PROGRAMME "GLOBAL CHANGE AND SUSTAINABLE DEVELOPMENT"
PRIME MINISTER'S SERVICES
FEDERAL OFFICE FOR SCIENTIFIC, TECHNICAL AND CULTURAL AFFAIRS

Research contracts nos. CG/DD/03A, CG/DD/03B and CG/DD/03C

SOURCES, PHYSICO-CHEMICAL CHARACTERISTICS, AND CLIMATE FORCING OF ATMOSPHERIC AEROSOLS

WILLY MAENHAUT
Universiteit Gent (RUG), Department of Analytical Chemistry,
Institute for Nuclear Sciences, Research group Tropospheric Aerosol Research
and Nuclear Microanalysis,
Proeftuinstraat 86, B-9000 Gent, Belgium

FREDDY ADAMS
Universiteit Antwerpen (UIA), Micro and Trace Analysis Centre (MiTAC),
Universiteitsplein 1, B-2610 Antwerpen, Belgium

and MAGDA CLAEYS
Universiteit Antwerpen (UIA), Department of Pharmaceutical Sciences,
Research group Bio-organic Mass Spectrometry,
Universiteitsplein 1, B-2610 Antwerpen, Belgium

FINAL INTEGRATED SCIENTIFIC REPORT

For the 4-year period from 1/12/1996 until 30/11/2000

TABLE OF CONTENTS

ABSTRACT

The overall goal of the project was to contribute to the reduction of the uncertainties in our knowledge of the sources, spatial distribution, and characteristics of the tropospheric aerosols that are of importance for climate. This was accomplished by performing studies at sites which are representative for large regions or are situated within (or downwind of) areas where it is expected that the radiative forcing by anthropogenic aerosols is very substantial. The studies were done (a) at selected sites in Europe within the framework of the EUROTRAC-2 AEROSOL subproject, (b) at sites in the eastern Mediterranean and in the Arctic, which are receptor areas of the European pollution plume, and (c) in tropical and subtropical regions.

The specific objectives of the project were: (1) to provide a comprehensive physico-chemical characterisation of the fine (submicrometer-sized) aerosol in the areas of study; (2) for some study areas, to complement this with purely physical aerosol measurements, with the determination of in-situ optical aerosol parameters and of vertical-column aerosol characteristics, and with measurements of atmospheric trace gases; (3) to determine the relative contributions of the three aerosol types (fine sulphate, organic aerosols, and mineral dust), which are mainly responsible for the aerosol forcing on climate; to differentiate between the natural and anthropogenic contributions to the fine sulphate and the organic aerosols; and to assess the sources, source processes, source areas, and transport mechanisms for the three important radiatively active aerosol types; (4) to investigate to which extent the fine aerosol mass can be reconstituted on the basis of the measured aerosol types, and thus aerosol chemical mass closure can be obtained; (5) to interrelate the various aerosol data sets and to utilise them for model calculations of optical aerosol characteristics or radiative forcing.

The project involved the development and implementation of novel methods and approaches for aerosol collection, for “bulk” and individual particle analysis, and for data interpretation and interrelation.

With regard to methodology, we implemented and evaluated a thermal-optical transmission technique for the determination of organic carbon (OC) and elemental carbon (EC) in aerosols. We participated in the EUROTRAC-2 AEROSOL Carbon Shootout Stages I and II and in other round-robins, which were organised to compare the methods of the various participants and to arrive at improved methods for the determination of and differentiation between OC and EC. We improved and evaluated methods for extracting organic compounds from aerosols for subsequent detailed analysis by capillary gas chromatography - flame ionisation detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS). We started developing a method for the quantitative determination of levoglucosan (which is a general marker for wood combustion) and related monosaccharide anhydrides in aerosol samples, and we implemented various types of derivatisations and solid-phase extraction in combination with GC/MS for the characterisation and structure elucidation of unknown compounds that were present in notable concentrations in urban and tropical aerosol samples. Methodological development work was done for transmission electron microscopy with selected area electron diffraction, and for two other microscopical analytical techniques,

namely microprobe X-ray fluorescence with laboratory and synchrotron radiation sources and static secondary ion mass spectrometry.

Aerosol research was conducted in Arctic and sub-Arctic areas. This included studies within the framework of the Arctic Ocean Expedition 1996 (AOE-96), for Summit in Greenland, at the Zeppelin mountain station in Ny Ålesund, Spitsbergen, at Sevettijärvi in Finnish Lapland, and for two sites (i.e., Birkenes and Skreådalen) in southern Norway. For AOE-96, we performed chemical mass calculations and examined the detailed mass size distributions of various elements and species. Chemical mass closure calculations were also done for Sevettijärvi and the two Norwegian sites. The data sets from the three sites were also subjected to absolute principal component analysis in order to examine the interrelations between the various chemical species and elements, and to identify the major aerosol components and/or source types. For Sevettijärvi, we also applied trajectory statistics in order to identify the major source regions of sulphate and of selected elements and heavy metals.

Our contribution to the AEROSOL subproject includes the development, evaluation and application of analytical methods for OC and EC and for detailed organic compounds. During 1998, the methods were evaluated and applied to aerosol samples collected in Gent, during two different seasons (winter and summer). In both seasons, daily samples were taken with three types of filter collection devices. Particulate mass (PM) was determined for all filters by weighing, and all quartz filters were subjected to analyses for OC and EC; selected filters from one sampler were analysed for detailed organic compounds by capillary GC-FID and GC/MS. About two thirds of the PM10 (that is particles smaller than 10 µm) aerosol mass was contained in the fine (<2 µm) size fraction at Gent during the sampling campaigns. During both winter and summer, total carbon (TC = OC + EC) was responsible for around one quarter of the aerosol mass and EC represented about 25% of TC. Considering that the organic aerosol also contains other atoms (such as hydrogen, oxygen, nitrogen) besides carbon, the OC data have to be multiplied by a conversion factor in order to obtain organic aerosol mass (organic matter, OM). Multiplication factors of 1.4 are commonly used for urban aerosols. Using this factor, one arrives at a percentage of carbonaceous aerosol (that is the sum of OM plus EC) of one third of the PM. By the detailed analyses for organic compounds, over 100 compounds belonging to different classes could be identified. Their total mass represented on average only 3% of the mass of the OM, though. *n*-Alkanes and fatty acids were the prevailing organic compounds in both seasons, but the distribution patterns of individual components within each class showed seasonal differences. The *n*-alkane pattern for summer aerosols was clearly affected by emissions from the vegetation, while that of fatty acids revealed a lower relative abundance of unsaturated fatty acids in summer than winter, that can be related to more extensive atmospheric oxidation of unsaturated fatty acids during summer. Concentrations of dicarboxylic acids and related products that are believed to be oxidation products of hydrocarbons and fatty acids were highest in summer aerosols. Some individual compounds in the latter class could only be detected in summer samples and showed the highest concentrations on hot summer days that were characterised by maximum temperatures above 25°C and increased ozone concentrations. The latter compounds included novel, recently identified glutaric acid derivatives. Several compounds were found that are markers of wood combustion, including diterpenoic acids, lignin pyrolysis products, and levoglucosan. The quantitative results obtained for diterpenoic acids and lignin pyrolysis products indicated that contributions from wood combustion are more important in winter than in summer. There was evidence that both soft and hard wood burning contribute to the organic aerosol, but that hard wood burning prevails during winter. Polyaromatic hydrocarbons were also more prevalent in winter than in summer.

