FINAL REPORT

COST 633

Particulate Matter – Properties Related to Health Effects

Scientific Report

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Preface

COST Action 633 has now finished. It was based on an initiative by Othmar Preining and Helger Hauck, both members of the Austrian Academy of the Sciences, in the late 1990-ies, who planned this Action as a basis for a multidisciplinary approach to the complex issue of particulate matter and health effects.

After the official start in October 2002 with Helger Hauck and Othmar Preining as chair and co-chair of the MC, there was an inactive period because no meetings could be held because of lack of funding. When the Action finally started again in May 2004, Helger Hauck and Othmar Preining retired, and Regina Hitzenberger (University of Vienna) was elected chair of the MC and Janja Tursic (now Environmental Agency of the Republic of Slovenia) was elected co-chair.

We are deeply grateful to Helger Hauck an Othmar Preining for bringing the Action into being and for chairing it during the rocky phase at the beginning. Both stayed interested in the Action, however, and participated at the COST 633 Conference we held in Vienna in April 2006. Sadly, Othmar Preining died in September 2007, so he did not see the completion of the Action and its results.

This Action could not have happened and could not have achieved its results without the hard work of the members of the Action, their willingness to listen to experts in other fields and their contributions to the multidisciplinary discussions in the joint WG meetings as well as at the COST 633 conference. We also thank the staff at the COST office for their administrative support.

This final report covers the main scientific results of the Action. It is introduced by an overview of the objectives and tasks of the Action as well as the structure and objectives of the working groups (**Introduction**).

The report starts with a **Position Paper** developed after the final public workshop in March 2008 in Brussels. This position paper gives the conclusions we draw in a very condensed form. It answers the questions where we are at the moment and what the challenges are for the next fifteen years in the field of Particulate Matter and Health Effects.

An important result of the Action was achieved already at the 2006 International Conference of COST 633 in Vienna, Austria. The conference was aimed mainly at discussions, so actually it was a series of five different workshops dedicated to interconnecting topics. The full report of this conference is available at the COST 633 website (http://cost633.dmu.dk). The **Executive Summary** of this conference containing the main results is given in this final report.

The report then presents results in the areas of the **working groups**. Although the chapters are under the headers of the working groups, members of other working groups contributed to these results by sending data and information as well as giving input in the multidisciplinary discussions. Supporting information and data for these chapters are given in **Appendix I** in tabular form. An overview of the data collected by Working Group 1 (**Part A**) is followed by plots of the temporal trends of black carbon (BC) obtained from Black Smoke data (**Part** B). **Part C** contains the list of interdisciplinary projects (finished and ongoing) that were performed in the last few years in the area of Particulate Matter and Health in Europe. The list also includes contact information for these projects where available.

Appendix II is an overview of the results of the Action achieved in the different participating countries. These results were presented at the COST 633 meeting in Barcelona in October 2007. Abstracts of the publications are given in this appendix.

Appendix III is a compilation of material collected at the public events organized by the Action (workshops, conferences, special sessions at conferences). It includes programs as well as abstracts of the presentations. As the abstracts of the Vienna conference were published in the scientific report of the conference, they are not reproduced here.

Regina Hitzenberger, Chair, MC
December 2008

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I. Introduction

The Action was originally initiated in the late 1990-ies, when the need for multidisciplinary studies became apparent. The importance of particulate matter (PM) for human health had already been recognized, but the studies performed up till then had their focus either on PM measurements or on health effects (epidemiology or toxicology). The Action brought together a large group of experts from the fields of research in PM, epidemiology, toxicology, emission inventory, source apportionment, and exposure and integrating assessment modelling. Only some of the experts had known each other previously, so the Action also provided a first time networking opportunity for many scientists from different fields.

The Action was first chaired by Helger Hauck and Othmar Preining (both from the Austrian Academy of the Sciences), who had also been the initiators. In 2004, Hauck and Preining retired from the Action and Regina Hitzenberger (University of Vienna, Austria) and Janja Tursic (then National Institute of Chemistry and now Environmental Agency of Slovenia) were elected chair and vice chair of the management committee of the Action.

The objectives of the Action were:

1) To increase the information on the particulate matter (PM) characteristics throughout Europe, describing the PM-system with respect to geographical and meteorological conditions, particle formation processes and their transport with special regard to the European aerosol situation (compared e. g. to the US).
2) To increase the information on health effects of PM throughout Europe with special regard to geographical, seasonal and source-related aspects.
3) To improve the scientific basis for setting environmental standards in Europe and for defining cost-effective abatement measures to reduce particle and particle precursor emissions.

Three working groups were instituted to work on the tasks

1) To review existing data and methods both with respect to particulate matter and health studies.
2) To identify methodological gaps and geographical areas without adequate COST 633 relevant data, as well as target component classes in different aerosol fractions and emission sources.
3) To consolidate and expand emission inventories.
4) To review and further develop models for source apportionment as well as integrated assessment models.
5) To propose future research activities.

The working groups were established roughly according to the scientific fields brought together by the Action – PM measurements, health effects and modelling.

Working group 1 was focussed on Air Quality and Instrumentation and was was co-chaired by Jean-Philippe Putaud, JCR Ispra, Italy, and Axel Berner, Austrian Academy of Sciences,Vienna, Austria.

Its objectives were:

1) To provide an overview of information available in Europe on data and measurement techniques of particulate matter (PM)
2) To give input to WG2 and WG3 on measurement aspects

WG 1's tasks included

1) Collecting the existing data in different countries to highlight regional differences in aerosol over Europe with special emphasis on the organic fraction.
2) Assessing the available analytical techniques with respect to the needs of the health-related aerosol research, including:
   - sampling techniques (filter artifacts, impactor efficiences, validity, etc…)
   - analytical methods.

We expected that the results of WG1 would:

- complement the existing data sets containing just PM (AirNet) or inorganic aerosol components (EMEP)
- provide a basis for linking regional differences in PM effects on health to regional differences in PM composition and size distribution
- suggest cost-effective abatement strategies for mass, surface and number aerosol concentrations on a regional basis
- contribute in defining normalized methods for future aerosol legal indicators
- motivate sound aerosol measurement programs at Member States level
- trigger the preparation of future EU projects for issues that cannot be tackled at national levels.

Working group 2 was designed to cover Health Related Issues of Particles and was co-chaired by Raimo O. Salonen, National Public Health Institute (KTL), Kuopio, Finland, and Wolfgang Kreyling, GSF - National Research Center for Environment and Health, Neuherberg / Munich, Germany.

Its objectives were:

1) To review European heterogeneities in epidemiological and toxicological health outcomes associated with ambient air particulate matter
   - regional differences in health outcomes (i.e., southern vs. northern, eastern vs. western countries, multicentre studies)
   - seasonal differences in health outcomes (i.e., variations in a given location over the seasons of the year)
   - heterogeneities in health outcomes related to specific sources (traffic, industries, residential heating etc.)

2) To give inputs to WG1 and WG3 on health aspects.

The first task was to reveal European heterogeneities in health outcomes on the basis of recently published studies and to consider how they are related to the observed differences in particulate matter characteristics. In these considerations, regional differences in the prevalence and control of local emission sources (e.g., diesel cars, small-scale wood combustion, industries, energy plants) as well as the impact of trans-national transport of aerosols was taken into account. In addition, the impact of typical meteorological phenomena in different regions and seasons had to be considered.

The second task was to draw conclusions on the review results and to assess the role of human exposure to ambient air particulate matter in the observed heterogeneities in health outcomes utilising results from the two other working groups (WG1 and WG3) of the Action.
The third task was to give recommendations for human health risk assessment and management (e.g., suggestions for regulations) as well as for future European multicentre studies (i.e., identifying research gaps and needs). This included recommendations for ambient air PM parameters to be measured as well as analytical concepts elaborated by WG1 and WG3 of the Action.

In each of the three tasks, the work was divided into three parts according to the nature of existing databases:

- epidemiological studies
- toxicological studies
- human exposure assessment studies

Working Group 3, which was co-chaired by Thomas Kuhlbusch, IUTA e. V., Duisburg, Germany, and Markus Amann, IIASA, Laxenburg, Austria, addressed the issues of Sources, Emission, Modeling and Economic Aspects of PM.

The specific objectives of WG 3 were:

1) To provide an overview of information available in Europe on modelling of particulate matter (PM) with special emphasis on emission inventories, source apportionment models (SoAp) and integrated assessment models (IAM)
2) To give input to WG1 and WG2 on modelling aspects

WG 3 set itself the tasks**:**

1) To compile results related to PM_1, $PM_{2.5}$, PM_{10}, $PM_{2.5\text{-}10}$, $N_{0.1}$
    - Emission inventories
    - Source Apportionment methods and models (used in EU / generally available)
    - Source Apportionment results
    - existing models in EU and model validation (process studies – model results)
    - modelling results →process studies → SoAp per regions/site types
    - integrated assessment models (IAM)
2) To review and categorize information obtained in Task 1
3) To identify gaps and future research fields
4) To recommend future research

In order to reach the objectives, WG3 brought together European experts specialized on modelling the processes acting on particulate matter in the atmosphere as well as on assessment models.

II. Members of COST 633

Management Committee Members	
Name	*Country*
Regina HITZENBERGER, chair	Austria
Anne KASPER-GIEBL	Austria
Pierre DELMELLE	Belgium
Magda CLAEYS	Belgium
Jiri SMOLIK	Czech Republic
Miroslav JICHA	Czech Republic
Matthias KETZEL	Denmark
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Tuomo PAKKANEN (till 2006)	Finland
Risto HILLAMO (from 2007)	Finland
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Serge DESPIAU-PUJO	France
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John SODEAU	Ireland
Abid NASSER	Israel
Francesco FORASTIERE	Italy
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Markus AMANN (co-chair, WG3)	Austria
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Maria del Mar VIANA, WG3	Spain
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III. COST 633 Position paper

COST Action 633 Particulate matter and health in 2020: Are we on the right track?

Policy advice and research directions

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Introduction

The revised EU air quality directive is now on track after numerous legislative and implementation efforts during the last few years. During the revision and discussion of this directive, several important issues especially related to particulate matter (PM) were taken up within the Clean Air for Europe (CAFE) Programme. Not all issues could be tackled in the revision process due to lack of scientific data. There are still major uncertainties and serious gaps in the present scientific knowledge that need handling by the next evaluation of the air quality directive in 2013. The changing PM pollution in Europe leads to further information needs by stakeholders, policy-makers and decision-makers. Much more emphasis should be put on the role of PM in health impact and climate change. It is widely accepted that PM is an indicator for a complex mixture of air pollutants and that PM is highly correlated to many gaseous pollution components. Yet, for targeted abatement strategies, new information is needed on the most toxic emissions and conditions. Given that PM includes harmless as well as harmful material, indicators that are better linked with biological effects were discussed for their additional use in standard setting.

The COST action 633 brought together experts in the field of particle measurements, transformation of atmospheric aerosols, exposure, epidemiology, toxicology and modeling of aerosol sources, atmospheric processing, and other fields and provided a genuinely interdisciplinary platform to formulate questions, discuss possible answers and identify research that needs to be performed in the near future and beyond.

In a two-day meeting (Brussels, March 13 – 14, 2008) COST action 633 members gathered information and provided guidance for dealing with current heterogeneities and future changes in Europe-wide PM levels and characteristics, as well as the health implications due to air pollution and climate change mitigation policies.

What is the problem of the changing source patterns and emission characteristics?

With regard to modelling and source apportionment

- Good emission inventory data and source profiles are lacking for some sources (e.g. modern tail pipe PM emissions from vehicles, (re)suspended dust, forest fire smoke PM, residential wood burning PM, etc.).
- Separation between natural and anthropogenic contributions is difficult for some constituents (e.g. OC, PM number).
- Vehicle emissions change fast due to new emission limits and technologies (e.g. PM traps, biofuels, metals from catalysts etc.). Therefore, it is difficult to be up-to-date in source modelling.

What is the value of alternative indicators for PM mass?

- Sources are misclassified due to changed source representation by some tracers (e.g. As: coal combustion vs. natural gas or liquid fuels, NaCl: sea salt vs. road de-icing salt, MgCl2: road de-icing (reduces dust resuspension) vs. other (mineral) sources).
- The contributions to PM from chemical transformations of emissions need to be reconsidered on the basis of new scientific information on atmospheric processes.

For assessing short-term and long-term health effects

- PM compositions will change rapidly (e.g. with increased use of solid and liquid biofuels for heating and transport), but we lack even the basic toxicological data needed for risk assessment.
- PM source - health effect relationships cannot be reliably assessed without updating and extending the source apportionment information (see above).

Several alternative indicators for PM mass (PM10, PM2.5) have been put forward in the scientific community: Black Smoke, elemental carbon, particle number and an oxidative stress index. The basic idea is that they are better at representing specific (health relevant) sources and/or have a closer connection to health effects, thereby provide a better opportunity to detect causality between certain air pollution types and sources and health effects.

Are we able to monitor these alternative indicators?

Yes, though there are major differences in measurement techniques used by the scientists and no European standardized methods. In addition, setting up standards takes currently too long.

Which parameters could be alternative indicators?

- Black Smoke has been and is still used in EU countries as an air quality indicator.
- Elemental carbon is preferred to Black Smoke. The only advantages of Black Smoke are the long historical datasets and low cost measurements.
- Ultrafine PM (or the number of particles per volume) in different microenvironments have differences in chemical composition. Despite concerns on the health risks related to ultrafines, little information is published.
- Particle numbers may not be alternative for PM mass, but a good additional parameter.
- The oxidative stress index (oxidative potential) of PM should be further investigated due to its potential to give valuable additional information about the health risks. No conclusions can be drawn yet about the likelihood to become a standard metric for legal limit values and administrative monitoring of PM pollution.
- An indicator of PM surface reactivity may be a good general measure for health risks but like the oxidative potential and particle number concentration, needs further validation.

When is an indicator a good indicator?

- A good indicator has direct connection to health effects and helps identifying contributions of different PM sources and/or harmful components in ambient air.
- PM1 (ultrafines) would be better than PM2.5 for a fine PM pollution measure. Larger size particles (>1 or >2.5µm) should be monitored in parallel to PM1 (or PM2.5) since these fractions are also linked to (albeit different) types of health effects.

Where should we go from here in European PM Research?

- Establishment of PM super centres with high-standard harmonized methodology to increase the quality of European-wide aerosol data (the regions do differ from each other in PM composition and health risks!) to be used to identify source contributions to and the oxidative potential of PM as well as the associated health effects.
- The interdisciplinary approach of the field achieved in COST 633 should be incorporated into integrated PM science with harmonised methodologies, i.e. combine the expertise from air quality, modelling and health effects including modelling of the whole chain of events.
- PM has a dual role in health effects as well as in climate change, which means that also the measurement techniques used in these two, currently separate scientific areas should be harmonised with each other.

Key messages

Why do we regulate PM? To reduce the associated health effects!

Current challenge

- Changing source patterns and emission characteristics are likely to change the dose-response
relationship. PM-mass is only a proxy for the PM-characteristics that cause the effects. What is the consequence for risk assessment and standard setting?
- We need (a) metric(s) that is (are) directly linked to the causative pathway leading to health effects. The current mass-based approach brings the focus on the most mass-intensive sources and to mass causal factor related to health endpoints. Mass per se may not be the most relevant metric to describe the concentration- dose-response relationships and may even neglect other specific health effects caused by PM i.e. particle number concentrations. This fraction is poorly correlated with PM mass (in time and space), whereas scientists have serious concerns about the impact of these small and numerous particles. If these particle numbers are stronger correlated to or have different impact on health effects, this would mean inefficient use of resources available for abatement strategies if the focus is only on PM mass.

What PM-properties cause the health effects? What are the indicators?

- We currently have several candidate characteristics, namely Black Smoke/elemental and organic carbon, particle number and surface, and an oxidative stress index.
- The oxidative stress paradigm offers a good explanation for the known health effects of ambient PM and thus favours an oxidative stress index.
- Several tests are currently available to determine an oxidative stress index, but these tests need further evaluations and harmonization.

Where do we go from here?

We need a validated new metric for the next legal cycle. Therefore, the following validation steps are needed:

- more mechanistic research on the toxicological aspects of PM;
- large epidemiological studies involving several old and new metrics in parallel with good time-space resolution linked with detailed information on emission sources including toxic potency of the whole (chemical) mixture;
- studies to understand how sources and emission patterns contribute to the novel metrics and indices;
- development / improvement to have reliable and easy-to-use (robust) measurement methods and devices;
- use well validated exposure models to propose new guidelines, based on scenarios, for the next generation of policy orientations.

IV. Executive Summary, COST 633 conference “Similarities and Differences in Airborne Particulate Matter: Exposure and Health Effects over Europe”.

April 2006, Vienna, Austria

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The impact of airborne particles on human health is currently seen as the most important environmental issue in Europe. Recent assessments showed a loss in life expectancy of about 9 months in the year 2000 (EU-25, central CAFE baseline estimate[1]) due to PM2.5 mass. The revisions of the Air Quality Directive and its daughter directives were discussed at the same time in Brussels which all form the background of this conference.

Various scientific areas are necessary when tackling the still wide open issues in this research on particulate matter and health. Scientific areas cover a range from e.g. chemistry, meteorology, engineering, toxicology, to epidemiology. Scientists with this diverse scientific background coming from all over Europe discussed the issue of particulate matter and health in 5 interconnected workshops each of which approached the main question from a different perspective.

The topics of the five workshops were:

Topic 1:	Particle characterisation and characteristics
Topic 2:	Sources of particulate matter
Topic 3:	Modelling and (personal) exposure
Topic 4:	Health effect - Epidemiology
Topic 5:	Health effect - Toxicology

Figure 1 shows a flow chart on information/research areas necessary to assess the health impact of airborne particulate matter. It also illustrates how the topics fit into this overall scheme.

Two major issues were clearly stated by all participants of the workshop:

- There has been tremendous increase in knowledge related to airborne particles and their effects on human health over the last decade.

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[1] Baseline Scenarios for the Clean Air for Europe (CAFE) Programme , Markus Amann, Imrich Bertok, Janusz Cofala, Frantisek Gyarfas, Chris Heyes, Zbigniew Klimont, Wolfgang Schöpp, Wilfried Winiwarter, Final Report to DG ENV, Feb. 2005

- Still some major open questions remain and it is seen that integrated approaches combining the different scientific areas covering environmental, socio-economic and medical research in selected regions in Europe are necessary to effectively tackle the open questions European wide.

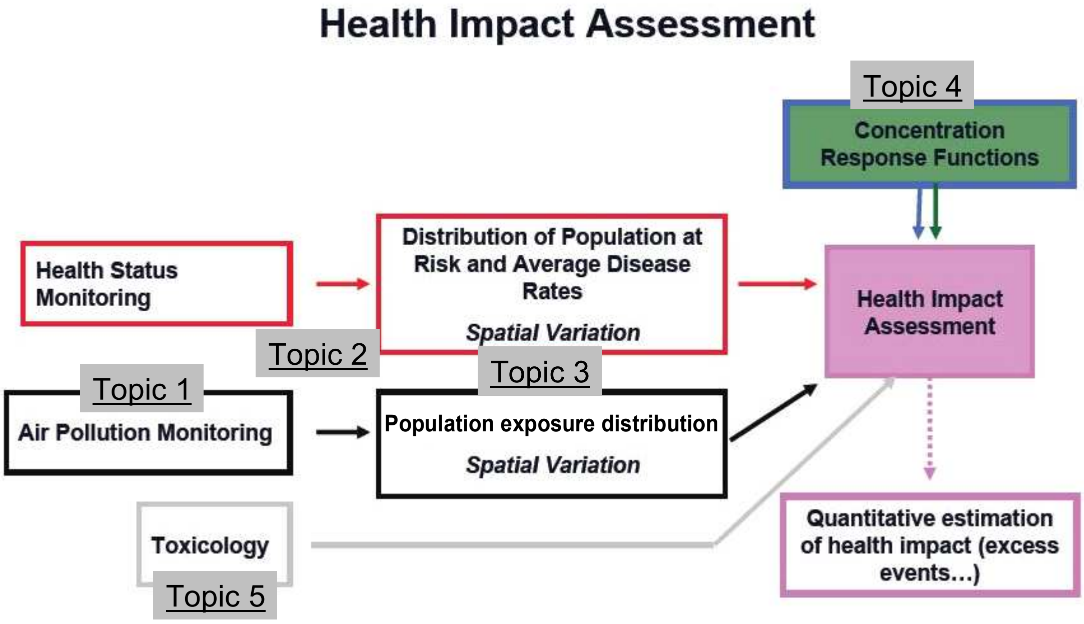

Figure 1: Scheme for health impact assessment [2]

Several major issues came up during the discussion in **Workshop 1** on particle characteristics and characterisation. One block of recommendation is linked to monitoring. Specific needs identified here are

- Extension of the current monitoring network to other particle parameters also in urbanized areas.
- Improvement of PM mass measurement accuracy. Also the reference method EN12341 suffers from sampling artefacts and analytical bias.
- Standardisation of analytical methods for aerosol measurements that cannot be validated because standards do not exist (e.g. EC, particle number concentration).

The points listed above would be best addressed by setting up about 3 aerosol (super)sites in urban areas located in different regions of Europe. These (super)sites would achieve a complete

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[2] Analysis and design of local air quality measurements, Towards European Air Quality Health Effect Monitoring, Thomas Kuhlbusch, Astrid John, Achim Hugo, Annette Peters, Stephanie von Klot, Josef Cyrys, H.-Erich Wichmann, Ulrich Quass, Peter Bruckmann, Report to DG ENV, http://www.iuta.de/Verfahrenstechnik/Luftreinhaltung/euraqhem_final_report.pdf, April 2006.

characterisation of the urban aerosol in relation with their health effect, and serve as platforms for instrument calibrations and intercomparisons.

Further important recommendations were

- Development of novel analytical capabilities related to aerosol-and-health e.g. PM oxidative stress, the surface area of the particles' insoluble core.
- Assessment of the effect of pollutant emission abatement strategies on PM characteristics.

The above recommendations are all linked to ambient air quality monitoring and its assessment while in **Workshop 2** the main focus was on the sources of airborne particulates and their assessment. The importance of source apportionment in view of health effects and planning of abatement strategies was clearly stated. Especial importance on future direction of source apportionment was put on

- A need for the development of a common methodology for certain questions/tasks is clearly seen, which shall be validated by comparison with secondary information and/or other methods.
- A possible new focus could be the use of emission inventories, chemical transport models and source apportionment methods in combination. Whereas each tool separately is not capable of answering all questions, in combination they could provide a more detailed insight to issues such as regional variability of contributions by traffic, wood burning, etc.
- The quantification of wood burning as a PM source is a concern for emission inventories. Source apportionment studies could help verify or reject the current statistics, in order to determine whether the large differences reported across the EU are a fact or whether wood burning is simply not reported for some regions.
- One of the biggest challenges for source apportionment studies are secondary organic aerosols (SOA). Current knowledge on their formation processes, or on the influence of natural or anthropogenic emitted precursors, is limited. Smog chamber experiments, modelling studies or the study of their polymerisation processes would provide an insight to this issue.

The linkage of source apportionment and health effect studies is seen as of specific importance which should include the following points:

- Separate focus on the coarse and fine grain-size fractions, given that the effects on health of these two fractions are clearly differentiated (respiratory vs. cardiovascular).
- Extension to particle number concentrations, ultra fine particles.
- Short- and long-term health studies should be linked to source apportionment studies, thereby facilitating the identification of possibly harmful sources and particle properties.

While ambient air and particle source apportionment studies are important tools linking particles and health a further major focus discussed in **Workshop 3** was the linkage of measurements to (personal) exposure and how modelling can facilitate this linkage. The intense discussion of this topic enabled the identification of following recommendations:

- There is a need to assess the uncertainty of existing models rather than development of new models.
- Long-term exposure estimates still need to be improved and developed, especially taking the indoor situation into account.
- PM outdoor-indoor penetration, the time spent indoors and indoor sources including health effects need further investigation.
- Air quality models should be used to complement monitoring data allowing a better spatial distribution characterisation.
- Exposure studies in Europe should take into account the different characteristics of climate zones, the specific behaviour of social groups, and national habits.

The last two workshops were complementary to the first three. The first three were focussed mainly on exposure (air quality monitoring, source apportionment, indoor/outdoor, air quality modelling, personal exposure) whereas the focus of the last two was on health effects due to particles. Epidemiology and its drawbacks and limitation were discussed in **Workshop 4**. The outcome of this discussion can be summarized in the statements below identifying future needs and possible directions.

- Better definition of physicochemical differences of particles and inclusion into health effect models that include genetic and socio-economic differences.
- Development of high resolution spatial exposure models for the estimation of chronic, long-term particle exposure. Europe-wide studies on the long-term effects of air pollution with standardized procedures in both health and exposure assessment are needed. To appropriately investigate chronic effects, such studies must focus on early anatomical or functional markers of chronic diseases rather than on terminal outcomes.
- Inclusion of socioeconomic and genetic differences when in studies of the exposure-response relationship between air pollution and pulmonary, cardiovascular or neurodegenerative diseases are investigated. The interrelation between socio-economic factors and the biologically relevant co-factors are poorly understood in Europe and need to be integrated in future air pollution research.
- Development of dosimetry models that can be used to refine the exposure-response function and for studying effects in secondary organs.
- Investigation of the consistency of concentration-dose-effect estimates for different sources, constituents, and regions.

The last **Workshop 5** dealt with the topic mainly from the toxicological point of view. Major gaps were identified while at the same time clear concepts on how particles interact with human health were presented.

- Need for better integration of epidemiology and toxicology, using for instance same health indicators (biomarkers of effect).
- Conduct source related toxicological studies preferably using real world mixtures.

- Long term exposure studies (that can also be used as toxicology-time series studies). Better animal models with the challenge for transgenic mice.
- Development of a test battery for oxidative stress that can ultimately be used to monitor the biological reactivity of air pollution.
- Development of tests to evaluate effectiveness of control strategies of vehicle emissions.
- The role of surface area of (the insoluble core of) PM has to be identified.
- The role of so-called non-toxic components (often also referred to as “natural”) in the total mixture of PM is still very week. Can such particles interact to become for instance carriers for toxic or allergic substances (not even a particle).
- Integration of air sampling in toxicological TEST: Usage of PM sampling techniques that reduces sampling artefacts to a minimum such that it really resembles PM in air

The need of collaboration and interdisciplinary approaches became obvious during the final discussion. Even though several urgent research needs were identified in specific research areas a clear recommendation to conduct well organized concerted research studies in several regions in Europe comprising monitoring and research of air quality, exposure, health status, exposure-response functions, source specific toxicological studies, evaluation of abatement actions, etc. is given by all members of COST 633 and participants of the workshop.

V. Results from Working Group 1: Air Quality and Instrumentation

Chairs: Jean-Philippe Putaud, JRC Ispra, and Axel Berner, Austrian Academy of Sciences

V.1 Aerosol data compilation - final report

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1. Scope and strategy

As increasing efforts are put on remote sensing and modeling of atmospheric particle properties, in situ measurements are still essential for determining the extent to which satellite data and model output are close to reality. The most recent compilations of aerosol physical and chemical data (Van Dingenen et al. 2004; Putaud et al., 2004) across Europe showed that the number of sites at which the aerosol has been fully characterized is still limited, especially in the Southern and Eastern parts of Europe.

The scope of WG1 – Task 1 was to compile the aerosol data obtained in the countries participating to the Action, and to sort these data in order to make them comparable for highlighting **differences and similarities in aerosol characteristics across Europe.** Indeed, while PM mass concentration is the only atmospheric particle related variable that has to be monitored according to European Directives (Daughter Directive on Air Quality 1999/30/EC), the aerosol consists of a complex mixture of particles with different size, chemical composition, etc.. Considering (i.e. monitoring and regulating) PM mass concentration ONLY might well be insufficient for tackling the PM health issue. To illustrate this, we aimed at showing how variable the aerosol characteristics for a given level of PM_{10} concentration can be, focusing on regional differences.

It was therefore decided during the first COST633 WG1 meeting in 2004 to compile aerosol data sets covering at least 3 weeks, and that would contain both:

- PM mass concentration, which is the metric adopted in Europe for assessing particulate matter air pollution
- PM chemistry or particle number data.

The strategy adopted during this meeting was to rely on COST 633 National Representatives for listing, getting, and submitting to the COST633 restricted access data bank the relevant aerosol data sets obtained in their countries.

In order to make comparisons easier, sites were classified according to the information provided by data providers according to:
- the type of site (rural, near-city, urban background, kerbside), following the classification established by the EEA (Larssen et al., 1999)
- their location in Europe, divided in 3 large sectors: North-Western, Southern and Central Europe (Fig. 1b).

We recognize here that determining the nature of each site is not always easy, as the border between two adjacent categories is often not very sharp.

2. Main results

2.1. Identified, selected and collected datasets

National Representatives and working group members from 16 countries reported the existence of 294 data sets (site x period), among which 181 fit to the selection criteria decided by COST633 WG1 (Fig.1a). Eligible data sets were uploaded to the COST633 data bank by representatives from Austria, the Czech Republic, Finland, Germany, Hungary, The Netherlands, Slovenia, Spain, UK and the WG1 co-chairman from the EC (Appendix I, Part A, Annex 1). Thirty-five (35) data sets contain PM mass concentrations and chemistry, twelve (12) contain PM mass concentrations and particle number data. Only a few include all of PM mass, chemistry, and particle number data (Fig. 1b).

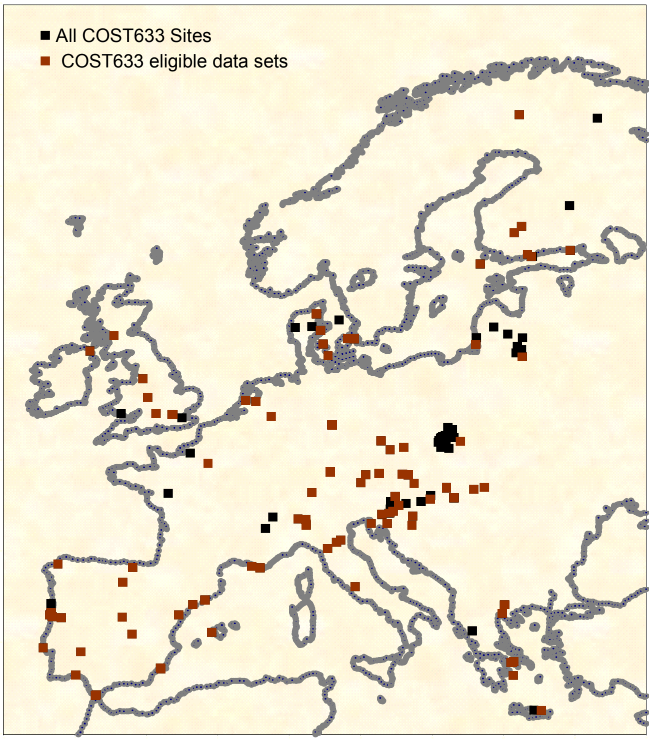

Figure 1.a: Sites for which aerosol data and COST633 eligible aerosol data were identified.

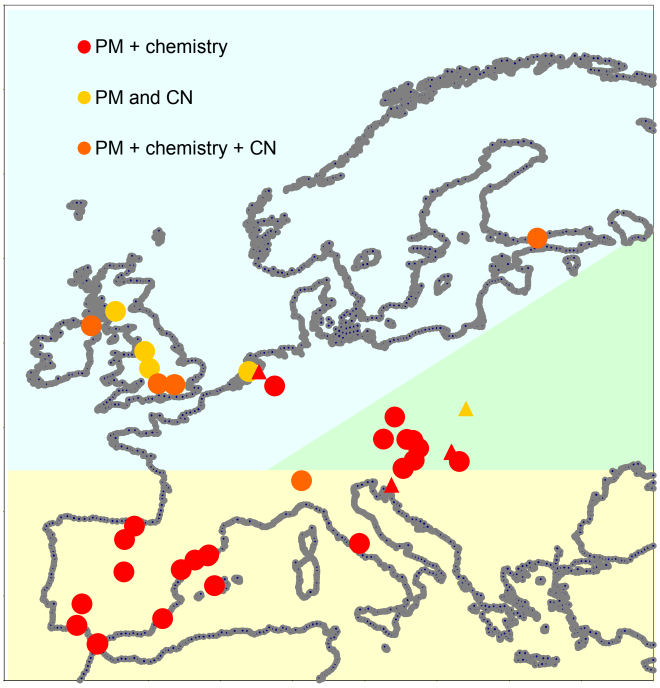

Figure 1.b: Sites from which aerosol data were reported to the COST633 data bank. Also shown are the 3 geographical sectors used for segregating data: North-Western (blue), Southern (yellow) and Central (green) Europe. Triangles indicate sites for which less than a full year of data is available.

2.2. PM mass concentrations

2.2.1. PM_{10} mass concentrations

Although we compiled only data sets where additional information on top of PM mass concentrations are available, we show here (Fig. 2a) statistics of PM_{10} mass concentrations to put the data we collected in a broader context (as PM_{10} mass concentrations have been monitored for years at hundreds of stations across Europe).

The range of PM_{10} concentrations observed at the COST633 sites is large. Annual averages range from 15 to 50 µg/m³. Annual averages are larger than the current EU directive (40 µg/m³) at a few sites, below the 20 µg/m³ 2010 target at 3 sites only. The EU 24-hr limit value (50µg/m³) is exceeded more than 18 days a year (95th percentile) at 19 sites, more than 90 days a year (75th percentile) at 5 sites. In each of the 3 sectors, PM_{10} generally increases when going from rural to kerbside sites, but not always. PM_{10} concentrations in urban background look larger in Southern Europe, whereas concentrations at rural sites look similar in the 3 geographical sectors.

PM_{10} seasonal variations are generally larger at continental sites compared to sites located at short distances from the sea shore (not shown).

2.2.2. $PM_{2.5}$ mass concentrations

The amount of $PM_{2.5}$ mass concentration data available across Europe is still limited as $PM_{2.5}$ was introduced in the EU Directives (http://ec.europa.eu/cyprus/news/air_pollution_en.htm) only recently. Among the COST633 sites, $PM_{2.5}$ annual averages range from 9 to 34 µg/m³ (Fig. 2b). Only 5 sites are above the 25µg/m³ EU target for annual average to be reached by 2010. Also $PM_{2.5}$ looks a bit larger in Southern Europe compared to the other sectors. The gradient in $PM_{2.5}$ when moving from rural to urban to kerbside sites is not as clear as for PM_{10}.

$PM_{2.5}$ seasonal variations are generally comparable to those of PM_{10}. These seasonal variations are mainly related to changes in pollutant horizontal and vertical dispersion driven by meteorology.

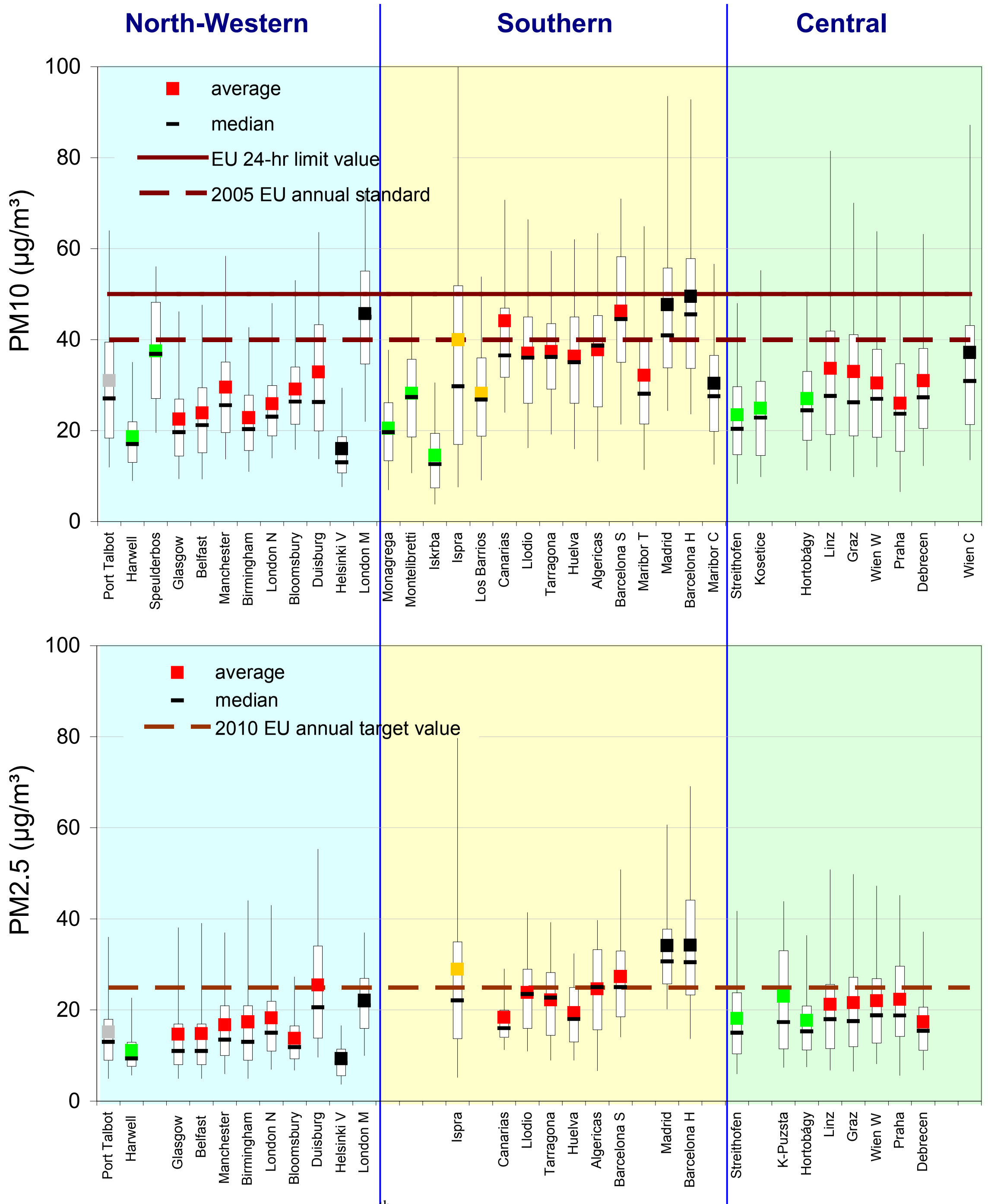

Figure 2: 5, 25, 50 (median), 75, 95th percentile and average (colored squares) of (a) PM_{10} and (b) $PM_{2.5}$ mass concentrations. Colors indicate the type of site: ⬜ industrial, 🟩 rural, 🟨 near-city, 🟥 urban background, and ⬛ kerbside. Also shown are the EU limit values and targets.

2.2.3. Relationship between $PM_{2.5}$ and PM_{10}

$PM_{2.5}$ and PM_{10} are generally related ($R^2 = 0.69$). However, the $PM_{2.5}$ / PM_{10} ratio is quite variable (ranging from 0.43 to 0.86 among the COST633 sites). For 2-3 sites, $PM_{2.5}$ concentration levels off when PM_{10} gets larger than 50 µg/m³ (Fig. 3). Differences in $PM_{2.5}$ / PM_{10} ratios cannot be clearly related to the site type or its location.

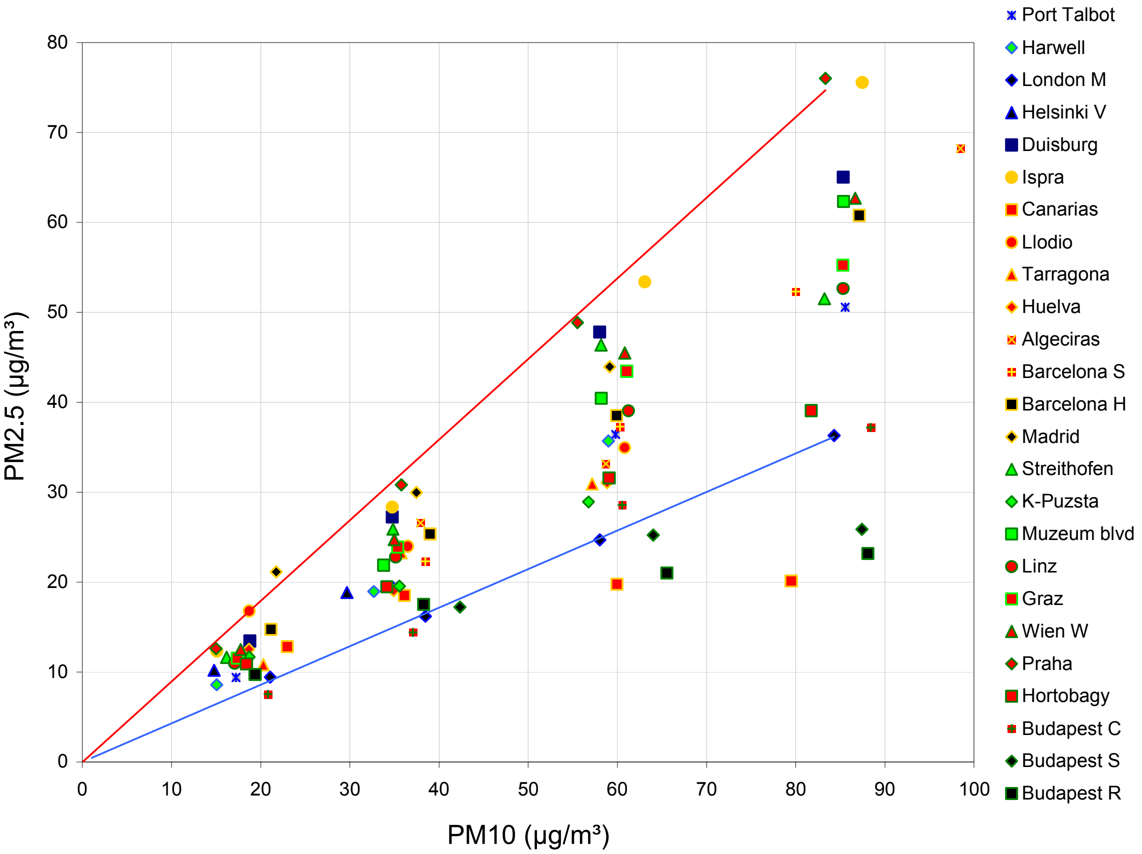

Figure 3: Relationship between $PM_{2.5}$ and PM_{10} mass concentrations. Data points represent $PM_{2.5}$ and PM_{10} averages of daily values calculated over the following PM_{10} concentration bins: 0-25, 25-50, 50-75, and 75-100 µg/m³. The blue and red lines show the lowest (0.43) and the highest (0.90) mean $PM_{2.5}/PM_{10}$ ratios, observed at London M and Praha, respectively.