Besides work on OC, EC, and detailed organic compounds, our contribution to the AEROSOL subproject includes intercomparison and evaluation of methods for measuring important aerosol parameters, such as the PM, carbon, determination of the detailed mass size distribution for the PM, OC, EC and other important aerosol species, chemical mass closure work, and source (type) apportionment. Various intercomparisons were made at Gent of filter collections and in-situ measurements for the aerosol particulate mass and elemental/black carbon (all for the PM2.5 aerosol, that is for the particles smaller than 2.5 µm). The in-situ instruments were a Rupprecht and Patashnick tapered element oscillating microbalance (TEOM) for the PM and a Magee Scientific aethalometer for black carbon (BC). The TEOM value was on average only two thirds of the gravimetric mass derived from quartz fibre filters. Discrepancies between TEOM and gravimetric aerosol data have been observed by others and are attributed to the heating to 50°C (and loss of semi-volatile aerosol) in the TEOM. Comparisons of gravimetric fine PM determinations were also done with filter holders that used different types of filters. It was found that the fine PM derived from Nuclepore polycarbonate filters and Teflo filters was only around 75% of that derived from the quartz fibre filters. The difference may be due to the loss of semi-volatile aerosol for the Nuclepore and Teflo filters or to the collection of gaseous species by the quartz filters or to a combination of both. Further investigations should clarify this. In fall 1999, we examined the detailed mass size distribution of the PM, OC, EC, and various elements at Gent, and used the data for aerosol chemical mass closure calculations as a function of particle size. Six aerosol types were considered in the mass closure calculations: (1) organic aerosol, (2) EC, (3) ammonium sulphate, (4) sea salt, (5) crustal matter, and (6) biomass smoke. The major aerosol types in the submicrometer size fraction were organic aerosol (on average responsible for 32% of the PM), ammonium sulphate (27%) and EC (10%). In the supermicrometer size range, organic aerosol (28% of the PM) and crustal material (24%) prevailed; ammonium sulphate and sea salt were responsible for about 10% each. On average, 74% of the gravimetric PM was accounted for by the aerosol types considered. The unexplained mass is likely attributable to ammonium nitrate and water.

In addition to our aerosol research at Gent, we conducted aerosol research at various other urban sites, including for Cracow, Helsinki, and Budapest. These urban studies were to some extent linked to the EUROTRAC-2 AEROSOL subproject. Furthermore, the work in Helsinki fitted within the EUROTRAC-2 project SATURN.

We also participated in the INTERCOMP 2000 experiment of the EUROTRAC-2 AEROSOL subproject. The field work for INTERCOMP 2000 took place in April 2000 at the Institute for Tropospheric Research (IfT) research station Melpitz, about 50 km north-east of Leipzig, Germany.

A large part of our project dealt with comprehensive studies on chemical, physical, and optical (radiative) aerosol properties in the eastern Mediterranean and the assessment of the direct radiative forcing by aerosols in the area. These studies were performed in close co-operation with foreign research groups, especially with the Biogeochemistry Department of the Max Planck Institute for Chemistry, Germany. Both long-term and intensive aerosol measurements were conducted at Sde Boker in the Negev desert, Israel. The long-term measurements started in January 1995 and are still going on. The intensive measurements were conducted during two campaigns (of about 4 weeks each), the first one, called ARACHNE-96, in June-July 1996, the other, ARACHNE-97, in February-March 1997. In the long-term measurements, aerosol samples are collected with a Gent PM10 stacked filter unit sampler according to a 2-2-3-day schedule and analysed for the PM, BC, and over 40 elements. From December 1995 through September 1997, an integrating nephelometer was used for the continuous measurement of the aerosol scattering and backscattering coefficients at 3 wavelengths (450, 550, and 700 nm), and it was then replaced by a unit which only measures the scattering at 550 nm. Furthermore, measurements of vertical column-integrated aerosol optical depth and aerosol properties are conducted at the site on a nearly continuous basis with an automatic tracking combined sunphotometer/sky radiometer. During the intensive campaigns, a wide array of instruments was used for measuring the aerosol chemical, physical, and optical (radiative) properties and for measuring selected atmospheric trace gases (CO, CO_2, SO_2, O_3). Comprehensive articles on the ARACHNE-96 and ARACHNE-97 campaigns were published. During ARACHNE-96, the average aerosol dry single scattering albedo (ω_0) characterising polluted conditions was 0.89, whereas during "clean" periods ω_0 was 0.94. The direct radiative effect of the pollution aerosols was estimated to be cooling. With regard to the long-term measurements, the data from the 3-wavelength nephelometer and the Gent PM10 stacked filter unit sampler were interrelated. This was done for the period December 1995 through September 1997. The total scattering coefficient at 550 nm showed a median of 66.7 Mm^{-1}, typical of moderately polluted continental air masses. Values of 1000 Mm^{-1} and higher were encountered during severe dust storm events. Mass scattering efficiencies were obtained by multivariate regression of the scattering coefficients on dust, sulphate, and residual components. An analysis of the contributions of the various aerosol components to the total scattering observed showed that anthropogenic aerosol accounted for about 70% of the scattering. The rest was dominated by the effect of the large dust events mentioned above, and of small dust episodes typically occurring during mid-afternoon. The radiative forcing by anthropogenic aerosols in the study region at the top of the atmosphere was estimated using two different approaches. The most detailed of these yielded an all-sky radiative forcing of -2.5 and -4.9 Watt m^{-2} over desert and ocean surfaces, respectively. These data are in good agreement with predictions from global models of aerosol radiative forcing. Overall, we concluded that our data provide strong support for a negative radiative forcing due to anthropogenic aerosols in the eastern Mediterranean region, and that the magnitude of this forcing is in good agreement with current model predictions. Further with regard to the long-term collections, we applied trajectory statistics in order to assess the source regions of some important aerosol constituents. The stacked filter unit data set for the 3-year period from 1995 through 1997 was used for this purpose. The air masses, which arrived at Sde Boker slightly above ground (i.e., at a level corresponding to 950/960 hPa), originated mainly from the north-west, and had remained in the atmospheric boundary layer (below 2000 meters) during the 5 days preceding their arrival. The same was true for the 900 hPa arrival level. The highest levels of fine sulphur were associated with air masses that originated in the North; the dominant source region appeared to be Ukraine, followed by the West coast of the Black Sea, and Greece. In contrast, fine V and fine Ni (two indicators of residual oil burning) were from local/regional origin, including from the power plants along the Israeli coast. Russia seemed to be the major source area of fine Zn. Coarse Ca, an indicator for the carbonate mineral dust, was highest for air masses coming from the south-east and west, consistent with the location of the desert source regions

Our aerosol research in tropical and subtropical regions included studies in Africa (the Republic of Congo, Zimbabwe, South Africa), the Brazilian Amazon region, northern Australia, and Indonesia. It involved both long-term and campaign-type measurements. The emphasis in the studies was placed on the impact of biomass burning and of natural biogenic emissions on the climatically active fine aerosol. Part of our work for Brazil was performed within the framework of the "Smoke, Clouds, Aerosols and Radiation - Brazil (SCAR-B) Experiment" and the "Large Scale Biosphere-Atmosphere Experiment in Amazonia" (LBA), and some of our research in South Africa was done as part of the Southern African Regional Science Initiative (SAFARI 2000).

With regard to the valorisation of our work, this is partly done through traditional channels, such as publications in international journals and presentations at international conferences. For our research that is done within intensive campaigns, we also relate our data with results of the other participants, which leads to joint publications and presentations. The results are further used in workshops, activities and reports that aim at transfer of knowledge to policy advisers and policy makers. Our long-term and other data sets with concentrations and compositions of fine atmospheric aerosols for various European sites are being used for advice to the European Commission, in particular within work for the 2003 revision of the EU Particulate Matter Directive.

Our research has shown that the determination of seemingly simple aerosol parameters, such as the PM, is much less straightforward than usually thought. The measurement of the PM is complicated by both positive and negative artifacts. Work on the control, elimination, and assessment of the artifacts is needed. This work will assist regulatory bodies which are setting and imposing guidelines for particulate matter. Carbonaceous particles make up a very large fraction (often over 30%) of the aerosol in many areas. Yet, our knowledge on the detailed molecular composition of the carbonaceous aerosol, its sources, and its effects on human health and climate is still quite poor. Further research on these topics is highly recommended. There are still large uncertainties associated with the radiative forcing of aerosols on climate. In the past few years, much progress has been made with regard to the *direct* radiative aerosol forcing. However, with regard to the *indirect* radiative forcing (that is through the effects of aerosols on clouds) much work remains to be done.

1 CONTEXT AND OBJECTIVES

Aerosols are tiny liquid or solid particles that are present in the atmosphere. They have diameters in the range from 1 nm to over 10 µm, but most of their mass is in the size range from about 0.1 to 10 µm. They originate from a wide variety of natural and anthropogenic (man-made) processes that exhibit a large spatial and temporal variability [Andreae, 1995; Jonas et al., 1995]. The production mechanisms are: (1) direct injection of particles in the atmosphere, mostly by dispersion processes, resulting in so-called primary (and coarse, that is >1 µm) aerosols, and (2) transformation of inorganic and organic gaseous precursors into secondary (and fine, <1 µm) aerosols. Aerosols play an important role in atmospheric chemistry, have effects on human and animal health and welfare, and they influence climate. In the 1990s renewed interest in the health risks of aerosols has been generated by the finding of a correlation between increased mortality and the concentration of (fine) airborne particles in metropolitan areas in the United States [Dockery et al., 1993].

The climatic effect of aerosols stems from the fact that they physically affect the heat balance of the Earth, both *directly* by reflecting and absorbing solar radiation and by absorbing and emitting some terrestrial infrared radiation, and *indirectly* by influencing the properties and processes of clouds, and, possibly, by changing the heterogeneous chemistry of reactive greenhouse gases (e.g., O_3) [Charlson and Heintzenberg, 1995]. Changes in the heat balance due to anthropogenic or externally imposed changes are referred to as forcings. The climatic effect of aerosols is in the direction of cooling (under most circumstances) and is of a magnitude comparable to that of the greenhouse gas warming [Charlson et al., 1992; IPCC, 1994]. Due to the spatial and temporal variability of anthropogenic aerosols, the forcing has strong regional character [Kiehl and Rodhe, 1995], so that also the climate response to the aerosol forcing is regionally heterogeneous [Taylor and Penner, 1994]. In 1995, the global mean radiative forcing by anthropogenic aerosols was estimated to be -(0.25-2.5) W m^{-2} [Houghton et al., 1996]. The large range of uncertainty associated with the aerosol forcing estimate reflects the poor state of knowledge regarding the sources, distributions, and properties of atmospheric aerosols. Kiehl and Briegleb [1993] stressed that studies on the regional characteristics of aerosols were urgently needed to reduce this uncertainty. Penner et al. [1994] suggested a research strategy which encompasses surface-based observations of aerosol chemical and physical properties.

Over Europe, fine sulphate, which is formed by the gas-to-particle conversion of SO_2 from fossil fuel burning and smelting activities, is thought to be mostly responsible for both the *direct* and *indirect* aerosol forcing on climate. Over tropical and equatorial continental regions, fine pyrogenic (biomass burning) particles and natural emissions from the vegetation, which both consist mainly of carbonaceous particulates, are the prevailing climatically active aerosol species. In addition, organic aerosols from anthropogenic continental origin have been shown to account for the major part of the cloud condensation nuclei (and thus the *indirect* forcing) in marine air [Novakov and Penner, 1993]. However, it is difficult to discriminate between the natural and anthropogenic contributions to the carbonaceous aerosols, and this is especially so for tropical and subtropical areas [e.g., Radzi bin Abas and Simoneit, 1996; Maenhaut et al., 1996c]. This difficulty stems partly from the difficulties in collection and preservation of carbonaceous particles (which are often semi-volatile), but even more from the lack of suitable analytical methods to measure polar organic compounds in the aerosols. In the studies on natural and combustion aerosols from the vegetation, one has until now mainly concentrated on the determination of solvent extractable organic compounds, including *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, and terpenoids [e.g., Rogge et al., 1993a; Radzi bin Abas and Simoneit, 1996]. A major component of the aerosol on a global scale is mineral dust (soil dust). While most of this dust is of natural origin (i.e., generated by dust storms in desert regions of North Africa and Central Asia), changes in land use must have increased the amounts of dust injected into the atmosphere [Andreae, 1995; Tegen and Fung, 1995]. Tegen et al. [1996] calculated the climate forcing of mineral aerosols from disturbed soils, and they indicated that additional field (and other) measurements are required to improve the estimates of the radiative forcing and to assess uncertainties.