2.3. PM chemistry

As PM mass concentrations mainly depend on pollution dispersion or dilution, only relative contribution of PM constituents to PM mass are presented in this section. Absolute seasonal average concentrations of major constituents of PM_{10} and $PM_{2.5}$ are provided in Appendix I, Part A, Annexes 2 and 3.

2.3.1. PM_{10} chemistry

PM_{10} chemical composition for 35 COST633 sites are shown in Fig. 4.The organic matter (OM) fraction was calculated assuming the same organic matter – to – organic carbon ratio (1.4) for all sites. At sites for which only total carbon (TC) was measured, TC concentrations were converted to CM (carbonaceous matter) concentrations assuming a constant EC/TC ratio = 0.1, and a constant OM/OC ratio = 1.4. Sea salt was calculated from Na^+ and Cl^- concentrations (when available) and a standard composition of seawater. Mineral dust was roughly estimated as 4.5 x Ca^{2+}. The unaccounted PM_{10} fraction results from the difference between the sum of the quantified PM components and PM_{10} mass concentrations determined independently. This fraction therefore includes the constituents that were not measured, and the amount of water associated with the collected aerosol at 50% RH (relative humidity at which aerosol samples have to be weighed according to the EN12341 protocol).

Seasonal averages are shown, so that sites for which < 1 yr –long data sets are available can be considered. The most obvious observation is that not all the main constituents of PM_{10} are measured at most sites. As a consequence, the unaccounted fraction of PM_{10} is often large. The contribution of mineral dust is much larger in the Southern sector compared to the North-Western and Central sector. Mineral dust can account for >30% of PM_{10} at many sites in Spain. Also sea salt contributes for up to 30% to PM_{10}, with largest contribution at sites located near the sea shore. SO_4^{2-} and NO_3^- generally account for <30% of PM_{10} each. NO_3^- contribution is larger in winter, SO_4^{2-} contribution larger in summer. Carbonaceous aerosol (OM + EC) can account for more than 50% of PM_{10}. The contribution of carbonaceous aerosol is larger in Central compared to North-Western Europe.

Yearly average contributions of PM_{10} main constituents to PM_{10} mass are listed in Table 1. Mineral dust is important mainly in Southern Europe, with relatively small differences among site types. The sea salt contribution is generally significant, except at Central European sites. SO_4^{2-} contribution increases when going from North-Western to Southern to Central Europe and decreases when moving from rural to kerbside sites. Also NO_3^- contribution decreases from rural to kerbside sites, but is generally larger in North-Western Europe. The ratio total carbon TC / PM_{10} clearly increases from North-Western to Central Europe, where it is quite comparable at urban and rural sites. In North-Western and Southern Europe, TC / PM_{10} ratios increase when moving from rural to kerbside sites.

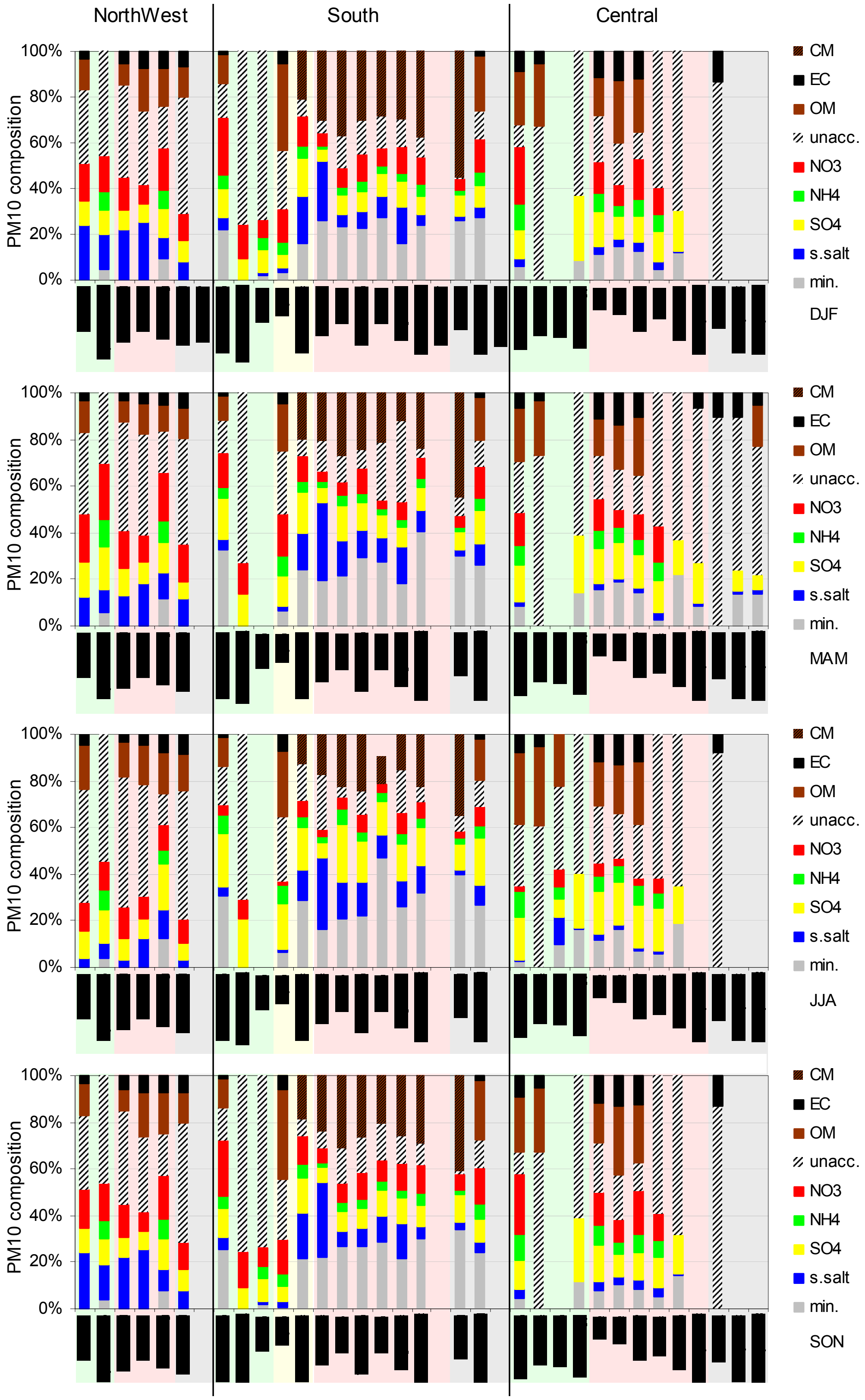

Figure 4: Chemical composition of PM_{10} from winter (top) to autumn (bottom). Sites are classified according to their location (North-West, South, Central) and type (rural: green, near-city: yellow, urban: red, kerbside: black pastel backgrounds)

Table 1: Annual mean of main constituents' daily contributions to PM_{10} mass in three large regions in Europe and 4 types of sites

PM10		rural	near-city	urban	kerbside
N-Western Europe	min. dust	4%			
	sea salt	11%		12%	6%
	SO4	13%		11%	8%
	NO3	17%		13%	12%
	OM	15%		15%	14%
	EC	4%		6%	8%
	TC	*14%*		*16%*	*18%*
Southern Europe	min. dust	27%	13%	24%	30%
	sea salt	5%	10%	11% ◥	5%
	SO4	16%	14%	11%	12%
	NO3	13%	10%	7%	8%
	OM	12%	32%		
	EC	1%	5%		
	TC	*13%*	*21%*	*18%*	*28%*
Central Europe	min. dust	9%		15%	
	sea salt	1%		2%	
	SO4	20%		15%	
	NO3	16%		7%	
	OM	26%		22%	
	EC	8%		13%	11%
	TC	*27%*		*29%*	

◥ Canarias excluded

2.3.2. $PM_{2.5}$ chemistry

$PM_{2.5}$ chemical composition for 21 COST633 sites is shown in Fig. 5. Calculations were made following the same rules as for PM_{10}. The unaccounted fraction of $PM_{2.5}$ is large at many sites because all of the main $PM_{2.5}$ constituents were not measured. Mineral dust contribution to $PM_{2.5}$ remains $\leq$ 10% in all circumstances. The contribution of mineral dust is much larger in the Southern sector compared to the North-Western and central sector. Sea salt also contributes less than 10% of $PM_{2.5}$, one site excepted (Canary islands). SO_4^{2-} contribution can reach 40% of $PM_{2.5}$, and NO_3^- up to 25% (generally less than 20% though). The contribution of NO_3^- is particularly small in summer, which can be explained by thermodynamics ($NH_4NO_3 \Leftrightarrow NH_3 + HNO_3$ equilibrium shifted towards the gas phase) but also by increased sampling artifacts, depending on sampling techniques. Carbonaceous species account for 30-70% of $PM_{2.5}$, with little or no seasonal variation at most sites.

Considering the limited number of datasets containing $PM_{2.5}$ chemistry data, the significance of the annual average contributions to $PM_{2.5}$ listed in Table 2 may be discussed. It appears that as for PM_{10}, the ratio $TC/PM_{2.5}$ clearly increases when moving from North-Western Europe to Southern and Central Europe, while the contribution of NO_3^- is much higher in the North-Western sector compared to the remainder of Europe.

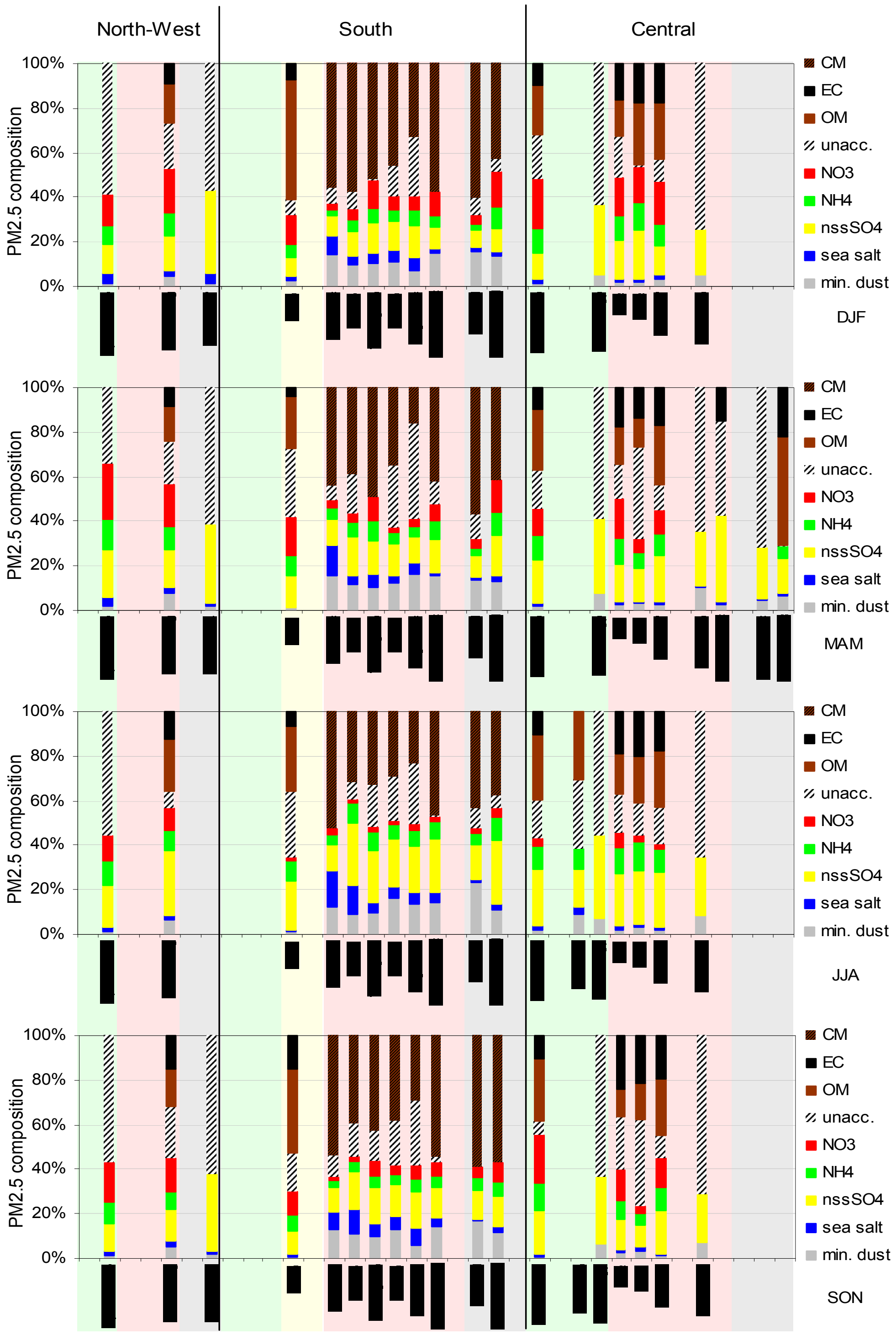

Figure 5: Chemical composition of $PM_{2.5}$ from winter (top) to autumn (bottom). Sites are classified according to their location (North-West, South, Central) and type (rural: green, near-city: yellow, urban: red, kerbside: black pastel backgrounds).

Table 2: Yearly mean contribution of main constituents to $PM_{2.5}$ in three large regions in Europe and 4 types of sites

PM2.5		rural	near-city	urban	kerbside
N-Western Europe	min. dust				
	sea salt			2%	
	SO4			19%	
	NO3			16%	
	OM			18%	
	EC			10%	
	TC			*23%*	
Southern Europe	min. dust		2%	12%	15%
	sea salt		1%	7%	1%
	SO4		14%	16%	12%
	NO3		11%	5%	4%
	OM		39%		
	EC		6%		
	TC		*34%*	*31%*	*42%*
Central Europe	min. dust	4%		4%	
	sea salt	1%		1%	
	SO4	26%		20%	
	NO3			5%	
	OM			21%	
	EC			19%	
	TC			*34%*	

2.3.3. $PM_{2.5}$ vs. PM_{10} chemistry

Comparing the chemical composition of PM_{10} and $PM_{2.5}$, it appears very clearly that both mineral dust and sea salt are much more abundant in PM_{10} than in $PM_{2.5}$. In contrast the ratio $TC/PM_{2.5}$ is larger than TC/PM_{10} in each cell of Tables 1 and 2. The contribution of SO_4^{2-} is only slightly larger in $PM_{2.5}$ compared to PM_{10}.

2.4. PM and particle number concentrations

Particle number and PM mass concentration data were collected for 12 sites. The distribution of these sites is very uneven since 10 are located in the North Western sector of Europe, and 9 are urban background sites.

2.4.1. PM_{10} and particle number concentrations

Figure 6 shows the relationship between PM_{10} mass and particle number concentrations. Generally both the total and ultrafine particle number concentrations increase with PM_{10}, although a few exceptions are apparent. The datasets collected from the North Western sector of Europe indicate that for a given range of PM_{10} concentrations, the particle number concentration is much larger at a kerbside site compared to urban background sites. Also, particle number concentrations at urban background sites in North-Western Europe are comparable to particle number concentrations at an urban background site in Central Europe for equal PM_{10} concentrations.

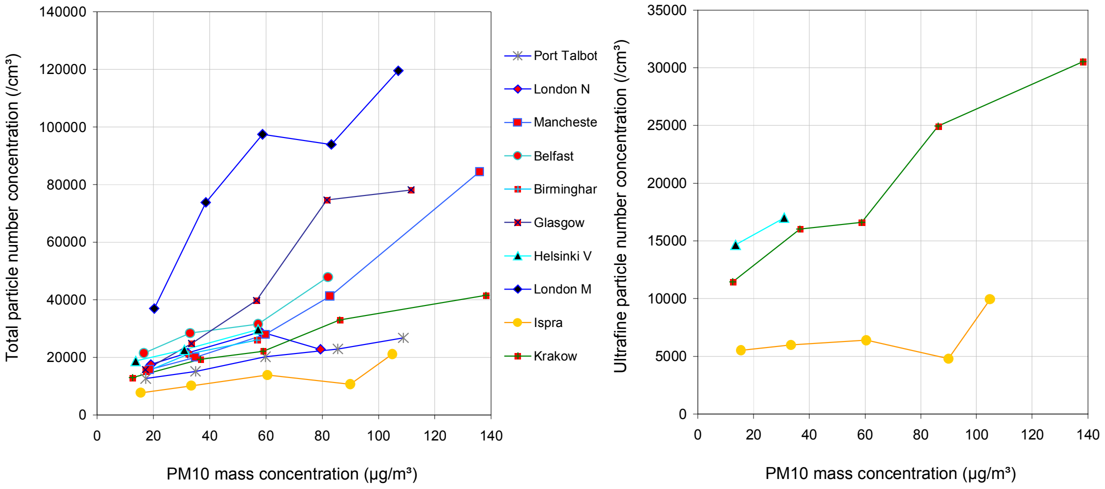

Figure 6: Average total (left) and ultrafine (right) particle number concentrations as a function of PM_{10} mass concentrations. Averages have been calculated for the following PM_{10} ranges: 0-25, 25-50, 50-75, 75-100 and >100 µg/m³. Line and symbol foreground colors are related to the site location (blue: North West, yellow : South, green: Central) and the symbol background color is related to the type of site (yellow: near-city, red: urban background, black: kerbside, grey: industrial).

For the 3 sites at which total, ultrafine particle number and PM_{10} mass concentrations were measured, we observe a large contribution of ultrafine to the total particle number, generally decreasing for increasing PM_{10} mass concentrations (Table 3).

Table 3: Ultrafine / total particle number ratio as a function of PM_{10} mass concentration ranges for 3 COST633 sites

	PM10	[0-25]	[25-50]	[50-75]	[75-100]	[100-+]
Helsinki V	urban	0.78	0.75			
Ispra	near city	0.72	0.59	0.46	0.45	0.47
Krakow	urban	0.88	0.83	0.75	0.76	0.74

2.4.2. $PM_{2.5}$ and particle number concentrations

Figure 7 shows the relationship between $PM_{2.5}$ mass and particle number concentrations. No linear correlation can be observed between $PM_{2.5}$ mass and both the total and ultrafine particle number concentrations at these 4 sites. Considering the two sites located in Finland (triangle symbols), it is obvious that for a given range of $PM_{2.5}$ mass concentration, particle number concentrations are larger at the kerbside compared to the rural site. However, the particle number concentrations measured in Amsterdam (NL) are even larger (but consistent with the particle number concentrations observed at London M). For each $PM_{2.5}$ mass concentration range, both the total and ultrafine particle concentrations are very similar at the rural site in North-Western Europe and the near-city site in Southern Europe.

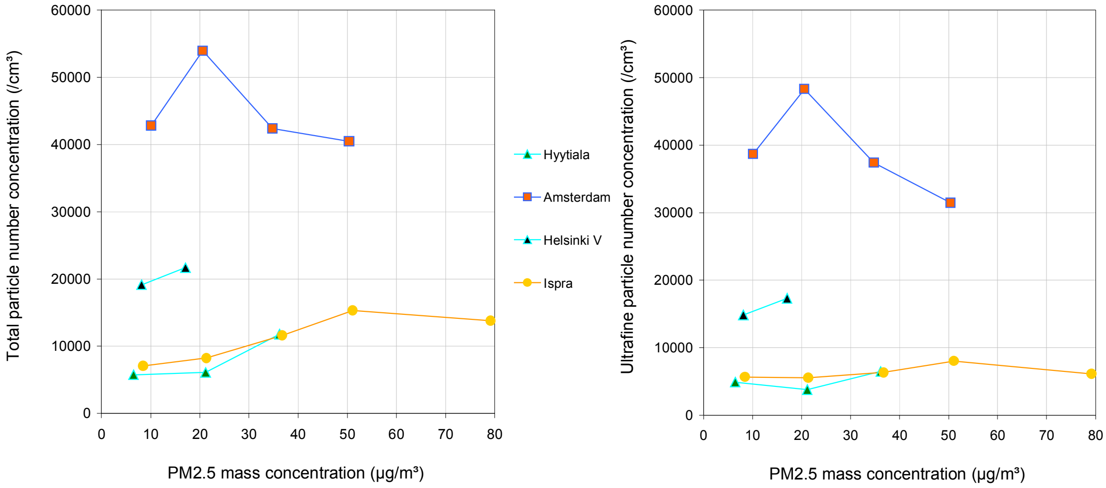

Figure 7: Average total (left) and ultrafine (right) particle number concentrations as a function of $PM_{2.5}$ mass concentrations. Averages have been calculated for the following $PM_{2.5}$ ranges: 0-15, 15-30, 30-45, 45-60 and >60 µg/m^3. Line and symbol foreground colors are related to the site location, (blue: North West, yellow: South) and the symbol background color is related to the type of site (green: rural, yellow: near-city, red: urban background, black: kerbside).

In contrast to what was observed at sites where PM_{10} was measured, the ultrafine / total particle number ratio does not always decrease with increasing PM mass concentration, except at the rural and near-city sites (Table 4).

Table 4: Ultrafine / total particle number ratio as a function of $PM_{2.5}$ mass concentration ranges for 4 COST633 sites.

	PM2.5	[0-15]	[15-30]	[30-45]	[45-60]	[60-+]
Hyytiala	rural	0.85	0.62			
Amsterdam	urban	0.90	0.90	0.88	0.78	0.85
Helsinki V	kerbside	0.78	0.80			
Ispra	near city	0.80	0.67	0.54	0.52	0.44

1- Conclusions

As a result of very different activities of the COST633 partners, aerosol datasets from >40 new sites (i.e. that were not part of previous compilations by Van Dingenen et al., 2004 and Putaud et al., 2004) have been collected that contain both PM mass concentration and chemistry (35) or particle number concentration (12) data. They represent a limited fraction of the existing original (i.e. not already reported to international open access data bases) aerosol data only. These data sets have been sorted as a function of site location (North-Western, Southern, Central Europe) and type (rural, near-city, urban background, kerbside, industrial). Chemical mass closure cannot be achieved at many sites because not all of the main constituents of PM were measured. This is limiting the possibility of checking data quality. There is also a dramatic lack of particle number information mainly for Southern and Central Europe, that is critical for assessing the possible role of ultrafine particles in aerosol health effects. In spite of these limitations, this compilation provides elements to answer the question: “What is hidden behind equal PM_{10} mass concentrations at various site types across Europe”.

The COST633 aerosol data compilation is to be published as a stand-alone report by the European Communities (2008). Main conclusions include:

1. At a given PM_{10} mass concentration, $PM_{2.5}$ concentrations range within a factor close to 2 across Europe, even if sites of the same type (e.g. rural, urban background,…) in the same geographical sector (e.g. Central Europe) are considered. However, PM_{10} and $PM_{2.5}$ are generally correlated at each site, with a few noticeable exceptions though (some kerbside sites and frequently desert dust-impacted sites).

2. PM_{10} and $PM_{2.5}$ chemical composition may be significantly different or may be similar, mainly depending on site locations. Mineral dust and sea salt, which are major constituents of PM_{10} at sites where sea spray and soil dust transport or suspension are important PM sources, make a minor contribution to $PM_{2.5}$. Total carbon (TC) and SO_4^{2-} account for a systematically larger fraction of $PM_{2.5}$ than PM_{10}, but this is not so for NO_3^-.

3. Both PM_{10} and $PM_{2.5}$ chemical composition change when moving from a rural to a kerbside site and from North-Western to Southern to Central Europe. The most obvious gradient regards the TC / PM ratio, which increases from North-Western to Southern to Central Europe. We also observe that on average TC / PM_{10} increases when going from rural to urban background to kerbside sites in all sectors in Europe. In contrast, secondary inorganic SO_4^{2-} and NO_3^- contributions to PM_{10} generally decrease when moving from rural to near-city to urban background to kerbside sites.

4. Both total and ultrafine particle number concentrations can differ by an order of magnitude at a given PM mass concentration when moving from rural or near-city sites to urban background or kerbside sites. The significance of this comparison may be weakened by the fact that these sites are not all located in the same geographical sector of Europe though. At similar sites (e.g. urban background, North-Western Europe), particle number concentrations can still differ by a factor of 2 at a given PM_{10} mass concentration. In contrast, total and ultrafine particle number concentrations are very similar when equal $PM_{2.5}$ concentrations are observed at a rural site in Finland and a near-city site in Italy.

5. At most COST633 sites, both total particle number and ultrafine particle number concentrations broadly increase with PM_{10}, although often not systematically. This relationship is not clear at sites where $PM_{2.5}$ was measured, especially for ultrafine particles. At all sites, the ratio ultrafine / total particle number tends to decrease when PM mass concentrations increase.

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Van Dingenen, et al., A European aerosol phenomenology–1: physical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, *Atmos. Environ.*, 38, 2561-2577, 2004.

V.2 Temporal Trends of in Black Smoke (BS) in Europe

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1. Introduction

One of the tasks of WG 1 was to investigate time series of black carbon (BC) or elemental carbon (EC) in Europe. To date, no long term data sets exist for these parameters in Europe, as they were measured in the past only in more or less intensive measurement campaigns of rather short duration, but not on a long-term basis. Working group 1 of COST Action 633 collected sets of EC or BC data from Action members to be added to the COST 633 data base set up by Jean-Philippe Putaud at the JRC Ispra. The report on this data base is given in section V.1 of this final report. "Black Smoke" (BS), however, has been measured for several decades in some air quality networks because it was easier to measure than total suspended particulate (TSP) concentrations. In later years, the link between BS and TSP was found to be insufficient, and some countries abandoned BS measurements in favour of more direct PM10 measurements with filter samplers, TEOMs or Beta-gauges. BS has been found, however, to be closely linked to the BC or EC concentration, as the method actually is based on a measure of the blackness of deposited aerosol samples, which is in turn caused mainly by BC in the aerosol. From an epidemiological point of view, BS is important because it better reflects combustion aerosols than PM2.5 and is still used in health effect studies (e. g. the APHEA study, Atkinson et al., 2001; or a study in the Netherlands, Fischer et al., 2008).

In this report, we present the results of an investigation of long-term trends and geographical similarities or dissimilarities of BC concentrations derived from measured BS data, which were either provided by individual members of our Action or obtained from AirBase. In some cases, Action members suggested links to BS data bases in their countries or contact addresses to possible data providers. We show here only a selection of the analyzed data and concentrate on common features and also some dis-similarities in the data sets. A full set of plots of BC derived from long term BS data is given in Appendix I, Part B. Although AirBase (http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1029) and some individual data sets also contain data on PM10, the focus here is solely on BS data.

2. Conversion of BS to BC concentrations

BC and EC refer to the optically absorbing (BC) and thermally refractive (EC) particles which are produced by incomplete combustion of carbonaceous material. The distinction between these parameters is purely operational and only based on the measurement techniques. BC and EC are suspected to cause adverse health effects, so time series of BC or EC could provide interesting information also for retrospective studies. As neither BC nor EC were measured on a continuous long term basis, a proxy for BC is needed. One possible proxy could be Black Smoke (BS) which has been measured for many years in several European countries. At the time the measurements were started, BS was actually used as a proxy for total suspended particulates (TSP), because it was much easier to measure filter reflectance than weighing the mass of filter deposits in reasonable time with adequate precision. The reflectance (or blackness) of the filters was converted to a mass concentration of TSP using a calibration curve (e. g. Coulson, McK. Ellison 1963) and given as mass concentration of "black smoke" BS.

Several studies investigated the relationship between BS and TSP or BS and EC or BC (e. g. Hoek et al., 1997; Muir and Laxen, 1995; Roemer and van Wijnen, 2001). Arguments were found both in favour and against using BS as a proxy for either parameter. Ten Brink (2009) found a very good agreement between BS and BC measured in several campaigns in Europe. In their recent study of BS and EC in the Netherlands, Schaap and van der Gon (2007) showed that BS is quite a good indicator for EC if a site-specific calibration curve is used. Two calibration curves are given for urban and rural sites, respectively, which were used also in this report. Of course this is only one possible conversion, and there are discussions whether BS can be taken as a proxy for BC; and, if so, which conversion factors to use, but here we take the pragmatic approach and simply show what is available and how the BS data would translate to BC concentrations under the assumption that the regression lines given by Schaap and van der Gon (2007) can be applied and have not changed over time with the changing BC source characteristics.

The conversion relations given by Schaap and van der Gon (2007) are (both BC and BS concentrations in units of $\mu g/m^3$):

Urban: $BC = 0.088 * BS + 0.32$
Rural: $BC = 0.056 * BS + 0.16$

The converted data in this report are discussed in terms of BC and not EC following the current nomenclature of using the term BC, although strictly speaking Schaap and van der Gon (2007) compared BS to EC measured with the Sunset Laboratory method (Birch and Cary, 1996). As there are still large uncertainties in comparing EC or BC concentrations measured with different techniques (for Europe see e. g. the studies by Schmid et al. 2001, ten Brink et al. 2004, Hitzenberger et al., 2006 and Reisinger et al., 2008), the BC concentrations shown in this report are only indications of what the "real" concentrations might have been.

3. Available data and available long-term data sets

For this investigation in temporal trends of Black Smoke (BS) in Europe, we used mainly the publicly available data from AirBase (European Environmental Agency) and data either provided by members of the Action, or data from other providers suggested by members of the Action. In some cases we could not access BS data as they were not available in electronic form. In the data analyses, common problems were incomplete data sets, data sets spanning just a few years, too few stations of similar type in some countries, and incomplete geographical coverage.

Table I gives an overview over the data analysed for this report. In most cases, the available data were hourly averages, which had to be converted to annual averages.

Table 1: Number of stations with BS data per country, station type and time span of data sets. Only the long term data sets used in this report are included.

Country	Total	Urban	Suburban	Rural	Years
Belgium	28	10	18	0	1990-2005
Denmark	7	7	0	0	1967-2002
United Kingdom	96	41	32	23	1961-2005
England	30	16	14	0	1961-2005
Northern Ireland	6	4	2	0	1961-2005
Scotland	28	9	12	7	1961-2005
Wales	32	12	4	16	1962-2001
France	14	14	0	0	1976-1990
Greece	4	4	0	0	1984-2004
Ireland	9	6	2	1	1973-1996
Macedonia	25	19	6	0	1997-2005
Netherlands	22	13	1	8	1964-2005
Poland	5	5	0	0	1997-2003
Portugal	6	5	1	0	1986-1991
Sweden	11	7	1	3	1997-2004
Spain	17	10	3	4	1986-2003
Slovenia	35	33	2	0	1968-2002
Finland (blackness of TSP-filters)	1	1	0	0	1992-1996

Figure 1 gives an overview of the geographical location of all stations with data sets either publicly available or provided by members of the Action.

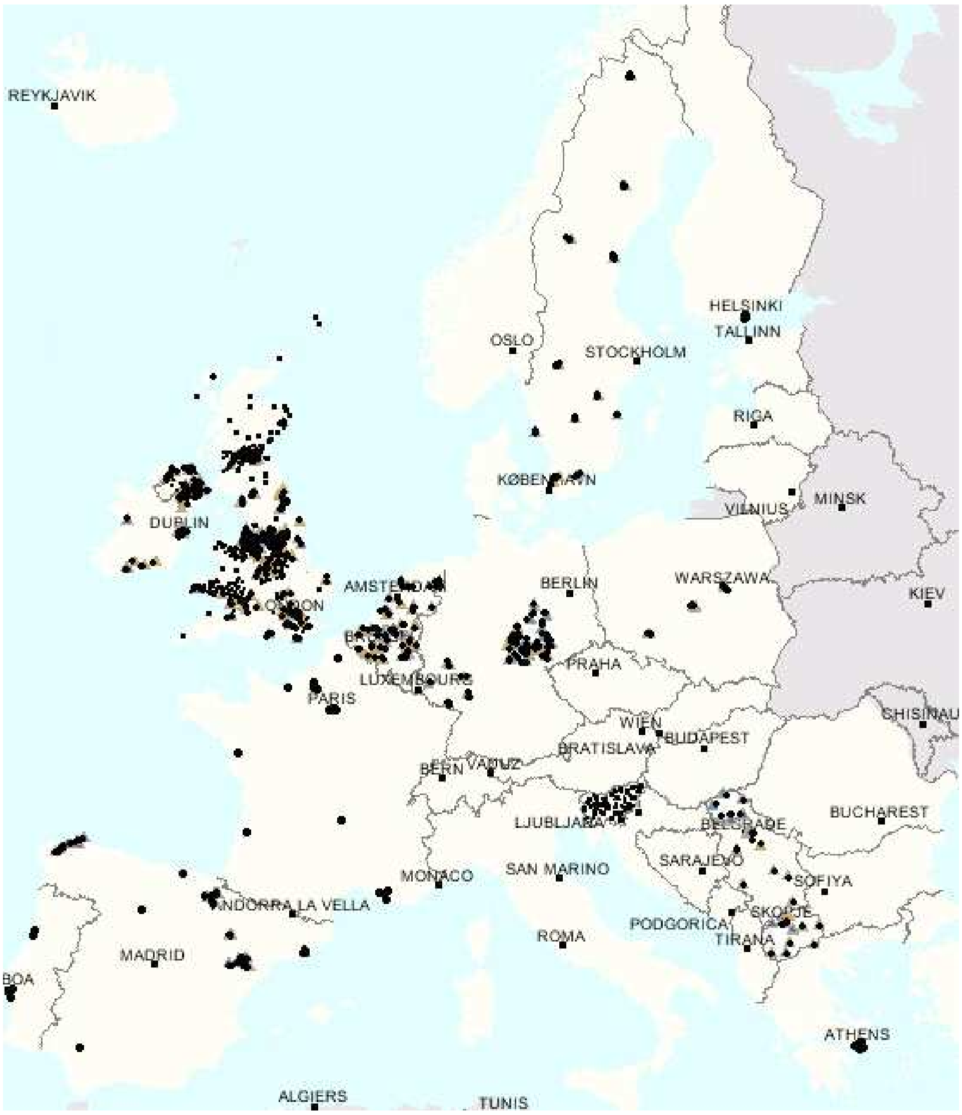


Figure 1: Stations with BS measurements available for this report. Green: 1969-1978, red: 1979 – 1988, orange: 1989 – 1998, black: 1999 - 2006

As can be seen, the geographical coverage is quite patchy. Most BS stations are in the UK, in Ireland, the Benelux states, Slovenia and Germany. In some countries, BS either was not measured or we did not find access to possible data sets. Most stations, unfortunately, have only rather short data series. Figure 2 shows the stations with long term (i. e. at least 5 year) data sets that were used in this report. These stations range from urban (kerbside) to remote background locations.

Figure 2: Geographical location of stations with fairly long-term data sets.

4. Results

The longest continuous data sets are available for Denmark (one station has measurements from 1967 – 2002), Slovenia (1968 – 2002) and the UK (1969 – 2005). Figure 3 shows these three data sets (all for urban stations).

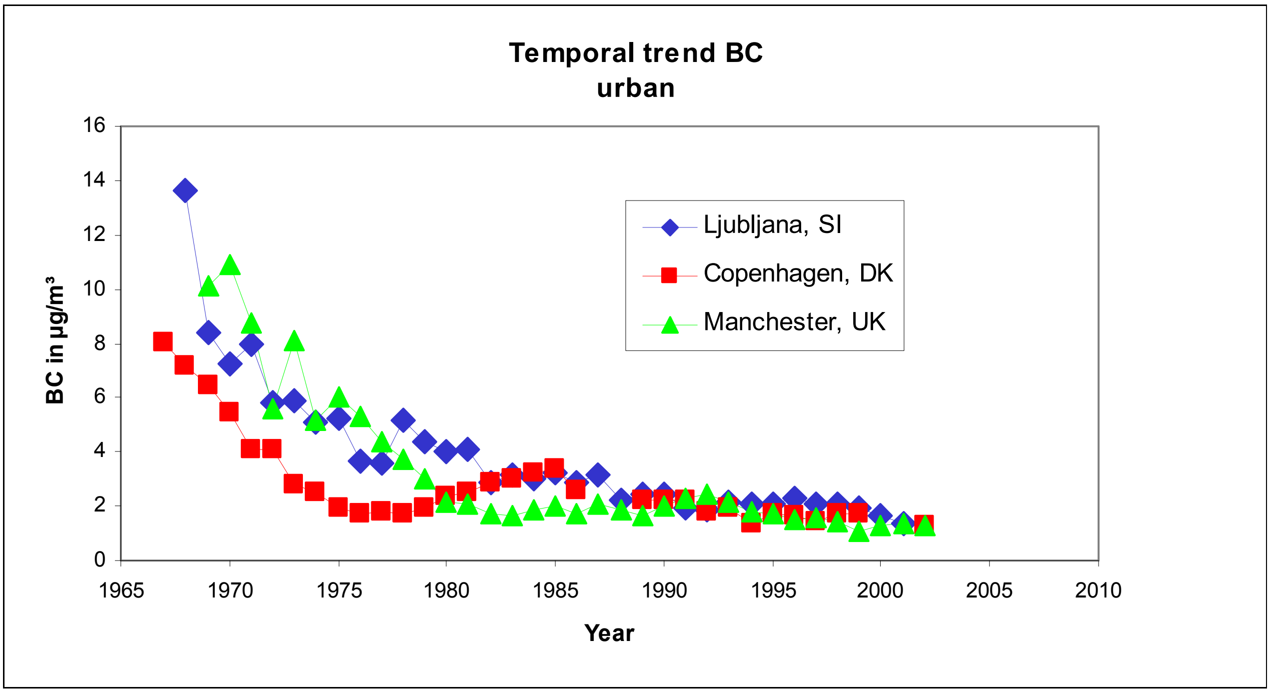


Figure 3: Comparison of three longest data sets (all stations: urban). BC concentrations are given in µg/m³. The values are all annual averages. The Manchester data are from AirBase (© EEA, Copenhagen, http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1029). The data for Copenhagen were obtained from the Environmental Protection Agency for the City of Copenhagen, http://www.miljoe.kk.dk/94d9a7a1-6f48-4c72-9c51-f3bc4f5bec4d.W5Doc

At all stations, concentrations were quite high at the start of the measurements. In Ljubljana and Manchester, the decrease in BC was fairly monotonic, while in Copenhagen concentrations had a local minimum in the mid-seventies (annual average concentration of 1.73 µg/m³), a value that was reached again twenty years later. In the mid-eighties, concentrations had a local maximum (3.4 µg/m³).

The general decrease of BC (and TSP, not shown) with time is seen at practically all stations, and some also show the local minimum in the mid-seventies. This minimum might be linked to the first oil crisis in 1973, after which consumption increased again. As concentrations measured at individual stations are also subject to changing local emission patterns, interpretations for single stations, however, are difficult without further local information. In later years, pollution control measures led to a Europe-wide reduction in emissions. BC emissions, e. g. decreased by a factor of about 7 in the years from 1960 to 2000 (Novakov and Hansen, 2004).

The Denmark data are from one station only, because only this station had the long time series. The long term data and the data obtained from AirBase, however (Figure 4) agree very well. This figure also gives an example of the pitfalls of having only short data sets. If only the Airbase data were considered, which span from 1976 to 1982, an increase of BC concentrations would be deduced. In reality, these data sets started within the minimum in the mid-seventies and stopped before concentrations decreased again in the mid-eighties. If the long-term data set is considered, a marked decrease of concentrations is seen from the mid-sixties till the mid-seventies with a levelling-off after the secondary maximum in the mid-eighties.