In principle, the radiative (optical) properties of atmospheric aerosols can be predicted from their physical and chemical characteristics by using theoretical formalisms (Mie theory) or empirical relationships [e.g., Kiehl and Briegleb, 1993]. This requires the knowledge of the contribution from the various aerosol types (sulphates, combustion particles, dust, etc.), of the size distribution of these aerosol types, their surface composition and their chemical composition as a function of size, the particle shape, and the state of particle mixing (external or internal). Conversely, the optical characteristics of the aerosol (scattering and absorption coefficients) can be measured experimentally. These experimental optical data can then be compared with the calculated values in order to examine to which extent agreement (“closure”) between them can be obtained. As indicated by Ogren [1995] and others, such closure experiments on various temporal and spatial scales are essential to minimise the uncertainties of current estimates of aerosol climate forcing.

In studies on the climatically active fine aerosol (and on fine aerosols in general), a major fraction of the fine particulate mass (PM) remains often unexplained by the particle types measured [e.g., Maenhaut et al., 1996a]. This observation formed the impetus for the EUROTRAC-2 AEROSOL subproject, which aims at obtaining chemical mass “closure” for fine aerosols in key urban and rural areas in Europe. Assessing the various fine aerosol constituents and their sources is needed for determining the role of aerosols in regional and global climate forcing (and incidentally also for elucidating the causes of the health risks of aerosols). The relative contributions from natural and anthropogenic particle types (and source identification and apportionment in general) are usually obtained by applying receptor models [Gordon, 1988] to multivariate data sets that result from “bulk” analyses. For such data sets, there are, however, severe difficulties in apportioning the contributions from source types with similar bulk compositions of the emitted particles. To arrive at a better discrimination one can resort to individual particle techniques [e.g., Van Borm and Adams, 1988]. Most commonly used is electron probe X-ray microanalysis (EPXMA). While EPXMA is undoubtedly of great value, it suffers from the fact that its detection limits are of the order of 0.1% only. Therefore, continuous efforts are directed towards the development of more sensitive micro-analytical techniques and their application to environmental samples. Besides the identification and apportionment of sources and source types, similar tasks are increasingly performed with regard to source regions, particularly for areas that are downwind of major source regions. In the 1980s attempts were made to address this issue with receptor models, but nowadays there is a clear tendency to utilise air mass back trajectories in combination with the aerosol data sets [e.g., Stohl, 1996].

The overall aim of the project was to contribute to the reduction of the uncertainties in our knowledge of the sources, spatial distributions, and properties of the aerosols that are of relevance for climate forcing. Therefore, studies were performed at a number of sites that are representative for fairly large regions, and that are located in (or downwind of) areas where the radiative forcing from anthropogenic aerosols is expected to be substantial. The studies were done (1) at selected sites in Europe within the framework of the EUROTRAC-2 AEROSOL subproject, (2) at sites in the eastern Mediterranean and in the Arctic, which are receptor areas of the European pollution plume, and (3) in tropical and subtropical regions.

As indicated above, over Europe and downwind of it, fine sulphate is thought to be mostly responsible for the aerosol forcing on climate. However, the forcing by carbonaceous aerosols from fossil fuel use may also be substantial, and over the Mediterranean, mineral dust from arid and desert regions in North Africa and Arabia forms an important radiatively active aerosol component. One objective of the research was therefore to determine the relative contributions from the three aerosol types at various study sites and to determine their sources, source processes, source regions, and transport pathways (and to examine how all these parameters vary with season). While most of the climatically active fine sulphate is undoubtedly from anthropogenic origin, at certain times of the year (i.e., spring and summer) and in certain regions (e.g., the Arctic), there may be a significant contribution from sulphate that is formed by gas-to-particle conversion of dimethylsulphide and other reduced sulphur gases emitted by marine and terrestrial plants. Similarly, the primary and secondary organic carbon (OC) component of the fine aerosol over Europe may also originate in part from natural emissions of the vegetation. In tropical and equatorial regions, the contribution from vegetative emissions to the OC particles may even be higher, especially during the wet season when biomass burning is much reduced. It was therefore a major objective to assess the relative contributions from natural and anthropogenic sources for both the fine sulphate and OC.

Because the submicrometer-sized aerosol particles are of major relevance for both the direct and indirect forcing of climate, the emphasis was placed on the comprehensive chemical and physical characterisation of the fine aerosol. This was done through collections with a variety of aerosol samplers, whereby the fine aerosol is collected in a separate fraction or is fractionated in several size classes (such as is the case with cascade impactors), and subsequent bulk chemical analysis of the fractionated aerosols. Depending upon the sampler used, the bulk analyses included determination of the particulate mass (PM), of organic carbon (OC) and elemental (or black or soot) carbon (EC or BC), of water-soluble inorganic species (sulphate, nitrate, ammonium) and some water-soluble organic compounds (e.g., methanesulphonate, lower molecular weight (MW) organic acids), of major, minor and trace elements, and of selected higher MW organic compounds. These bulk analyses were complemented by microscopical analyses on selected samples, which aimed at determining the shape (morphology) and composition of individual particles, the state of particle mixing (external versus internal), and the presence of water-soluble or hydrophilic coatings on mineral and carbonaceous particles (such coatings have the effect that the particles can act as cloud condensation nuclei (CCN)). At a number of sites, the physico-chemical aerosol measurements were complemented by purely physical aerosol measurements (of the number of condensation nuclei, of CCN, and of the detailed aerosol number size distribution), with the determination of in-situ optical (radiative) aerosol parameters (scattering, backscattering, absorption coefficients) and of vertical-column integrated aerosol properties (optical depth, aerosol size distribution, and scattering), and with measurements of aerosol precursor gases (SO_2) or of useful tracers for polluted air (CO, CO_2, O_3). The research involved both long-term measurements and intensive campaigns, and a much wider array of instrumentation was used in the latter. Most of the work consisted of surface-based aerosol measurements, but some measurements were performed with an airplane in order to examine the vertical structure of the physical, chemical, and optical aerosol parameters.