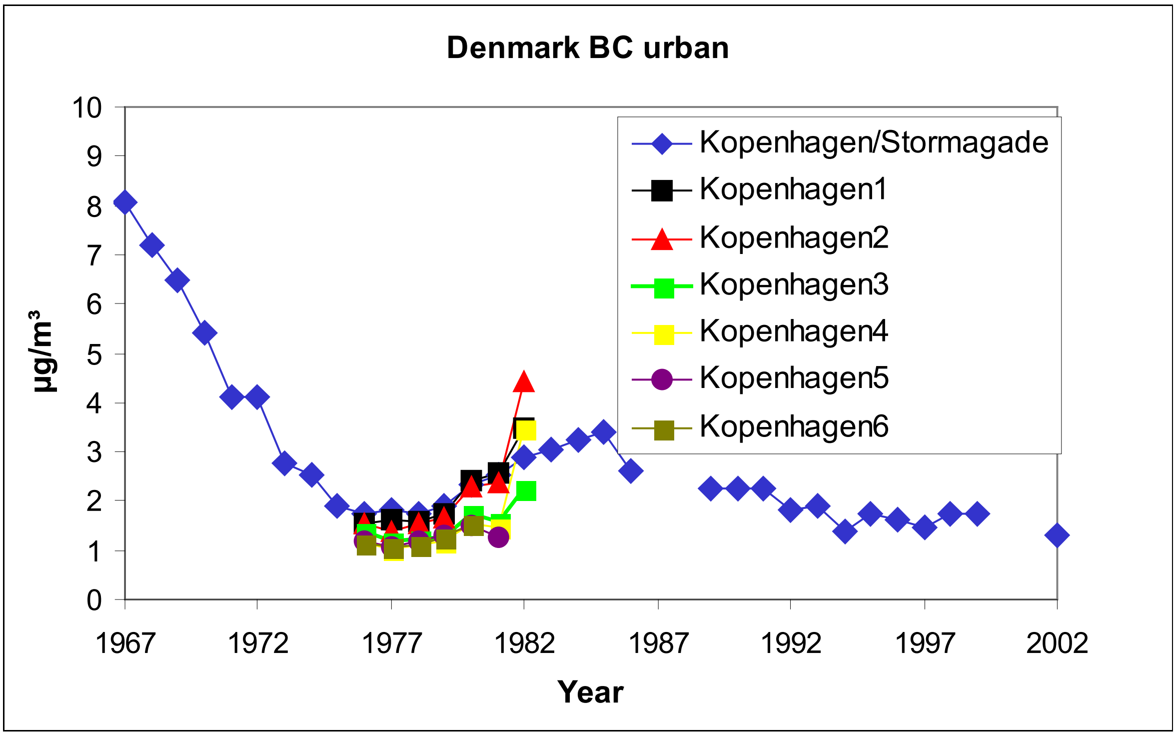


Figure 4: Temporal trends of BC in Copenhagen. Blue: obtained from the Environmental Protection Agency for the City of Copenhagen, http://www.miljoe.kk.dk/94d9a7a1-6f48-4c72-9c51-f3bc4f5bec4d.W5Doc; all others: AirBase (© EEA, Copenhagen, http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1029).

In general, practically all data sets show the decrease of BC with time. Figure 5 shows data collected in the UK at several stations from the late sixties nearly up to present. Figure 5a contains data collected at urban stations and Figure 5b data collected at background stations. Concentrations at the beginning of the measurements were generally quite high (around 10 µg/m³) but decreased rapidly at both urban and background stations. The UK stations are roughly comparable in terms of concentration to the Copenhagen and Ljubljana stations.

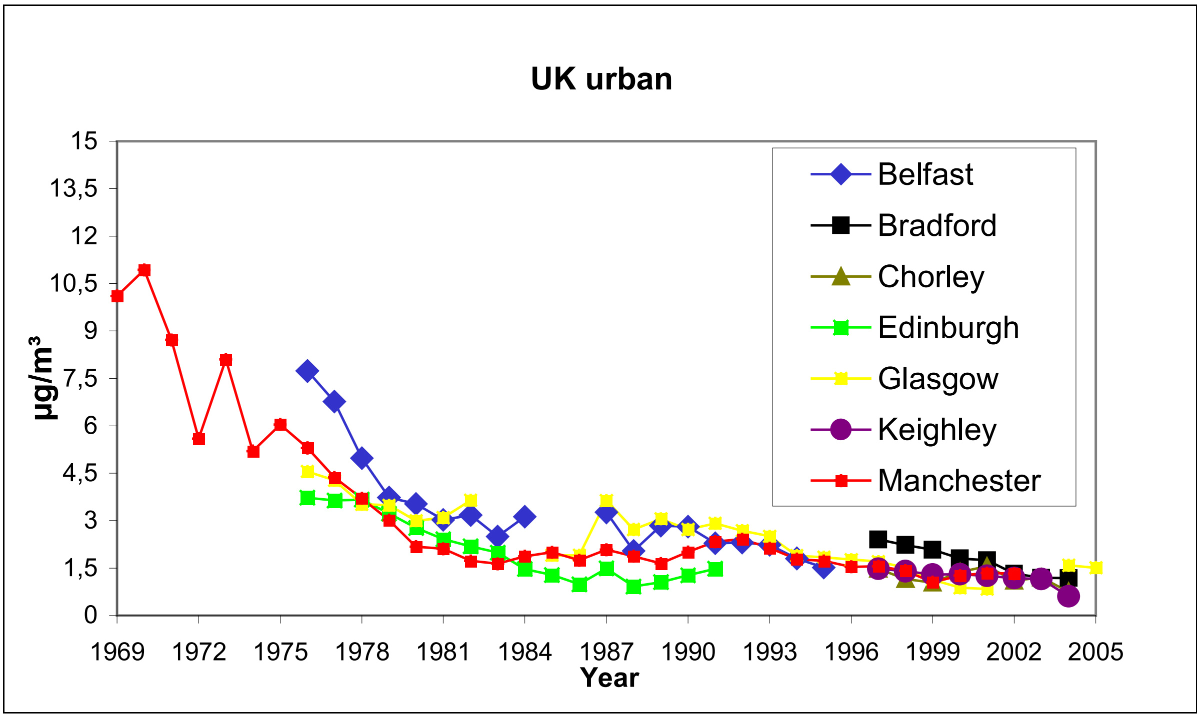
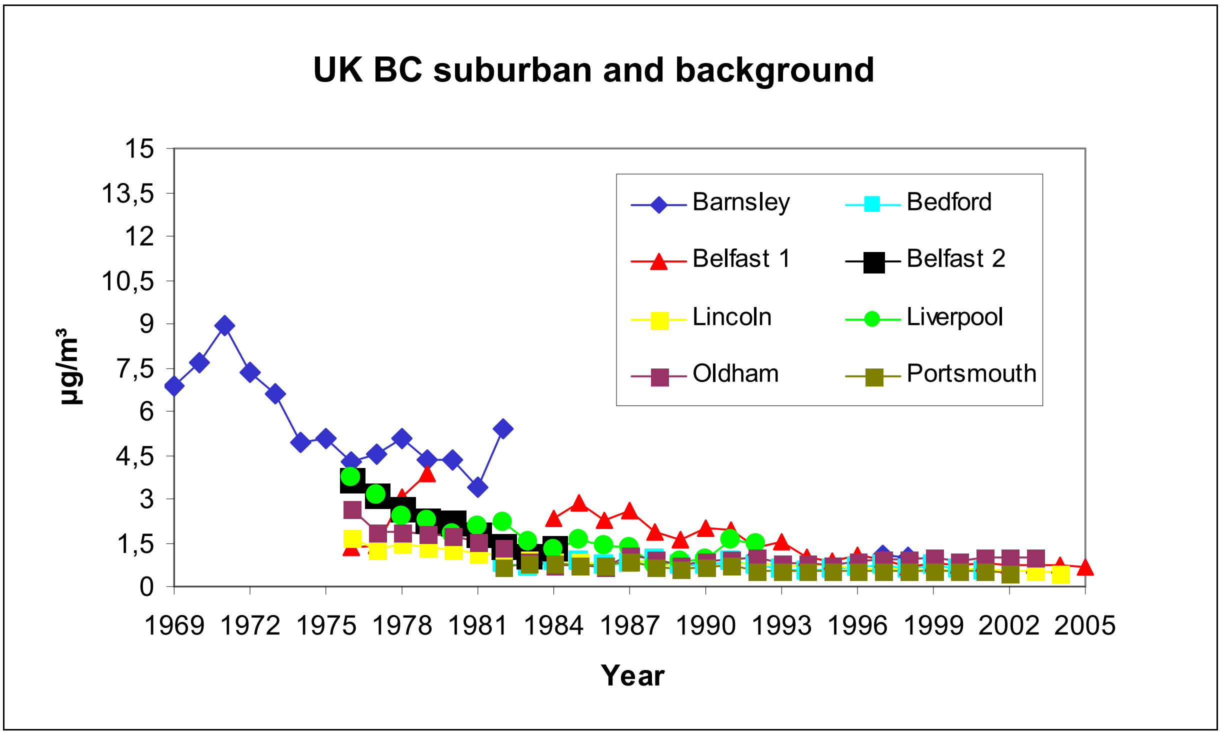


Figure 5a (above): Temporal trend of BC obtained from BS data measured at urban stations in the UK.

Figure 5b (below): same as 5a; background stations. All data inn Figure 5a and 5b were obtained from AirBase (© EEA, Copenhagen, http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1029)



The highest BC concentrations of all cities were measured in Athens (Figure 6), while the lowest BC concentrations were found in Sweden. Urban concentrations in Sweden (data set only 1997 – 2004) are below 1 µg/m³, while background concentrations are even lower. The data set from Athens starts only in the mid-eighties, at a time when BC concentrations in urban Manchester, e. g. were around 2 µg/m² and in Copenhagen and Ljubljana around 3 µg/m³. Although the situation improved in later years, BC concentrations in Athens are still as high as they were in e. g. rural England in the late sixties or in Manchester in the mid-eighties. As all these data are annual averages, concentrations on individual days will exceed these (high) average concentrations by far.

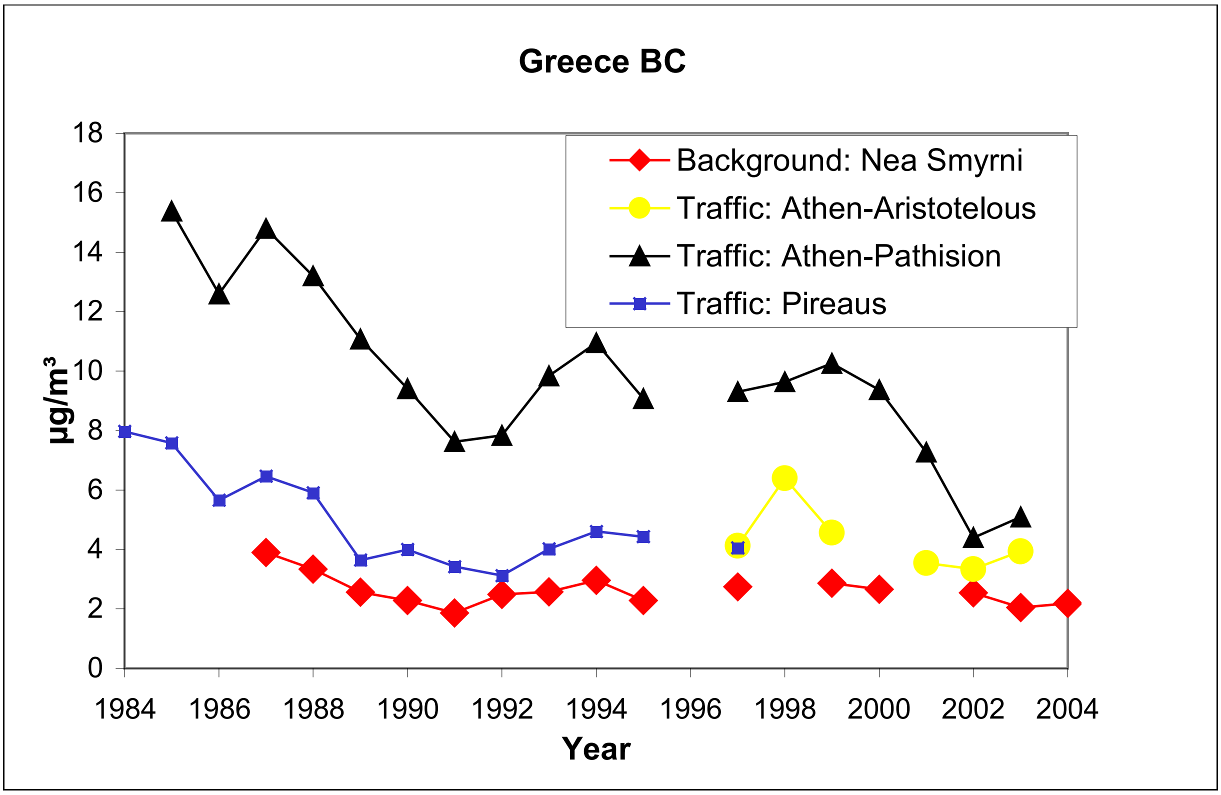


Figure 6: BC obtained from BS in Athens and at a background station (all stations: AirBase, © EEA, Copenhagen, http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1029).

Only few stations show different trends. In Macedonia, e. g., background stations show a reduction in concentration (data set 1990 – 2005), while at some urban and industrial stations concentrations increased. An interesting feature is also seen in Figure 7 in the data from the Netherlands. The general trend of decreasing concentrations in the left part of the figure is superimposed by spikes at two stations and increasing concentrations in the long data set obtained at Schiedam. The data for the stations in Utrecht start in 1989. The traffic I station in Utrecht has very high annual averages compared to all other stations. Concentrations decrease here, too, but approach those of the other stations only after ca. 2000.

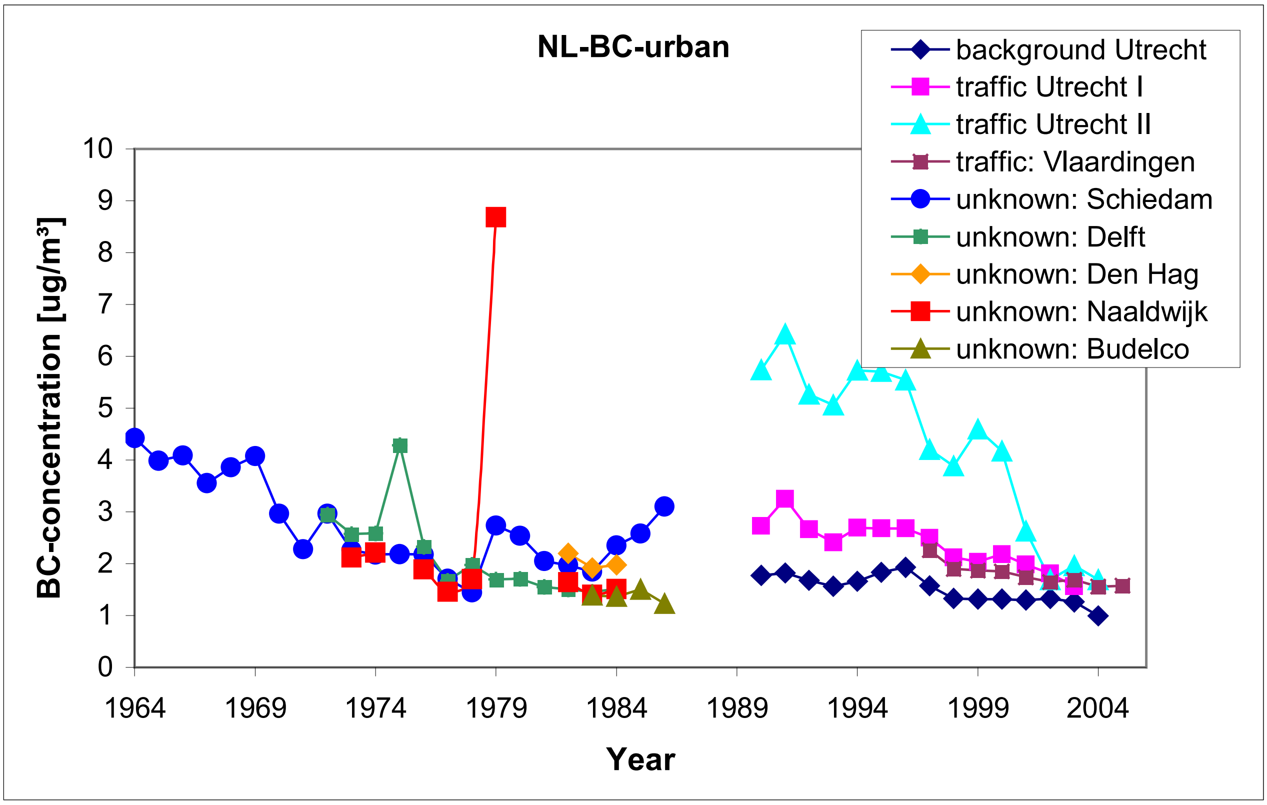


Figure 7: BC concentrations obtained from BS measurements in the Netherlands, 1964 – 2005. All data except from the sets labelled “unknown” were obtained from AirBase (© EEA, Copenhagen, http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1029).

5. Summary and conclusions

The BS data sets were quite variable both in time span and geographical coverage. In this report, all BS data were converted to BC data using the conversion relations given by Schaap and van der Gon (1997) for urban and background sites in the Netherlands. This conversion quite certainly depends on the total aerosol situation as well as on the local (and temporal) source characteristics for BC, but as no long-term data sets of directly measured EC or BC are available, BS is the only way of obtaining at least estimates for the earlier BC or EC situation in Europe.

In order to track general long-term trends of BC concentrations in Europe, only the longest data sets are useful. Among the available data sets, BS data from Denmark, Great Britain, the Netherlands and Slowenia span from the early to mid sixties up till today. As trends at the other stations follow the general trend seen in the data from the long term stations in those years where measurements were made, one might be tempted to extrapolate these data sets also for the years where no data exist. This should be done with extreme care, however, as there are some stations where the trends do not follow the general trend, e. g. because of changed industrial activities or changes in local emission patterns.

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V.3 Selected Aspects of Chemical and Physical Sampling Artefacts

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1. Introduction

The atmospheric aerosol is a multi-phase system containing condensed particles of different size and different composition, and gas phase material.

Under ordinary atmospheric conditions part of the PM is rather non-volatile because of low equilibrium vapour pressures. Examples are elemental carbon, some salts (sulphates, sodium chloride), also oxides of metals. Other species are semi-volatile, e.g. ammonium nitrate and many organic species and they are found in both the vapour and the aerosol phase, in variable proportions depending on temperatures and pressures. Gas-to-particle partitions lend for modelling by thermodynamic equilibrium, as has been shown for the nitrate and others. Other semi-volatile species, especially the organics, are still under investigation, mainly because of lacking speciation and thermodynamic data. It must be mentioned that semi-volatiles, and volatiles, can absorb on porous structures of particles and deposits of particles, and may dissolve in a liquid phase. Both absorption and dissolution make thermodynamic modelling rather complex.

Sampling, the process of selecting and analysing particles, is a necessary step when monitoring and characterising the atmospheric aerosol. It may be pointed out that sampling reduces the information on the aerosol almost inevitably. Even a perfect sample which would preserve the ambient state of the aerosol before analysis stands for only part of a much larger population. The statistical problem what a sample is representative for is not easily answered. At a site the concentrations of the aerosol usually undergo substantial variations. Main reasons are short-term fluctuations generated by incomplete mixing of ground based emissions with the air shed to a sampling site and of aerosols formed in the atmosphere, and long-term trends of a background aerosol. Practically PM concentrations at a site are often reported as averages over space and time. These averages are useful in many regards. However they are certainly not necessarily representative for all purposes, e.g. personal exposure, because of the fluctuations of the aerosol concentrations. In addition, the partitioning of volatile species is subject to continuous variations due to the temporal and spatial changes of atmospheric conditions.

In terms of physical and chemical properties, a sample usually does not perfectly represent the air borne state of an aerosol. Already the aggregation of particles on a substrate or a filter destroys the identity of the individual particle. When collecting PM over extended periods of time, evaporation and condensation of volatiles and semi-volatiles change the composition of the deposits. Furthermore, chemical reactions in PM deposits contribute to the transformation of the PM material or can also generate new material which had not been carried into the sample on air borne particles. Analytical procedures may also cause transformations of part of the aerosol material.

Artefacts can be regarded as systematic errors, caused by a sampling procedure, by a transformation of a sample during extended sampling periods and by an analytical process. In this sense artefacts are not being reduced by increasing the precision of an instrument. Instead, they affect the accuracy of the sampling method.

Artefact formation is well known. The situation has been laid out recently to quite some extent in a WHO report on guide lines for concentration and exposure-response measurement of PM (WHO, 2002). (Another WHO report on guide lines on monitoring ambient air quality (WHO, 1999) focus on "strategies and methods for providing information on ambient air quality that is adequate for health impact assessment"; these guidelines do not provide a detailed discussions of sampling problems.) An extremely brief, but rather acceptable summary of the WHO (2002) report concerning the artefacts is this: Sampling procedures must be directed towards unambiguous measurements of aerosol parameters, e.g. mass or number concentration; artefacts should be reduced to a minimum when they can not be avoided. Another option is this: Artefacts can be tolerated in as much as they do not disturb, deteriorate or destroy relations among aerosol parameters and relations to other systems. In this sense it is evident that the individuality of an aerosol particle is meaningless when going for the average mass of the aerosol. But it is not self understanding that regional back ground aerosols do exhibit a high degree of correlation even on a short time basis, (Berner et al., 2004), with short interruptions indicating a change of the weather situation.

Are there reasons to deal with artefacts in more detail? In the preparation of the COST 633 action the idea had been promoted to look into the physical and chemical differences of the atmospheric aerosol over Europe. Meanwhile looking into the similarities of these aerosols became another point of view. The scopes do not seriously differ however, because the understanding of similarities covers also the understanding of differences, and vice versa. Regional heterogeneities of the atmospheric aerosol must exist due to the different climatic and geographic conditions involved in the formation of the European aerosols, and the sampling. This becomes even more important anticipating the influence of climate change on the ambient aerosol. Meanwhile it became known that health effects of ambient PM exhibit heterogeneities over Europe. This result certainly calls for research focussed on heterogeneities of the ambient aerosol, also in its evolution, because the differences in the aerosols would be part in the explanation of heterogeneous health effects. This involves also a closer look on artefacts, because of two postulates: their dependence on climatic and geographic factors, and their relation to the reactivity of atmospheric aerosol material and its products during sampling.

Scientists are always confronted with artefacts and must be aware of them. Surprising results may occur at any time. An example is the measuring of the coarse fraction, PM(10-2.5), by the difference of two TEOMs, a TEOM PM_{10} and a TEOM $PM_{2.5}$ operated simultaneously side by side: The PM(10-2.5) signal may become negative (Berner, 2003). This must occur when both PM_{10} and $PM_{2.5}$ are close to the detection limits of either or both instruments. Sporadically however, the PM(10-2.5) signal becomes highly negative for hours. The problems are: Were both instruments wrong? If not, which one of the TEOMs went off and for what reasons? Can the malfunction be recognised in the data set of a single instrument? Another example is a recent comparison of two low-pressure cascade impactors, a Berner LPI and a Dekati LPI (Wang et al., 2007). The collection efficiencies of the impactors differ systematically by large factors. The explanations given so far, that these differences are caused by the slip correction factors, are absolutely dissatisfactory. Due to a lack of reported data it is pure speculation though to suggest this artefact reflects differences in the design of the impactors and consequently in the evolution of the specific aerosols inside the impactors.

Systematic investigations into artefacts have been started about two decades ago and it is worthwhile to take a look into recent research.

- The problem of monitoring nitrates in atmospheric PM, well known since the eighties of the twentieth century, has been repeatedly addressed in the recent literature.
- Semi-volatiles in PM are another matter of quite some concern, as reported by WHO (WHO, 2002). This work which is still going on as demonstrated by Eatough's and others' work (e.g. Eatough et al., 2003) can be seen as an approach to aerosol mass closure in geographically and climatically different regions in the US.
- The formation of new aerosol material when diluting emissions from stationary sources is another topic. The sampling methods have been very successfully refined as to suppress the formation of new or intermediate PM during a sampling process when dilution is involved. (England et al., 2007a; England et al., 2007b). Bringing such emissions to a close-to-atmospheric state allows these sources to be handled in source apportionment models.
- In this regard the comprehensive and on-going work on real-world emissions from mobile sources must also be mentioned. There is quite a progress, but this work is certainly far from being completed.
- There is only little material on formation and transformation of aerosol material in deposits of ambient aerosols.

2. Aspects of chemical artefacts

Problems of transformation and formation in deposits of PM are obviously not in the scope of research, according to the lack of discussions in the WHO report (WHO, 2002). This includes artefact formation by absorption on substrates and on particulate deposits. There are substantial indications however, that such reactions are important, at least for some species of the atmospheric aerosol. Organic matter in aerosol deposits is far from being completely oxidised and is therefore reactive.

2.1 Absorption

Filters and deposits of particles on substrates possess a large number of "pores", not only cavities in a solid or liquid medium, but also contact sites formed by crossed fibres, by particles on fibres, and by particles on particles. These pores have quite different sizes and shapes. Substances with suitable properties, e.g. the ability to adhere to other material, build monomolecular layers and films on a substrate (physi-adsorption, chemi-adsorption) and form liquid phases when the absorbed material, the adsorbate, is filling up the pores (capillary condensation).

For water the pores must be small, 100 nm by diameter and less, in order to produce a considerable reduction of water vapour pressure (see section 3 – capillary condensation). This explains that glass fibre filters do not evaporate all of adsorbed water even at reduced ambient relative humidity. They will always retain some liquid when the pores are fine enough.

The molecules adsorbed and condensed in a porous medium can be replaced by the molecules of another kind when these adhere better to the substrate. Consequently related parameters, e.g. the interface tension and the capillary forces, become only stronger. When imbedded in a new medium a porous particle hold together by absorption does probably not disintegrate: Either new molecules enter the pores replacing the former ones in the course of time, thereby strengthening the coherence, or the new medium, as not being absorbed, leaves the particle unchanged. It would need chemical reactions to take the agglomerate apart. (In the course of aging, agglomerates may change their shape and become more spherical.)

The atmospheric aerosol contains ultra fine particles with porous structures. Already the very first particles formed in combustion may be porous. Due to their high number concentrations these primary particles coagulate rapidly. They form particles with modal diameters of about 10 nm to 20 nm (nucleation mode) and contribute to the Aitken mode particles in the 100 nm size range. These ultra fine particles of the ambient aerosol contain absorbed material. The particles may get into the circulations and metabolisms of a biological system. The questions are:

- Do these particles preserve their identity?
- Do these particles exchange and release their absorbed matter in the new system?
- Are the particles sequestered somewhere in the biological system?

Absorption plays another role. In chemi-adsorption the adsorbent may change the structure of the adsorbed molecule; when the adsorbent is electrically conductive it may enhance chemical reactions among the adsorbates (catalysis).

2.2 Formation of PM constituents on concentrated electrolytic solutions

2.2.1. Formation of sulphate

About three decades ago sulphate artefacts became a matter of some concern. Artefacts have been reviewed by Pankow (1987) already. As has been pointed out by Appel (Appel, 1993), positive sulphate artefacts were recognised when sampling atmospheric aerosol on glass fibre filters. Bearing in mind the absorption of water on filters, it is understandable that at least part of this sulphate was formed on the filter matrix. There are two aspects: The freshly formed sulphate would increase the amount of PM on the filter. It also increases the volume of the active medium. Due to Raoult's law more water goes to the filter, because the system is in equilibrium with ambient relative humidity (self dilution). Moreover this formation of sulphate, when continuous, occurs at relative humidity below 100%, that is, in rather concentrated solutions.

Also deposits of ambient aerosols may well contribute to the formation of sulphate or other new PM material which had not been carried into the sample by the particles. Deposits of the accumulation mode aerosol, and also sea salt aerosols, contain quite some amount of acids and their salts. Depending on relative humidity, this material undergoes deliquescence and takes up a certain amount of water according to Raoult's law. At low relative humidity this material may not readily form crystals, but might stay liquid, supersaturated however and preserving part of its water even below the point of deliquescence. It is the question whether highly concentrated solutions of salts, as found in the deposits of ambient aerosols, contribute to the formation of sulphate at relative humidity as found in haze and under dryer conditions. This is in some contrast to reactions in aqueous solutions as met in fog and cloud. Such aqueous phase reactions play a role in the oxidation of atmospheric pollutants, as has been reviewed recently (Blando and Turpin, 2000).

There may be other implications which are rather unexplored though. Material formed in concentrated solutions of salts, on airborne particles or in deposits, may change composition when being diluted with water, e.g. in the lung or in an analytic procedure.

The role of concentrated solutions of salts in the formation of sulphates has been investigated recently in some detail. In a specific reactor salt mixtures simulating isolated deposition spots as in an impactor were exposed to a humidified gas with traces of SO_2 (Turšič et al., 2003a; Turšič et al., 2003b). The samples were prepared on Tedlar substrates in order to prevent or suppress reactions of the gases with the substrate. The experiments demonstrated the formation of sulphate in the presence of Mn on NaCl and on $NaNO_3$ at relative humidity above 75%. The reactions were enhanced by NH_3. During introduction of a gas mixture containing $[SO_2] = 2$ ppm and $[NH_3] = 1$ ppm measurable concentration of sulphate (above limit of quantification) was formed in about 1.5 hours at a relative humidity of 80% and in about 15 minutes at a relative humidity of 90%. First results on the reactivity of ambient aerosol samples were presented at the EAC 2004 (Turšič et al., 2004).

For salts at 80% r.h. exposed to a gas mixture of $[SO_2] = 2$ ppm and $[NH_3] = 1$ ppm at 80% r.h. the production rate of sulphate is 1 % h^{-1}. This means that 1% of gaseous phase SO_2 was transformed into sulphate or that at these conditions about 10 μg of sulphate was formed. In general, oxidation of dissolved SO_2 in cloud water can be done by ozone, hydroperoxide, OH radicals and catalytic reactions involving ions of transition metals. According to Warneck (1999) the most effective oxidant in aqueous phase processes is H_2O_2. Therefore, the studies of transformation of SO_2 in the work of Turšič et al. (2004) represents only one reaction pathway. However, current concentrations of ambient SO_2 are in the range of a few ppb and therefore we assume that the amount of sulphate formed at higher humidity can become significant after rather long sampling periods (e. g. several days).

When sampling ambient aerosols, particles containing aqueous solutions are deposited and sulphate is formed at the same time. The concentration and composition of the ambient aerosol may be constant over a sampling period. In the aerosol, sulphate may contribute a quarter to the water soluble substances, by the mol. With the reaction rate given above ($[SO_2] = 2$ ppm and $[NH_3] = 1$ ppm), an increase of sulphate by 20% is reached in about 3 hours. However, as ambient SO_2 concentrations are much lower than those used in our experiments, a significant sulphate production is not expected for sampling times of several hours.

The experiments demonstrate and suggest the following:

- Transformation of atmospheric trace gases to aerosol material does occur on concentrated solutions of salt above 80% r.h., as has been shown for SO_2/H_2O and $SO_2/NH_3/H_2O$ systems.
- It is not clear as yet whether these reactions are taking place inside the salt solutions or on the surface. When taking place on the surface, the reactions may become much more effective for the airborne aerosols due to their higher specific surface, even at low relative humidity close to a point of deliquescence. (Discussions of respective scenarios are beyond the scope of this report.)
- For ambient aerosols the excess of sulphate formed on the sample can increase to measurable levels after 24h and 48h sampling periods, depending on reactions rates and the amounts of water soluble material.
- These sampling artefacts do not necessarily disturb relations among aerosol parameters, as has been pointed out above.
- In general, other reactions on concentrated solutions of salt may contribute to the formation and transformation of PM, possibly the water soluble organics.

2.2.2 Formation of dicarboxylic PM on deposits

In 2000 Kerminen et al. (2000) reported remarkable data on dicarboxylic acids in the atmospheric aerosol. These aerosols were sampled size-segregated with an 11-stage BLPI low-pressure cascade impactor with seven stages below 1.8 µm, and with a two-stage virtual impactor with a cut at 2.3 µm. The impactors were set up inside a warmed cabin at temperatures around 25°C in summer and in winter. Sampling times were 234h for VI and 24h or 48h for the BLPI.

The comparison of concentrations of mass and compounds during summer and “off-summer” indicates the formation of PM on the deposits. “Off-summer” is the time after and/or outside July and August. The data are represented in the Table 1 (after Kerminen et al., 2000).

Table 1. The VI to BLPI concentration ratio (average ± standard deviation) for fine-particle mass and ions at Sites 1 and 2. Samples collected during the summer (June-August) are separated from those collected outside the summer season. The number of samples used in the comparison is given in parenthesis.

VI/BLPI	Mass	Na^+	$SO_4^=$	MSA^-	$Ox^=$	$Mal^=$	$Suc^=$
Site 1 (urban)							
summer (6)	1.06±0.16	1.16±0.26	1.25±0.10	1.37±0,08	1.60±0.18	2.11±0.56	1.20±0.51
off-summer (7)	1.07±0.10	1.23±0.10	1.07±0.06	1.12±0,14	1.60±0.42	2.90±1.63	1.42±0.79
Site 2 (rural)							
summer (3)	1.51±0.09	1.17±0.06	1.45±0.52	1.73±0,438	1.50±0.25	4.77±2.06	2.27±1.30
off-summer (7)	1.15±	1.29±1.14	1.13±0.05	1.08±0.20	1.58±0.65	2.79±0.57	2.09±0.96

Obviously the samples of the VI contain more material than the BLPI; the VI/BLPI ratios are all larger than unity, they depend however on the compounds. Kerminen et al. (2000) discuss a couple of reasons for the super-unity VI/BLPI ratios:

- **Analytical uncertainties** are within narrow limits.
- **Contamination** of the samples is strictly avoided.
- **Systematic differences between the sampling procedures** are probably important. As is pointed out later, the complete mixing of different aerosol modes in the VI sample, in contrast to the BLPI samples, becomes an essential systematic difference, when assuming that a reactivity of the aerosol would depend on the sources, therefore on size.
- **Wall losses** in the impactor must produce super-unity VI/BLPI ratios. They do not explain though the rather large scattering ranges of the ratios. Therefore wall losses, and their effects, are marginal.
- **Evaporation** in the instruments, especially in the low pressure stages of the BLPI impactor, can produce super-unity VI/BLPI ratios. Kerminen et al. (2000) understand that evaporation is not the main reason for the super-unity ratios. Other aspects of evaporation (see section 4) support this assumption;
- **Reactions of gaseous compounds with deposits and with the filter matrix** may explain the super-unity VI/BLPI ratios to some extent.
- Beyond these points, **Reactions in the deposited material by mixing different aerosol modes** must also be considered.

In the BLPI evaporation must occur because of the reduced pressures in the BLPI, especially the ultra fine stages of the BLPI which operate at strongly reduced pressures. The losses however would become massive only in the ultra fine aerosol. For Kerminen's BLPI impactor the total residence time of the flow is 0.38 s. A time of 0.14 s is spent in the uppermost stages (size range; 8µm-16 µm; pressures: close to ambient); in the next six stages (size range: 0.125 µm – 4 µm; pressure range: 75% - 99% of ambient pressures) the residence time is 0.22 s; in the three low pressure stages (size range: 0.03 µm – 0.07 µm; pressure range: 30% - 9% of ambient pressures) the time is 0.02 s. It is not thought that particles would loose too much material during the passage thorough the impactor.

Thermal effects must also be taken into account. In the inter-stage sections the temperature is at ambient because of the low velocities of the flow. In the aerosol jets however the temperatures drop considerably depending on the jet velocity (see section 4). Deposits are kept under a flow of cooled air, and material which had evaporated in the inter-stage sections may re-condense on particles and the cooled deposits.

This might explain that the total amounts of nitrates collected in a BLPI are in rather good agreement with the nitrates collected on a filter (Wang and John, 1988). (That impactor had a volumetric flow rate of 30 l/min, therefore shorter residence times by factor of 5/6. The size range is 0.07 µm to 16 µm; the lowest pressure is 30% of ambient.). This result is a clear indication that evaporation losses in the BLPI, of material associated with accumulation mode particles and coarse particles, are not very important. Liquid deposits, probably aqueous solutions, are often observed in the upper submicron stages of BLPI impactors. Even large amounts of water on the deposition spots may be found in these stages when collecting ambient aerosols at high relative humidity. This topic has been discussed before (Berner et al., 1998).

It is another consequence that evaporation losses, when they are to explain VI/BLPI ratios of 1.2 up to 4 or 5, would call for a rather massive mode of semi-volatiles in the ultra fine particle size range. First, such modes do not appear in the size distributions measured (see Kerminen et al., 2000). Second, due to coagulation this mode would probably not exist in the atmosphere for longer periods of time. These additional arguments support Kerminen's assumption that evaporation is probably not the main factor behind the super-unity VI/BLPI ratios.

Chemical transformation of gaseous compounds with the deposits during 24h and 48h sampling is probably a main reason for the super-unity VI/BLPI ratios. Kerminen et al. (2000) suggest that the larger specific surface of the VI deposits improves the reaction rates of gas-phase reactants. Following the results for SO_2 obtained by Turšič et al. (2004) though, the reaction rates may be rather low. This may hold also for formation of the di-carboxylates. The question is whether diffusion of gas-phase precursors to the deposits is a limiting factor for the reaction rates. When this is not the case, that is, when the reactions are slow enough as not to exhaust a reservoir of reactants replenished from the gas phase, a larger specific surface is not the cause for different VI/BLPI ratios.

The systematic difference of the sampling techniques may also be responsible for super-unity VI/BLPI ratios. In the VI particles of different origin, composition and size are lumped together; in the BLPI this mixing is rather incomplete. For the lumping to be effective, the aerosol particles must have different chemical properties, depending on size, source, and history in the atmosphere.

It is worthwhile to discuss the indication of the scattering ranges of the VI/BLPI ratios. First, the scattering can be produced by changes of reaction conditions caused by systematic differences of the instruments, including the effects of changes of external conditions like ambient relative humidity. (An example is discussed later.) Second, VI/BLPI ratios around 1.0 do not necessarily mean that the production of PM on deposits has stopped; it may tell that the conditions for forming a specific compound are equally good in both instruments.

The seasonal differences of the sulphate VI/BLPI ratios are remarkable; they are higher in summer than in off-summer. Moreover, at the urban site the scatter in the VI/BLPI ratios is smaller. This might indicate that the conditions for the formation of sulphate on deposits are more homogeneous at the urban site.

- Given the formation of sulphate on deposits of PM at relative humidity above 80% (Turšič et al., 2004), why should the VI/BLPI ratios become larger than unity? The transformation of SO_2 studied by Turšič et al. (2004) requires aqueous solutions. It seems that these solutions must contain some free water in excess of the water used in the hydration of the dissolved ions. In the BLPI stages these solutions contain less water, they are more concentrated in the BLPI than in the VI, because of increased evaporation of water under more reduced pressures. Also the ambient relative humidity controls the content of water. During a sampling period, ambient humidity undergoes diurnal variations: In the BLPI the deposits would dry earlier than in the VI, and recover later. For this reason the VI can form sulphate for longer periods of time.

- Both instruments are operated in a cabinet at 25°C. In off-summer periods the ambient temperatures are probably lower than the temperatures in summer (July and August), on average, and the samplers are warmed. Therefore the deposits tend to be dryer for longer periods of time in the off-summer seasons than in summer and produce less sulphate during sampling.
- The MSA data follow the same trend. Hypothetically, they can be interpreted in a similar way.

Considering the super-unity VI/BLPI ratios of sodium, it must be remarked that this element is not subject to chemical transformations. Most of the sodium is contained on coarse sea salt aerosols with MMDs above the cut sizes of the impactors. The instruments split this aerosol differently; due to the cut diameter at 1.8 µm the BLPI samples contains less sodium than the VI (cut size 2.3 µm). We understand that these differences have not been compensated for in the data, e.g. by including part of the material found above 1.8 µm into the BLPI deposits. Therefore the VI/BLPI ratios of sodium are larger than unity.

The VI/BLPI ratios of the di-carboxylates do not show seasonal differences, nor do they depend on the urban or rural character of the sampling site. However the di-carboxylate ratios are larger than the sulphate ratios of sulphate. There is a (weak) trend that they increase from oxalate to malonate and succinate. The scattering ranges of the VI/BLPI ratios are marginally smaller at the urban than at the rural site. What are reasons for the super-unity VI/BLPI ratios of the carboxylates and the scatter of the VI/BLPI ratios?

- Higher evaporation rates in the BLPI would increase these ratios. But evaporation is probably not the main reason, as has been discussed above.
- The role of the specific surface must be discussed in more detail than can be done here. Not only diffusion of reactants from the gas phase, but also relative humidity may control the formation rates of the di-carboxylates reactions on the deposits; this would imply that the reactions are processing in an aqueous medium with highly concentrated solutions, at relative humidity in the range below 90% (see the work of Turšič et al., 2004). Detailed lab studies on di-carboxylates are not available though. The di-carboxylates are semi-volatile; therefore they participate in the evaporation-condensation cycles.
- When these mechanisms, that is, evaporation and condensation, diffusion and relative humidity, control the amount of di-carboxylates found on the deposits right after sampling, super-unity VI/BLPI ratios can be expected, but also a large scattering depending on the efficiency of either one of the controlling mechanisms.
- When mixing of aerosols in the VI is responsible for the super-unity VI/BLPI ratios, the involved aerosol modes must have different chemical properties. The two modes contributing to the fine PM are the accumulation mode with mean diameters at about 0.6 µm and the Aitken mode with mean diameters at about 0.15 µm. The accumulation mode is an aged aerosol which mainly consists of material formed and transformed in the atmosphere. Main constituents are inorganic acids and their salts (sulphate, nitrate), secondary organics in different states of oxidation and elemental carbon. The Aitken

mode consists mainly of carbonaceous material (elemental carbon, soot, hydrocarbons) formed by incomplete combustion of fuels. Most of this material is emitted as such directly by the vehicles; in urban atmospheres the formation of Aitken mode particles by coagulation of finer particles is less important. At urban sites these particles are also rather fresh. The electronic properties must probably also be taken into account, because soot and elemental carbon, due to electric conductivity, facilitate the exchange of electrons between adsorbed molecules which are not in direct contact with each other. Catalytic effects of elemental carbon are well known and have often been addressed in the literature.

- The chemical properties of organics formed by incomplete combustion must be taken into account. It can be postulated that this material contains hydrocarbon radicals in different amounts and different composition.

2.2.3 Radicals formed by incomplete combustion of organic material

Tobacco smoke is a very good example for a product formed by pyrolysis, a special kind of incomplete combustion. In a cigarette, also in a cigar or a pipe, the finely cut and rather dry tobacco is lighted; it burns without a flame. Air is drawn through the tip and makes it glow. In the tip the oxygen is more or less completely consumed to burn a tobacco matrix which has lost most of its volatiles before. The matrix may consist mainly of char coal. The hot gas entering the cooler zone of the cigarette contains rather low levels of oxygen and low levels of water vapour. Downstream of the tip the hot gas heats the fresh tobacco, producing volatile material by thermal decomposition of the tobacco. These volatiles can not burn because of lack of oxygen and low temperature. Instead, the volatiles may condensate in the cigarette to form the smoke. In breaking chemical bonds, pyrolysis produces radicals, organic molecules with one or more unpaired electrons. These radicals can be characterised by electron resonance spectroscopy (EPR).

The gas dawn into the tobacco has low levels of oxygen and low levels of water vapour. Therefore the condensates forming in the smoke have not been in contact with these gases before leaving the cigarette. In the air, in the lung and on tissues the smoke may react with these gases. This oxidation changes the chemical composition of the smoke.

Wood smoke is also an example for an incomplete combustion of organic matter. Wood is used in different ways. For heating the wood is usually dried over extended periods of time. Still this wood produces smoke before it has been heated to higher temperatures. It might be another indication of organic radicals, that wood smoke has been used traditionally in the conservation of fish and meat. We expect that wood smokes of different kind and age expose very good EPR signals.

Incomplete combustion of liquid fuels can produce smokes; they leave the tail pipes of motor vehicles as dark clouds. Indeed theses particles of the Aitken mode are not produced in the atmosphere by coagulation of finer aerosols. These smokes also are expected to contain radicals which would show in EPR spectroscopy. If so, these radicals contribute to the reactivity of these particles.

Last not least, coal produces smoke by incomplete combustion, especially in the initial phases of burning. In the past, the London smog was well known and also its impacts on health. The problem: organic radicals might have a role in the evolution in these hazardous effects.

In discussions the question of radicals in particles of urban is often dismissed because the life times of radicals are usually rather short. In a metabolism, their life times are of the order of microseconds and less. In other situations life times of radicals are much longer, up to seconds. On PM of ambient aerosols life times of radicals may amount to hours and days as has been suggested in a recent paper (Arellanes et al., 2006).

The reasons for this rather large range of life times are probably not fully understood. A radical is an atom or molecule possessing one or more unpaired electrons. These are very apt to react with other radicals and molecules. When two radicals react with each other the unpaired electrons form a bond; the radicals have vanished. A reaction of a radical and a molecule produces a new molecule and leaves a radical which may possess the same or a different reactivity. This may be the start of a chain reaction. Short life times may indicate that a radical is able to react with a variety of partners.

Organic radicals formed by thermal decomposition during incomplete combustion come probably in a rather wide range of molecular sizes, and perhaps with more than one unpaired electron, at different sites though. It might be difficult or impossible to saturate all of these electrons at once; nevertheless these sites may play continuously a role in chemical transformations via absorption and electric conductivity of carbonaceous agglomerates. An organic radical may therefore preserve its character for quite some time.

- Do Aitken mode particles and accumulation mode particles of the ambient aerosol contain radicals, even after longer residence times in the atmosphere?
- Do radicals when absorbed on agglomerated particles get into the circulations and the metabolisms of biological systems?
- Are these radicals chemically active as long as the agglomerate exists?

2.3 Conclusions and outlook

PM is steadily formed and transformed on deposits of ambient aerosols. This has been shown for sulphate, and is suggested for di-carboxylates. For sulphate the reaction rates are slow; the excess sulphate formed on the deposits may become important after sampling times of 24h and 48h. In regard of PM mass, such contributions are perhaps not very important, especially when the aerosol components represent minor constituents. In regional aerosol samples, these changes of a material are very likely proportional to the amounts of this material carried on the aerosol particles; thus the excess material would not disturb relations of these aerosols, e.g. linear regression, correlation, and others.

Chemical artefacts may point to new pathways of PM formation and transformation. It is unclear whether the reaction of SO_2 on aqueous solutions of salts is a surface reaction on the aqueous solution or a reaction in the bulk of the solution. Specific reactions in rather concentrated electrolytes must be considered very carefully; water may become a reactant under such circumstances as met on ambient aerosol particles for a good part of their life time.

The nature of smokes, especially their contents of radicals, is a point of special interest. Such particles are supposed to occur also in the ambient aerosols. When mixed with other particles, predominantly with the particles of the accumulation mode, they may contribute to the transformation of secondary organics.

EPR spectroscopy can be used to quantify and specify radicals on smoke particles. Deposition of aerosols on samples of live tissues, and recording the tissues' reactions, promises to be a very successful step of characterising the harmfulness of these aerosols. Addressing the sensitivity of such methods, it may well be remarked that these special tissues are not necessarily of human origin.

3. Capillary condensation

Capillary condensation refers to the behaviour of liquids in capillaries. The laboratory experiment is represented in Figure 1. The capillary with diameter r dips vertically into the liquid. In the left part of the figure, the liquid is wetting the inner surface of capillary. The liquid rises to a certain height, h^+, above the level of the bulk liquid. The liquid column is in equilibrium with gravity. The surface of the liquid column, the meniscus, is negatively curved. On the right side of the figure, the liquid does not wet the capillary. The liquid in the capillary is depressed by the height h^-. The meniscus of the depressed column has a positive curvature. In both cases the liquid columns reach an equilibrium height determined by gravity and by the interface tension which depends on the properties of the capillary and the liquid.

The interactions of the molecules of the liquid and the capillary produce these phenomena. In the case of attraction the molecules of the liquid adhere to the capillary when being in direct contact with its surface. These molecules tend to cover the surface, pulling the liquid into the capillary. In the experiment equilibrium is reached when the force at the interface is balanced by the weight of the liquid column. For repulsive interactions the molecules do not adhere on the capillary. It needs some force to press the liquid into the capillary. In the experiment equilibrium establishes when this force on the liquid compensates the weight of the missing column above the meniscus. On the macroscopic scale, these phenomena reflect the molecular interactions.

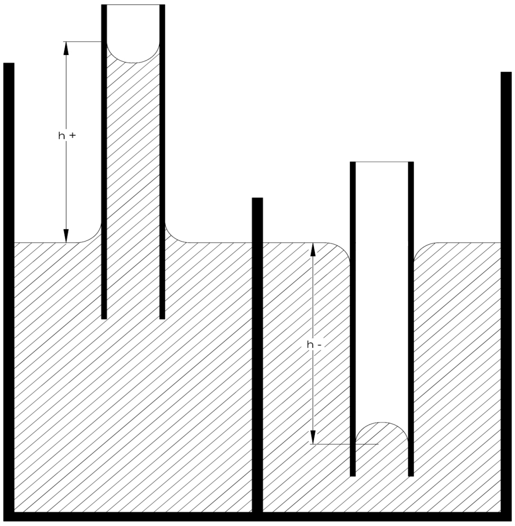

Figure 1: Schematical representation of the raise (h^+) or the depression (h^-) of a liquid in a capillary.

In case of the rising liquid the weight of the column, $m \cdot g = \rho \cdot g \cdot r^2 \cdot \pi \cdot h$, is balanced by the force $F_\sigma = \sigma_a \cdot 2 \cdot \pi \cdot r$, where σ_a is the interface tension. Formally this yields the "pressure" p_a, where a stands for the adhering liquid,

$$p_a = 2\sigma_a/r = -\rho \cdot g \cdot h.$$

This relation follows also from the balance of pressures. In the capillary, at the level of the bulk liquid, the pressure is $p_0+p_a+\rho \cdot g \cdot h$; this balances the pressure p_0 on the bulk liquid. The result is $p_a = -\rho \cdot g \cdot h$.

Under non-adhesive conditions the meniscus of the liquid in the capillary drops below the surface of the bulk liquid. The curved surface of the meniscus develops a force which compensates the missing weight of the column. Therefore

$$2\pi \cdot r \cdot \sigma_r, = m \cdot g \cdot h,$$

yielding, with p_r for non-adhesive conditions,

$$p_r = 2\sigma_r/r = \rho \cdot g \cdot h.$$

The pressures, p_a and p_r, are opposite in sign.

Remarks:

- Whether a liquid is adhesive or repellent in a capillary is determined by the interaction of the liquid molecules with the molecules of the capillary.
- Gravity does not rule adhesion or repulsion. The curvature of a meniscus develops also in the absence of gravity.

- Gases influence interface tension only when they dissolve in the liquid or in the capillary.

The vapour pressure over a curved surface like the surface of a drop or a meniscus is related to the pressure $\mathcal{P}$, produced by an interface or a surface, as demonstrated by the Kelvin equation for the vapour pressure of a liquid droplet,

$$\frac{p}{p_\infty} = \exp\left(\frac{2\sigma}{r} \cdot \frac{V_m}{RT}\right) = \exp\left(\frac{pV_m}{RT}\right)$$

In the Kelvin equation the term $(p\cdot V_m)/(R\cdot T) = (+|p|\cdot V_m)/(R\cdot T)$ is positive, indicating an increase of pressure on the droplet. The result is an increase of the vapour pressure of the liquid forming the droplet. The meniscus in capillaries is treated analogously (Brezesinsky et Mögel, 1993). The radius r is now the radius of the meniscus. For a negative curvature the sign of p is negative, and the vapour pressure at the meniscus falls below the vapour pressure for the plane surface. The relation of the vapour pressure produced by an interface with negative curvature is then

$$\frac{p}{p_\infty} = \exp\left(-\frac{2\sigma}{r} \cdot \frac{V_m}{RT}\right) = \exp\left(-\frac{pV_m}{RT}\right)$$

For the surface tension of water which equals the interface tension under conditions of perfect wetting, the vapour depression becomes is appreciable for small pores only, with radii below 100 nm.

Remarks:

- Because the vapour pressure of a liquid over a surface with negative curvature falls below the vapour pressure of the plane surface, vapours of this liquid can condense in a narrow capillary or a pore and fill it. This condensation process is selective, because it requires the liquid molecules to adhere on the wall of the pore.
- This condensation process does not represent a perpetuum mobile.
- The smaller the size of the pores the stronger the reduction of the vapour pressure of the condensable vapour. A structure made up of nano pores may keep its condensates also at low pressures as met in sampling instruments.
- The process of condensation is controlled by the diffusion of the vapours to site of condensation. Depending on the size of the pores it may take some time that a porous structure fills.
- A liquid which is unable to wet or to cover the surface of the underlying material, does not condense in pores of this material.
- Capillary condensation, as is absorption, is a selective process.
- A liquid condensed in a pore can not be replaced by a liquid of less interface tension.

Capillary condensation is part of the absorption, the taking up of matter in bulk by other matter, as in dissolving of a gas by a liquid. The exponent $-(p\cdot V_m)/(R\cdot T)$ plays an essential role in the theory of absorption. Capillary condensation, however, is only part of an absorption process. The first step in this process is adsorption, that is, the formation of an interface based on the intermolecular forces of the molecules of the liquid with the molecules of the solid substrate.

In a hexagonally densest packing of equally sized spheres the free volume is about 25.9% per particle, yielding an average pore volume of 4.32% with an average pore size of 35.1% in units of the of the diameter of the spheres. By the order of magnitude these numbers are indicative for the amount of material which can be absorbed in a porous medium of densely packed spheres. Also the average size of the pores is about 1/3 of the size of the particles.

We can probably say that attractive intermolecular forces between the two kinds of molecules generate a negatively curved meniscus, in terms of capillarity, after films of adsorbed molecules have formed. This may imply that non-attractive or repellent intermolecular forces are responsible for a positively curved meniscus.

4. Temperatures and pressures of the flow in a cascade impactor

In impactors, temperatures and pressures of the aerosol flow vary. In a stage the nozzles forming the aerosol jets accelerate the fluid to a certain velocity, the jet velocity, Uj; in the inter-stage sections the velocities of the fluid break down to an average velocity which is low compared to the velocities of the jets.

The velocity determines the temperature in a jet. For the ideal gas, temperature and velocity are related by the conservation of energy. For the impactor the most important energies are the enthalpy, H, and the kinetic energy, $(1/2)\cdot U^2$, of the gas. For two different states we have

$$\Delta H + \Delta\left(\tfrac{1}{2} U^2\right) = 0 \ ;$$

ΔH is the change of enthalpy from a point “1” to a point “2” in the fluid. Specifically, point “1” is a point in the inter-stage fluid, upstream of the nozzles of a stage, point “2” is a point in the aerosol jet at the end of a nozzle. The velocity of the fluid in point “1” is close to zero; at this point the kinetic energy of the fluid is negligible compared to the kinetic energy in point”2”. Consequently

$$H_1 = H_2 + \tfrac{1}{2} U_j^2 = 0 \ .$$

In terms of the observables (p,V,T) the change of enthalpy of the ideal gas is given by $\Delta H = c_p \cdot \Delta T$, with c_p for the specific heat at constant pressure as a factor.

$$\Delta H = H_1 - H_2 = c_p \cdot \Delta\left(T_1 - T_2\right) = \tfrac{1}{2} U_j^2$$

That is, the gas in the jets falls below the temperatures in the inter-stage section. In the inter-stage sections the velocities of the fluid are close to zero; the temperatures in the inter-stage sections are almost identical with the ambient temperatures.

For points "i", "j" in two different inter-stage sections, the change of enthalpy is given by

$$\Delta H = \Delta(pV) + c_v \Delta T = 0 \;;$$

with c_v, the specific heat at constant volume. For the considered points, $T_i = T_j = T_a$; so $\Delta(T)=0$ and $p_i \cdot V_i = p_j \cdot V_j$.

The aerosol jet impinges on the collection plate and creates a radial pressure distribution. The highest pressures occur in the point of stagnation (round nozzles) or in the line of stagnation (slit nozzles). There the velocity drops to zero. In the impinging jet and in the wall leaving the region of stagnation the pressures are close to the pressure measured at the end of the nozzle. There are also temperature gradients. The temperature is highest in the point of stagnation and equal to the inter-stage temperature upstream of the stage. The temperatures are lowest in the high speed flow in the impinging jet, in the outer parts of the stagnation flow, and in the wall jet leaving the region of stagnation. The regular deposits under the nozzles are covered by a flow of cold air.

Semi-volatile species may evaporate in the inter-stage sections of the impactor, due to the gradual reduction of pressures in the impactors. In these sections the temperatures are close to the ambient temperatures, and the residence times are relatively large. In the jets however the temperatures fall below ambient, depending on the velocity of the jet. The saturation vapour pressure, P_s, of a semi-volatile decreases, much stronger though than its vapour pressure, P_j, in the jets. The pressure ratio P_j/P_s may amount to values of about 10 and more (see Figure 2) for jet velocities above 200 m/s typical in low pressure cascade impactors.

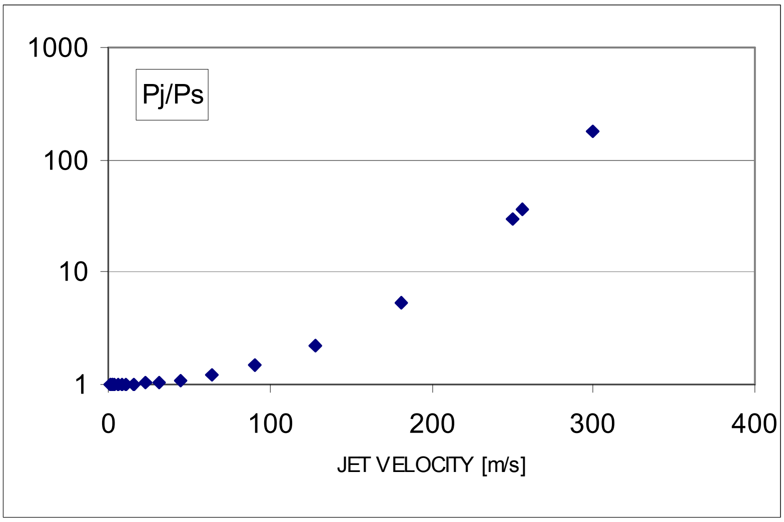

Figure 2: Pressure ratio p_j/p_s of an organic semi-volatile (100g/mol) vs. velocity of the aerosol flow (air).

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VI. Results from Working Group 2: Health Related Issues of Particles

Chairs: Raimo Salonen and Wolfgang Kreyling

VI.1 Heterogeneities in health effects of particulate air pollution: Epidemiological and toxicological evidence

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1. Introduction

The Clean Air for Europe (CAFE) Programme of the European Commission (2005) made an integrated assessment of the health impacts, and consequent direct and indirect economical losses due to population exposures to outdoor fine particulate ($PM_{2.5}$; particle size < 2.5 µm) air pollution in 25 Member countries (EU25). The assessment resulted in an estimate of nearly 350000 premature deaths annually due to current ambient $PM_{2.5}$ levels and that the statistical life expectancy of a citizen in the EU was shortened by about eight months (range 4-13 months in different countries) (Commission staff paper 2005; Watkiss et al. 2005).

The CAFE estimates were heavily influenced by subjects with chronic cardio-respiratory diseases, in whom the shortening of life expectancy was assessed to be up to 10 years. Moreover, roughly tens of millions of subjects with chronic cardiovascular or respiratory diseases as well as tens of millions of children were estimated to suffer from short-term disease exacerbations leading to increased symptoms and medication use, restricted activity, absences from work, and increased use of medical care services including emergency department visits. The overall direct and indirect economical losses due to the current $PM_{2.5}$ exposures and subsequent adverse health effects were estimated at 278-780 billion euros per year. The large range in economical losses was due to valuation of a premature death in two different ways. The direct and indirect losses due to disease treatment and exacerbations were about 90 billion euros per year. The substantial variations between the EU countries reflected the differences in their annual outdoor $PM_{2.5}$ concentrations (Commission staff paper 2005; Watkiss et al. 2005).

The CAFE assessment has given important background information to the Commission, European Parliament and the member countries on the extent of the health, social and economical impacts of particulate air pollution, which has also influenced the recent decision-making on abatement strategies. However, the database that formed the core information in the impact assessment on this most important environmental health problem in Europe needs urgent improvement in order to guarantee a favourable progress in the regulation of outdoor air pollution in the future. The areas of the largest gaps and uncertainties in the CAFE data were as follows:

1) The Europe-wide modelling of $PM_{2.5}$ exposure was made on a regional scale (50x50 km) with little data on increments originating from local emission sources.
2) The assessment was based only on fine particulate mass ($PM_{2.5}$), although there is increasing evidence from aerosol sciences that the chemical compositions vary by type of location (urban, suburban, rural) as well as season and climate, and that these variations are reflected in the magnitude of health effects among susceptible population groups.
3) Updated health effect assessment data (WHO 2004) were utilized, but little information was then available on source-specific $PM_{2.5}$ exposures and health effects.
4) Exposures to and health effects of coarse thoracic particles ($PM_{10-2.5}$) were not included in the CAFE assessment.

The main purpose of the interdisciplinary scientific work of the participants from 21 countries in the COST Action 633 'Particulate matter: properties related to health effects' (http://cost633.dmu.dk) has been to co-operate in production of novel research data in original national and multinational studies in order to reduce important gaps and uncertainties in the present knowledge on the health effects of urban particulate air pollution. On the basis of the most recent publications, we have reviewed heterogeneities reported in the epidemiological and toxicological health outcomes associated with urban air particulate matter. With heterogeneity, we mean in this context *"a significant variability in the particulate mass-based concentration-response or dose-response relationship"* as observed with the same methodology in a single study or as assessed in critical meta-analysis. Thus, increasing or decreasing prevalence or magnitude of health outcome with increasing or decreasing particulate mass concentration or mass dose of outdoor air particles does not represent "heterogeneity", unless the slope of the particulate mass-based exposure- or dose-response relationship is also changed. In addition to studies that have directly investigated this issue, we also evaluated selected literature that provides indirect suggestions of heterogeneity.

A special emphasis of this interdisciplinary scientific review is to pay attention to heterogeneities in health outcomes that could influence current concepts of health risk assessment as well as the air pollution control or monitoring strategies in the EU. Examples of such are regional, spatial and temporal heterogeneities and, most importantly, heterogeneities in health outcomes related to specific particulate sources and constituents. In the selection of representative literature, we have given preference to recent European studies and complemented those with studies conducted elsewhere, mainly the United States. As the heterogeneities in health effects related to particle size have been systematically reviewed in recent years (WHO 2003 and 2005; USEPA 2004; Brunekreef and Forsberg 2005; Pope and Dockery 2006), the knowledge gained from these reviews is only shortly summarized in each section.

2. Epidemiological evidence of heterogeneity

The by far largest and best known database on heterogeneities deals with the influence of particle size on the epidemiological health outcomes of urban air particulate matter. There is vast evidence that thoracic particles (PM_{10}; diameter < 10 μm) and, more strongly, fine particles ($PM_{2.5}$; diameter < 2.5 μm) are consistently associated with premature mortality, hospital visits and functional decrements among respiratory and cardiovascular patients (WHO 2004 and 2005). Coarse thoracic particles ($PM_{10-2.5}$; diameter 2.5-10 μm) do not seem to associate as frequently with mortality and cardiovascular outcomes as fine particles, but they have consistently associated with hospital visits and functional decrements among respiratory patients (WHO 2004 and 2005; Brunekreef and Forsberg 2005). These three size ranges of particles have been measured as gravimetric mass concentration in the health studies. In contrast, ultrafine particles (UFP; diameter < 0.1 μm) have been usually measured as particle number concentration. Also they have been associated with health effects, including mortality, among the respiratory and cardiovascular patients, although the associations have not been as consistent as with $PM_{2.5}$ (WHO 2004 and 2005; Pope and Dockery 2006).

2.1.Temporal, seasonal, spatial and regional heterogeneity

The large bulk of epidemiological evidence on the health effects of urban air PM_{10} and $PM_{2.5}$, and to a smaller extent UFP number concentrations, are from daily time-series studies that have investigated the association of particle concentrations with mortality, hospital admissions and functional decrements among subjects with chronic respiratory or cardiovascular disease. Most often significant effects are seen with one to two days lags from the anticipated exposure to outdoor particles (WHO 2004 and 2005; USEPA 2004; Pope and Dockery 2006). However, there has been temporal, regional and spatial heterogeneity in the effects of urban air PM_{10} and $PM_{2.5}$ in recent epidemiological studies as summarized in Table 1.

Both shorter and longer averaging times than 24 hours seem to cause variability in the particulate concentration-response relationship. It has been known for a long time that asthmatic subjects react quickly to increased pollutant concentrations (WHO 2004 and 2005; USEPA 2004). Recently, it has been reported that 1- to 4-hour personal or central site $PM_{2.5}$ concentration can also associate with exercise-related myocardial ischemia (Lanki et al. 2008) and with changes in cardiac rhythm (Henneberger et al. 2005). This suggests that the urban air $PM_{2.5}$ may have both immediate and delayed effects on the onset of myocardial infarction.

In general, there seem to be signs of accumulated health effects from urban particulate air pollution, when the averaging time of the PM_{10} and $PM_{2.5}$ concentration in the analyses has been made longer. For instance, the mortality estimates per 10 $\mu g/m^3$ $PM_{2.5}$ or 20 $\mu g/m^3$ PM_{10} roughly double within 5 days and can be 10-20 times higher in chronic exposures of several years. This suggests not only a worsening of an existing chronic disease but possibly also a contribution to the induction of the disease, e.g. allergic sensitization in asthma and progression of atherosclerosis in ischemic heart disease (Pope and Dockery 2006).

Small area modeling of $PM_{2.5}$ concentration seems better connected to the real-life exposures than a single value obtained for a large area from one or few central site monitoring stations.

At least, the mortality estimates from this kind of analysis have led to much higher values of the risk of chronic effects than in cross comparisons between communities (Jerrett et al. 2005).

The APHEA 2 project has shown regional heterogeneities in the PM_{10} and black smoke concentration-response functions for the short-term mortality (Samoli et al. 2005) and hospital admissions (Atkinson et al. 2001) in Europe. Samoli et al. (2005) reported steeper concentration-response functions for the PM_{10} and black smoke-associated total and cardiovascular mortality with the higher ambient temperature, NO_2 and PM_{10} levels present in southern European cities compared to the northern European cities. In the study of Atkinson et al. (2001), there were steeper concentration-response functions for PM_{10}-associated respiratory hospital admissions in the eastern than the western European countries. Potential effect modifiers, in addition to the air pollution characteristics in each city, included the health status of the population, the geographical area, and the climatic condition (Katsouyanni et al. 2001). There have been similar observations on the heterogeneity of $PM_{2.5}$-associated mortality and respiratory hospital admissions in the US (Peng et al. 2005; Dominici et al. 2006).

Subsequently, several epidemiological studies have shown an association of the urban air PM_{10} and $PM_{2.5}$ concentration with mortality or other health outcomes only during the warm season of the region (Roberts 2004; Ren et al. 2006; Lanki et al. 2006a; Kettunen et al. 2007) (Table 1). Riediker et al. (2001) have also reported in human subjects living in an urban centre that outdoor air PM_{10}, NO_2 and O_3 may strongly increase the intensity of allergic rhinoconjunctivitis symptoms during pollen-season.

2.2. Source-related heterogeneity

There are still only few epidemiological studies in Europe that have systematically compared the contributions of different sources and chemical constituents to urban air particulate-induced health effects. This is due to a lack of sufficient chemical characterization of the aerosol particles with harmonized methods that is elaborate and expensive in studies lasting for several months or years at multiple sites. Therefore, large studies of this kind have been mainly conducted in the US, where there has been a systematic urban air $PM_{2.5}$ speciation program for some time. The short-lasting panel studies in Europe have made black carbon measurements, and ionic and elemental speciation, but are lacking measurements of organic carbon that constitutes a large part of the fine particulate mass. These measurement data allow particulate source analysis by modeling speciation data together with simultaneously measured gases such as carbon monoxide and nitrogen dioxide (Viana et al. 2008). In these studies, local combustion sources have been most strongly associated with the measured short-term health outcomes, while long-range transported secondary pollutants, sea salt and soil-derived dust have shown no significant associations (Table 2).

There is also suggestive epidemiological evidence without direct comparison to other sources that living close to a major local source of incomplete combustion, producing soot measured as black smoke or elemental carbon, increases the risk of respiratory or cardiovascular health outcomes. Studies on the harmfulness of residential heating with wood, and of regional or long-range transported wildfire smoke have been recently reviewed by Boman et al. (2003) and Naeher et al. (2007). Cardiopulmonary mortality (Hoek et al. 2002) and respiratory symptoms in Dutch children (Brauer et al. 2002, Janssen et al. 2003) have been more prevalent in subjects living in vicinity to a major road. In addition, these is evidence of a substantial, rapid decline in black smoke and mortality in association with a ban of coal sale for residential heating in Dublin (Clancy et al. 2002). A similar change has also been seen with PM_{10} and hospital admissions of children and mortality in connection to a temporary closing of a steel mill in Utah (Pope et al. 1991 and 1992). In this case, the reduced levels of transition metals in PM_{10} have been suggested to contribute to the decreased prevalence of health outcomes (Ghio 2004). The data of Heinrich et al. (1999) from the former eastern Germany supports this, as the children living near mines and metal-smelters had a higher prevalence of respiratory symptoms and allergy than the children in non-industrialized areas. Tsai et al. (2000) have associated oil burning, vehicular traffic, industry and sulphate aerosols with daily mortality in New Jersey.

In general, the urban air sulphate concentration in PM_{10} or $PM_{2.5}$ that correlates highly with fine particulate mass has been rather consistently associated with mortality in the US studies (WHO 2005; USEPA 2004), but a causal relationship has been much doubted due to the relatively low toxicity of sulphate aerosols (Schlesinger and Cassee 2003, Schlesinger et al. 2006). The levels of elemental and organic carbon and oxygenated hydrocarbons in $PM_{2.5}$ have been associated with increased prevalence of bronchitis in asthmatic children and cardiovascular emergency room visits in the US (McConnell et al. 2003; Metzger et al. 2004). Metals like Cu, Ni, V, Fe and Zn from metal industries (Ghio 2004) or car brakes (Riediker et al. 2004) have been associated with cardio-respiratory health outcomes. Also the soil mineral constituents in PM_{10} have been associated with symptoms of the upper respiratory tract (Tiittanen et al. 1999) and asthma (Meister and Forsberg 2007), and occasionally mortality (Ostro et al. 1999).

Inflammation has been suggested as a major biological mechanism mediating particulate-associated respiratory effects, such as exacerbation of asthma and chronic obstructive pulmonary disease (Brunekreef and Holgate, 2002), as well as cardiovascular effects such as atherosclerosis, increased blood coagulation and disturbances in cardiac rhythm (Brook et al., 2004; Pope et al., 2004). On the other hand, exposure to particulate air pollution has been associated with oxidative DNA-damage that may increase the risk of lung cancer (Møller et al. 2008).

2.3 Sources for heterogeneity at individual level

Outdoor fine particles are known to penetrate indoors to a substantial degree. This greatly increases the lung burden of particles, as people in well-developed countries spend nearly 90% of their daily time indoors. In the study of Hänninen et al. (2004), the average infiltration properties of the building stocks in four European cities (Athens, Basel, Helsinki, and Prague) were quite similar to each other, ranging from 0.6 to 0.7 for $PM_{2.5}$, despite the climatic differences. This supports the findings of Lianou et al. (2007) on consistently higher $PM_{2.5}$ concentrations inside residences in the vicinity to a major road in another set of four European cities. Mechanical air filtration and air conditioning have been shown to decrease home indoor $PM_{2.5}$ concentrations, which can be subsequently reflected in reduced personal exposure and health outcomes (Janssen et al. 2002; Brauer et al. 2008).

On the other hand, life styles can affect personal exposure to outdoor air particles and subsequently increase the risk of health effects. Time spent in busy traffic increases personal exposure not only to combustion-derived soot and organics but also to coarse and fine dust from car brake, tyre and body wear (Riediker et al. 2004; Yli-Tuomi et al. 2005). Eager cycling in city traffic can lead to increased exposure to UFP and cause oxidative DNA damage in white blood cells (Vinzents et al. 2005).

3. Toxicological evidence of heterogeneity

The main toxicological endpoints of urban air particles, regarded as important from the human disease point of view, include local and systemic inflammation as well as cytotoxicity and genotoxicity causing tissue damage and increasing cancer risk. Inflammatory processes in the bronchi and alveoli have been traditionally connected to increased risk of chronic bronchitis and asthma, but these processes in the alveoli and blood circulation may also affect the arterial walls and the heart in many ways, e.g. via increased blood clotting, enhanced atherosclerotic plaque formation, acute rupture of the plaque leading to infarction, and cardiac dysrythmias due to influences on the autonomic nervous system. Finally, penetration of ultrafine particles to the brain may disturb the central nervous system (Calderón-Garcidueňas et al, 2008; Mills et al. 2009; Campbell et al, 2009).

Most of the toxicological studies have been made using aqueous suspensions of particulate samples previously collected in field campaigns using either common low-volume particulate samplers or specially designed high volume cascade impactors with large collection capacity (Sioutas et al., 1997; Demokritou et al., 2002; Sillanpää et al., 2003). A much smaller number of studies have used concentrated urban air particles in direct exposures of humans, animals or cultured cells (Ghio and Huang 2004). In comparisons of intratracheal instillation method with aerosol exposure method in rodents, the particulate distribution patterns and inflammatory responses in the lungs have been similar to each other (Driscoll et al. 2000; Costa et al. 2006).

Another methodological issue, often discussed in association with toxicological animal and cell studies, is the particle dose per surface area of tissue or inflammatory / respiratory epithelial cells in culture. Generally, the doses producing effects are regarded as much higher than those received daily into human lungs in real-life conditions. However, the pulmonary deposition of inhaled particles in a human subject is not even, but can show up to thousand-fold variation per surface area between different lung sites. Especially, pulmonary disease can enhance the uneven distribution (Phalen et al., 2006).

Overall, toxicological studies on the urban air particulate mixture should be regarded as controlled bioassays that can give valuable information about the biological properties of the particles in connection to their sources and physical and chemical properties. This can help finding plausible explanations to epidemiological study results and, thus, facilitate important abatement measures. However, human health risks cannot be quantified on the basis of toxicological cell and animal studies.

3.1. Heterogeneity with particle size

Several studies have reported systematic differences in the toxic potency between the three particulate size ranges of health interest: coarse thoracic particles ($PM_{10-2.5}$), fine particles (usually $PM_{2.5-0.1}$ or $PM_{2.5-0.2}$), and ultrafine particles ($PM_{0.1}$ or $PM_{0.2}$). When the comparisons between particulate samples in different size-ranges have been made with one representative mass dose that is the same for all, we cannot define an exact potency difference that needs a full dose-response curve but can define a difference in the "inflammatory activity", "cytotoxic activity" or allergy-related "adjuvant activity" between the samples. However, testing a wide range of mass doses is a prerequisite for the selection of a single representative mass dose of the particulate samples in different size-ranges.

It can be stated as a summary from several animal studies (Schins et al. 2004; Gerlofs-Nijland et al. 2007 and 2009; Happo et al. 2007) and cell studies (Becker et al. 2003; Pozzi et al. 2003; Dybing et al. 2004; Hetland et al. 2005; Jalava et al. 2006 and 2007) that the coarse particulate samples from a number of European locations and meteorological conditions have a higher inflammatory activity than the fine or ultrafine particulate samples. Moreover, it seems that intermediate size-range ($PM_{2.5-1}$) particles resemble much the coarse thoracic particles and have a clearly higher inflammatory activity than accumulation ($PM_{1-0.2}$) or ultrafine ($PM_{0.2}$) particles (Jalava et al. 2006; Happo et al., 2009). In contrast, fine particulate samples have enhanced the allergen-specific IgE responses more than coarse particulate samples (Alberg et al. 2009). Interestingly, there has not been such reduction of biological activity with smaller particle size, when the same urban air samples have been investigated for cytotoxicity and apoptosis (so-called programmed cell death), or nitric oxide production that has connections to both of these biological end points (Jalava et al. 2006 and 2007).

An obvious mechanistic reason for the positive association of particle size with inflammatory activity in single-dose studies both in the animal lungs and in cultured macrophages is that these two have a link with each other. Alveolar macrophages prefer to take up particles over one micrometer in diameter and they have a key role in orchestrating an acute inflammatory response to such particles (Kreyling and Scheuch, 2000). In contrast, solid ultrafine particles are not effectively cleared by the macrophages but are translocated into the epithelial cells or interstitium for at least months (Semmler-Behnke et al., 2007). The latter may contribute to the harmful cardiovascular effects of particles, which become even more likely in situations, where ultrafine particles enter the blood circulation (Nemmar et al. 2006).

One reason proposed for the higher inflammatory activity of larger size-range particles in the lungs or macrophages is that they contain more solid material than accumulation and ultrafine particles (USEPA 2004). Indeed, it has been shown that the inflammatory activation of the macrophages by both the $PM_{10-2.5}$ and $PM_{2.5-0.2}$ samples is largely due to the uptake (phagocytosis) of insoluble particulate material and not due to water- or lipid-soluble materials separated thereof (Jalava et al. 2008). Of course, this does not mean that inorganic or organic soluble constituents could not have important biological effects, especially when attached to solid particles and taken up by target cells. In addition, a water-soluble fraction of urban air fine particles has disturbed the phagocytic function of cultured macrophages (Zhou and Kobzik, 2007) and a lipid-soluble extract rich in PAHs has been highly mutagenic, genotoxic and embryotoxic in various cell studies (Binková et al. 2003). In the study of Steerenberg et al. (2005), either a water-soluble or a water-insoluble particulate fraction was responsible for the IgE-mediated allergy adjuvant activity in the mouse lung depending on the site of particulate collection in Europe. Furthermore, in another inhalation study, exposure of previously ovalbumin-sensitized mice to rather pure ultrafine carbon black (CB) particles led to a stronger allergic response when the mice were exposed to the ultrafine CB aerosol prior to the final ovalbumin challenge compared to vice versa (Alessandrini et al., 2006).

It is also possible that some organic and inorganic constituents on particle surface are capable to produce highly reactive oxygen or nitrogen radicals that evoke toxic effects on the target cells such as alveolar macrophages, other inflammatory cells and respiratory epithelial cells. The candidates of organic constituents for such effects include oxy- and nitro-PAHs and quinones (Squadrito et al., 2001), but also transition metals like copper, nickel, vanadium and iron can be involved in acellular production of toxic intermediates (Shi et al. 2003).

3.2. Seasonal and geographical heterogeneity

It is not surprising that the urban air PM_{10} samples collected in different sites and seasons have shown heterogeneity in inflammatory or cytotoxic responses, because the sources of PM_{10} are numerous and the particle size distributions within PM_{10} are likely to vary greatly with meteorology (Monn et al. 2003; Salonen et al. 2004). However, there is evidence, that also the coarse and fine particulate samples collected in different seasons at one place or in different regions of Europe have profound within-size-range heterogeneity in their toxic activities. Dybing et al. (2004), Hetland et al. (2005), Gerlofs-Nijland et al. (2007 and 2009) and Happo et al. (2009) have demonstrated seasonal variation in the in-vitro and in-vivo inflammatory activity of coarse and fine particulate samples collected in a variety of central and northern European sites. The inflammatory activity of warm season samples has been generally higher than that of the winter samples. In contrast, winter season samples have shown higher allergy adjuvant activity than summer season samples in the mouse lung (Steerenberg et al. 2005). Accordingly, the lipid-soluble extract of winter samples has had higher mutagenic, genotoxic and embryotoxic activities in cells than the extracts of samples from warm seasons (Binkova et al. 2003). Happo et al. (2007) and Jalava et al (2007) have shown that the inflammatory activities in the mouse lung and mouse macrophage cell line of urban background $PM_{10-2.5}$ and $PM_{2.5-0.2}$ samples from warm and dry season Barcelona and Athens are much higher than those of the respective samples collected in central and northern European cities during cool and wet seasons.

3.3. Heterogeneity with source and chemical composition

Perhaps the most severe limitation to the utilization of toxicological study results in search for causative particulate sources is that only few studies have made a thorough chemical characterization of the urban air particulate samples, to which the rodent lungs or cultured target cells, most often macrophages and respiratory epithelial cells, have been exposed. Table 3 summarizes some of the key findings from three EU-funded toxicological projects on size-segregated urban air particles with chemical characterization:

- Health effects of particles from motor engine exhaust and ambient air pollution (HEPMEAP)
- Respiratory allergy and inflammation due to ambient particles (RAIAP)
- Chemical and biological characterisation of ambient air coarse, fine, and ultrafine particles for human health risk assessment in Europe (PAMCHAR).

The overall picture that was derived from these three multi-centre projects is that both coarse and fine particles are capable of inducing toxicity. Particulate matter from traffic, oil combustion and biomass / coal combustion seem to have high toxic potential. The chemical composition of particles seems to play an important role and, although the view on causative components is not definite, metals and hydrocarbons appear to be strongly associated with the biological responses. Outdoor air particles have also been potent inducers of allergic responses in animals (Sandström et al, 2005). The often different toxicity of coarse particles underlines the need to consider this particle size-range together with fine particles in human health risk assessment and in standard-setting.

Results from similar animal and cell studies conducted in the US mostly agree with the results obtained in these European studies. This includes positive associations of the traffic-related and heavy oil combustion-related (Ni, V, organics) material, road dust crustal material, and a series of metals (e.g. Fe, Zn, Cu, Pb) with the inflammatory and cytotoxic activities of the collected urban air fine particulate samples in various cell and animal models. Correspondingly, secondary fine particulate sulphate has shown inconsistent associations with the toxicity endpoints in these models (Seagrave et al. 2006; Veranth et al. 2007; Gilmour et al. 2007; Duvall et al. 2008). The associations of identifiable coarse particulate sources and constituents with the inflammatory and cytotoxic activities of these samples have also been inconsistent. This involves also endotoxin that is the best known representative of the relatively large and poorly known biogenic fraction of urban air coarse particles.

Stöger et al. (2006 and 2008) have identified different biochemical pathways of inflammation in healthy mice exposed by inhalation to generated ultrafine CB particles with and without a substantial surface load by organic compounds.

Table 4 summarizes a number of physical and chemical characteristics of urban air ultrafine, fine and coarse particles anticipated to contribute to their harmfulness to health. There is a variable amount of experimental evidence on the associations of each of them with toxicity endpoints in either cell or animal studies. Therefore, it is no wonder that scientists have been looking for some simple characteristic like the oxidative capacity of collected particles as a candidate for the overall toxicity. However, it seems that urban air particles can induce oxidative stress and subsequent inflammatory, cytotoxic and genotoxic activation of the key defence cells in the lungs, i.e. macrophages and epithelial cells, via diverse biochemical pathways. More research is needed on the feasibility and associations of acellular tests of oxidative capacity of collected particles with human health outcomes. At this moment, tests of oxidative stress in cellular systems seem more appropriate markers of the overall harmfulness of urban air particles (Ayres et al. 2008).

4. Conclusions and implications

The present review has shown that there is considerable heterogeneity with regard to the health effects of urban air PM_{10} and $PM_{2.5}$ in epidemiological studies. The hypothesis that at least some of the observed heterogeneities are due to particulate properties is supported by a series of toxicological studies that have investigated collected, size-segregated urban air particulate samples in experimental human, animal and cell studies.

It has become clear that there is heterogeneity in toxicity and health effects due to particle size, i.e., coarse vs. fine vs. ultrafine particles. These heterogeneities have also been connected to the common sources of urban air particles (traffic, coal/oil/wood combustion, metal industries, sea spray, soil dust, long-range transport). Within the same size-range, (most often in fine particles), these heterogeneities have been associated with varying chemical composition of the urban air particles due to geographical, spatial and meteorological differences between study sites. However, there are still only few integrated studies that have combined epidemiological panel studies with simultaneous toxicological and in-depth chemical characterization of the urban aerosol particles at the same site. This setup, of course, can provide the strongest evidence on the particulate-associated causes in relation to heterogeneities in epidemiological findings.