The various aerosol data sets were interrelated to each other and used for model calculations of the aerosol optical properties or radiative forcing. The objectives hereby were: (a) to investigate how well the experimentally measured radiative properties of the aerosol could be predicted from the measured chemical and physical aerosol characteristics (and thus closure can be obtained between measurement and theory), (b) to assess the direct radiative forcing by aerosols, and (c) to assess to which extent the ground-level in-situ aerosol characteristics are related to or can be used for the prediction of the chemical, physical and optical aerosol properties in the entire vertical column. Another major objective was to examine to which extent the fine PM could be reconstituted on the basis of the various aerosol types measured, and if it appeared that a substantial fraction of the PM is unexplained, to take appropriate actions for identifying that “missing” mass.

The aerosol collections and chemical analyses were largely performed with instrumentation that was already available at the start of the project, but some new developments were also necessary and were made, especially for the bulk analysis of OC/EC and organic compounds and for the microscopical examination of submicrometer-sized individual particles. The developments were needed to obtain chemical mass closure for the PM, to extend the range of marker compounds or species for discrimination between natural and anthropogenic particle types, and to obtain the information required for the calculation of the optical aerosol characteristics.

To determine the relative contributions from the major aerosol types and/or source categories to the total aerosol concentration and to discriminate between the natural and anthropogenic contributions for the important particle types, we relied mostly on receptor modelling by chemical mass balance and multivariate techniques. In addition, efforts were made for assessing the dominant source regions and transport pathways. This work involved the use of air mass back trajectories.

The overall goal of the project was thus to contribute to the reduction of the uncertainties in our knowledge of the sources, spatial distribution, and characteristics of the tropospheric aerosols that are of importance for climate. In summary, the objectives of the project were:

(1) to provide a comprehensive physico-chemical characterisation of the fine (submicrometer-sized) aerosol in the areas of study;

(2) for some study areas, to complement this with purely physical aerosol measurements, with the determination of in-situ optical aerosol parameters and of vertical-column aerosol characteristics, and with measurements of atmospheric trace gases;
(3) to determine the relative contributions of the three aerosol types (fine sulphate, organic aerosols, and mineral dust), which are mainly responsible for the aerosol forcing on climate; to differentiate between the natural and anthropogenic contributions to the fine sulphate and the organic aerosols; and to assess the sources, source processes, source areas, and transport mechanisms for the three important radiatively active aerosol types;
(4) to investigate to which extent the fine aerosol mass can be reconstituted on the basis of the measured aerosol types;
(5) to interrelate the various aerosol data sets and to utilise them for model calculations of optical aerosol characteristics or radiative forcing.

The project involved the development and implementation of novel methods and approaches for aerosol collection, for “bulk” and individual particle analysis, and for data interpretation and interrelation.

2 METHODS AND TECHNIQUES

2.1 Aerosol collections for subsequent “bulk” chemical analysis or investigation by individual particle techniques

A wide variety of aerosol collectors are employed, but those actually used at a given site depend on the logistical support, on the type of measurement (long-term, campaign, aircraft), on the subsequent analyses, and on the co-operating institutions. The collection devices used in the current project included “total” filter samplers, PM10 (particulate matter <10 µm equivalent aerodynamic diameter (EAD)) and PM2.5 (particulate matter <2.5 µm EAD) devices, and several types of cascade impactors. Most commonly used was the “Gent” PM10 stacked filter unit (SFU) sampler [Maenhaut et al., 1994b; Hopke et al., 1997]. This device separates the aerosol particles into a coarse and a fine size fraction, with the division between the two fractions at around 2 µm EAD. Filters of organic material (polycarbonate, Teflon, cellulose, cellulose esters) were used for measuring major, minor, and trace elements and water-soluble inorganic and organic species. For organic and elemental carbon and higher molecular weight organic compounds, the filter material consisted of quartz fibre, glass fibre or Teflon-coated glass fibre. As cascade impactors we mainly used the 8-stage, 1-L/min PIXE Int. cascade impactor (PCI) [Bauman et al., 1981] or reduced versions thereof, the 12-stage, 11-L/min small deposit area low pressure impactor (SDI) [Maenhaut et al., 1996b], and the 10-stage rotating microorifice uniform deposit impactor (MOUDI) [Marple et al., 1991].

2.2 Measurement of in-situ optical and physical aerosol characteristics and of vertical column integrated parameters

The optical (radiative) parameters of the in-situ aerosol are measured by means of an aethalometer (Magee Scientific) and a 3-wavelength integrating nephelometer with backscatter shutter (TSI 3563). The aethalometer [Hansen et al., 1984] is used for the measurement of the absorption coefficient (b_a). The TSI 3563 nephelometer [Anderson et al. 1996; Anderson and Ogren 1998] is used for the continuous measurement of the total scattering and backscattering coefficients at 3 wavelengths (450, 550, and 700 nm).

The physical characteristics of the in-situ aerosol are measured with a condensation nuclei (CN) counter (TSI Model 3022A) to determine the total number of particles (with diameter> 10 nm), a laser-optical particle probe to determine the aerosol number size distribution, and a cloud condensation nuclei (CCN) counter.

The column-integrated optical and physical aerosol parameters (optical depth, scattering, and volume size distribution) are determined by means of an automatic tracking combined sunphotometer/sky radiometer (CIMEL Electronique 318A) and by an automated multifilter rotating shadow-band radiometer [Harrison et al., 1994].

Most of the optical and physical aerosol measurements were performed through international co-operations, in particular with the Biogeochemistry Department (director: Prof. Dr. M.O. Andreae) of the Max Planck Institute for Chemistry (MPIC), Mainz, Germany.

2.3 Bulk chemical analyses

The bulk analyses included determination of the particulate mass (PM), of organic carbon (OC) and elemental (or black or soot) carbon (EC or BC), of water-soluble inorganic species (sulphate, nitrate, ammonium) and some water-soluble organic compounds (e.g., methanesulphonate (MSA), lower molecular weight (MW) organic acids), of major, minor, and trace elements, and of selected higher MW organic compounds. Many of these species and elements were measured with techniques and methods which were already used by us before the start of this project. The techniques include gravimetry (for PM), a simple light reflectance technique (for BC), ion chromatography (IC), particle-induced X-ray emission (PIXE) and instrumental neutron activation analysis (INAA). More details on them can be found in Maenhaut [1993, 1996]. For other species, in particular OC, EC, and organic compounds, methodology was developed as part of the current project.

2.4 Microscopical (individual particle) analyses

Selected aerosol filter samples and/or cascade impactor samples were examined by individual particle analysis techniques. The techniques include electron probe X-ray microanalysis (EPXMA), transmission electron microscopy (TEM), nuclear microprobe (NMP) analysis, synchrotron microprobe X-ray fluorescence (µ-XRF), and static secondary ion mass spectrometry (S-SIMS). EPXMA, TEM, the NMP and µ-XRF were used for the determination of the size, shape (morphology), and elemental composition of the individual particles. EPXMA was already a well-established technique at the start of the project, but for the other techniques methodological work was carried out as part of the current project.

2.5 Chemical mass closure calculations. Identification and apportionment of the major aerosol types and/or source categories and assessment of the dominant source regions and transport pathways. Determination of the relative contributions from natural and anthropogenic sources

The chemical analysis of the aerosol samples provides concentration data for several indicators and tracers of major aerosol types and source categories, and for discriminating between the natural and anthropogenic contributions. It is especially examined to which extent the measured fine PM can be reconstituted by the various aerosol types and/or components (and thus chemical mass closure can be obtained). The aerosol types and/or components include crustal material (which may consist of soil dust, road dust, and coal fly ash in variable proportions, depending upon the site), sea salt, carbonaceous aerosols, sulphate, nitrate, ammonium, and water. In the chemical mass closure calculations, we obtained the mass of crustal material from the mass of Al and other crustal elements, whereas the mass of sea salt was estimated on the basis of the sea-salt elements Na and Cl. By examining the relationships and correlations among the various variables in aerosol composition data sets, the major aerosol types and/or source categories (e.g., mineral dust dispersal, sea spray, fossil fuel combustion, industrial emissions, biomass burning, waste burning) are identified. Subsequently, we calculate the contribution from each aerosol type and/or source category to the concentrations of the fine PM and of the various species and elements. The calculations involve the use of chemical mass balance (CMB) models and of multivariate receptor models (such as absolute principal component analysis (APCA)) [Henry et al., 1984; Lowenthal et al., 1987; Maenhaut and Cafmeyer, 1987].

The concentrations of the aerosol types and/or source categories, as obtained by APCA or CMB, or of good indicators for the aerosol types are related to air mass back trajectories in order to assess the source regions and transport pathways. For large data sets (of at least 100 samples collected over long time spans), we also implement statistical approaches to pinpoint the source areas [Seibert and Jost, 1994; Stohl, 1996].

For aerosol types, such as sulphate and carbonaceous particles, the natural and anthropogenic contributions are resolved by relating their concentrations to data of suitable indicator species. The apportionment involves the use of multiple linear regression (MLR) analysis [Maenhaut et al., 1994a], APCA or CMB.

2.6 Interrelation of the radiative and physicochemical characteristics for in-situ aerosols. Calculation of the direct radiative forcing of aerosols

From the nephelometer and aethalometer data, we obtain the extinction coefficient for up to 3 wavelengths and some other radiative characteristics for the in-situ aerosol. The radiative characteristics can also be calculated (modelled) from Mie theory [Bohren and Huffman, 1983] and the physicochemical aerosol properties, and it can be examined to which extent agreement (closure) is obtained between the experimentally determined and model-predicted radiative aerosol characteristics.

The optical/radiative aerosol characteristics can also be used to calculate the direct radiative forcing. For these calculations, one can employ the approaches of Penner et al. [1992, 1998], Kiehl and Briegleb [1993], Haywood and Shine [1995], Key and Schweiger [1998], Anderson et al. [1999] or modifications and/or extensions thereof.

This interrelation and modelling work was done in close collaboration with the MPIC.

3 DEVELOPMENT AND IMPLEMENTATION OF NOVEL TECHNIQUES AND METHODS FOR COLLECTION AND BULK AND MICROSCOPICAL (INDIVIDUAL PARTICLE) ANALYSIS OF ATMOSPHERIC AEROSOLS

3.1 Development of analytical methods for organic and elemental carbon

The carbonaceous fraction of atmospheric aerosols consists of elemental carbon (EC) and a variety of organic compounds (organic carbon (OC)). The distinction between OC and EC is mostly based on the difference in temperature at which they volatilise. For measuring OC and EC we acquired an OC/EC thermal-optical transmission (TOT) carbon aerosol analyser from Sunset Laboratory (Oregon, U.S.A.). This instrument is built for analysing aerosol samples collected on quartz filter samples. During the stepwise heat treatment in different atmospheres (first in pure He, then in an O_2/He mixture) the light transmission through the filter is continuously monitored, so that one can correct for the artifact EC that is formed by charring during the pyrolysis of organic material [Birch and Cary, 1996]. Our analyses were generally performed using temperature, time and other instrumental parameters suggested by the manufacturer, and OC and EC were derived from the thermogram with the calculation software that was supplied with the instrument. This software sets an automatic EC/OC “split point” at that point (time) in the thermogram when the transmission through the filter is the same as the initial transmission, but one can override this and set the “split point” manually. The software also allows one to correct the OC concentration for the contribution from inorganic carbonate carbon (CC), provided the CC consists essentially of calcium carbonate and the peak arising from it is clearly identifiable in the thermogram. An alternative correction for CC is to perform the OC/EC analyses on sample sections that have been subjected to an HCl treatment to convert the inorganic carbonate into CO_2 and thus to volatilise it prior to analysis.

The capabilities and limitations of the instrument were examined by analysing filter samples from different locations and different seasons and by participating in international intercomparison exercises. We participated in the EUROTRAC-2 AEROSOL Carbon Shootout Stages I and II, which were organised by Prof. Dr. H. Puxbaum (Technical University, Vienna), and in an intercomparison, organised by Dr. X.D. Liu (National Research Centre for Environmental Analysis and Measurements (NRCEAM), Beijing, China). In the Carbon Shootout Stage I, urban aerosol samples were collected on quartz fibre filters at a site in Berlin and distributed to participants from about 20 universities and research institutions. For the Shootout Stage II the filters were collected at a rural site in Austria and there were again about 20 participating groups. The objectives of the Shootout were to compare the OC/EC analysis methods of the various participants and to arrive at improved methods for the determination of and differentiation between OC and EC. Good agreement was obtained for total carbon (TC = OC + EC), but there were large differences for the differentiation between OC and EC. The differences were clearly worse for the rural samples from Austria (with high biopolymer content) than for the urban samples from Berlin. Furthermore, for the rural samples, the EC/TC ratio depended strongly on the temperature program used. Higher EC/TC ratios were obtained when a lower maximum temperature was used in the first stage of the analysis (in pure He) or when the maximum temperature was sustained for a shorter time. This phenomenon also existed to some extent for the urban samples, but not as much as for the rural samples. Among the participants of the Shootout there is a consensus that methods which rely on an optical correction (as is the case with our method) provide more accurate results, at least for urban samples [Schmid et al., 2001]. For samples with high biopolymer content, further research is in progress. In the intercomparison of Dr. Liu, quartz fibre filter samples with aerosol collected in Beijing were distributed to participants from China, Japan, France, and ourselves. The results of this exercise were similar as for the Carbon Shootout Stage I.