Another important factor, causing heterogeneity in human health effects, seems to be the period of exposure. High hourly and daily mean concentrations of urban air particles seem to be hazardous, not only to subjects with chronic respiratory disease but also to those with ischemic heart disease. Moreover, year- or decade-long living in an environment with elevated outdoor particle concentration seems not only cause disease exacerbation but it may actually induce new cases of chronic pulmonary and cardiovascular diseases. The overall outcome from this is shorter life-expectation, when compared to people living in cleaner environment.

The current scientific evidence makes us to ask several questions that are highly relevant from the point of view of the present EU air pollution abatement strategies and the society at large:

(i) Would populations living in Mediterranean countries and other countries during warm and sunny weather benefit from stricter than usual air pollution limit or guideline values to protect their health?

(ii) Is living in suburban areas and commuting healthier than living in city centres in vicinity to major sources of particles (e.g. busy traffic lanes, industries)? How much does the way of commuting (e.g. car vs. bus vs. train) affect personal exposure to hazardous particles and does it affect the health risks?

(iii) Should car traffic be massively reduced in large cities to protect populations not only against engine emissions but also against other potentially hazardous particulate emissions (e.g. from brake, tire and chassis wear)? How do these various car emissions attribute to the burden of disease?

(iv) Does changing from current fossil fuels to biodiesel or bio-ethanol in vehicles cause a health-wise favourable or unfavourable change in urban air quality, especially in particles? We know from previous experience that each source of urban air particles has a characteristic toxicity profile and adverse health effects. This means that no new source of particles should be introduced in large numbers to urban environments without pre-existing knowledge of the potential health risks that it may cause.

(v) To what extent would more effective mechanical ventilation and particle filtration in buildings reduce personal exposures of urban populations to harmful particles of outdoor origin? What would be the health benefits from this action?

(vi) What is the role of particles and gaseous (separately and as complex mixture) pollutants from current residential heating with wood in personal exposures to and adverse health effects of fine particles in Europe? What would be the health benefits from strict EU-wide regulation of the emissions?

(vi) Will the planned increase in biomass-based energy increase or decrease personal exposures to and adverse health effects of fine particles in Europe?

Given the fact that there is substantial heterogeneity in PM-associated health effects and toxicity due to size and composition, it is recommended that large epidemiological studies involving several old and new metrics in parallel with good time-space resolution will be launched. New air quality monitoring methods should also be developed in order to assess the overall hazardousness of urban particulate air pollution. In this regard, the measurement of oxidative potential of the airborne particles seems like a good candidate.

It is obvious that many more epidemiological, toxicological and aerosol science studies are needed to answer the questions listed above and other important questions on particulate air pollution and health. Interdisciplinary studies involving all these areas of science would probably be the most valuable ones, because they can provide the strongest evidence on causal relationships. Based on these studies, the decision-makers are requested to integrate air pollution research findings into further refinement of particulate risk assessment, as well as into designing and improving the air quality management strategies.

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Table 1. Temporal, regional and spatial heterogeneity in the mass-based concentration-response relationships of urban air particulate matter (PM) with respiratory and cardiovascular health outcomes in selected European and US epidemiological studies and reviews.

PM metrics	Variable	Health outcome with heterogeneity	Key findings	Reference
$PM_{2.5}$, ultrafine particles (UFP), accumulation particles (ACP)	Central site / personal PM averaging time: hours	Heart rate variability (HRV), electrocardiographic (ECG) changes, myocardial ischemia	0-24 hour central site UFP, ACP, and most consistently $PM_{2.5}$, associated with reduced HRV and abnormal ECG changes. 1-hour personal and 4-hour outdoor $PM_{2.5}$, but not UFP, associated myocardial ischemia during exercise.	Gold et al. (2000) Henneberger et al. (2005) Lanki et al. (2008)
PM_{10}, black smoke (BS)	Central site PM averaging time: days - weeks - years	All-cause, cardiovascular (CV), cardio-respiratory (CR) or respiratory mortality in multiple studies / cities mainly in the US	Percentage increase of all-cause mortality per 10 $\mu g/m^3$ $PM_{2.5}$ or 20 $\mu g/m^3$ PM_{10} or BS increase: 0.8–1.3% for 1-day, 0.4–2.1% for 1 to 3 days, 2.6–3.3% for 5 to 40 days, and 3.2–17% for months to years. Percentage increase of CV/CR mortality per 10 $\mu g/m^3$ $PM_{2.5}$ or 20 $\mu g/m^3$ PM_{10} or BS increase: 0.8% for 1-day, 0.6–1.4% for 1 to 3 days, 2.7–4.0% for 5 to 40 days, 5.7–28% for months to years. Percentage increase of respiratory mortality per 10 $\mu g/m^3$ $PM_{2.5}$ or 20 $\mu g/m^3$ PM_{10} or BS increase: 1.8% for 1-day, 0.6–1.5% for 1 to 3 days, 3.4–8.6% for 5 to 40 days, 8.7% for months to years.	Review by Pope and Dockery (2006)
$PM_{2.5}$	Spatial resolution in assessment of chronic exposure	All-cause, ischemic heart disease (IHD) and lung cancer mortality over a 10-year period in Los Angeles (US)	Percentage increase per 10 $\mu g/m^3$ of small area modeled $PM_{2.5}$: 17% for all-cause mortality (CI: 5–30%) and 24–60% (depending on model) for IHD & lung cancer mortality. Both nearly 3 times higher estimates than in comparisons between communities.	Jerrett et al. 2005
PM_{10} / BS / $PM_{2.5}$	Different regions in Europe	Daily mortality in many European cities	Percentage increase of all-cause mortality per 10 $\mu g/m^3$ PM_{10}: < 1% in most Northern European cities vs. 1-3% for several Southern European cities. Positive trend between the estimate and mean daily PM_{10} concentration.	Samoli et al. 2005 Review by Anderson et al. 2004; WHO 2005

Table 1 (cont.)

TSP / PM_{13} / PM_{10} / $PM_{2.5}$	Different regions in Europe	Daily hospital admissions in many European cities	Percentage increase in daily respiratory hospital admissions per PM mass unit (PM_{10} or BS) higher in Eastern European cities vs. Western European cities.	Atkinson et al. 2001 Review by Anderson et al. 2004
PM_{10} / $PM_{2.5}$	Season in the same location	Daily mortality in the US and Australia, and Helsinki (FI)	Significantly increased daily CV, stroke and respiratory mortality per 10 $\mu g/m^3$ or interquartile range increase in $PM_{2.5}$ or PM_{10} only during warm season.	Roberts (2004) Ren et al. (2006) Lanki et al. (2006a) Kettunen et al. (2007)
PM_{10} / $PM_{2.5}$ / particle number counts (PNC)	Season in the same location	Daily hospital admissions in the US and Australia, and Helsinki (FI)	Significantly increased daily hospital admissions due to myocardial infarction only or more pronounced during warm season.	Roberts (2004) Ren et al. (2006) Lanki et al. (2006b)

Table 2. Source and chemical composition related heterogeneity in urban air fine particle ($PM_{2.5}$) concentration-response relationships with various health outcomes in selected European and US epidemiological studies.

PM metrics	Variable	Health outcome with heterogeneity	Key findings	Reference
$PM_{2.5}$	Central site PM source modeling from ionic and elemental composition with gases	Daily cardio-respiratory (CR) mortality over a 10-year period in six eastern US cities	Significantly increased daily CR mortality per 10 μg/m^3 increase in $PM_{2.5}$ (2-day mean): mobile source 3.4% (1.7–5.2) and coal combustion 1.1% (0.3–2.0)	Laden et al. (2000)
$PM_{2.5}$	Central site PM source modeling from ionic and elemental composition with gases	Myocardial ischemia in coronary heart disease patients in Helsinki (FI)	Significantly increased myocardial ischemia during exercise per 1 μg/m^3 increase in daily source-specific $PM_{2.5}$ (2-day lag): 22% for local traffic and 19% for oil combustion PM. No significant increase with soil (4%), sea-salt (-24%) or long-range transported secondary PM (2%).	Lanki et al. (2006b)
$PM_{2.5}$	Central site PM source modeling from ionic and elemental composition with gases	Decrease in peak expiratory flow rate (PEFR) of asthmatics in Helsinki (FI)	Significantly decreased evening PEF per interquartile range (μg/m^3) increase in 5-day average of local combustion $PM_{2.5}$. No significant increase with soil, sea-salt or long-range transported secondary PM.	Penttinen et al. (2006)
$PM_{2.5}$	Central site PM source modeling from ionic, elemental and organic carbon (OC) composition with gases	Cardiovascular (CV) and respiratory emergency department visits in Atlanta (US)	Significantly increased emergency department visits per interquartile range (μg/m^3) increase in the same day $PM_{2.5}$: 1.2-2% in respiratory visits for sulphate-rich secondary PM and 1.3-3.3% in CV visits for mobile sources, biomass combustion, other OC sources, and metal processing..	Sarnat et al. (2008)

Table 3. Source and chemical composition related heterogeneity in urban air ultrafine ($PM_{0.1}$ / $PM_{0.2}$), fine ($PM_{2.5-0.1}$ / $PM_{2.5-0.2}$) and coarse ($PM_{10-2.5}$) particle induced toxicity in selected European and US cell and animal studies.

PM metrics	PM variables and particulate sampling sites	Toxicological end points tested for heterogeneity	Key findings	Reference
$PM_{10-2.5}$, $PM_{2.5-0.1}$	Inorganic ions, total elements, PAHs, hopanes, steranes, endotoxin. Particulate samples collected in four Dutch sites and two German sites with varying nearby traffic volumes and in Dutch freeway tunnel, urban site in Rome and wood smoke environment in Lycksele.	Acellular oxidative capacity (ascorbate depletion in synthetic RTLF, DNA damage) and proinflammatory activity (arachidonic acid, IL-6) of isomass $PM_{2.5-0.1}$ and $PM_{10-2.5}$ samples in mouse macrophage cell line; proinflammatory activity and cell damage in the lungs of exposed rats (cell number, total protein, LDH, uric acid, TNFα, MIP-2 in BALF; histopathological examination of the lungs); pro-coagulation activity in blood (fibrinogen).	$PM_{2.5-0.1}$ markers of vehicle brake dust (Cu, Ba) and tire dust (Zn) and wood smoke (K^+), and $PM_{10-2.5}$ markers of vehicle brake dust (Cu, Ba) positively associated with some inflammatory endpoints and cell damage in the rat lungs. A trend of greater PM toxicity with higher traffic volumes.	HEPMEAP project: Gerlofs-Nijland et al. (2007)
$PM_{10-2.5}$, $PM_{2.5-0.15}$	Ions, total elements, PAHs, endotoxin Combined clustering of chemical constituents in both size-ranges on the basis of correlation pattern with biological responses. Particulate samples collected in four European cities (Rome (IT), Oslo (NO), Lodz (PL), Amsterdam (NL)) during spring, summer and winter seasons.	Proinflammatory activity (TNFα, MIP-2, IL-6, IL-8) of isomass $PM_{2.5-0.2}$ samples in primary rat alveolar macrophages and alveolar epithelial cell, and human alveolar epithelial cell line. Proinflammatory activity and cell damage in the lungs of exposed rats (albumin, Clara cell protein, TNFα, MIP-2 in BALF). Adjuvant activity in allergic sensitization of mouse lungs (IgE antibodies in blood, histopathology of the lungs).	Clusters of traffic, industrial combustion and/or incinerators, and combustion of black and brown coal / wood smoke positively associated with adjuvant activity for respiratory allergy. Clusters of crustal soil material and sea spray positively associated with measures of inflammation and acute toxicity. Cluster of secondary inorganic aerosol and long-range transport aerosol exclusively associated with systemic allergy.	RAIAP project: Steerenberg et al. (2006)

Table 3 (cont.)

$PM_{10\text{-}2..5}$, $PM_{2.5\text{-}0.2}$	Inorganic ions, dicarboxylic acids, water-soluble elements, PAHs, EC, OC, total elements, levoglucosan, endotoxin. Chemical mass closure Particulate samples collected in six European cities during contrasting air pollution situations by local sources and meteorology: Duisburg (DE), Prague (CZ), Amsterdam (NL), Helsinki (FI), Barcelona (ES) and Athens (GR).	Proinflammatory activity (TNFα, MIP-2, IL-6) and cytotoxicity (cell viability by MTT test) of isomass $PM_{2.5\text{-}0.2}$ samples in mouse macrophage cell line and proinflammatory activity in the lungs of exposed mice (cell number, total protein, TNFα, KC and IL-6 in BALF).	Photo-oxidized organic compounds, possibly together with transition metals (most consistently Ni and V) originating from fuel oil combustion, and soil-derived crustal material positively associated with inflammatory activity of fine particulate samples. PAHs from incomplete biomass and coal combustion positively associated with cytotoxicity and immunosuppression. Negative or inconsistent association of regionally and long-range transported secondary inorganic ions (NO_3^- , NH_4^+, SO_4^{2-}) with the inflammatory or cytotoxic activity of fine particulate samples. The results from cell and animal studies similar to each other.	PAMCHAR project: Jalava et al. (2009) Jalava et al. (2008) Happo et al. (2008)

Table 4. Summary of physico-chemical and biological properties of urban air particles with health interest in future studies.

PM property	**Determinants**
Size class / distribution	Number, length, surface area, volume / mass
Fraction by solubility	Non-soluble solid fraction vs. water-soluble and lipid-soluble fractions
Chemical composition	Transition metals (e.g. Cu, Ni, V, Fe) Reactive organic compounds (e.g. PAHs, quinones)
Bioavailability	Active or passive penetration to key defence cells (e.g. macrophages, other inflammatory cells, epithelial cells
Biological reactivity	Oxidative potential; inflammatory, cytotoxic and genotoxic activities

VI.2 Document of Research Needs; formulated after the COST 633 meeting at Ispra, May 2004

COST ACTION 633

Particulate Matter:
Properties Related to Health Effects

STATEMENT

RESEARCH NEEDS IN THE AREA OF PARTICULATE AIR POLLUTION AND CHILDREN'S RESPIRATORY HEALTH IN EUROPE

Management Committee Meeting in Ispra, May 13 -15, 2004

1. Introduction

The COST Action 633 focuses in 2002-2007 on the development and evaluation of scientific methodologies and databases that would improve the scientific understanding and regulatory basis of the physico-chemical characteristics and emission sources of ambient air particulate matter responsible for current substantial mortality and morbidity among European populations. It also promotes multidisciplinary collaboration between European research groups. COST 633 has 18 participating countries: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Italy, Lithuania, Netherlands, Norway, Portugal, Slovenia, Spain, Switzerland and United Kingdom . In addition, the European Commission DG Joint Research Centre (Ispra) and IIASA (Laxenburg, Austria) participate in the Action.

2. Scientific background

The current scientific understanding of the health impacts of ambient air particulate matter in Europe has been largely reviewed in the project 'Systematic Review of Health Aspects of Air Quality in Europe' conducted by the WHO European Centre for Environment and Health in 2002-2004 for the EC-DG Environment 'Clean Air for Europe' (CAFÉ) Programme. The published and currently prepared reports confirm the susceptibility of several large population groups to particulate air pollution: fetuses and children, child and adult asthmatics, and elderly subjects with chronic obstructive pulmonary disease (COPD) or ischemic heart disease. We acknowledge that children's health and respiratory diseases will be priorized in the first phase of the European Environment and Health Strategy 2004-2010 and, therefore, our subsequent formulation of research needs deals only with impacts of particulate pollution on children's respiratory health.

The European and US studies reviewed by the WHO expert group on particulate matter, ozone and nitrogen dioxide in 2003 indicate a whole range of adverse impacts that particulate air pollution can potentially cause on children's respiratory health: increased symptoms and bronchitis, decreased lung functions and retarded lung growth as well as increased medication use and hospitalization of asthmatic children. Living in an area with high regional background of particulate air pollution and ozone (US), living in home and going to school in immediate vicinity of busy highways (NL), and living in vicinity of poorly controlled metal industry (US) have all been associated with adverse impacts on children's respiratory health, but the causative nature of these or other common emission sources and their particulate constituents is unconfirmed in a broader European setting.

3. Suggestion of research needs in Europe

Improved characterization of the increased exposure to physico-chemical constituents of ambient air particulate matter, and of the associated respiratory health risks with the help of epidemiological and toxicological studies, are needed in relation to combustion and non-combustion emissions from traffic, combustion emissions from residential heating and large emissions from poorly controlled industries in vicinity of children's usual living environments. Similarly, the sources, physico-chemical characteristics and health impacts of high regional background levels of particulate pollution should be investigated.

4. Rationale for air quality topics

4.1 A substantial portion of total fine particulate (diameter < 2.5 μm) emissions in European countries is derived from traffic and residential heating (wood, coal) -related combustion processes.

4.2 Day-care centres and schools are often located along busy roads in residential areas in order to provide good traffic connections for the parents.

4.3 Traffic is an emitter of, not only very small fine and ultrafine (particle diameter < 0.1 μm) particles from combustion engines, but even larger masses of fine and coarse (particle diameter > 2.5 μm) abrasion type particles are produced from brake, tyre and asphalt wear. In addition, traffic resuspends other deposited dust from the ground into the atmosphere.

4.4 Traffic and residential heating -derived emissions as well as the non-stack emissions from poorly controlled industries are released at low heights above the ground, which makes them likely to cause large impacts on the local ambient air quality.

4.5 The impacts on local outdoor air quality are likely to be reflected on the indoor air quality in the residencies. This applies well to numerous constituents of ambient air fine particulate matter.

4.6 There is little scientific information in Europe on the air quality and health aspects in relation to residential heating and effective national or EU strategies for its control do not exist. However, one intervention study from Dublin has shown a large reduction in mortality in the 1990's, when coal sales were banned and heating with coal was stopped.

4.7 The national and European strategies against global warming include increasing use of biomass combustion for residential heating, which can potentially increase exposures to numerous particulate and gaseous pollutants and impair health of large populations (including children).

4.8 Uncontrolled biomass combustion in agriculture and in wildfires can have substantial contributions to the background particulate pollution in large areas of Europe.

5. Rationale for children's susceptibility

5.1 Young children spend more time in their residential areas than adults (home, day-care centres, schools) which increases their outdoor and indoor exposures to particulate and gaseous pollutants from local sources. They spend also more time exercising outdoors than adults, which increases pollutant doses in their lungs.

5.2 Increased prevalence of respiratory allergies and asthma in children enhances the sensitivity of their lower respiratory tract to irritant air pollutants such as particulate matter.

5.3 Previous epidemiological studies in Europe have shown significant associations between ambient air fine particulate matter and respiratory health effects among asthmatic children living in suburban areas but the responsible particulate constituents and emission sources are not fully understood.

5.4 Previous epidemiological studies in US have shown significant associations between ambient air particulate matter concentration and adverse effects among asthmatic children living in residential areas polluted by emissions from residential heating.

VII. Results from Working Group 3: Sources, Emission, Modelling, Economic Aspects

Chair: Thomas Kuhlbusch

VII.1 Emission inventories, source apportionment, modelling, and integrated assessment modelling

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** A. Miranda lead author for Exposure Modelling
*** W. Winiwarter lead author for Emission Inventory
**** R. Friedrich lead author for Integrated Assessment Modelling

Health effects caused by PM can only be studied by proper exposure descriptions. This includes a detailed characterization of particles in ambient air as was discussed in the previous section. This section tries to combine all necessary information for assessing the possible impacts caused by airborne particles – either as PM mass, number concentrations or possible other metrices. This section is structured starting with emission inventories. Emission inventories are prerequisites for source apportionment studies as well as dispersion models, both used for exposure and abatement strategy assessments. Hence the second and third part of this section deals with source apportionment studies in Europe and models used in Europe for exposure assessments. The last part of this section, dealing with integrated assessment modelling, integrates the information given in this section as well as in the previous sections.
Each part in this section gives its own recommendations which were taken up in the discussion leading to the COST 633 position paper (chapter III of this report).

VII.2 Emission inventories – Availability and Limitations

Release of particulate material into the atmosphere: quality considerations of PM emission inventories

1. Summary

Transfer of material into the atmosphere is a key factor influencing atmospheric concentrations of trace constituents. Emission inventories provide the information needed to understand and quantify this process. Both regulatory interests and scientific needs require high quality emission data. In contrast to inventories of gaseous pollutants, which are well-established, inventories of particulate matter (PM) suffer from a low level of reliability. While considerable efforts for improvements are underway, the major obstacles are specific properties of PM. PM is not a unique substance, but an internal and/or external mixture of a multitude of compounds from very different origin, different effects on substrates, and different size. Quantification of emission rates is hampered by their strong dependencies on measuring conditions (temperature, lapse time) and process state (start-up vs. equilibrium). Successful efforts to abate emissions have lead to a situation where emissions very strongly depend on the technology of PM abating equipment used – for which information often is not available on an aggregate level. Furthermore, abatement measures have very different effects on different particle size classes, and typically rather influence larger particle sizes. Emission rates, e.g. in domestic heating from small installations, are strongly determined by national and regional habits, making it difficult to identify appropriate emission factors and use them for a larger domain. Information on fugitive emissions is sparse, i.e. suspension of particles which are not contained in an exhaust air duct, caused by wind shear, material transfer processes or other mechanical forces. This concerns activities in industry and agriculture, but also motorized vehicle traffic in addition to exhaust (Diesel) particles. Important PM emissions derive from natural processes, like sea salt and wind blown dust. Comparing independent efforts in assessing emissions, here national data (from Austria) to the trans-national estimates of IIASA's GAINS model, allows to better understand and quantify an inventory's significance. Methodological improvements and harmonization efforts currently under way in Europe will focus activities and allow for more reliable PM inventories in the near future.

2. Introduction

Emission inventories describe the release of trace constituents into the atmosphere. They have been established as a tool to environmental planning and therefore are often driven by policy needs. Any policy to reduce the impact of air pollution needs to address the polluter. Emission inventories identify polluters and thus provide means for an effective development of reduction measures. Even indirect methods to assess sources for air pollution from ambient air measurements using statistical methods of source apportionment (for an overview see Viana et al., 2008) often require emission inventories as input data. Furthermore, emission inventories are indispensable background information for atmospheric modelling and thus subject to scientific scrutiny. Knowledge on the release rates of trace compounds into the atmosphere, in their spatial and temporal resolution, is indispensable to derive their atmospheric transport and transformation.

Particulate matter as an air pollutant has long been recognized as a serious air quality problem, but in connection with large scale installations and mostly due to stack emissions. This type of emissions could relatively easily be measured – in order to provide reliable emission estimates – and controlled by applying appropriate abatement devices (e.g. by cyclones, filters, including electrostatic precipitators, and scrubbers).

As a consequence of the relative new discovery of health relevance of ambient air level concentrations of fine particulates (Dockery et al., 1993), the focus of attention moves from the point sources to the fugitive emissions, from a small number of installations to a vast number of individual release points (or even an indiscriminate release area), which as such provide a tiny contribution to total load each, but combined are responsible for a major fraction of the pollution level observed, while their emission behaviour largely differs.

While some information on PM emission has been available in U.S. emission assessment guidelines for some time (EPA, 1999), an adequate European standard has been added to the Atmospheric Emission Inventory Guidebook (EEA, 2007) only recently. Such guidelines, compilations of available information from measurements, are the foundation of national inventories; thus also such national inventories only start to be developed as a country-led approach. PM inventories as a useful tool to describe the fluxes of material into the atmosphere thus are rather in their infancy, despite of the long history of PM considered as air pollutants.

The following considerations will be limited to inventories of PM emissions. Emissions of gaseous compounds, which may give rise to PM formation in the atmosphere – secondary inorganic aerosol, SIA, or secondary organic aerosol, SOA – are not covered. These emissions of gases in general are believed to be better understood than PM emissions (see e.g. Rypdal, 2002, for an uncertainty estimate).

3. Specific obstacles in assessing PM emissions

Emissions of atmospheric trace constituents are, in absence of measurements, estimated from the extent of a statistical entity, the so-called activity, and specific emission factors describing their relationship towards emissions:

$$E = A * EF$$

Emission estimation is performed by source or source sector, using a specific emission factor representing a certain compound (here: PM). A major underlying assumption in this operation is that the emission factor chosen adequately reflects an activity's emission behaviour, so that in consequence this simple algorithm describes emissions under a variety of realistic conditions (e.g. spatial and temporal variability). Unfortunately this is not always the case for PM:

- As a product of incomplete combustion, PM composition and quantity largely depends on the exact combustion conditions and efficiency of the process. Increased efficiency will largely reduce emissions.
- In the case of suspension of fine particulate material, e.g. by wind, its levitation behaviour may be strongly influenced by the "stickiness" of individual particulates driven by water content of surfaces. In very dry conditions, fine clay particles which normally would draw water might separate more easily and thus remain airborne.

- In both cases, any emission abatement leads to partial removal of particles, the extent of which again very strongly depends on operating conditions and is difficult to exactly foresee.

In cases where emission factors inadequately describe emitting conditions the emission factor approach can not be used. So the set of available (measured) situations needs to be separated into homogeneous clusters. This procedure just requires knowledge on specific emission factors for each cluster, and on the respective activity distribution into each of the clusters. Separating combustion into flame and smoldering conditions, for example, would require knowledge on the amount of material undergoing each of those two processes.

Moreover, while typical PM emission measurements report just on the weight (or sometimes just on the number concentration) of particles, PM exhibits a number of characteristics that needs to be accounted for a full description. Most notably are

- particle size
- particle composition in terms of
    - deliquescence or hygroscopicity
    - volatility
    - chemical speciation in general

The particle size, and parameters influencing particle size (hygroscopicity and volatility) will influence the release properties and the atmospheric behaviour, with large particles in general exhibiting smaller atmospheric residence times. Volatility affects measurements of both emissions and ambient air. The chemical composition is important in terms of deliquescence/volatility, but also if source apportionment studies are used to trace specific sources (see Viana et al., 2008). The commonly used Lenschow approach for source apportionment (Lenschow et al., 2001) relies on availability of chemical composition data.

While the release process for particles may be reasonably well described in plumes, PM often also derives from not so well characterized release points. Fugitive emissions make it difficult to actually quantify a flux, even when concentration measurements near the release site are available. Moreover, the release into the atmosphere, where the PM is being "picked up" by atmospheric models, may be hampered by so-called canopy effects, when emitted material re-deposits immediately after its release (see Fig. 1). In that case, a specific interface to describe the fate of the emission until it actually becomes airborne needs to be created.

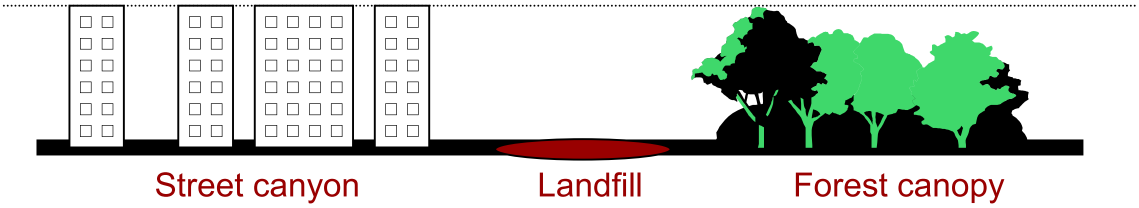

Figure 1: Concept of "canopy effects" causing re-deposition of material immediately following its release. Emitted substances need to be transported across the dotted line before they are adequately covered by atmospheric models

4. Examples demonstrating limitations in understanding PM release

4.1 Construction

Construction is one of the major sectors in European economy. In terms of its effects on the atmosphere, specific characteristics are that it is mainly an outdoor activity, which is occurring intermittently and on varying locations. This fact both makes limitations difficult, and reduces neighbors' protest as it may be seen an only temporary nuisance.

PM pollution from construction derives both from construction machinery, and from fugitive sources. Construction machinery is an investment for many years. Diesel engines operated at a construction site are typically many years older than trucks delivering goods. Old test bench emission factors for such engines are available, but not for situations of many years in-use. New engines that would accord to EURO standards are being introduced only at the slow rate of replacement. One difficulty is also to estimate the penetration rate of new equipment as well as the operation time (or fuel consumption) of such intermittent operation.

Even more difficult is an estimation of PM released from soil or from construction material during building or especially demolishing. Depending on the type of construction, large areas of land can be exposed to wind and/or to lifting (mostly) soil matter by ground operation of machinery. It is common practice to keep surfaces wet in order to reduce high dust concentrations on a construction site. In estimating emissions we would need to know the extent to which such methods are being applied in practice. So abatement methods effectively decrease the quality of inventories (while of course increasing the quality of the air).

4.2 Road dust emissions

Emissions from road dust (suspension of particles from the road, in connection with road abrasion) have been assessed many years ago in several U.S. studies (EPA, 1999). Unfortunately the results offered are highly disputable, and also would indicate that road dust is by far the most important source of PM pollution in the atmosphere – a statement which at this extent can not be confirmed by atmospheric observations or source apportionment analysis. Moreover, re-visiting the original dataset used by EPA to derive their recommended equations proved that their method was not extremely robust (Venkatram, 2000)

According to the original EPA equation, PM10 mass from road dust would be about 6 times as high as the tailpipe emissions. Re-evaluation (using the identical set of data) proved that at the same plausibility half the emissions (3 times tailpipe emissions) could be assumed.

As this still did not provide satisfactory results for Europe, additional measurements were taken, especially in Switzerland (Gehrig et al., 2004) and in Germany (Lohmeyer et al., 2004). These measurements now indicate (for tailpipe conditions as of 1995) approximately the same amount of PM is released from tailpipes and from road dust. More results are coming up, which seem to confirm these previous analyses (Ketzel et al. 2007).

4.3 Fugitive emissions from material handling in industry

Handling operations of dust generating material (rock, ore, sand, fertilizer, hay, corn, etc.) will inevitably release particulate material. The amount of release again is very difficult to capture, as concentration measurements alone will not suffice to estimate the emission flux. Thus this is an activity that in many cases has not received sufficient attention, even while the amount of material being moved in industry is extremely large. While the reliability may be a matter of debate, there exists a consistent tool that allows estimating emissions directly from activity data. VDI (1999) distinguishes the generation of emissions by material (humidity, brittleness, bulk density) and by the relevant process (height of fall, number of transfers and/or transports during process). At least a consistent set of data can be derived while adequate validation will not be provided.

5. Issues that remain yet to be solved

5.1 Agricultural activites

Extremely high PM concentrations as observed inside animal housing has been extrapolated to assess its release into the atmosphere (see e.g. Takai et al., 1998; Seedorf, 2007, and references therein). Animal housing is known to be the cause of local impacts to air quality, but the sheer relation between volume of air inside buildings and outside may put an effect from mere dilution of inside air on the outside air quality in question. Further deposition may potentially occur while air is leaving the building. The issue will have to be investigated in more detail.

Likewise, operations on open fields (plowing, harrowing, disking, harvesting) are known to lift particles into air. Algorithms for quantification have been made available by the US EPA. Again this algorithm seems to point towards extremely high emissions.

In a recent study, Öttl and Funk (2007) were able to show for the same soil and operation type, under different environmental conditions very different emission behavior will take place. Drying out of soils was a reason for a tenfold increase of emissions. European conditions, which tend to be more humid than those of the western U.S.A., thus will tend to produce distinctively less PM emissions.

While further investigation is needed, it may be speculated that dryness of topsoils (only a layer of a few cm is relevant, deeper soil layers will remain humid anyway) may cause dry-up of water in between clay particles, which under more humid conditions keeps them stick together. Clay particles, with a typical size of a few µm, are prone to remain airborne when lifted as single entities.

5.2 Natural emissions

On a global scale, the source terms of atmospheric particles have been estimated by IPCC (Penner et al., 2001). According to the figures presented, atmospheric PM should be expected to derive almost in its entirety to natural sources (Fig 2). By far the most prevalent sources are sea salt and wind-blown (mineral) dust. Again, this assessment contradicts both atmospheric observations and pollution levels.

Possibly, the algorithms used to derive the global picture are adequate to specific situations, but not to be extrapolated. The sea salt algorithm (Gong et al., 1997) provides the mass of small sea spray particles, i.e. wet droplets above the sea surface. Under normal conditions such droplets will dry up within seconds. At an average ocean salt content of 3.5%, real emissions into the atmosphere will immediately be reduced by a factor of 30 in volume (factor three in diameter).

In a similar way, mineral dust emissions have been calibrated to understand the release of desert dust. Large clouds of desert dust have been observed to strongly affect the Amazon rainforest, Europe (both from the Sahara), Eastern China and Korea (Gobi desert). As described for agricultural processes above, this approach might not be fully adequate for barren area other than extremely dry conditions at ultra-fine soils. While the results of NatAir (Korcz et al., 2008) indicate that for Europe a calibration of the standard algorithms is possible to match atmospheric conditions, definitely more research is needed to understand the release process of soil material into the atmosphere.

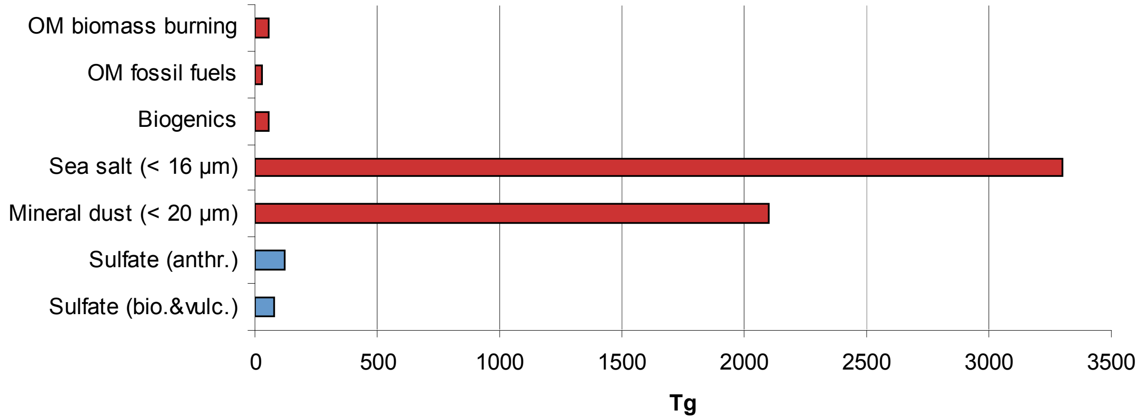

Figure 2: Source terms for atmospheric particles according to Penner et al. (2001). Blue bars denote secondary particle formation

Emissions of natural sources are of specific interest, as by definition they are not subject to abatement. Any action to provide health protection to the citizen requires to even more focus on anthropogenic emission activities. The scientific background to the political discussion on how to treat naturally emitted aerosols in terms of ambient air threshold values has been compiled by Marelli (2007). Natural PM sources also include Primary Biological aerosol Particles (PBAPs); their emissions have been estimated recently by Winiwarter et al. (2008).

6. Other important sources of PM emissions

Emission inventories in general are able to cover combustion emissions. Due to effective abatement measures, the contribution of formerly large single sources (industry, power plants) has been effectively reduced in Europe. Also modern Diesel engines (EURO4 and later, i.e. essentially vehicles from model year 2006 and later) have started a decreasing trend of PM emissions. This is consistent with EU regulations of ultra-low S-content (10 ppm) in Diesel fuel.

Vestreng et al. (2007) provide an estimated sectoral split of emissions. Tab. 1 shows fugitive sources as “PMcoarse”, and combustion emissions as PM2.5. In addition to the sources covered in the discussion above, considerable emissions occur from “non-combustion plants” (almost a third of the PM2.5 emissions). These emissions predominantly derive from solid fuel use in domestic heating. Emission factors for this sector are available (e.g., EEA, 2007) and the processes are reasonably well understood. However, efficient modern technology exists which is able to burn solid fuels at very low emissions (Obernberger and Brunner, 2005). In order to adequately address this improvement, information on the extent of fuel consumption in these modern installations (with respect to the total consumption) is required.

Table 1: PM emission in Europe (in Gg, 27 EU member countries) as of 2005, expert estimate (Vestreng et al., 2007). "PMcoarse" denotes particles larger than PM2.5, but included in PM10.

SNAP SECTOR	PM2.5	PMcoarse	PM10
01: Combustion in energy and transformation industry	137	110	247
02: Non-industrial combustion plants	517	125	642
03: Combustion in manufacturing industry	150	66	216
04: Production processes	219	183	402
05: Extraction and distribution of fossil fuels	26	49	75
06: Solvent and other product use	22	11	33
07: Road transport *	267	82	349
08: Other mobile sources and machinery	140	17	157
09: Waste treatment and disposal	59	14	73
10: Agriculture	87	213	300
Sum	1625	870	2495

7. Existing PM inventories

Creation of an emission inventory is a tedious task. A detailed inventory thus becomes available only when policy interest is sufficiently high. As described above, PM was not considered a priority issue, and thus was not included in the national obligations of emission reporting. Only the latest versions of the Atmospheric Emission Inventory Guidebook (EEA, 2007) provide guidance needed for countries to be able developing an own national inventory. As a consequence, country estimates on "official" PM emissions still are not fully consistent.

Instead, a number of "top-down" estimates exist, which attribute emissions to European countries. The first such estimate is probably a report by Berdowski et al. (1996). The CEPMEIP inventory was derived from this work (Tab. 2), like also some national studies (e.g. Winiwarter et al., 2001). The GAINS dataset is an independent Europe-wide top-down assessment, the EMEP set reflects expert estimates based on national emissions officially submitted. EMEP also provides a scheme for spatial disaggregation to the EMEP grid (50x50 km^2).

For illustrative purposes only a global dataset is shown. The BC inventory prepared for GEIA has been established in order to understand global warming, health issues are not considered.

A considerable number of urban inventories have been established by local agencies and their contractors in Europe. Both SATURN and City-Delta have attempted to compile this information. However no comprehensive list of areas providing PM inventories is available. More recent urban inventories tend to consider also PM10 and PM2.5 size fractions, and benefit from the improved availability of realistic emission factors.

Table 2: Some PM inventories in Europe.

	source	Spatial resolution	Species considered*
CEPMEIP (Europe)	Pulles, 2001	country	TSP, PM10, PM2.5
GAINS (Europe)	Kupiainen and Klimont, 2004	country	BC, OC, TSP, PM10, PM2.5
EMEP (Europe)	Vestreng et al., 2007	50x50km²	PM2.5, PM10
GEIA (global)	Penner et al., 1993	1°x1°	BC only
SATURN (urban)	Sturm et al., 2000	Individual cities (1x1km² - 5x5km²)	TSP
City-Delta (urban)	Thunis, 2006	Individual cities 5x5km²	PM2.5, PM10

*) Species considered are Total Suspended Particles (TSP), Particles with aerodynamic diameters smaller than 10 µm (PM10), Particles with aerodynamic diameters smaller than 2.5 µm (PM2.5), Black Carbon (BC), Organic Carbon (OC)

8. Quality checks

PM inventories require detailed quality assessment in order to establish confidence. Detailed descriptions of quality checks in emission inventories are available (e.g. Sturm and Winiwarter, 2004). The main element of all these checks is locating relevant independent data to be compared with. Independent data in this sense can be

- emission data prepared for another time period, while emissions remain comparable
- emission data for a different area/region/country, as long as conditions are similar
- alternate emission data for the same area and time period (see Fig. 3)
- data from ambient measurements

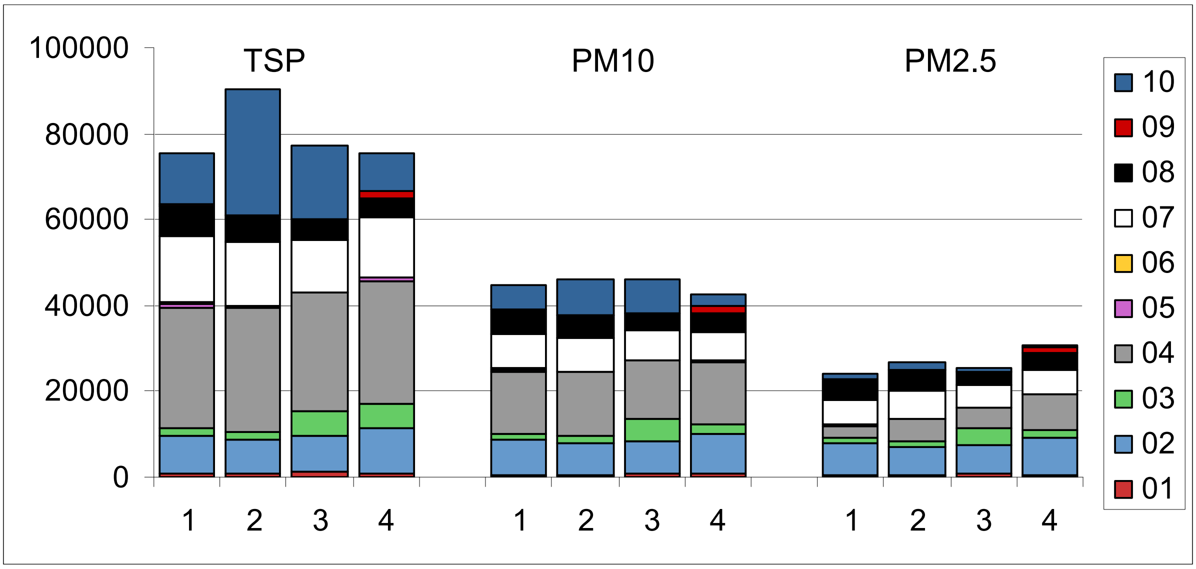

Figure 3: Comparison of Austrian PM emission estimates. Emissions are in tons, presented by SNAP sector (see Table 1 for description). (1) is data from Winiwarter et al., 2007, (2) is the official Austrian inventory (Umweltbundesamt, 2007), (3) is an older assessment for Austria (Winiwarter et al., 2001), and (4) stands for the GAINS set (Kupiainen and Klimont, 2004)

It is evident that a comparison of an emission inventory with measured data, if at all possible, is the most convincing approach. Measurements most closely reflect the exposure of humans and their health risk, which is the topic to be considered. Two options seem possible to bridge the gap between these otherwise unrelated datasets.

- Use emission data in an atmospheric model, and compare concentrations to measurements
- Use ambient measurements and source apportionment to estimate emission fluxes, to be compared with the inventory

Any of these methods, if thoroughly applied, will create opportunity to improve the PM inventory and thus greatly increase the confidence into such an inventory.

9. PM emissions that will require further attention in future

The primary focus of most existing PM inventories is assessing PM mass released. The majority of measurements available are on total mass, and discrimination by species is first of all being made by differentiation of sources. In terms of health impacts, such an assessment is justified by the links of air pollution to health based on PM10 and PM2.5 mass (Dockery, 1993; Pope, 1995). Typical effects to the human body are inflammations caused by insoluble particles enclosed by body tissue.

There is however also effects due to bioaerosols, which affect biological processes in a much more direct way, thus much lower concentrations may need consideration. This is the case for pollen (especially in terms of allergic reactions), bacteria or virus which may be directly interfering with human metabolism. Winiwarter et al. (2008) report on emissions of bioaerosols (mass based) and state that pollen at typical diameters of 10-60 µm will be too large to undergo significant long range transport. Still pollen fragments may be carried over long distances and become the cause for allergic reactions.

Combinations of compounds may also be a reason for health related effects. Endotoxins as compounds of bacteria's cell membranes may enhance allergic and non-allergic reactions caused by air pollutants leading e.g. to asthma (Peden, 2002; Riediker et al., 2001). At present, no detailed assessments of bioaerosol emissions are available, but they certainly deserve further attention.

Specific health relevant particles may also derive from new technology. A recent article by Poland et al. (2008) presents nanotubes as a potential health risk. Carbon nanotubes are cylindrical carbon molecules which exhibit promising material properties. At their length-to-diameter ratio of 10^6 they may resemble the health risk of asbestos. This issue and other, still unknown issues will have to be observed further.

10. Outlook

The focus on particulate matter, initiated by the understanding that PM at ambient levels is health relevant, considerably supported activities to improve the understanding on emission sources. Only in the recent years national authorities have started to compile national inventories, based on scientific support. Traditionally such policy orientated activities have been the foundation of inventories used in atmospheric models, and have given rise to scientific critique and improvement. More is to be expected also in the case of PM.

- Considerable additional efforts will be needed to understand the behavior of fugitive emission sources. While a more elaborate coverage of point sources tends to lead to decrease their estimated emission, fugitive sources become more dominant.
- Source apportionment will help to validate the respective contributions assessed for individual sources. More source related measurements of species composition will be needed to provide adequate species fingerprints.
- Differentiation of PM emissions by chemical species may be required also in terms of potential effects of PM.
- Assessing number distribution in addition to mass distributions provides similar information in terms of different aerosol qualities. However, as aerosol number distributions tend to change quickly in fresh plumes, it will be a matter of future definition to define a proper release point, which allows comparable results and a proper integration into atmospheric models.
- Resolving emission patterns temporally (annual cycle / weekly cycle / daily cycle) will be required to be used in exposure assessment.
- Environmental policy to abate emission will lead to mandatory low PM technology. New product standards will facilitate keeping track of new emission factors in databases, thus contributing also to improved inventories.
- Further challenges concern adequate coverage of emissions from natural source, as well as properly safeguarding citizens' health in events dominated by natural PM which can not be addressed by emission reduction.
- Improving the reliability of PM emission inventories as outlined above is urgently required for policy as well as for science. This concerns the proper source identification as well as coverage of abatement strategies.

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VII.3. Methods and results of source apportionment studies in Europe

1. Introduction

In the field of atmospheric sciences, source apportionment (SA) models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants, e.g., particulate matter (PM), based on ambient data registered at monitoring sites (Hopke & Song, 1997; Watson et al., 2002; Bruinen de Bruin et al., 2006). There are three main groups of SA techniques:

a) **Statistical approaches**: Methods based on the evaluation of monitoring data. Basic numerical data treatment is used to identify sources: e.g. (1) correlation of wind direction and composition data (Henry et al., 2002); (2) the correlation of gaseous pollutants with PM components; (3) subtraction of levels measured at the different site types from regional background to local hot-spots (Lenschow et al., 2001), or (4) quantification of natural PM contributions (e.g., African dust, Escudero et al., 2007). The main advantage is the simplicity of the methods and the consequent low impact of mathematical artefacts due to data treatment.

b) **Dispersion modelling**: Methods based on emission inventories and/or dispersion models to simulate aerosol emission, formation, transport and deposition (Eldering & Cass, 1996; Visser et al., 2001). Detailed emission inventories that are not always available are needed for this approach. A significant advantage is their use in assessing different scenarios e.g. to define the ‘best’ abatement strategy.

c) **Receptor modelling**: Methods based on the statistical evaluation of PM chemical data acquired at receptor sites (receptor models). There is a wide range of statistical models and modelling approaches which are currently available in the literature (Schauer et al., 2006). One of the main differences between models is the degree of knowledge required about the pollution sources prior to the application of receptor models. The two main extremes of receptor models are Chemical Mass Balance (CMB) and multivariate models. The fundamental principle of receptor modelling is that mass and species conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere (Hopke et al., 2006).

Despite the widespread need for these data, there is little information available on receptor modelling results from different European countries, the type of models applied or the input data utilised. Furthermore, comparability of the available SA results is limited given that parameters such as time resolution, type of monitoring site and PM sampler, and analytical methods vary widely from one study to another. Consequently, even though numerous SA results are available in the literature, general European-wide conclusions cannot yet be extracted. In addition to this lack of harmonization in the published studies, a large amount of valuable material is currently available in the grey literature only.

The need to tackle this issue was detected by the COST Action 633 (“Particulate Matter: Properties related to health effects) and subsequently addressed by compiling a database of SA studies available in Europe, more specifically in COST633 member countries (http://www2.dmu.dk/atmosphericenvironment/COST633/). Both meta-data on publications and data on PM sources and source contributions were collected, with the aim to obtain an overview of the results and analyse their comparability. The issue of the comparability between receptor modelling results is considered essential if SA data are to be used for the design of multinational mitigation strategies, the assessment of human exposure to PM from specific sources, and investigations of long-term changes in exposure situations over Europe.

2. Methodology

The compilation of meta-data on SA publications was carried out by means of a questionnaire, distributed via e-mail among researchers from COST633 member countries and based on already existing publications in international scientific journals or public reports. The authors were asked to report on the meta-data specified in Table 1.

Table 1: Meta-data reported in the questionnaires.

Field	**Description**
Publication	Reference of the paper, report, etc.
Technique	Receptor modelling technique or approach used
Study area	Number and location of monitoring sites
PM data	Type of sampler (high-volume, impactor, etc.), sample duration (hours), etc.
Additional data	E.g., meteorological parameters, gaseous pollutants, etc.
Target metric	PM10, PM2.5, PM1, etc.
Analytical methods	Type of analyses performed (ICP, PIXE, XRF, etc.)
Time coverage	Duration of sampling period (X months, Y years, etc.)
Receptor sites	Type of site (urban background, industrial, regional, etc.)
Software	Software needed to run the model, if any
Technique	Theoretical principle
Main advantages	Main advantages of the technique
Main limitations	Main limitations of the technique
Origin of technique	Original publication where the technique was described
Contact	Contact person

Despite the fact that replies to the questionnaires were not obtained from all the member countries, the return may be seen as a useful overview on SA activities in Europe up to the end of the year 2005 (date of meta data collection). Furthermore, a literature search was carried out by the authors for SA-related papers published in 2006 and 2007 (thus extending the data to the current status), the results of which are also included in this paper (Table 2). It should be noted, however, that this overview does not claim to provide a review of all SA studies performed in Europe or the COST633 Action member countries.

Table 2: Publications reported in the questionnaires (up to year 2005, and unpublished data at that point in time) and results from the literature search (marked with *, published in 2006-2007). Numbers in superscript indicate the study site as listed in Figure 6a caption.

Results from questionnaires and literature search				
Almeida et al. (2005) ^{12}	Harrison et al. (1997) ^{16,33}	Maenhaut & Cafmeyer (1998) ^{8,9}	Quass et al. (2004) ^{14}	Vallius et al. (2003) ^{32}
Almeida et al. (2006) ^{12}	Harrison et al. (2003) ^{16}	Maenhaut et al. (1999) ^{8,9}	Querol et al. (2001) ^{3}	Vallius et al. (2005) ^{28,29}
*Andersen et al. (2007) ^{17}	Harrison et al. (2004) ^{16}	Maenhaut (2000)	Querol et al. (2002) ^{4}	Viana et al. (2006a) ^{6}
Bauer et al. (2007a)	Hueglin et al. (2005)	Marcazzan et al.	Querol et al.	Viana et al. (2006b)

		(2001) [21]	(2004b) [2,5]	[3]
Bauer et al. (2007b)	John et al. (2004a)	Marcazzan et al. (2003) [21]	Raes et al. (2005) [30,31]	Viana et al. (2006c) [6]
Borrego & Pio (1991)	John et al. (2004b)	*Marenco et al. (2006) [23,24]	*Ragosta et al. (2006)	Viana et al. (2007) [3]
Brüggemann et al. (2000).	Kaiser & Scheifinger (2003)	*Mazzei et al. (2006).	Rodríguez et al. (2004) [2]	Viana et al. (2008) [27]
*Canepari et al. (2006).	Kaiser & Scheifinger (2005)	*Mazzei et al. (2007).	*Salma & Maenhaut (2006)	Wåhlin & Palmgren (2005) [17]
Castro et al. (1999)	Kaiser et al. (2002)	*Minguillón et al. (2007b) [27]	Salvador et al. (2004) [1]	Wåhlin et al. (2006) [17]
D'Alessandro et al. (2003) [22]	Kaiser et al. (2004)	Mossetti et al. (2005) [21]	*Salvador et al. (2007) [1,26]	Yin et al. (2005) [18,19,20]
D'Alessandro et al. (2004) [22]	Kuhlbusch et al. (2004)	Öttl et al. (2005) [25]	Schnelle-Kreis et al. (2006)	Zabalza et al. (2006) [7]
Düring et al. (2003) [13]	*Lanz et al. (2008)	Pio et al. (1989) [10]	Spindler et al. (2004) [15]	
Ebert et al. (2007)	*Lonati et al.(2007)	Pio et al. (1996) [11]	Stölzel (2003) [15]	
*Gerasopoulos et al. (2006)	Lucarelli et al.(2004) [22]	*Pratesi et al. (2007).	Szidat et al. (2004a)	
Gerwig (2005) [15]	Maenhaut & Cafmeyer (1987)	Prendes et al. (1999) [26]	Szidat et al. (2004b)	

2. Results and Discussion

3.1 Receptor models in use in Europe

The number of European publications reported in the questionnaires as a function of the receptor modelling approach used is summarised in Figure 1. PCA was the most frequently used model up to 2005 (30% of the studies), followed by the Lenschow approach (11%) and back-trajectory analysis (11%). Other models commonly used were PMF (8%), CMB (7%) and mass balance analysis (addition of chemically analysed PM components, 7%). The data from the last two years (2006-2007, resulting from the literature search and not grouped with the data from <2005 because they were not reported in the questionnaires) show a continued use of PCA (50% of the new publications) and an increase in the use of PMF (13%) and the mass balance analysis of chemical components (19%). No new publications applying CMB or the Lenschow approach in Europe were obtained for 2006-2007.

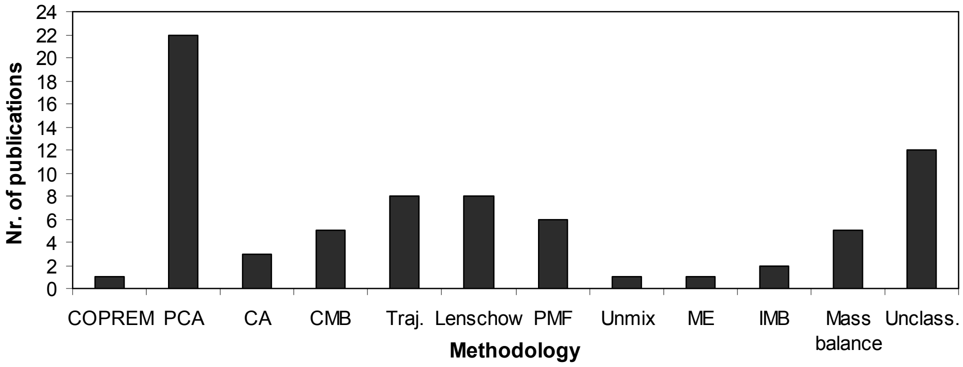


Figure 1: Number of publications (up to 2005) as a function of the receptor modelling approach used. COPREM (Constrained Physical Receptor Model); PCA (Principal Component Analysis); CA (Cluster Analysis), CMB (Chemical Mass Balance); Traj. (Trajectory analysis); Lenschow (Lenschow approach); PMF (Positive Matrix Factorisation); UNMIX (UNMIX receptor model); ME (Multi-linear Engine); IMB (Isotopic Mass Balance). Unclass.:unclassified.

3.2 Target metric, sampling and analytical methodologies, receptor sites

3.2.1 Target metric

Until 2005, PM_{10} was on average the preferred target metric (46% of the publications reportted, Figure 2a) followed by $PM_{2.5}$ (33%). Studies focusing on other size fractions were reported with much lower frequencies: $PM_{2.5\text{-}10}$ (9%), TSP (4%), PM_1 (3%), PM_2 (1%) and $PM_{0.1}$ (1%). Based on the year of the publications (Figure 2b), results evidence a slow but progressive increase in the use of PM_{10} from 1997 to 2003, whereas models were applied to $PM_{2.5}$ only after 2000 and increased sharply in 2003 (first year with more studies on $PM_{2.5}$ than PM_{10}). In 2006 and 2007 (not included in Figure 2) 38% of the new studies found in the literature targeted $PM_{2.5}$ while only 29% focused on PM_{10}, thus confirming a change in focus in SA studies in Europe. This focus on the sources of fine aerosols is most probably related to stronger recent evidence on the adverse effects of fine particulates on health (Lanki et al., 2006; Pope & Dockery, 2006) as opposed to coarser particles. As a result, an increase in the number of papers published from Europe on smaller particle size fractions ($PM_{2.5}$, PM_1) is likely in the coming years. Such studies from the US are already available in the literature (Pancras et al., 2006). The detailed source apportionment of very fine grain size fractions (PM_1 and smaller) will also require the characterisation of specific tracers and chemical profiles for this fraction, given that source profiles should not be expected to be the same for coarse and fine aerosols.

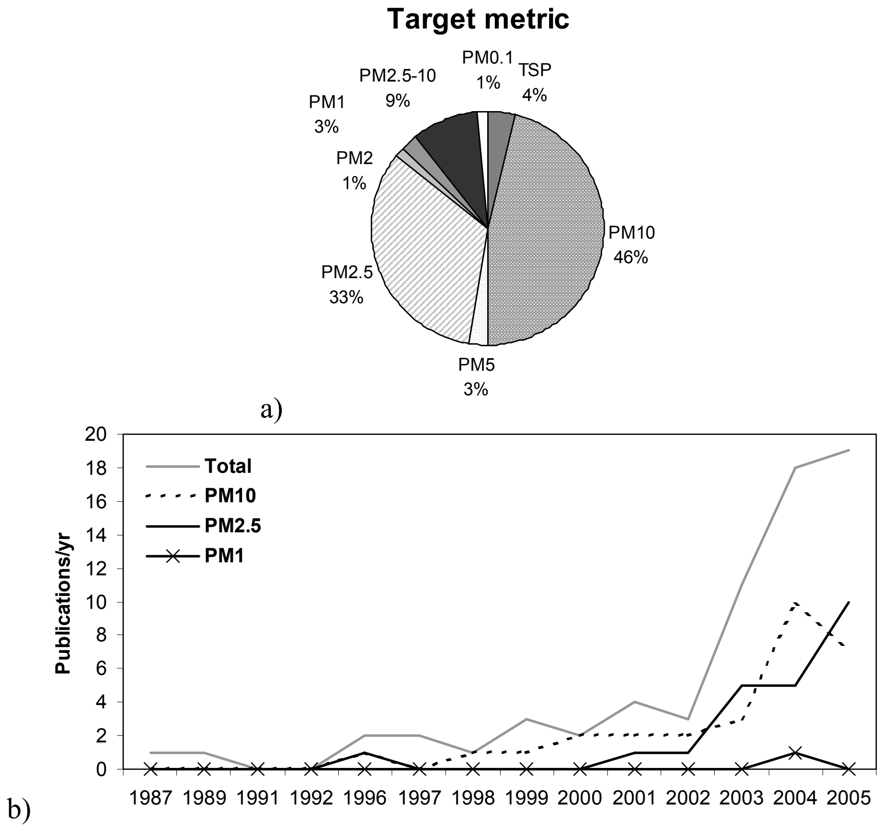
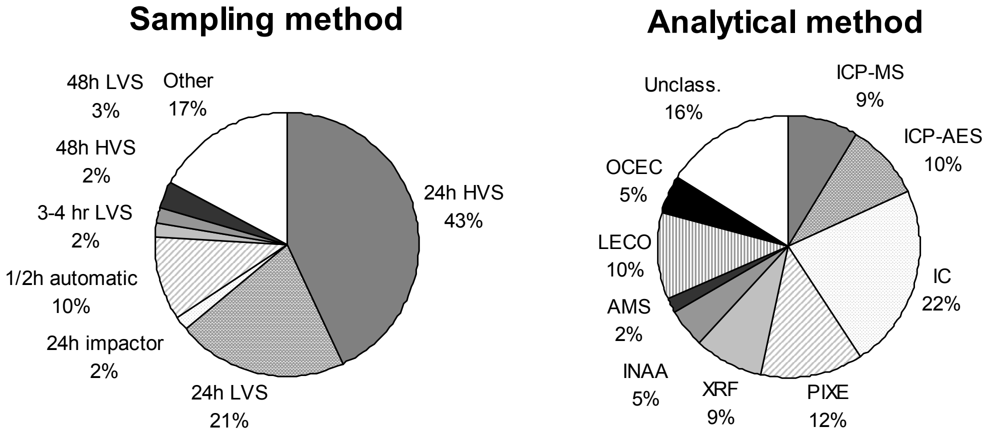


Figure 2: a) Target metric of reported SA studies until the year 2005 (included). b) Time evolution of publications on SA of PM_{10}, $PM_{2.5}$ or PM_1 between 1987 and 2005.

3.2.2 Sampling methodology

A large variety of sampling methodologies was recorded throughout Europe for the different PM fractions analysed (Figure 3a). The choice of method will influence the PM and chemical data extracted, as the different methodologies are subject to the impact of different sampling artefacts (magnitude and type, Turpin et al., 2000). High-volume samplers (typically >30 m^3/h) were used in the majority of the SA studies reported (43%), with 24h as the standard sampling period (66% of the total). This duration was the most commonly used as it allows for the comparison with the daily limit value for PM concentrations. Longer sampling durations (48h) were also reported, although less used (5%) due to the larger influence of (mostly negative) sampling artefacts. The second widespread method of sampling was for 24 hours with a low-volume sampler (typically 1 m^3/h, 21%) both in terms of number of studies and of groups applying this methodology. Semi-hourly automatic data represented 10% of the studies reported, mostly used in combination with back-trajectory data, and were essentially used by two research teams. In the last two years (2006-2007), the number of studies using 24h low-volume samplers increased (31% of the total, 5 new studies) while there were only two new studies (13%) using high-volume samplers. The use of new sampling and monitoring methodologies (e.g., streaker sampler, particle number, particle size distribution, etc.) were reported for 50% of the 2006-2007 studies.



a) b)

Figure 3: a) Sampling methodologies reported until the year 2005 (included). b) Analytical methods reported until the year 2005 (included). Unclass.: unclassified. Inductively Coupled Plasma - Mass Spectrometry (ICP-MS); Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES); elemental analysis (LECO analyser); Particle Induced X-Ray Emission (PIXE); X-Ray Fluorescence (XRF); Ion Chromatography (IC); Instrumental Neutron Activation Analysis (INAA); Accelerator Mass Spectrometry (AMS); organic and elemental carbon analysis (OC-EC).

3.2.3 Analytical methodology

A broad spectrum of techniques was described for the determination of different chemical components (Figure 3b), ranging from destructive to non-destructive techniques. Ion Chromatography (IC) was the most commonly used technique for the determination of ionic species (22% of the studies), while major and trace elements were determined in similar proportions (9-12%) by means of ICP-AES (Inductively-Coupled Plasma Atomic Emission Spectrometry), ICP-MS (Inductively-Coupled Plasma Mass Spectrometry), PIXE (Particle

Induced X-Ray Excitation spectrometry) and XRF (X-Ray Fluorescence). Discrimination between organic (OC) and elemental (EC) carbon was only carried out in 5% of the studies, evidencing the large potential remaining for the determination of vehicular sources (e.g., diesel vs. gasoline vehicles). As novel applications, it is essential to highlight the use in the years 2006-2007 of Aerosol Mass Spectrometry (AMS) and ^{14}C analyses. These techniques allow for the distinction of primary and secondary organic fractions and the distinction of fossil versus non-fossil particulate carbon, respectively.

The extent and quality of the chemical data is also a determining factor with regard to the potential of SA methods to clearly separate sources. As an example, the general lack of an appropriate uncertainty estimates is a clear limitation when applying models such as PMF, COPREM or CMB, given that uncertainty matrices are required as input for these models. To overcome this, the missing uncertainty data must be estimated using algorithms based on detection limits or reproducibility of the results, that may result in the restriction of the potential of the models to resolve the sources.

Another example is the absence of major tracer species in the compositional datasets, when certain PM components are not analysed or their analyses are not reliable enough using a given technique (e.g., Na concentrations when analysed by XRF, Götschi et al., 2005; Viana et al. 2007). Even though these tracers may be determined in parallel using correction factors or by additional techniques (in the case of Na, Rhodes & Hunter, 1972; Maenhaut & Cafmeyer, 1998), this might introduce a bias in the analysis.

3.2.4 Receptor sites

Receptor sites where the models were applied also constitute a differentiating factor. As shown in Figure 4 (top), urban background locations were clearly preferred (53% of the studies) probably due to the fact that SA studies aim mostly to represent maximum population exposure. However, the issue remains whether monitoring and/or SA studies should be carried out at locations where a smaller proportion of the population is exposed, but where PM levels and composition present potentially higher health risks, e.g., industrial or kerbside sites. These types of sites were the target of 11 and 20% of the studies reported, respectively. The opposite situation was found regarding rural sites (16%), given that rural environments are not generally representative of the population's exposure but are nevertheless extremely useful locations to investigate the origin and properties of background and long-range transported aerosols. The studies which applied the Lenschow approach included at least two site-types, given that in this method the spatial variability of PM concentrations is used.

However, this distribution is dependent on the country (Figure 4, bottom). The dissimilarities in the distribution of monitoring site types between national networks in Europe have already been noted (Querol et al., 2004a), referring to the overall number of urban, industrial or rural sites. When looking at SA studies, these differences are again evident and reflect both the structure of national monitoring networks and living patterns such as the proximity of residential areas to heavy traffic (urban topography). Furthermore, the proportional differences could also be partly due to the still rather low total number of SA studies per country (thus proportions are sensitive), and the fact that in some countries SA studies may be more of a side-product of other type of studies (e.g., epidemiological) while in others they may have been specifically planned as SA studies, thus possibly affecting the selection of the sites.

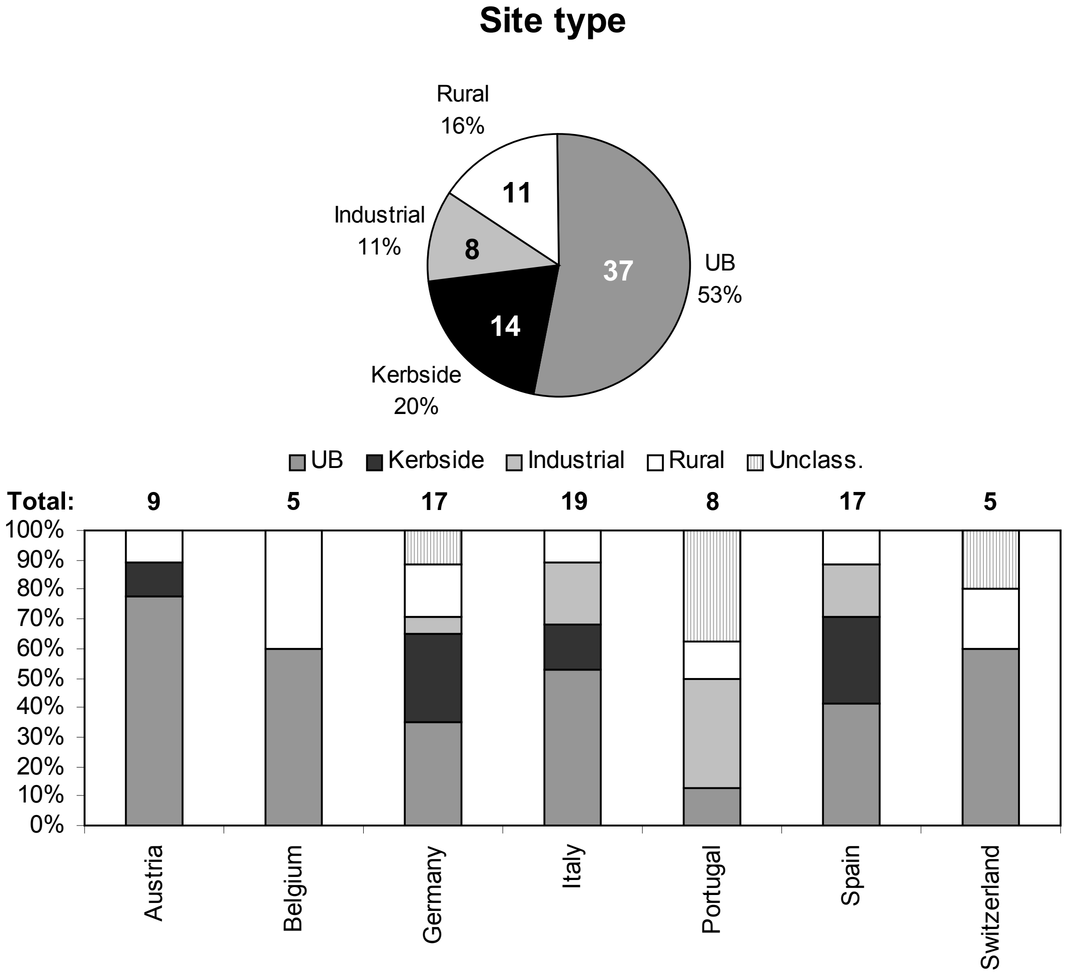


Figure 4: Receptor sites reported until the year 2005 (included): total mean (top, % and total number including only sites with original classification by authors) and classified by country (bottom, only countries with >5 sites reported are shown).

According to the meta-data reported, >75% of the SA studies in Austria were carried out at urban background locations, and <15% at kerbside sites. In Germany, Italy or Spain, with similar distributions, there is a lower proportion of urban background sites (<50%) and a larger number of kerbside (20-30%) and industrial sites (5-20%). The largest proportion of SA studies carried out at rural sites was reported for Belgium (40%).

3.3 SA results in Europe

The entire set of publications reported in the questionnaires was collected and analysed in search of the sources and source contributions described by the authors. The aim of this analysis was to compare PM sources throughout Europe, and to evaluate the geographical variability of the common sources and the specificity (if any) of sources detected only in certain regions. The results of these analyses are plotted in Figures 5 and 6.

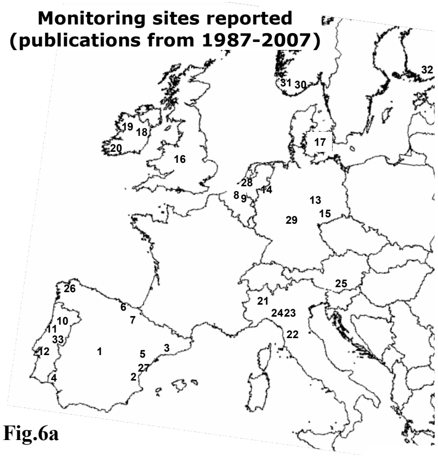


Fig.6a

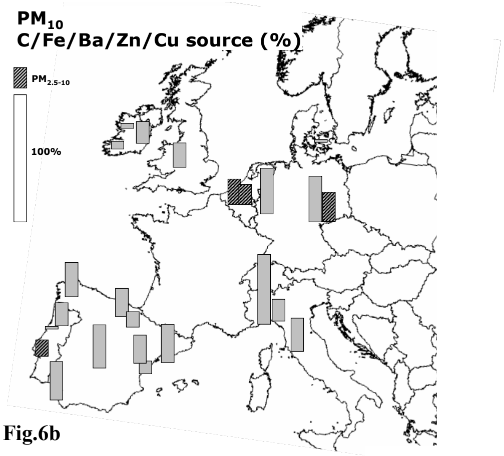


Fig.6b

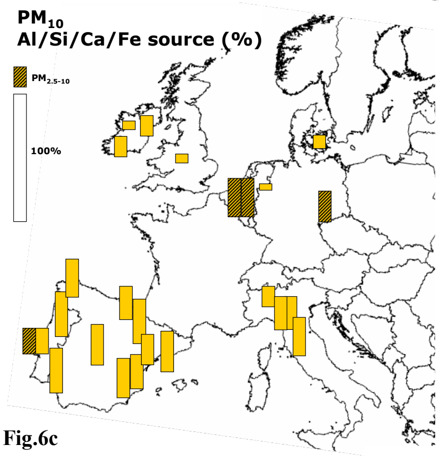


Fig.6c

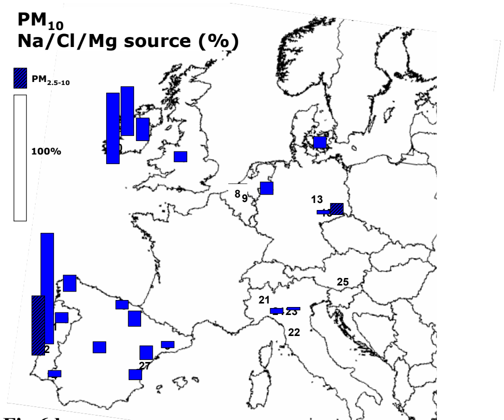


Fig.6d

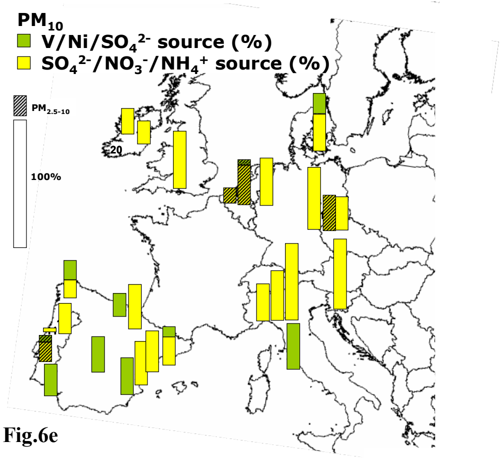


Fig.6e

Figure 5: a) Location of monitoring sites reported: Madrid, Spain (1), Onda, Spain (2), Barcelona, Spain (3), Huelva, Spain (4), Monagrega, Spain (5), Llodio, Spain (6), Alsasua, Spain (7), Ghent, Belgium (8), Waasmunster, Belgium (9), Estarreja, Portugal (10), Areao, Portugal (11), Lisbon, Portugal (12), Leipzig, Germany (13), Duisburg, Germany (14), Dresden, Germany (15), Birmingham, UK (16), Copenhagen, Denmark (17), Dublin, Ireland (18), Balinasloe, Ireland (19), Cork, Ireland (20), Milan, Italy (21), Florence, Italy (22), Modena, Italy (23), Mt. Cimone, Italy (24), Klagenfurt, Austria (25), A Coruña, Spain (26), L'Alcora, Spain (27), Amsterdam, The Netherlands (28), Erfurt, Germany (29), Birkenes, Norway (30), Skreådalen, Norway (31), Helsinki, Finland (32), Coimbra, Portugal (33).
b) Contribution (as % of the PM$_{10}$ mass) of the C/Fe/Ba/Zn/Cu source.
c) Contribution (as % of the PM$_{10}$ mass) of the Al/Si/Ca/Fe source.
d) Contribution (as % of the PM$_{10}$ mass) of the Na/Cl/Mg source.
e) Contribution (as % of the PM$_{10}$ mass) of the V/Ni/SO$_4^{2-}$ and SO$_4^{2-}$/NO$_3^-$/NH$_4^+$ sources.

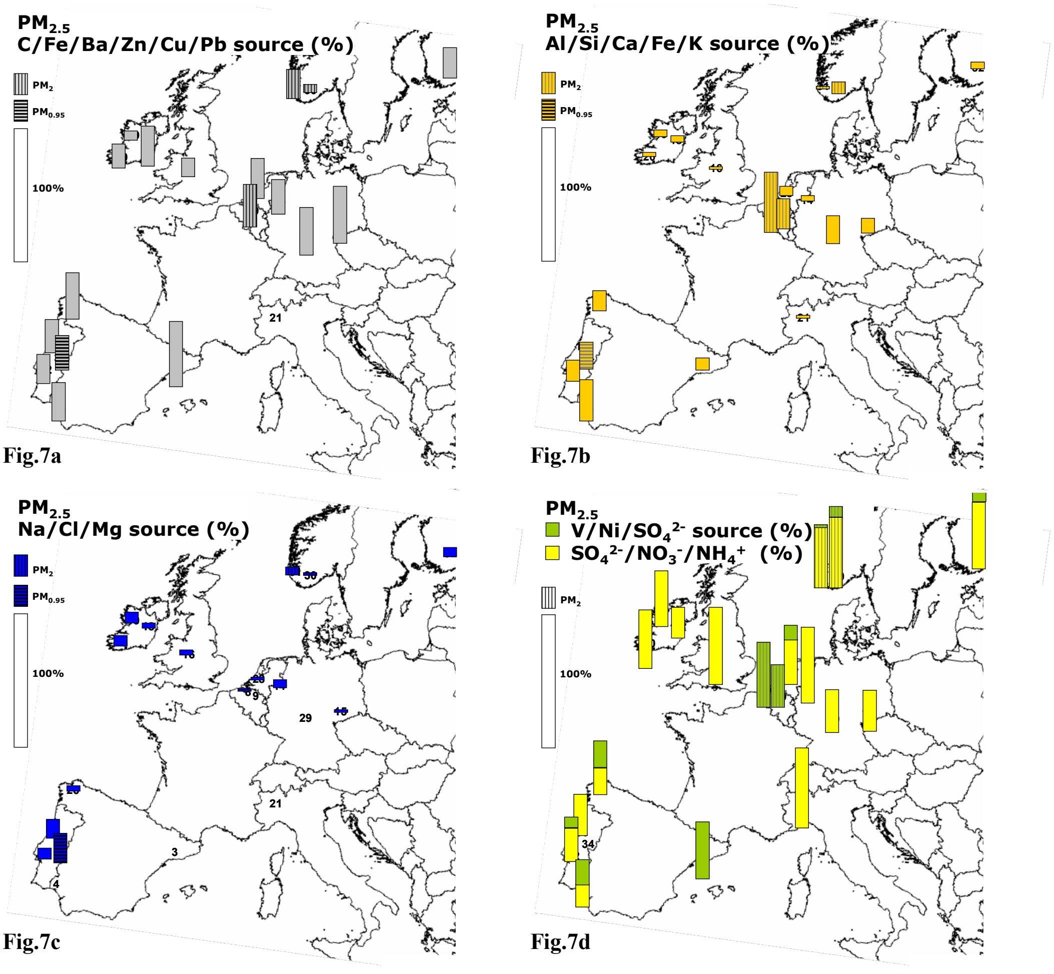


Fig.7a Fig.7b

Fig.7c Fig.7d

Figure 6: a) Contribution (as % of the $PM_{2.5}$ mass) of the Carbon/Fe/Ba/Zn/Cu source.
b) Contribution (as % of the $PM_{2.5}$ mass) of the Al/Si/Ca/Fe source.
c) Contribution (as % of the $PM_{2.5}$ mass) of the Na/Cl/Mg source.
d) Contribution (as % of the $PM_{2.5}$ mass) of the $V/Ni/SO_4^{2-}$ and $SO_4^{2-}/NO_3^-/NH_4^+$ sources.

There is a relatively good spatial coverage of SA studies over Europe, especially regarding the Northern, South-Eastern and South-Western dimensions. The fact that no data are shown for certain countries (e.g., France) does not imply that no SA activities have been conducted, but rather that none were reported. Figure 5a shows the location of the monitoring sites, both for PM_{10} (28 sites) and $PM_{2.5}$ (20 sites). The spatial coverage is thus clearly better for PM_{10} than for $PM_{2.5}$ due to the fact that fewer case studies are published for $PM_{2.5}$. Limited data were also available for $PM_{2.5-10}$, PM_2 and $PM_{0.95}$, which are also plotted in Figures 5 and 6. The discussion of the results, however, focuses on PM_{10} and $PM_{2.5}$.

The preliminary account of the sources described by the authors indicated the difficulty to compare source categories throughout Europe, given their large variability (>20 sources and source categories were found). Furthermore, some authors reported sources which were interpreted as combinations of tracer species (e.g., a source characterised by OC, Cu and Ba and interpreted as "traffic") whereas others reported chemical components (e.g., a source defined as "EC"). Clearly, these differences limit the comparability of the results. Within the sources reported as combinations of tracer elements, different authors provided different interpretations or source labels to the same or similar underlying sources, based on informed and subjective decisions affected by each researcher's knowledge of local circumstances (e.g., meteorological phenomena or specific industrial emissions in the region). The most evident example of this problem is the source characterised mainly by SO_4^{2-} levels, identified in most of the studies and interpreted with such different labels as "industrial emissions", "secondary aerosols", "regional background", "transboundary pollution" or even "general pollution". This heterogeneity in source categories was also observed in the contrast between very specific (e.g., "domestic heating") and very general (e.g., "general pollution") source categories. Finally, certain source profiles could represent the same source but change chemically and physically during atmospheric transport and depending on variable meteorological conditions (temperature, humidity, etc., e.g. a secondary aerosol source dominated by sulphate in summer and nitrate in winter).

In order to make the data comparable across Europe the results provided by the authors were sorted and rationalised according to the tracer elements used to identify the source-related components. Therefore, sources were classified as a function of combinations of common tracer elements instead of source names or labels given by the authors of original papers. Four main sources were thus found to be common to most of the studies reported, both for PM_{10} and $PM_{2.5}$ (Figures 5b-e and 6a-d, respectively):

- <u>Carbon/Fe/Ba/Zn/Cu source</u>: this source was detected at 23/28 PM_{10} monitoring sites and in 19/20 $PM_{2.5}$ sites (Pb also reported in this fraction). Interpreted as a vehicular source ranging from vehicle exhaust to traffic, combinations of its major markers were also found jointly with Br and NO_3^-, and less frequently with Cr and Mn. If interpreted as total traffic, the major tracers were reported in combination with mineral elements such as Fe, Ca or Al from road dust. In these cases, this source could be clearly differentiated from the Al/Si/Ca/Fe source (described below) due to the presence of trace elements linked to brake abrasion (Cu, Ba, Sb; Sternbeck et al., 2002; Schauer et al., 2006) and combustion of lubricating oil (Zn, Ca). As expected, the contributions in terms of mass from this vehicular source showed a dependency with the volume and mixture of traffic emissions at the receptor sites, with higher values reported at major cities and urban agglomerations (Figures 6b and 7a). The largest contributions in PM_{10} were thus recorded in Milan (27-55%, Marcazzan et al., 2003; Mossetti et al., 2005), Dresden (36%, Stölzel, 2003), Duisburg (36%, Quass et al., 2004), Madrid (34%, Querol et al., 2004b) or Barcelona (32%, Querol et al., 2001), while the lowest values were reported for rural sites in Ireland (4%, Yin et al., 2005) and Portugal (1%, Pio et al., 1996). The low value reported for Copenhagen is linked to the fact that this contribution strictly refers to road dust. In the cases of Birmingham and Ireland, these should be considered as minimum values. In the $PM_{2.5}$ fraction, the spatial distribution of contributions from this source showed a similar but enhanced pattern to the one described for PM_{10}, dependent on traffic volume. On very specific occasions the tracers of the vehicular source were reported clustered with a mixture of more general anthropogenic tracers, especially V, Ni or SO_4^{2-}, in which cases the source was interpreted as anthropogenic pollution or industry/traffic.

- <u>Al/Si/Ca/Fe source</u>: these were the major tracers of this source in PM_{10}, in addition to K in the case of $PM_{2.5}$. Additional tracers (Ti, Mg and Sr) were not common to all the source profiles in both size fractions. Combinations of these tracer species, mostly interpreted as mineral/crustal matter (local or regional re-suspension, city dust, crustal material, road dust, etc.), were reported at 24/28 PM_{10} monitoring sites and 19/20 $PM_{2.5}$ sites, indicating that this may be considered a major common source contributing of PM throughout Europe. In Southern Europe, this source would also include African dust contributions. In PM_{10} (Figure 6c), contributions from this source (as % of the PM_{10} mass) showed a marked spatial pattern, with the highest contributions being recorded in South-Western (Portugal, Spain, 20-37%, Querol et al., 2004b; Almeida et al., 2005, Viana et al., 2006a,b) and South-Eastern Europe (Italy, 16-32%, Lucarelli et al., 2004; Mossetti et al., 2005), and lower contributions being reported in UK (7%, Harrison et al., 2003), Ireland (7-16%, Yin et al., 2005), Germany (5%, Quass et al., 2004) and Denmark (10%, Andersen et al., 2007). This source was not identified in Austria or certain studies from Germany. As for $PM_{2.5}$ (Figure 7b), contributions were lower on average but still larger in Portugal and Spain (15-30%) than in UK, Ireland, Germany or Finland (<5%). It is important to remember, however, that many studies do not present bulk contents of mineral dust but only soluble fractions or extractable levels of typically mineral elements, thus biasing the mineral dust contribution. Assessing bulk levels of crustal material requires specific analytical approaches (XRF, PIXE and wet chemistry using $HF:HNO_3:HClO_4$ dissolution).