From the other evaluation work with our instrument it appeared that the automatic “split point” is set too late and provides too low EC/TC ratios for urban samples when their TC loading becomes larger than 100 µg cm^{-2}. This was concluded from the analysis of samples which had been taken in parallel with a high-volume sampler (with large areal aerosol mass density) and a low-volume sampler (with about 10 times lower areal aerosol mass density) at Gent during 1998 [Kubátová et al., 1999] and 1999. However, by manually adjusting the split point for the heavily loaded samples to the same time as automatically obtained for the lightly loaded samples collected in parallel, good agreement could be obtained between the EC/OC ratios for both types of filter samples. Another weak point of our instrument is that the HCl treatment led to a decrease in the response of the FID detector used for quantifying the carbonaceous compounds (after their conversion into methane). This problem is also seen in other instruments from the same company, it is unclear why it occurs, but because of it, the HCl treatment cannot be recommended for routine use [Cary, 1998]

We also developed procedures for measuring the water-soluble and the organic solvent extractable OC in aerosol filter samples. As the OC/EC instrument is built for analysing filter sections, it had to be adapted, so that also a quartz vessel (boat) with the residue of the solute or extract could be introduced into it. The reproducibility of this “boat” technique was evaluated with standard solutions of sucrose and EDTA and was typically better than 5%. The technique was applied to determine the water-soluble OC (WSOC) in total filter samples collected in summer and fall of 1998 in Gent. About 20% of the total OC appeared to be WSOC.

It should be indicated here that the OC, as obtained with the TOT technique, represents only the carbon in the organic aerosol and that other atoms (such as H, O, N) besides C are also present. Therefore, the OC data have to be multiplied by a conversion factor in order to obtain organic aerosol mass (organic matter, OM). For urban aerosols, one commonly uses a multiplication factor of 1.4 [Seinfeld and Pandis, 1998; Turpin et al., 2000].

3.2 Development of analytical methods for organic compounds in aerosols

The objectives of the analyses for organic compounds were to achieve a more complete molecular characterisation of the carbonaceous aerosol, to identify and quantify the compounds that provide the largest contribution to the OM, and to provide data for marker (indicator) species which allow one to differentiate between the natural and anthropogenic contributions to the carbon aerosol.

At the outset of the project it was decided to measure the organic compounds by capillary gas chromatography (GC) - flame ionisation detection (FID) and by GC/ mass spectrometry (MS), whereby GC/MS is used for qualitative analysis (identification) and GC-FID for the quantitative analysis, and to start by implementing and adapting a method which was originally described by Mazurek et al. [1987]. This method was selected because it was designed to monitor component losses during sample work-up, it can be applied to quantify low-microgram levels of extractable organic matter in aerosol samples, and allows one to determine over 100 compounds simultaneously. For the development work, we mostly used samples that were taken on Whatman QM-A quartz fibre filter with a total filter sampler (Qtot) at Gent. Special emphasis was placed on attempting to increase the fraction of extractable and elutable organic aerosol mass (EEOM). The EEOM is the sum of the resolved and unresolved mass in the GC-FID chromatograms. We compared the EEOM yields of (a) extraction with dichloromethane (CH_2Cl_2), (b) extraction with benzene, and (c) extraction with dichloromethane followed by extraction with the more polar solvent 2-propanol. Using (c), the EEOM yield was approximately 15-20% higher than with (a), but the increase was mainly in the unresolved complex mixture (UCM). Disadvantages of 2-propanol are that it gave rise to contamination, even when using a high-purity solvent, and that evaporation of the extracts is more difficult, and it was therefore not retained. Evaluation of benzene as extraction solvent showed that the EEOM and the composition of the extracts were very similar to those obtained with dichloromethane. Considering the high toxicity of benzene, preference was given to the use of dichloromethane as extraction solvent.

The yield of EEOM, relative to the OM, as derived from the TOT instrument, was of the order of 17% for the total filter samples from Gent, but only around 4% for the total filter samples from Amazonia. Taking into account that organic acids can also occur in the salt form, it was evaluated whether acidification of the filters results in an enhancement of the EEOM yield. In preliminary tests with total filter samples from Gent, the filters were first extracted with dichloromethane, then acidified with acetylchloride and extracted again. By this additional step, another 5% of the OM was recovered as EEOM. Following up on this good result, it was decided to evaluate the extraction yield itself for 5 different extraction procedures. For these experiments we used again total filter samples that were collected at Gent and were analysed for OM and EC with the TOT instrument. After the extraction, the filters were (when possible) again analysed for OM and EC, and also the organic extracts themselves were analysed for OM and EC. The five extraction procedures were:

i. 3 x 30 min ultrasonic extraction in CH_2Cl_2;

ii. 2 x 30 min + 1 x 16 hours ultrasonic extraction in CH_2Cl_2;
iii. in a Soxhlet apparatus: 4 hours in CH_2Cl_2;
iv. acidification with acetylchloride, followed by 3 x 30 min ultrasonic extraction in CH_2Cl_2;
v. soft saponification with NaOH.

The extract of procedure (i) contained on average 40% of the original OM, that of procedure (ii) 45%, that of procedure (iii) 40%, that of procedure (iv) 40%, and after procedure (v) 8% of the OM was found in the saponified (acidic) fraction and 35% in the non-saponified fraction. It is striking that for each of the 5 procedures a similar percentage of 40% of the OM was found in the extract. Although acidification does not result in a higher yield of extracted OM (at least not for urban samples from Gent), it was nevertheless decided to retain it since more compounds could be identified and quantified by GC-FID and GC/MS in the extracts and it also gave higher EEOM yields, especially for tropical samples [Kubátová et al., 2000]. However, it was also found that acidification with acetylchloride resulted in partial methylation of the fatty acids of the OM, which is undesirable. It was therefore decided to replace extraction procedure (iv) by:

vi. acidification with acetic acid, followed by 3 x 30 min ultrasonic extraction in CH_2Cl_2.