- Na/Cl/Mg source: detected at 20/28 PM_{10} monitoring sites, and 15/20 $PM_{2.5}$ sites (Figures 6d and 7c), this source showed the smallest variations regarding marker elements (mostly Na, Cl and/or Mg), and only rarely included Br, K, SO_4^{2-} or Sr. The main interpretations obtained for these elements were sea-salt, sea-spray and marine source. Mg was mostly reported as a tracer in Central and Northern European sites, while it was grouped with the mineral elements in Southern Europe (influence of dolomite in the aerosol). Contributions from this source showed a spatial pattern in PM_{10}, with highest levels at Atlantic coastal sites in Western Europe such as Portugal (88%, rural site, Pio et al., 1996) and Ireland (56%, Yin et al., 2005), levels ranging between 5-15% at Mediterranean and Northern Atlantic locations, and <5% at inland sites. In $PM_{2.5}$ the effect of this marine source was <5% at all sites except for locations in Ireland and Portugal (5-15%, Pio et al., 1996; Yin et al., 2005), thus confirming the pattern observed for PM_{10}.

- V/Ni/SO_4^{2-} and SO_4^{2-}/NO_3^-/NH_4^+ sources: as described above, the rationalisation and interpretation of SO_4^{2-}-related sources revealed the largest complexity, and therefore they have been grouped in a single category but separated as two individual sources (Figures 6e and 7d). The first combination (with SO_4^{2-}, V and Ni as common markers) was detected at 21/28 sites for PM_{10} and 16/20 for $PM_{2.5}$, whereas the second combination (SO_4^{2-}, NO_3^- and NH_4^+) was less frequent and detected only at 9/28 sites for PM_{10} and 10/20 sites for $PM_{2.5}$. The V/Ni/ SO_4^{2-} source was occasionally found in combination with trace elements such as Pb or Cu (interpreted as regional-scale pollution), NH_4^+ and Na, OC and K, or Zn and Pb (then interpreted as long-range transport or anthropogenic pollution). Most authors interpreted the common V/Ni/SO_4^{2-} combination as fuel-oil/petcoke combustion or industrial emissions based on the characteristic V/Ni signature of crude oil and its derivates (e.g., shipping emissions), but this interpretation was seen to be quite subjective given that the same authors during different studies labelled this combination as industrial or regional background even though the tracers were the same, based on their knowledge of the monitoring sites. On the other hand, a second type of source was reported, based strictly on the contribution from ammonium sulphate and nitrate (whether separately or in combination) and interpreted by most authors as secondary aerosols, regional background or long-range transport. The results from this analysis underline the difficulty to clearly discriminate between these two sources (V/Ni/ SO_4^{2-} and SO_4^{2-}/ NO_3^-/NH_4^+), probably because such differences are difficult to define conceptually. In order to circumvent this issue, the contributions from these sources are presented stacked in Figures 6e and 7d. In this way, the overlapping between these two sources is evident in cases such as Estarreja (Portugal) and A Coruña (Spain), where the added contributions of both sources provide similar results (24 vs. 14+15%), or Modena and Florence where the sources are labelled differently but their contributions add up to similar proportions of the PM_{10} mass (37 and 39%; Lucarelli et al., 2004; Marenco et al., 2006). The same is observed in $PM_{2.5}$, where the contribution from these sources along the coast of

Portugal and Spain or The Netherlands and Northern Germany is relatively constant (30-40% and 45-57%, respectively) but expressed as the addition of two different sources. No clear spatial pattern is observed for these sources in either PM_{10} or $PM_{2.5}$. These sources account for high proportions of PM_{10} and $PM_{2.5}$ (>30%) at most of the monitoring sites.

In addition to these four main sources common to the majority of the studies reported, a number of specific sources were also detected. These emissions were mainly linked to industrial processes observed at single sites: Cu/K/Ca (Cu smelters, Pio et al., 1989), As/Cu/Pb/Ba/Sb (Cu smelters, Alastuey et al., 2006; Querol et al., 2007a), Se/Hg (unidentified industrial process, Almeida et al., 2005), Cr/Ni/Mo/Cu/Co/As (pigment manufacture, Viana et al., 2006a), Cr/Ni/Cu (oil combustion, Pio et al., 1989), As/Pb/Zn/Cs (frit manufacture, Minguillón et al., 2007a), Se/Si/Cu/Fe (clay emissions from ceramic production, Querol et al., 2007b). The only industrial process observed repeatedly at 4 monitoring sites in 2 different countries was interpreted as metallurgy, with Mn, Zn, Pb and Cd as marker elements and contributing with a maximum of 10% of the PM_{10} mass. Finally, biomass burning was detected in Denmark (K/As, Andersen et al., 2007), and in Spain (K/C/O_3, Rodríguez, 2002). The fact that biomass burning was rarely detected in studies included in this report while recent studies have found relatively large contributions ((in Switzerland but also during the Carbosol project) suggests that this specific source was not discriminated by the models and thus incorporated in other sources.

3.4 Current research trends

Based on the analysis of the available SA data until 2005, and in comparison to those published in 2006-2007, four main current research trends were identified:

3.4.1 Inter-comparison of SA methods:

The comparison of SA results from different European regions is complex. However, this complexity is not only detected when comparing geographical regions, but also when different receptor models are applied to a single dataset. Recent publications focus on this issue (Almeida et al., 2006; Ilacqua et al., 2007; Vallius et al., 2008, Viana et al., 2006c, 2008), most of them agreeing on the difficulty to obtain coinciding results with different receptor models for the same dataset. The main reason for these disagreements is the different theoretical approaches behind the models. SA models and, if feasible, also data collection and analytical schemes, should thus be evaluated, harmonised and standardised, and further research is needed to ensure that SA methods are robust enough for their application to PM health effects assessment. The combined application of different types of receptor models could possibly solve the limitations of the individual models, by constructing a more robust solution based on their strengths. Inter-comparison exercises between different receptor models have recently also been carried out in the US (Hopke et al., 2006; Lane et al., 2007; Rizzo & Scheff, 2007) and China (Song et al., 2006).

3.4.2 Receptor modelling of particle size distribution and meteorological data:

The application of factor analytical techniques to size distribution data (Ruuskanen et al., 2001; Wåhlin et al., 2001) suggested that particle size data can be quantitatively apportioned to sources. Particle size distributions in the atmosphere are dynamic with the potential for coagulation and size dependent deposition. Zhu et al. (2002a,b) have made studies near major highway sources, suggesting that within a few hundred meters of the roadway, there are significant changes in the size distributions as the smallest sizes coagulate and dry deposit.

However, at a reasonable distance from the road, these processes slow significantly as the particle numbers decrease and thus, a quasi-stationary profile can be anticipated. The first quantitative apportionment was performed by Kim et al. (2004) for Seattle, who identified factors associated with surrounding particle sources of wood burning, secondary aerosol, diesel emissions, and motor vehicle emissions. Zhou et al. (2004, 2005) applied PMF to particle size data from the Pittsburgh Supersite, finding that it is important to analyse relatively limited time interval data (one to two months) because of the changes in size arising from changing physical and chemical conditions. Correlations with simultaneously measured gaseous pollutants help to identify the likely source types. PMF was also applied to particle size distribution data in Rochester (Ogulei et al., 2007a) and Buffalo, NY (Ogulei et al., 2007b) and to particle size distributions measured in indoor air (Ogulei et al., 2006). Absolute principal components analysis has been applied to particle size distributions and gaseous data from sites in Southern Ontario (Chan & Mozurkewich, 2007)

3.4.3 SA analysis of specific PM fractions:

3.4.3.a Carbonaceous aerosols using aerosol mass spectrometry

An improved understanding about the sources of organic aerosols (OA) was identified as one of main future topics related to the environmental effects of OA (Fuzzi et al. 2006). High-time resolution data of the chemical composition of aerosols as provided by aerosol mass spectrometers (AMS) have been used in several SA studies. In contrast to most SA studies, the AMS allows for a SA in time-resolution of minutes compared to typically daily samples.

Using AMS data, Zhang et al. (2005a,b) developed and applied a technique based on two mass spectral tracers and an iterative linear regression technique to apportion the organic carbon in PM1 into hydrocarbon-like aerosol (HOA) and oxygenated organic aerosol (OOA). HOA and OOA result mainly from combustion-related emissions and from secondary processes, respectively. Marcolli et al. (2006) applied a cluster analysis to an AMS dataset and found different classes of organic particles that could be interpreted in terms of sources and origin. PMF was then applied to AMS data from an urban site in Zurich (Switzerland) to quantify main sources and processes of organic carbon in PM1 (Lanz et al., 2007).

An interesting aspect of utilising AMS data for SA is the fact that a rich library of reference spectra for aerosols from a variety of sources and near-source measurements exists. These reference spectra are extremely helpful for SA studies using multivariate receptor models, because the similarity between estimated factors and reference spectra can be tested (Lanz et al., 2007), and the interpretation of retrieved factors can be justified.

In a follow-up SA study by Lanz et al. (2008), a hybrid receptor modelling approach using ME which incorporates a priori known emission source profiles (Figure 1) was applied to AMS data. During the considered time period in winter, wood burning and fossil fuel combustion accounted on average for 35-40% and 3-13% of the organic PM1, respectively. The major component of organic PM1 was again OOA (52-57%). Collocated radiocarbon measurements of organic carbon indicated that the dominating fraction of OOA originated from non-fossil sources.

The combination of different SA concepts like the combination of multivariate receptor model and the radiocarbon method by Lanz et al. (2008) is very promising, because (a) additional insight about sources of organic aerosols can be gained, or (b) the results of either method can be cross-checked.

3.4.3.b Carbonaceous aerosols using isotopic mass balance (IMB) and ^{14}C

As a unique and powerful IMB tracer, radiocarbon (^{14}C, $T_{1/2} = 5730$ years) offers the possibility for unambiguous apportionment of fossil and non-fossil sources for carbonaceous aerosols (Currie, 2000; Szidat et al., 2004b). Whereas ^{14}C has completely disintegrated in fossil material, primary and secondary organic particulate matter originating from fresh biomass is on the contemporary radiocarbon level. By separated analysis of ^{14}C in EC and OC (Szidat et al., 2004a), these fractions are quantified: EC_{wood} (wood burning, the only major origin of non-fossil EC), EC_{fossil}, OC_{fossil}, and $OC_{nonfossil}$. The last fraction comprises OC from wood burning as well as primary biogenic OC and biogenic SOA. In order to assess their contributions to $OC_{nonfossil}$, OC_{wood} is estimated from EC_{wood} using an average EC/OC emission ratio and OC_{bio} is calculated by subtraction (Szidat et al., 2006).

This ability to directly quantify fossil and non-fossil sources is unique among other apportionment approaches. A detailed attribution of emissions, however, is only possible in combination with other techniques, especially when high time resolutions are necessary. Here, most promising are combinations with methods enabling relative source apportionment information, which needs to be calibrated independently by ^{14}C. Three examples of such combinations with high time resolutions (a few minutes) are: a) joined determinations of ^{14}C and m/z 60 by AMS (Alfarra et al., 2007), b) verification of PMF receptor modeling results with ^{14}C (Lanz et al., 2008), and c) parameter analysis of wavelength-dependent aethalometer measurements using the EC_{fossil} vs. EC_{wood} distinction of ^{14}C (Sandradewi et al., 2008).

3.4.3.c Mineral dust

Many major, minor and trace elements are associated with the earth's crustal material. Most notable amongst them are Al, Si, Fe and Ca, but other elements such as K, Ti, Sr and Mn are present, and soils also contain organic matter. Abrasion products from road traffic also contain elements such as Fe (brake wear), Al (car body and engine parts), OC and EC (tyre wear) and Ca, Fe, Al, Si and carbon (road surface wear). Furthermore, Sb, Cu, Zn and Ba are also found in many studies as tracers of emissions from tyre and brake abrasion. Additionally, road traffic leads to the resuspension of road dust, of which soil is a major component. The precise elemental content of road dusts is location-dependent, due to differences in local geochemistry, the composition of road surface materials, and the composition of brake pads (F. Amato, unpublished data). Harrison et al. (2004) in UK found a roadside enhancement of Fe, but not Ca, whilst Wåhlin et al. (2006) in Denmark found a roadside enhancement in Ca which appears to have derived from road surface materials.

Wind-driven suspension of surface soils and desert dusts gives rise to airborne particles whose composition has much in common with road dusts, the main difference being a different trace element profile. Thus trace elements such as Ba and Cu (brake pads) and Zn (tyres) are enriched in traffic-generated particles relative to natural soils and dusts (Birmili et al., 2006; Hjortenkrans et al., 2007). However, there are such strong overlaps between the elemental composition of natural and anthropogenic crustal matter-based dusts that receptor models based upon elemental profiles have great difficulty in distinguishing them. Rodriguez et al. (2007) estimated mineral dust concentrations in $PM_{2.5}$ from the sum of $Al_2O_3 + SiO_2 + Ca + CO_3^{2-} + Ti + Fe + Sr$, and found major differences in concentrations between Barcelona (highest concentrations), Milan and London (lowest).

One other type of natural dust contribution is the transport of mineral dust from the African continent, which affects especially Southern European countries. Due to the overlap between the elemental composition of local soil dust and anthropogenic mineral dust, the identification and quantification of these contributions is complex. Methodologies for addressing this issue were presented by Collaud Coen et al. (2004) and Escudero et al. (2007).

Finally, coal fly ash has also a composition that may resemble that of soil dust, and this contribution may be important at some sites in Europe. In certain study areas this could represent an additional source of bias in the receptor modelling results (Viana et al., 2007).

3.4.4 Receptor modelling for epidemiological and health-related studies

Historically, epidemiological studies on the associations between PM and health effects have relied on fixed site measurements of mass concentrations (TSP, PM_{10} and, more recently, $PM_{2.5}$). However, during the last decade an increased pressure has emerged to uncover the specific PM constituents responsible for the observed health effects. If specific constituents were found to be more harmful than others, this would inevitably lead to new legislation and mitigation actions, and more efficient control of the sources of these constituents. When correctly linked to epidemiological studies, SA of PM can therefore play a significant role in attempts to answer this crucial question.

The use of receptor modelling in epidemiological PM health studies is still very young and therefore it is difficult to detect clear trends in this research area. Reports from epidemiological studies utilising PM SA results as input have been published during the last decade especially from Europe (Lanki et al., 2006; Andersen et al., 2007, Yue et al., 2007) and Northern America (Laden et al., 2000, Mar et al., 2005). In the studies performed in Europe, SA analyses have been applied to investigate the associations of particulate matter with cardiac but also respiratory endpoints, all of which studies indicated that the adverse health effects were primarily associated with exposure to traffic-related particles.

Ambiguity in source classification and misclassification of sources is a major problem in contemporary SA analyses and may have serious implications with regard to use of SA results in epidemiological studies. Implications of inadequacies of SA methods and the use of results from SA analyses in epidemiological research have been discussed by Grahame & Hidy (2007).

More precise estimates for human exposure and, if possible, personal exposure to source specific PM fractions are a prerequisite for obtaining new information on the potentially differential effects of PM from different sources. This goal can only be achieved by incorporating in epidemiological studies extensive air pollution measurements which allow efficient application of the latest and most powerful SA models.

4. Gap analysis and possible Research Directions

As the conclusion of the present overview, a gap analysis was carried out and the following gaps and possible research directions were outlined:

- Geographical representativity: This report does not intend to include all SA studies and/or countries in Europe. The authors are aware that the geographical coverage of the studies presented is limited. This may have implications regarding the applicability or representativity of the findings, and therefore this should be taken into account by the readers.

- Comparability between SA methodologies: Further research should be carried out in this direction.
- Evaluation and harmonisation of data collection and analytical schemes: in order to allow better comparability across individual sites, data should be evaluated and harmonised, and measurements should aim to provide data on PM chemical composition (tracers and source profiles) which facilitate identification and separation of complex source components.
- Combination of back-trajectory modelling with SA analyses: the further utilisation of back-trajectories (TS and PSCF, Lupu & Maenhaut, 2002) in combination with receptor models holds a large potential to confirm SA results and to overcome some of the above-mentioned difficulties (e.g., the identification of African dust).
- Apportionment of specific anthropogenic emission sources: certain anthropogenic combustion emission sources (e.g., shipping emissions, diesel/gasoline exhaust) were not discriminated by any of the SA studies described above. This is most likely due to the absence of marker species in the input datasets (OC, EC or PAH concentrations) and/or the inability of the models to separate sources with common tracers (e.g., V, Ni and SO_4^{2-} are tracers of oil combustion, shipping and industrial emissions). Additional data on source-specific marker species and their combined application with meteorological parameters (wind speed, wind direction, etc.) and/or particle number and size distribution data may provide new insights to this problem.
- Differentiation between SO_4^{2-}-containing sources: one of the major gaps detected in this analysis is the difficulty to clearly interpret and discriminate SO_4^{2-}-containing sources (secondary regional-scale aerosols vs. local- or meso-scale anthropogenic emissions such as industry or shipping).
- Quantification of natural source contributions (e.g. African or windblown dust, secondary organic material): the difficulty to quantify the contribution from natural mineral dust sources is once more related to the fact that different emission sources are characterised by similar tracer elements, thus limiting the potential of the models to separate source profiles and contributions. However, a methodology is already available to identify and quantify African dust contributions (Collaud Coen et al., 2004; Escudero et al., 2007). As regards biogenic secondary organic material, its composition is not well known and cannot be traced by inorganic compounds.
- Identification of the biomass combustion source: this source may be a very important PM source in Europe (wood combustion in stoves in winter, open fires of agricultural residues, garden refuse, forest fires, pit fires, etc.). Biomass burning episodes are generally episodic, thus complicating their identification on longer time-scales. The large organic fraction of PM may be partly due to secondary particle formation from volatile compounds emitted by biomass combustion. The use of more specific tracers as levoglucosan might help identify the biomass combustion source.
- Identification of the nitrate component: receptor models applied to European air quality data have been very poor in identifying a nitrate component of airborne particles. Identification of this component is a high priority for the following reasons: (1) due to changing profiles of precursor emissions, western European secondary inorganic aerosol is progressively becoming dominated by nitrates, whereas sulphates were historically more important (AQEG, 2005); (2) whilst sulphate and nitrate concentrations are frequently well correlated (r^2 up to 0.25), there are occasions when the two components are entirely uncoupled (Abdalmogith & Harrison, 2006); (3) work in the UK shows that nitrate makes a much greater contribution to $PM_{2.5}$ and PM_{10}

composition on days when the EU daily PM_{10} limit value is exceeded, relative to all days (Harrison et al., 2004).

- Use of single particle aerosol mass spectrometry: in addition to AMS to characterise organic matter, there is considerable potential in the use of single particle aerosol mass spectrometers in SA studies of both inorganic and organic constituents. Single particle mass spectrometers such as the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) are able to determine the aerodynamic diameter and major component chemical composition of large numbers of individual aerosol particles. The use of single particle mass spectrometry methods within Europe has been more limited, but Dall'Osto & Harrison (2006) identified five main classes of particles in the atmosphere of Athens, from the mass spectra of 166,000 particles. Whilst the results were not used to derive a quantitative SA, they were qualitatively comparable with data obtained by traditional chemical methods. Because of the fast response of the technique, diurnal variations in semi-volatile aerosol components were readily identified. Owega et al. (2004) has applied PMF to single particle data to identify and quantify their contributions to particle number concentrations.
- SA of indoor air concentrations, and relation to exposure: the current increase in publications reporting indoor air particle concentrations and composition suggests that the application of receptor modelling techniques to indoor air datasets constitutes an upcoming research direction.

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VII.4 Population Exposure Modelling to Particulate Matter

1. Introduction

Particles in the atmosphere arise from natural sources, such as windborne dust, sea spray and volcanoes, and from anthropogenic activities, such as combustion of fuels. Emitted directly as particles (primary aerosol) or formed in the atmosphere by gas-to-particle conversion processes (secondary aerosol), atmospheric aerosols are generally considered to be the particles that range from a few nanometres to tens of micrometers in diameter (Seinfeld and Pandis, 1998).

Increased understanding of the health issues associated to high concentrations of particulate matter (PM) have contributed to the identification of PM as the reason for one of the most critical air pollution problems. Estimates from the European Environment Agency (EEA, 2003) indicate that exposure to PM causes approximately three million deaths per year in the world. PM threshold exceedances have been reported by the majority of the European Union (EU) member states, mainly in urban agglomerations. These areas are of high exposure relevance due to the population density (EEA, 2005). Especially the fine particulates ($PM_{2.5}$) in PM_{10} are currently considered to be responsible for increased mortality over Europe. Anthropogenic $PM_{2.5}$ levels are expected to be responsible for a loss of ten months of life expectancy in some regions of Europe by 2020, in spite of current ongoing abatement measures to control air pollution (Amann *et al.*, 2005). It is also recognized that adverse effects from PM long-term exposure occur independent of the concentration level (WHO, 2006; Pope *et al.*, 2002).

Health effects of air pollution, namely of PM levels in the air, are the result of a chain of events, starting with the release of pollutants resulting in elevated ambient atmospheric concentration, then personal exposure, uptake, and finally leading to an internal dose with subsequent health effect (Figure 1).

Figure 1: Chain of events: from emission of pollutants to health effects.

The conditions for these events vary considerably and have to be accounted for, in order to ensure a proper assessment (Hertel et al., 2001). Ambient concentrations and exposure are the stages of the chain that are mainly covered within this report.

Human exposure refers to the individual contact (not uptake) with a pollutant concentration. It is, then, important to distinguish between concentration and exposure. Concentration is a physical characteristic of the environment at a certain place and time (here e.g. amount of material per unit volume of air), while the term exposure stands for the interaction between the environment and a living subject (Sexton and Ryan, 1988). The pollution pathways may be external (e.g., skin contact) or internal (e.g., consumed or respired, which is usually the principal pathway for uptake when air pollution is considered). For personal exposure to take place two events need to occur simultaneously; pollution concentration at a particular time and place and the presence of a person in that same place and time. Exposure has the dimension of "(unit[3]) × (time) / (volume)" or "(concentration) × (time)".

Exposure studies can be carried out aiming to estimate exposure of one individual (personal exposure) or of a larger population group (population exposure), through direct or indirect methods. Direct methods are measurements made by personal portable exposure monitors or biological markers. These can be, however, invasive and expensive techniques. The personal exposure monitoring devices that people carry with them must be lightweight, silent, highly autonomous and allow representative sampling. Still one week is about the maximum time that any population representative sample of individuals will comply with personal exposure measurements (Hertel et al., 2001; Sexton and Ryan, 1988).

When using indirect methods, the exposure is determined by combining information about the time spent in specific locations, called micro-environments, and the pollutant concentrations at these places. A micro-environment is defined as a three-dimensional space where the pollution concentration at some specified time is spatially uniform or has constant statistical properties (Hertel et al., 2001). The microenvironment can be the cabin of a car, inside a house, inside an office or school, outdoors, etc. Thus total exposure is the sum of the exposure in all microenvironments during the time of interest.

A constraint for using the indirect method is that the residence time of the person (termed time-activity pattern) needs to be known together with the pollution concentrations in each of the microenvironment at the time the person is present.

This paper will focus on ambient PM concentrations, which are a key variable for exposure models, and are generally obtained by direct measurements in air quality monitoring stations. However, depending on the location and dimension of the region to be studied, monitoring data may not be sufficient to characterize PM levels or to perform population exposure estimates. Numerical models are alternatives to derive concentration data. These models simulate the changes in concentrations in air using a set of mathematical equations that translate the chemical and physical processes in the atmosphere.

In this scope the purpose of the present work is to critically review PM modelling activities, concerning both ambient concentrations and exposure, going on mainly in Europe, aiming to identify advantages and gaps and to recommend future use and developments.

2. Particulate Matter Modelling

Air quality models use mathematical and numerical techniques to simulate the physical and chemical processes that affect air pollutants, namely PM, as they disperse and react in the atmosphere. Based on meteorological and emission data inputs, these models are designed to characterise primary particles emitted directly into the atmosphere and, in some cases, secondary particles formed as a result of complex chemical reactions within the atmosphere.

They are important in air quality management systems because they are widely used to provide the identification of source contributions to PM air quality problems and to assist in the design of effective strategies to reduce this pollutant in the air. Moreover, air quality models can also be used to predict future PM concentrations from multiple sources after the

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[3] Unit e.g. mass or number of particles.

implementation of a new regulatory program, in order to estimate the effectiveness of the program in reducing harmful exposures to humans and the environment.

Aerosol air quality models are also used in the analysis of acute episodes like the 2003 heat wave (Hodzic et al., 2006) and in the assessment of the impacts of emission control strategies at the European level (Cuvelier et al., 2007).

2.1 Type of models

Dispersion aerosol air quality models are usually simple; they calculate the concentration of particles at specified ground-level receptors, considering only the dispersion and not the chemical transformation processes. They simulate the atmospheric transport, the turbulent atmospheric diffusion, and some are also include deposition. The most simple dispersion models use the Gaussian approach (ISC3, AERMOD, AUSPLUME are examples of Gaussian models currently in use to estimate PM concentration values), which is perhaps the oldest (Bossanquet and Pearson, 1936) and perhaps the most commonly used. Notwithstanding the simplicity of this approach, Gaussian models have already been used to estimate particle concentrations for exposure estimates. For example, Johansson et al. (1999) evaluated population exposure to PM using information from multiple-source emissions and a Gaussian dispersion modelling system.

Chemical aerosol models simulate the changes of particles in the atmosphere using a set of mathematical equations characterizing the chemical and physical processes in the atmosphere. They became widely recognised and routinely utilized tools for regulatory analysis and attainment demonstrations by assessing the effectiveness of control strategies. The simulation of the dynamics of multicomponent atmospheric aerosols is an impressive problem that includes new particle formation by homogeneous heteromolecular nucleation, gas-to-particle conversion, coagulation and dry deposition (Zannetti, 1990). Figure 2 illustrates the complexity associated to aerosol modelling.

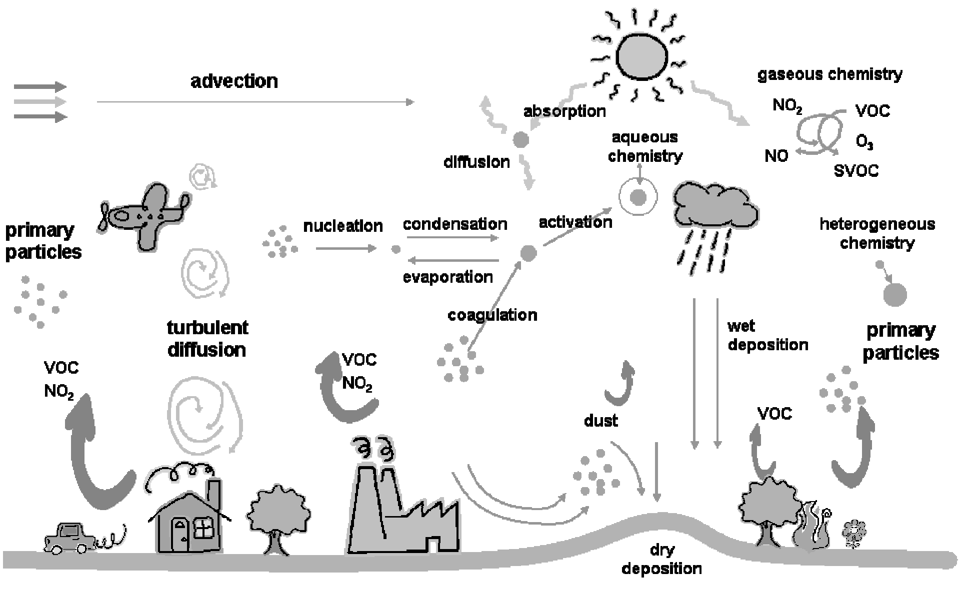


Figure 2: Simplified scheme of processes considered in aerosol (Monteiro, 2007)

There are two main techniques to model air quality: the Lagrangian trajectory model that employs a moving reference frame, and the Eulerian grid model that uses a fixed coordinate system with respect to the ground.

Lagrangian models consider air parcels, which travel with the wind (i.e., they are advected). These models are often also called as trajectory models, since the air parcel under consideration follows a trajectory defined by the winds. Examples of current in use Lagrangian models include CALPUFF, VADIS and HYSPLIT.

Eulerian models consider a mathematical framework anchored to the surface of the earth, as shown in Figure 3. They are often also referred to as grid models, since the framework is a three dimensional grid, with pollutants being emitted into the grid at the appropriate points. Pollutants travel through the grid, under the influence of the atmospheric flow, undergoing chemical and physical transformations as they go. Eulerian models include Models-3/CMAQ, CAMx, CHIMERE, LOTOS-EUROS and EURAD.

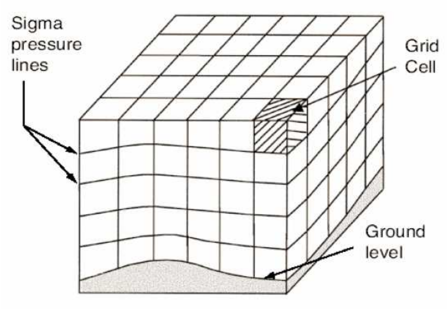


Figure 3: Eulerian modelling framework (Reid *et al*., 2007).

Most of the current operational chemical aerosol models have adopted the three-dimensional Eulerian grid modelling mainly because of its ability to better and more fully characterise physical processes in the atmosphere and predict the species concentrations throughout the entire model domain (Reid et al., 2003).

Air quality models can also be classified with respect to the scale of the phenomena they are developed to simulate. In fact, scale separation has proven to be a quite successful approach for atmospheric modelling, because different approximations and parameterisations can be applied for the different phenomena occurring in the different scales. Hence, models can be classified into global, mesoscale (including regional and urban) and local. Figure 4 shows the time and time scales associated to each class of models. It has to be noted that only local to urban scale models can actually be used for PM related assessments (exposure assessment, abatement strategy evaluation…) since only these models allow for a relatively correct calculation of near surface particle concentrations. Missing topography and the lower atmospheric levels often limit the use of larger scale models.

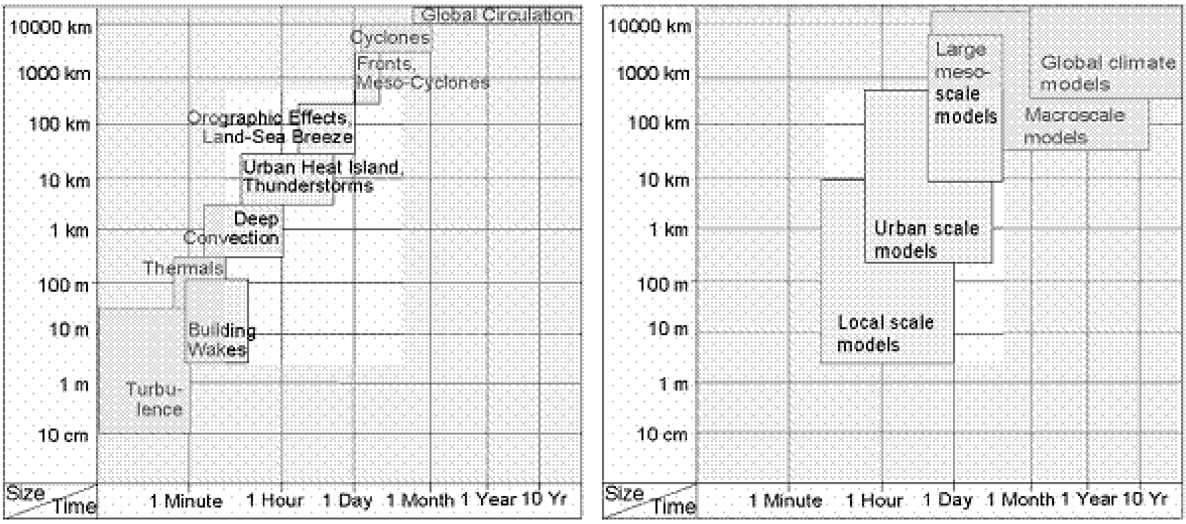


Figure 4: Characteristic time scale (abscissa) and characteristic horizontal scale (ordinate) of common atmospheric models (Moussiopoulos, 2003).

As the name implies, global models consider the transport of pollutants throughout the atmosphere, with no artificial restriction of the domain. The large spatial extent of these models dictates that the spatial resolution (grid spacing) must be relatively coarse to keep the computational demands within reasonable bounds. At the beginning most global modelling has been confined to carbon dioxide and the climate change issue, meaning that chemical transformation was not treated. However, expansion to other pollutants has taken place and nowadays there are already several applications of chemistry climate models considering aerosols (Ginoux et al., 2001).

Mesoscale models, which include regional and urban models, consider spatial scales ranging from a few hundred to a few thousand kilometres, over which many of the most pressing PM concerns are important. Models on these scales are generally the most important for policy makers. Monteiro et al., (2007) evaluated the skill of the CHIMERE aerosol chemistry-transport model simulating aerosols over Portugal and comparing with observations during the full year 2001. This work showed that besides the complexity of the formation mechanism of aerosols and the great number of individual chemical species involved, this modelling system can be used in the future as a tool for assessing air pollution abatement strategies as well as for scientific purposes to investigate the transport of PM and its formation at regional scale.

Local scale modelling is typically used to assess the impact of single sources, or small groups of sources, over distances ranging up to tens of kilometres. VADIS and FLUENT are examples of Computational Fluid Dynamics (CFD) local models. CFD modelling is a general term used to describe the analysis of systems involving fluid flow, heat transfer and associated phenomena (e.g. chemical reactions) by means of computer based numerical methods. Studies were recently published relating human exposure estimation in urban areas with ambient air concentrations determined with CFD modelling applications. The three-dimensional CFD model MISKAM has been successfully implemented to provide better assessment of exposure to traffic related air pollutants in urban areas (Lohmeyer et al., 2002). Borrego et al. (2006) developed a methodology to estimate population exposure to traffic related PM in urban areas based on the estimation of ambient pollutant concentrations with the CFD model VADIS. McNabola et al. (2008) also used a CFD to investigate whether pedestrians using the boardwalk would have a lower air pollution exposure than those using the adjoining footpath along the road. The results show considerable reductions in pedestrian exposure to traffic derived PM along the boardwalk as opposed to footpath.

Some examples of PM air quality modelling applications are given in Figure 5, for different goals and thus, covering various scales.

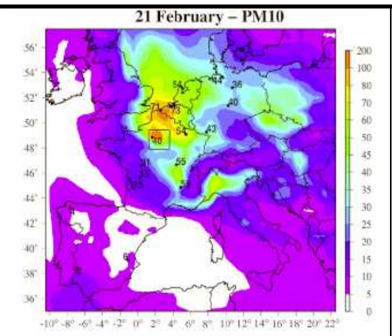
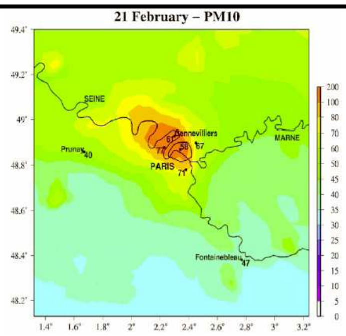
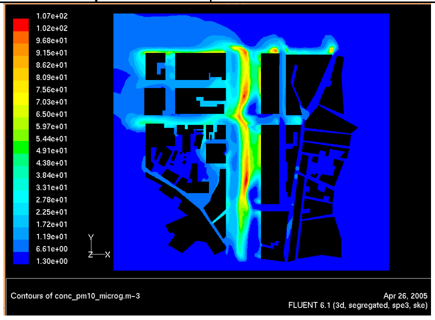
Type of Model	**Example of results**	
Mesoscale/Regional Eulerian model (CHIMERE) (Bessagnet *et al.*, 2005)	 Occidental Europe	 Paris region
CFD local model (FLUENT) (Martins *et al.*, 2005)	 Liberdade Avenue, in Lisboa city centre	

Figure 5: Examples of air quality modelling applications.

The choice of an appropriate model is heavily dependent on the intended application. Even though a model may be freely available, it does not follow that it is necessarily the most appropriate for the situation under investigation. In particular, the science of the model must match the pollutant(s) of concern. If the pollutant of concern is fine particulate matter, the model chemistry must be able to handle reactions of NO_X, SO_2, volatile organic compounds (VOC), ammonia, etc.. Reactions in both the gas and aqueous phases must be included, and preferably also heterogeneous reactions taking place on the surfaces of particles. Apart from correct treatment of transport and diffusion, the formation and growth of particles must be included, and the model must be able to track the evolution of particle mass as a function of size. The ability to treat deposition of pollutants to the surface of the earth by both wet and dry processes is also required.

2.2 Input, Output Data and uncertainty

Modern models require a considerable volume of data. The specific needs reflect the science incorporated in the model and typically includes the following:

- Emissions - For all sources treated by the model (for each grid square of an Eulerian model) the rate and time pattern of emission is required for each of the chemical species modelled by the model. These emissions should relate to the specific time period being studied. For the modelling of fine particulate matter formation and transport, emission data are also required for primary particle emissions as a function of particle size, as well as emissions of ammonia. Neither of these is particularly well categorised yet.

- Geophysical data - Information is required on a range of surface parameters, including topography, land use category and vegetation type.
- Meteorology - Meteorological information is typically required to drive the transport in the model. This information is needed at several vertical levels in the atmosphere, and must also be for the period to be modelled.
- Initial and boundary conditions - It is usual to specify the initial chemical concentrations for a number of the major species in the model. These will be taken from typical or average values measured, or previously modelled, for the region of interest. It is also necessary to specify concentrations at the boundaries of the model, except for global models. It is relatively simple to estimate initial and boundary conditions at the surface based on measurements, these values are also required at higher levels in the atmosphere, where measurements are sparser. Current practice, which addresses the specification of initial and boundary conditions, is to nest the model. In nesting an initial run is carried out for a large domain at relatively coarse resolution. This is followed by a run at finer resolution for a smaller subdomain, using predictions from the first run to provide initial and boundary conditions.

If the model is not so complex, needed input data would also not be so demanding. A particular situation has to be stressed: CFD models applied to urban areas need very detailed information about the buildings and any other obstacles within the simulation domain.

Output data are usually the temporal and spatial distribution of PM concentration values and sophisticated modelling approaches are available, which allow assessing PM at high spatial and temporal resolution for several source groups or even individual sources. These sophisticated models also calculate the chemical composition of particles, giving as output data sulphate, nitrate, black carbon, etc. or number concentrations. There is a need to assess the uncertainty of such models.

Because of the effects of uncertainty and its inherent randomness, it is not possible for an air quality model to ever be “perfect”, and there is always a base amount of scatter that cannot be removed (Chang and Hanna, 2004). Nevertheless, air quality models need to be properly evaluated before their predictions can be used with confidence, since model results often influence decisions with health and economic consequences. Therefore, information about uncertainties should be correctly estimated and interpreted since it is as important as modelling data (Borrego et al., 2008).

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

Uncertainties can be characterized and air quality model evaluation can be determined by statistical analysis, where model predictions are examined to see how well they match the observations. Discussion on the evaluation of air quality models and on the development of general evaluation methods has been carried out by many scientists; however, standard evaluation procedures and also performance standards still do not exist. Traditionally, model predictions are directly compared to observations, but this direct comparison method may cause misleading results because uncertainties in observations and model predictions arise from different sources (Chang and Hanna, 2004). As already mentioned, the uncertainty in observations may be due to random turbulence in the atmosphere and measurements errors, whereas the uncertainty in model predictions may be due to input data errors and model physics. Delle Monache et al. (2006) propose a decomposition of the root mean square error in two parts, a systematic component that reflects the portion of the error that is due to model errors an unsystematic component that reflects dependency on random errors, initial conditions errors and errors that result on a model skill deficiency in predicting a given situation.

Borrego et al., (2008) presented a systematic description of the modelling uncertainty analysis methodologies, based on bibliography review, analysed the different methodologies and concluded that despite all parameters are important, it was possible to define a subset of parameters able to reproduce the general uncertainties estimation. The defined parameters were the correlation coefficient, the fractional bias and the root and normalized mean square errors. Borrego et al., (2008) concluded that parameters that reflect the capability to simulate peaks should be taken into consideration in air pollution episodes simulation. Concerning the quality indicators defined by EU directives, the results showed that the legislated uncertainty estimation measures are ambiguous and inadequate in several aspects, mainly in what concerns the error measures for hourly and daily indicators based on the highest observed concentration. A relative error at the percentile (RPE) correspondent to the allowed number of exceedances of the limit value was suggested and tested, showing that is a more robust and appropriate parameter for model performance evaluation. The proposed guidelines can be useful for local and regional authorities, in order to estimate modelling uncertainty and guarantee the correct information about measured or predicted exceedances of limit values and/or alert thresholds, the geographical area affected and the duration period to be available to the public.

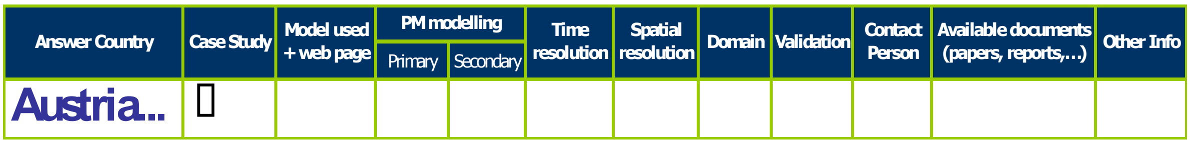
Uncertainties in PM modelling have already been estimated in some works. Borrego et al., (2007) applied the suggested methodology for the estimation of the air quality total modelling uncertainty over Berlin at two different scale model approaches. PM10 hourly concentrations over Berlin were simulated for the year 2002 and compared with air quality concentrations provided by the measuring stations. The uncertainty estimation methodology described was applied separately for each numerical model scale application. The results obtained with both scale modelling applications combined with the measuring data from the air quality network allowed determining the uncertainties following the basic recommendations: according to the EU Directives, performing statistical analysis and uncertainty mapping. At the regional/urban scale, the applied RCG chemistry-transport model was able to simulate PM10 with a satisfactory uncertainty level, according to the quality objectives defined by the EU Directive and to the statistical parameters calculated. The uncertainty spatial mapping showed that all the analysed indicators are adequate to perform the spatial representation of the uncertainty.

This study case constitutes an application example of the basic recommendations, regarding model uncertainty, defined in the scope of Air4EU project.

2.3 PM modelling in COST633 Action Member States

Aiming to provide an overview of the application of PM models in European COST633 Action member states in a common usable framework, modellers were asked to answer to a questionnaire (Miranda et al., 2006). This questionnaire was distributed via e-mail among researchers from COST633 Action member states. Table 1 shows the information required.

Table 1: Information required from COST633 member states.



Answer Country	Case Study	Model used + web page	PM modelling		Time resolution	Spatial resolution	Domain	Validation	Contact Person	Available documents (papers, reports,…)	Other Info
			Primary	Secondary							
Austria…	▯										

The information collected was compiled in a database. Ten member states replied to the questionnaire reporting a total of 30 case studies applications. The information collected with the questionnaire is synthesised in Table 2.

Table 2: Synthesis of the information collected by the questionnaire

Member State	Used Model	Primary	Secondary	Scale
Austria	CAMx	Yes	Yes	Mesoscale
	NEMO/GRAMM/GRAL	Yes	No	Local
Denmark	DEHM	Yes	Yes	Mesoscale
	THOR	Yes	Yes	Mesoscale
Finland	CAR+MONO32	Yes	No	Local
	SILAM	Yes	Yes	Mesocale
Germany	EURAD	Yes	Yes	Mesoscale
Norway	AirQuis	Yes	No	Mesoscale
	EPISODE	Yes	No	Mesoscale
Poland	CALMET/CALPUFF	Yes	No	Mesoscale
	AQPS	Yes	No	Mesoscale
Portugal	VADIS	Yes	No	Local
	FLUENT	Yes	No	Local
	MEMO	Yes	No	Mesoscale
	CAMx	Yes	Yes	Mesoscale
	CHIMERE	Yes	Yes	Mesoscale
Spain	DREAM	Yes	No	Mesoscale
	CMAQ	Yes	Yes	Mesoscale
	CALMET/MELPUFF	Yes	No	Mesoscale
	CALMET/CALPUFF	Yes	Yes	Mesoscale
	MELPUFF	Yes	No	Local
	SLP-2D	Yes	No	Local
	CHIMERE	Yes	Yes	Mesoscale
Switzerland	CAMx	Yes	Yes	Mesoscale
The Netherlands	CARII	Yes	No	Local
	OPS	Yes	Yes	Mesoscale
	LOTOS-EUROS	Yes	Yes	Mesoscale

Figure 6 shows the distribution and classification of models used by COST633 member countries, as reported to the questionnaire.

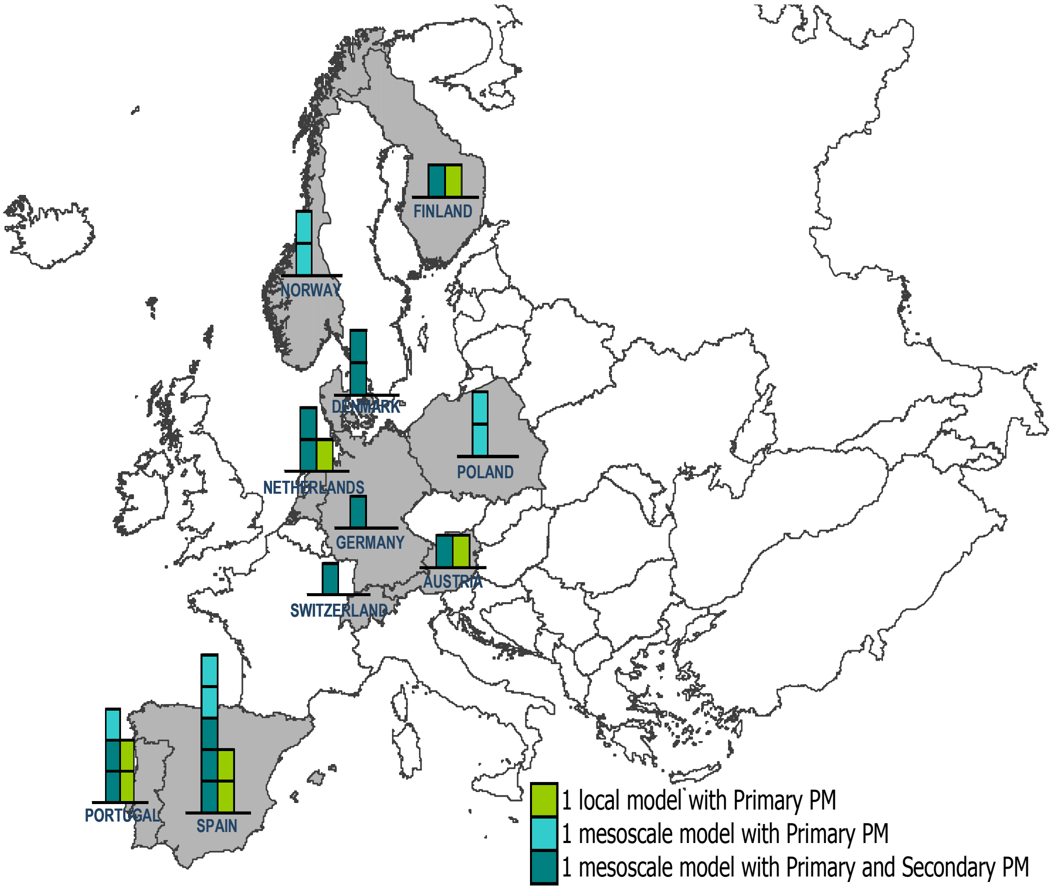


Figure 6: Distribution and classification of types of models used by COST633 member countries.

A total of 30 case studies and 20 models were reported, covering different scopes and different modelling scales, from local to regional scale. Primary aerosols were simulated in all case studies, whereas secondary aerosols were included in 50% of the cases, calculating not only PM10 and/or PM2.5, but also secondary organic aerosols (SOA).

Air quality models are widely applied in Europe for various purposes. As diagnostic tools, they are used to improve knowledge of the chemical and physical behaviour of the atmosphere, to help decision makers on the development of policies and air quality management systems for protection of ecosystems and human health. Models are also important instruments for prognostic, applied to a future situation, in order to evaluate the efficiency of a policy or a taken measure to reduce a certain type of emissions, or for air quality forecast, and consequently human exposure and health effects prevention.

Several examples of air quality modelling application have been given, for different goals and thus, covering various scales. Air pollutants concentration fields, as modelling outputs, are estimations of outdoor microenvironments that combined with gridded population and microenvironments information, should be used for exposure modelling and estimation of doses and health effects, concluding the source to dose assessment (Figure 1).

3. Exposure modelling

For population exposure assessment, a combination of the spatial distribution of both air quality, namely PM levels, and population density is required. However, nowadays chemical-transport models (known as CTM) can provide more detailed information regarding chemical composition and/or number size distributions of particles and we should start taking profit of all the available modelling results to improve exposure estimation and to go further in our knowledge. Numerical models are useful tools for the mapping of air pollutants, once the monitoring networks are able to assess the air quality in the single stations of the monitoring network, and not the whole area of interest. Dispersion and photochemical models have been applied, at different scales, to evaluate air pollution due to particulate matter concentrations and its effects on human exposure and health.

3.1 Type of models

According to the IPCS (2004) an exposure model is a conceptual or mathematical representation of the exposure process, designed to reflect real-world human exposure scenarios and processes. There are many different ways to classify exposure models. A consensus appears to be developing around the following classification scheme, which has been adopted in this paper: 1) mechanistic or empirical; and 2) deterministic or stochastic (probabilistic) (Table 3) (WHO, 2005). However, alternative classifications may be considered as well.

Table 3: Model categories (WHO, 2005)

	Mechanistic	Empirical
Deterministic	Mathematical constructs of physical/chemical processes that predict fixed outputs for a fixed set of inputs.	Statistical models based on measured input and output values (e.g. regression models that relate air concentrations and blood levels of a chemical or ambient pollutant concentration with personal exposures).
Stochastic	Mathematical construction of physical/chemical processes that predict the range and probability density distribution of an exposure model outcome (e.g. predicted distribution of personal exposures within a study population).	Regression-based models, where model variables and coefficients are represented by probability distributions, representing variability and/or uncertainty in the model inputs and parameters.

Koussaa et al. (2002) classified exposure models as statistical, mathematical and mathematical-stochastic models. Statistical models are based on the historical data and capture the past statistical trend of pollutants (Goyala et al., 2006). The mathematical modelling, also called deterministic modelling, involves application of emission inventories, combined with air quality and population activity modelling. The mathematical-stochastic approach attempts to also include a treatment of the inherent uncertainties of the model (Burke et al., 2001).

Most recently, mathematical exposure models applied to urban areas have been presented by Jensen (1999), Koussaa et al. (2002), and Wu et al. (2005). The model presented by Jensen

(1999) is based on the use of traffic flow computations and the operational street pollution model (OSPM) for evaluating outdoor air pollutants concentrations in urban areas. The activity patterns of the population have been evaluated using various administrative databases and standardised time-activity profiles. The modelling system uses a GIS in combining and processing the concentration and population data activity. The model was applied to evaluate population exposure in one specific municipality in Denmark.

An Individual Exposure Model (IEM) was developed by Wu et al. (2005) to retrospectively estimate the long-term average exposure of the individual children from Southern California to several pollutants, including PM10 and PM2.5. In the IEM model, pollutant concentration due to both local mobile source emissions and meteorologically transported pollutants were taken into account by combining a Gaussian line source model (CALINE4) with a regional air quality model (SMOG). Information from the Southern California Children's Health Study (CHS) survey was used to group each child into a specific time-activity category, for which corresponding time-activity profiles were sampled.

Once the outdoor concentration has been calculated by air quality models, the indoor pollutant concentration can also be modelled based on an understanding of the ways in which indoor air becomes exchanged with outdoor air, together with the deposition or decay dynamics of the pollutants, and with indoor emission source rates characteristics. Several methodologies exist to estimate indoor air pollution concentrations from outdoor modelled concentrations. These include a variety of empirical approaches based on: statistical evaluation of test data and a least-square regression analysis; deterministic models based on a pollutant mass balance around a particular indoor air volume; or a combination of both approaches. Most of the current available studies (Baek et al., 1997; Monn, 2001; Chau et al., 2002; Wu et al., 2005; Borrego et al., 2006) are based on experimental data, resulting from measurements of outdoor and indoor concentrations for different microenvironments in order to establish a relation between indoor and outdoor (I/O) concentrations. Morawska and Congrong (2003) presented a review of studies conducted in different countries concluding that in the absence of known indoor sources the I/O ratios range from 0.50 to 0.98. These values show that, firstly the contribution of outdoor air as a source of indoor particles is very significant, and secondly that is rather consistent across all the studies.

3.1 Input and Output Data

Besides the spatial and temporal distribution of PM concentrations (out and in doors) the information needed in such exposure studies include location of the activity, the period or time when the activity took place (e.g. time of the day, phase in life), and the duration of the activity. A review of time-activity patterns in exposure assessment is given by Ackermann-Liebrich et al. (1995).

A number of exposure modelling studies based on air quality modelling results have already been performed, namely in the scope of the European Project FUMAPEX. As an example, Figure 7 presents the results of the estimation of children (< 15 years) exposure in Turin city area. A mesoscale model was used to obtain PM10 ambient concentrations in a 1*1 km horizontal resolution grid, that were than used to estimate the indoor concentrations necessary for exposure calculations (Hänninen et al., 2005).

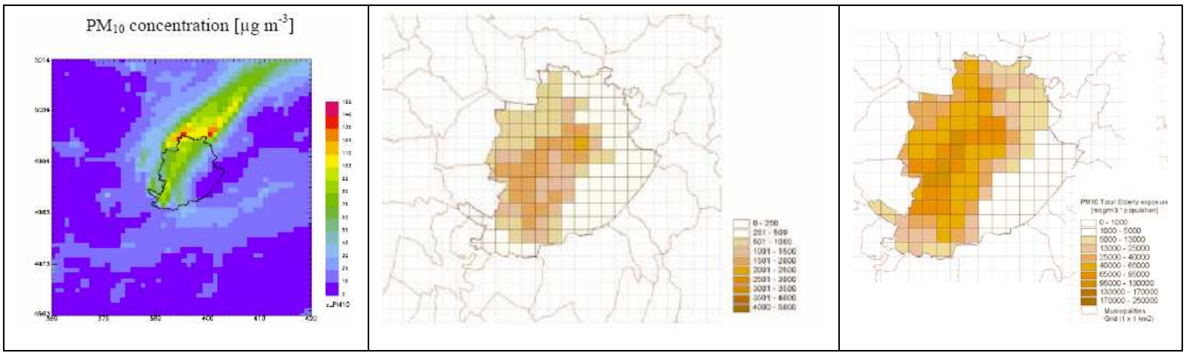


Figure 7: PM$_{10}$ simulated concentration field, children population living in each grid cell and spatial distribution of 24-hours total PM$_{10}$ exposure (Hänninen *et al.*, 2005).

Borrego et al. (2006) developed a methodology to estimate the population exposure to PM10 in urban areas, which is schematically shown in Figure 8.

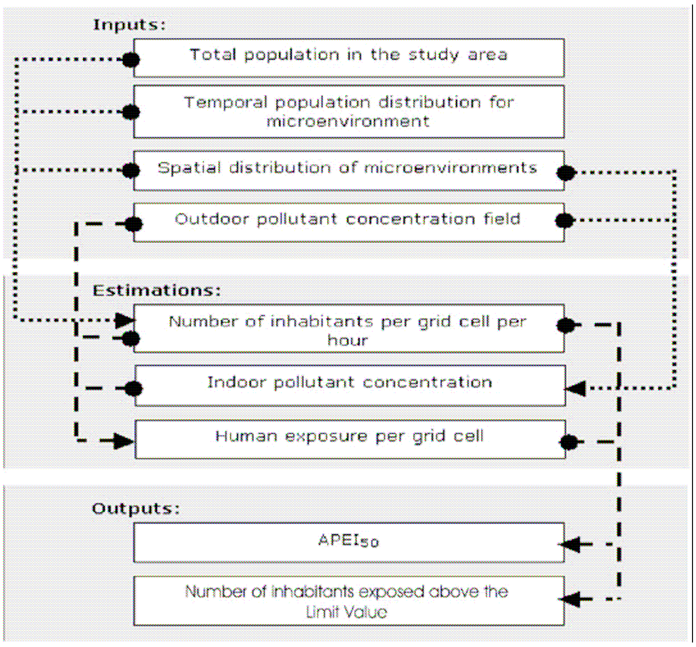


Figure 8: Schematic representation of the exposure model (Borrego *et al.*, 2006).

This methodology combines information on concentrations at different microenvironments and population time–activity pattern data. A link between a mesoscale meteorological and dispersion model and a local scale air quality model was developed to define the boundary conditions for the local scale application. Simple I/O relations were used by Borrego et al. (2006) to determine PM10 indoor concentrations from outdoor concentrations. These empirical functions, which were extrapolated from outdoor and indoor measurements, are different for each microenvironment and distinguish between diurnal and nocturnal periods. The day/night time is classified not as a function of sunlight, but in relation to the human activity pattern.

The time–activity pattern of the population was derived from statistical information for different sub-population groups and linked to digital city maps. Finally, the hourly PM10 concentrations for indoor and outdoor microenvironments were estimated for the Lisbon city centre, which was chosen as the case-study, based on the local scale air quality model application for a selected period.

The required input information includes the total population and its temporal distribution for the different microenvironments, the spatial distribution of microenvironments and the outdoor pollutant concentration. The prime objective of the model is the quantification of an integrated exposure expressed as an Accumulated Population Exposure Index (APEI). The APEI index is defined as the daily accumulated exposure over the pollutant concentration threshold and weighted by the number of inhabitants exposed. Therefore, is calculated as a sum of the positive differences between the hourly mean PM10 concentration and a threshold, multiplied by the number of inhabitants exposed, and then integrated over 24 h.

Results of PM10 field predicted by VADIS local dispersion model and the population exposure expressed in terms of an accumulated index (APEI50) are presented in Figure 9.

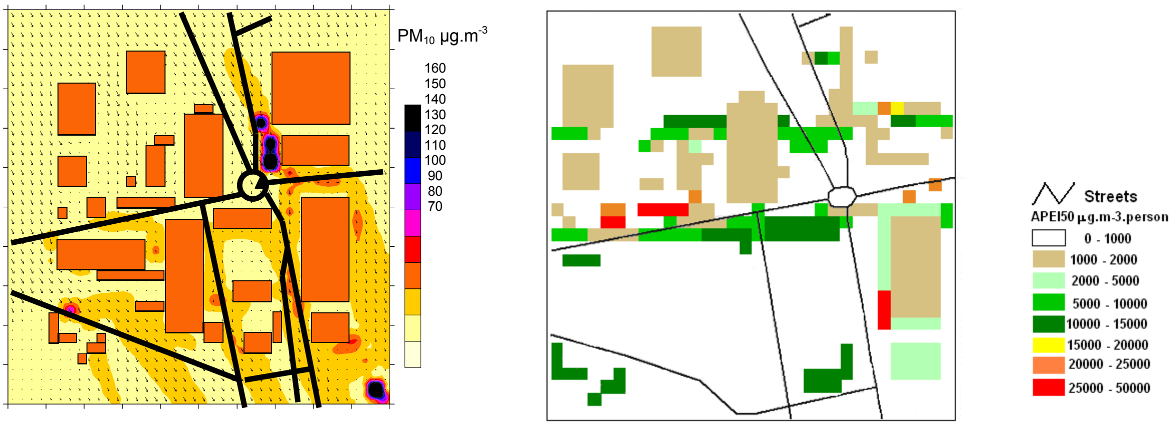


Figure 9: PM_{10} simulated field and exposure results for an urban area in Lisbon (Borrego *et al.*, 2006).

This methodology was a first approach to estimate population exposure, calculated as the total daily values above the thresholds recommended for long- and short-term health effects. Obtained results reveal that in Lisbon city centre a large number of persons are exposed to PM levels exceeding the legislated limit value.

4. New Developments

Aerosol modelling tools registered a fast development during the last years. Nowadays, and besides the complexity of the formation mechanism of aerosols and the great number of individual chemical species involved, it is possible to simulate particles and consequently to estimate population exposure based on chemical transport model results. However, improvements still have to be done, regarding the chemical and physical processes, especially in the case of SOA, which currently can only be modelled with a high level of uncertainty (Pun et al., 2003). Also special care should be taken to reduce uncertainties on emission data and measurements. Usually PM models' validation is focused on PM10 concentrations. The validation of an aerosol model also requires the analysis of the aerosol chemical composition for the main particulate species (ammonium, sulphate, nitrate and secondary organic aerosol). To find data to perform this kind of more complete evaluation is not easy. The same applies to emissions data. The lack of detailed information regarding the chemical composition of aerosols obliges modellers to use previously defined aerosols components distributions, which are found at literature. Present knowledge in emission processes is yet very lacunal, especially concerning suspension and resuspension of deposited particles (Vautard et al., 2007).

Moreover, the large diversity of environments and sources of aerosols makes difficult to obtain a general evaluation for a given model all over a large region like Europe, simultaneously at urban and regional scales. Northern Europe undergoes a very different climate than southern Europe, and sources mostly result from combustion in large cities and industrial areas, while southern Europe may be significantly influenced by wind-blown dust and photochemical transformations.

The issue of modelling scales and objective is very important. City-Delta exercise allowed concluding that fine-scale models show better performance for PM10 in the cities than large-scale models. However, these improvements are limited because models do not generally use small-scale meteorology, and still have limited vertical resolution. A further increase in horizontal resolution, down to 1 *1 km instead of 5 * 5 km may be necessary to increase further the skill. No given model is superior to the others (Vautard et al., 2007).

Dynamical downscaling, from regional till local scale, could be a way to increase the simulation resolution, taking into account the influence of large scale phenomena in micro-scale.

Aiming to understand an episode of very high levels of PM10 registered in central Europe, Builtjes et al. (2005) applied different CTMs and verified that, for this particular case study, all the CTMs showed low correlation factors and underprediction of PM. To overcome current modelling deficiencies a combination of observations and model results could be used. Combining model results with measurements reduces uncertainties inherent to both, and is strongly recommended in order to achieve a better depiction of the real situation in the areas of interest (Builtjes, 2006).

According to Walker et al. (2006) species such as PM and aerosols however, have so far only been indirectly assimilated via aerosol optical depth (AOD), either using satellite data alone, or in combination with ground based data. PM2.5 concentrations over Europe have been estimated using the LOTOS model in combination with AOD observations from the ATSR-2 satellite. This is, however, confounded by a number of difficulties due to the complex character of the different constituents of PM. It is thus not possible to use such assimilation systems yet to assess the PM concentrations in cities or urban areas.

Before using more sophisticated techniques of data assimilation it is, however, of vital importance that the model is thoroughly evaluated and validated, using proper model input data and measurements. This part of the work should not be underestimated, as it often forms the key to success in combining monitoring and modelling. Ideally, the model should show little or no bias as compared to the measurements, i.e., the model should not underestimate or overestimate concentrations systematically, or as an average, as compared to the measurements. Most data assimilation methods work best if there are little or no bias between the model and the measurements. There should also be a reasonable good time correlation (perhaps 0.5 or higher) between the two before attempting to use such methods.

The ensemble approach should also be further investigated (Builtjes, 2006) as a way to improve PM estimates.

Exposure modelling may be a promising approach to exposure assessment, using ambient air concentration modelling and the respective spatial and temporal distribution, combined with population statistics, to get a statistical assessment. Still information may become more personalized, using traffic models' information on optimized daily trips (work, school, shopping) or even tracking individuals mobile phone positions. Technology for exposure assessment is available; it is a matter of costs, data handling, and data privacy regulations to access such information. Anyway, a statistical assessment may prove sufficient for many purposes.

Indoor environments are (in the absence of strong indoor sources) assumed to be much less exposed to PM than outdoor air, due to the filtering effect of the building. Still data show that ambient concentration levels reflect also the temporal variation that is seen indoors, at least for PM10. This supports the use of ambient data as a proxy for the overall exposure. However, just "baby-steps" have been done in separating indoor and outdoor particles generation. How can the exposure to indoor sources (cooking, cleaning, candle lights, smoking) be assessed and what are the health implications of those sources are still questions to investigate, taking into consideration PM outdoor-indoor penetration and the dependency between life time indoor and the particles size, composition and physical properties (e.g. volatility, hygroscopicity).

Moreover, it is clear that the fraction of time people spend indoors changes between seasons, between places (especially northern vs. southern Europe) and also depends on work habits that may change with time (mechanisation of outdoor labour, but also leisure activities). Finally, influence of the outdoor environment to indoor air quality, or the indoor particle formation will strongly depend on age and national habits, partly again triggered by environmental conditions (need for heat insulation). Together with the need to look into other metrics than PM10 alone, this indicates the importance of better understanding the extent people are exposed to particulate matter – with exposure as the potential to inhale and retain a certain dose of material.

5. Final Comments

Air quality numerical models are useful tools for the mapping of PM, once the monitoring networks are able to assess the air quality in the single stations of the monitoring network, and not a whole area of interest. Mathematical models which simulate the evolution of both gaseous and aerosol species have only recently started to appear, due to the complexity and variability of the processes in which particulate matter is involved (Nenes, 1999).

- Nowadays, highly sophisticated modelling approaches are available, which allow assessing PM at high spatial and temporal resolution also for several source groups or even individual sources. Some can also provide chemical composition of PM and particle size distributions. Thus no new models need to be developed (models predicting transport and transformation of aerosols in the atmosphere are available). Instead, methods need to be devised which are able to forward uncertainty to modelled outputs. The respective results made available for a certain use allows understanding if answers to specific user questions can or can not be supplied reliably.
- Before being used for policies and health evaluation, PM models must be evaluated, a process which can now be carried out over long time periods (see e.g., Vautard et al., 2006 or Monteiro et al., 2007), due to the increase in computer power and memory.

- All models are useful and the choice of an appropriate model is heavily dependent on the intended application: the type and dimension of the area, the pollutants to simulate, and the final goal of the study (air quality management, exposure and health estimations, etc).
- During the last two decades or so several chemistry-transport models have been developed in Europe and elsewhere. They are already widely applied for exposure and health related issues, but an effort is still needed to take more advantage of this third generation models (Chemical Transport Models including aerosol chemistry) on epidemiological studies.
- One major field of improvement of modelling is seen in its linkage to exposure of the population and of individuals. This application was so far limited but may lead to significant improvements in e.g. exposure assessments in cohort studies.

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VII.5 Integrated Assessment Modelling

1. Introduction

Integrated assessment is a methodology used for helping decision makers to make decision by providing all 'relevant' information. The basic idea is, that we life in a highly complex cross-linked world, where any decision has a lot of different impacts. And of course at least all important impacts should be taken into account when making the decision. Thus Integrated Assessment (IA) is defined as a multidisciplinary process of synthesizing knowledge across scientific disciplines with the purpose of providing all relevant information to decision makers to help to make decisions.

2. Integrated Assessment: the example of PM10/PM2.5

What is relevant and thus should be integrated depends on the question to be answered respectively the decision to be taken. Thus we illustrate the different levels where integration takes place, with the example of PM10/PM2.5 health impacts.

2.1. Integration

If our primary aim is to reduce health impacts caused by fine particles in an efficient way, firstly all sources of PM emissions should be taken into account, as we should select the most efficient measures, however we do not know in advance, for which emission sources the most efficient reduction measures are available. This includes as well anthropogenic sources like transport, industry, energy conversion, households, agriculture as biogenic and natural sources like sea salt, particles from erosion, a.s.o. Of course, natural emission can in most cases not be reduced, but they cause a base concentration, that can not be changed and thus limits the effect of measures to reduce anthropogenic emissions. Furthermore PM10 consists to a large part of secondary particles that are formed by chemical transformation in the air, especially ammonium nitrate, ammonium sulphate and organic secondary aerosols. Thus, not only primary PM emissions, but also emissions of the precursors of secondary aerosols like SO_2, NO_x, NH_3, NMVOC have to be considered.

Secondly, having identified emission reduction measures or policies, we find, that nearly all measures have an effect not only on PM or PM precursor emissions, but also on emissions of other substances like greenhouse gases. For instance if we reduce electricity demand, this will reduce PM emissions from electricity production, e.g. in a coal fired power plant, but it will also reduce emissions of many other pollutants including CO_2 emissions and/or emissions of radioactive substances. And in a full assessment, these 'secondary' benefits should also be taken into account when assessing the efficiency of the measure. Other measures, like the reduction of wood stove use or the burning of VOC in flue gases have a positive effect on particle or precursor emissions, but on the other hand lead to a substantial additional emission of CO_2, thus partly or fully compensating the positive effect of the measure. So, these secondary benefits or burden have to be taken into account in an integrated assessment.

Thirdly, primary particles contain various heavy metals, e.g. lead, cadmium, zinc, arsenic, mercury and others. After emission into the atmosphere, these substances are deposited to soil, and eventually parts of it will be taken up by crops, which are further processed into food, that is eaten and thus leads to intake of heavy metals via ingestion, which imposes certain health risks on humans. Similarly, other impact pathways lead through ground and surface water to the contamination of drinking water and fish. Thus in a full integrated assessment, not only the atmospheric transport, but also pathways through soil, water and crops have to be considered, thus in many cases a multimedia approach is needed.

Thus, within an integrated assessment, depending on the question or problem integration might be necessary:

- across sources and pollutants: transport, energy conversion, industry, households, agriculture, natural sources;
  PM, ozone, acid substances, nutrients, heavy metals, greenhouse gases, SO_2, NOx, VOC, CO, POPs
- across impacts: health, crops, ecosystems, materials, climate change, macroeconomic (and social) impacts
- across environmental media: air (incl. indoor), soil, water, flora and fauna
- across scales: local, regional, hemispheric, global
- across all types of abatement and mitigation measures, including primary and secondary technical and non-technical measures.

2.2. Assessment

Having defined what is meant by 'integrated', we now analyse the term 'assessment'. Either there is one specific decision to be made, than the assessment tries to find out whether to make the decision is beneficial to society or not. More often, there are many alternatives to choose; than the question is which of the alternatives is the optimal decision. To be able to assess this, it is important to transform environmental impacts into effects that affect the utility of individuals and thus can be assessed. For example, the emission of x tons of a pollutant can not be assessed, as the damage associated with this emission is not known. However a risk of y to get a cough or even chronic bronchitis during the next year can be valued. Thus it is important to transform pressures or emissions into damages and risks. This is done with an approach that is known as impact pathway or full chain approach. Starting with scenarios of activities, that cause emissions and using emission factors, emissions of all relevant substances to the relevant media (air, indoor air, soil, water) are calculated. Then the transport and the chemical or physical transformation of the emitted substances in the environmental media is modelled. As a result the concentration of the substances and the transfer of pollutants between the media is analysed. In a next step, the exposure of the population and its subgroups, but also of materials and plants is modelled. In addition, the intake of pollutants via ingestion is estimated. Having established the exposure or the intake, the damage to human health, ecosystems, crops and materials is estimated using exposure-response-relationships or intake-response-relationships.

The result of this step consists of a list of many different risk and damage endpoints, which have different units and thus can not be directly added or compared. The next step could thus be to reduce the number of damage endpoints by aggregating similar endpoints. Well known examples are the aggregation of greenhouse gas emissions into t of CO_2 equivalent by using GWP (global warming potential) factors. Health endpoints can be transformed into DALYs (disability adjusted life years), ecosystem damage into pdf (potentially disappeared fraction of species). Material and crop damage is already expressed in monetary units, so can be directly aggregated.

After this step still a number of, not a priori comparable, endpoints remain. To be able to compare or aggregate them, these endpoints have to be transformed into a common unit; preferably a monetary unit, i.e. €, as this unit is already established for expressing the costs of measures. This is usually done by using the results of contingent valuation studies, i.e. by finding out, what the effected population would be willing to pay to avoid a certain risk or damage; either by carrying out surveys (stated preferences) or by observing peoples behaviour (observed preferences).

Thus, damages and risks can be transformed into monetary units and then directly be used for cost-benefit analyses.

2.3. Modelling

The model system that is used to carry out all these steps of an analysis is called an integrated assessment model. The main elements of such a model are presented in Figure 1.

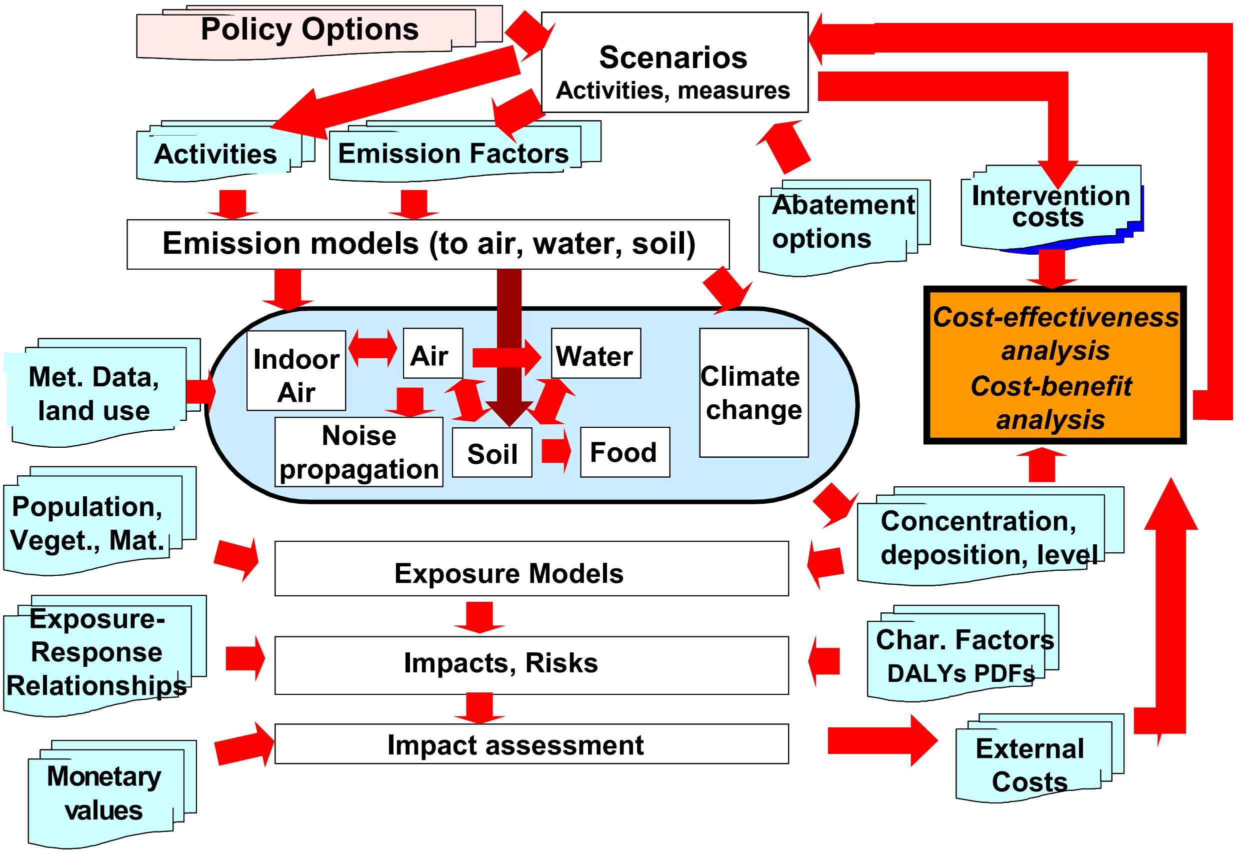


Figure 1: Main elements of an integrated assessment model

Only a handful of integrated assessment models exists, however none covers yet the full range of integration as outlined above. If we focus on atmospheric pollution and the European scale, two models could be especially mentioned:

(1) The GAINS (www.iiasa.at) model of IIASA (International Institute for Applied Systems Analysis) covers 'classical' pollutants like PM10, SO_2, NOx as well as greenhouse gases and is widely used for policy support for example for preparing the protocols of the UN-ECE CLRTAP program and also for supporting EU programs like Clean Air for Europe and the National Emissions Ceilings Directive.

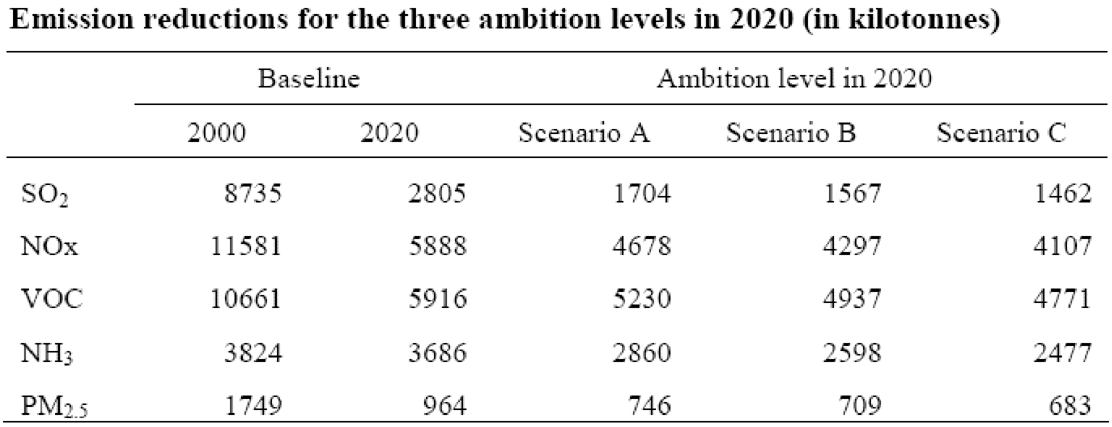
(2) The ECOSENSE model (www.externe.info) of IER, Universitaet Stuttgart that additionally to the pollutants mentioned for RAINS covers heavy metals and also includes a multimedia model for modelling the pathway through soil and water to food and drinking water. ECOSENSE is also widely used for decision support in project appraisal in the energy and transport sectors and for carrying out cost-benefit analyses for a number of environmental directives for the EU.

Other European wide models, that are however smaller in scope, i.e. analyse a much smaller number of pollutants, are CASM from the Stockholm Environment Institute and ASAM from Imperial College, London. A number of further modelling systems is primarily used for integrated assessment on a national scale.

The uncertainties of the results of integrated assessment modelling still are quite high; the standard deviation could roughly be estimated as a factor of three around the central value. Thus sensitivity analyses have to be made, to analyse whether the basic conclusions remain valid despite varying input parameters and model results, which fortunately is quite often the case.

As an example for applications, we first show results of GAINS used for supporting the CAFE strategy of the EC (http://cafe-cba.aeat.com/reports/). In this work, first a number of emission reduction scenarios have been set up for 2020 (see Table 1).

Table1: Emission reduction scenarios



Emission reductions for the three ambition levels in 2020 (in kilotonnes)

	Baseline		Ambition level in 2020		
	2000	2020	Scenario A	Scenario B	Scenario C
SO_2	8735	2805	1704	1567	1462
NOx	11581	5888	4678	4297	4107
VOC	10661	5916	5230	4937	4771
NH_3	3824	3686	2860	2598	2477
$PM_{2.5}$	1749	964	746	709	683

Then the costs for these scenarios and the avoided monetized risks for these scenarios have been calculated. Results are shown in Table 2 (http://cafe-cba.aeat.com/reports/) (MTFR= maximal technically feasible reduction, i.e. with technical measures).

Table 2: Calculations of costs and avoided monetized risks

In billion €/a	**A**	**B**	**C**	**MTFR**
EU Annualised benefits (health, materials and crops) change over base				
Low estimate	38	46	50	57
High estimate	120	147	160	182
EU-25 Annualised Costs - change over base line				
Total	5.9	10.7	14.9	39.7
NET benefits				
Low estimate	32	35	35	17
High estimate	115	136	145	142
Benefit to Cost Ratio				
Low estimate	6.3	4.3	3.4	1.4
High estimate	20	14	11	4.6

As can be seen, the optimal strategy lies somewhere between scenarios B and C. Most of the benefit comes from the reduction of health impacts due to the PM2.5 emission reductions. Based on these results, a 'thematic strategy' was identified and agreed upon, that with costs of around 7 billions € per year achieves benefits of at least 42 billion € per year.

Another example is the application of the ECOSENSE model to identify cost-effective measures for a strategy to reduce health impacts from PM10, but with a view on reducing health impacts from NO_2 and ozone and impacts from eutrophication of ecosystems (http://www.parest.de/impressum.html). This resulted in the following list of additional priority measures (additionally to the already planned or implemented measures like EURO VI for vehicles):

Energy and Industry
- FGD, where not yet implemented
- Optimisation and improvement of bag houses
- Optimisation and improvement of electrostatic precipitators
- Substitution of coal and heavy fuel oil with natural gas
- Improved primary measures (LowNox + over fire air)
- Selective Catalytic Reduction, where not yet implemented
- Leak detection and repair programs (Refineries, fugitive)

Households
- Substitution of coal and wood with light fuel oil and gas
- State of the art stoves
- Energy saving (e.g. reduction of stand-by electricity demand, use of BAT)

Transport
- City toll, reduced parking space regime or fuel tax increase 20%
- Switch to CNG, electric and hybrid engines
- Particulate filters in existing and new off-road vehicles (building machinery, tractors,..)
- Retrofitting particulate filters for HDV diesel engines,
- Reduction of emissions from ships (currently under negotiation)

Solvent Use
- Substitution of solvents in sprays
- Emission reduction
    - Offset printing (less isopropanol, high boiling point cleaners)
    - Degreasing processes
    - Paint application in mechanical engineering branch
    - Production of solvent based goods
    - Paint application – wood (carpenter)

Agriculture (reduction of secondary aerosols)
- Cover of manure storage
- Improved slurry application technique (slurry injection, band spreading)

Of course, an integrated assessment can only be as good as the available basic information. One of the most important gaps is the missing information about which feature (number, size, weight) and which species contained in PM10 are responsible for the human health impacts. This information would however be crucial for identifying efficient strategies for reducing PM10 health impacts.

3. Summary and recommendations

As explained above, an integrated view taking into account all relevant information and relationships is a necessity and prerequisite for identifying efficient policies. Integrated assessment model systems to carry out such assessments are available, although further model improvements are needed. Current developments, e.g. within the EC projects INTARESE (www.intarese.org) and HEIMTSA (www.heimtsa.eu), focus on exposure modelling and on coupled multimedia modelling, the latter linking models for the media water, soil, food, outdoor air, indoor air and integrating future climate change effects. Furthermore, interfaces between the models of the process chain, i.e. from emissions to concentrations to exposure and intake to health effects and ecosystem damage to valuation of these endpoints should be defined and implemented. A big challenge is the estimation of the uncertainties and the representation of these uncertainties together with the results.