This extraction procedure is currently used for our routine analyses by GC-FID and GC/MS.

The extraction efficiency was not only dependent on the actual extraction procedure used, but to a much larger extent on the sampling location and thus on the type of carbonaceous aerosol. This became evident by reanalysing filter samples from various locations (Balbina and Rondônia in Brazil and Sde Boker in Israel) for OM and EC, after they had been analysed for OM and EC and subsequently extracted for detailed organic analyses with procedures (i) and (iv). The OM extraction yield was much lower for total filter samples from Brazil than for similar samples from Israel (the results for Israel were similar to those for Gent). Also the particle size of the aerosol plays an important role. For filter collections from Balbina, whereby the aerosol was separated in two size fractions, a much larger extraction yield was noted for the fine size fraction than for the coarse. This was essentially due to the difference in composition between the two size fractions.

As to the GC-FID and GC/MS analyses themselves, they were done after concentrating the combined extracts to 1 mL, filtering and drying this, and redissolving the residue. Part of this solution was then analysed directly, and the remainder was methylated with diazomethane and also analysed. Our GC/FID and GC/MS procedures for routine analyses have changed somewhat over the years. Those originally used are described in detail in Kubátová et al. [2001b]. The more recent procedures are presented in Kubátová et al. [2000].

There is a substantial difference between the extracted OM yield and the EEOM yield (these are respectively 40% and 17% of the OM for total filter samples from Gent). On the other hand, it appeared from our routine GC-FID and GC/MS analyses that certain compounds, such as levoglucosan (which is a general marker for wood combustion), were present in high concentrations, but could not be quantified. Therefore, we started developing a method for the quantitative determination of levoglucosan and related monosaccharide anhydrides in aerosol samples. The method involves addition of a recovery standard (1,2,3-trihydroxyhexane), extraction with the new extraction procedure (vi), and trimethylsilylation.

In the course of our GC-FID and GC/MS analyses of urban and tropical aerosol samples it was found that several unknown compounds were present in notable concentration. Various types of derivatisations and solid-phase extraction in combination with GC/MS were employed for the characterisation and structure elucidation of these unknowns [Kubátová et al., 2000; Zdráhal et al., 2001a, 2001b].

3.3 Analytical-methodological development on individual particle analysis

Methodological development work was done for transmission electron microscopy (TEM) with selected area electron diffraction (SAED), and for two other microscopical analytical techniques, namely microprobe X-ray fluorescence (µ-XRF) with laboratory and synchrotron radiation sources and static secondary ion mass spectrometry (S-SIMS).

The TEM investigations were carried out on a JEOL JEM 1200EX at 80 kV, whereby EDX analyses were done with a Tracor Northern TN5500 X-ray microanalysis. The electron diffraction measurements were performed on a Philips CM 20 at 200 kV (EMAT-RUCA-University of Antwerp) [Sobanska et al., 2000].

With regard to µ-XRF and related techniques, methodological studies with aerosol particles were done at Hasylab in Hamburg and at the European Synchrotron Radiation Facility (ESRF) in Grenoble. As a preparation for the activities with beam line ID 22 of ESRF and to test the methodology, a number of measurements were performed on fly ash particles with dimensions of 10 to 50 µm. This was done, on one side, with a laboratory µ-XRF and µ-tomography instrument based on a rotating anode X-ray tube and capillary X-ray optics (built in the laboratory), and, on the other side, with the microfocus beam line, BL 1, of ESRF. The samples investigated were fly ash particles from a lignite fired power plant in Japan. This material was selected because it had been studied earlier with other microanalytical methods amongst others at other synchrotron facilities. Also, the particles were of a size (i.e., in excess of 10 µm EAD) which is compatible with the X-ray beam size of beam line BL 1. In accordance with the earlier measurements it was found that the particles are inhomogeneous in composition and structure. Two-dimensional images with µ-XRF and microprobe X-ray diffraction (µ-XRD) were obtained with a lateral resolution of the order of 1 µm [Rindby et al., 1997]. The methodology, which also includes preliminary measurements with the tube excited system, is further described by Adams et al. [1998] and Vincze et al. [1998].

With the new beamline ID 22 we performed preliminary measurements on fallout particles from the Chernobyl explosion sampled in rural areas in Norway. The intention was to test the possibilities of imaging with X-ray absorption spectrometry, namely with X-ray absorption fine structure analysis (XANES). The 3 D repartition of uranium in 10 to 30 µm size particles and its different valence states could be established. Inside the particles, uranium seemed to be reduced to the elemental state, probably as a result of reactions with graphite or elemental carbon at the moment of the explosion.

S-SIMS allows the determination, with a lateral resolution of the order of 100 nm, of the elementary composition, the chemical composition of elemental constituents (speciation), and organic compounds at the surface of the microscopical object and in a subsurface shallow layer. In May 1997, a S-SIMS instrument (Cameca TOF SIMS) was acquired. The analytical methodology of SIMS for atmospheric particles had not been explored previously and was therefore studied within the current project. In a first phase, the characteristics of a number of collection substrates for aerosol sampling (aluminium foil, indium foil, and silver membranes) were studied with scanning electron microscopy with energy-dispersive X-ray analysis attachment (SEM-EDS) and the TOF-SIMS instrument. The results with SEM showed that the Ag-membranes are not appropriate as their pore size of 2-3 µm interferes with the observation of the particles. The purity of the three substrates was studied with TOF-SIMS and it was found that the impurity levels are comparable for the three substrates. It was concluded that indium foils are the best substrates for the collection of the air particulates. Aluminium substrates are less suitable as they prevent the determination of Al, which is one of the most important elements in aerosols. The general aspects of the methodology were described by Van Vaeck et al. [1998a]. Subsequently, we concentrated on the speciation of pure inorganic compounds as a preparation stage for obtaining molecular information on real atmospheric samples. A set of binary salts was analysed in which the mass spectra were systematically studied to characterise the different type of features, such as fragment ions, adduct ions, molecular ions, cluster ions and recombination clusters. Special attention was given to the development of a suitable sample preparation procedure and the influence of the instrumental parameters on the reproducibility of the measurements. Results showed that the SIMS spectra yield sufficient qualitative information to deduce the molecular formula of the salts. In addition, fine speciation is possible (e.g., to distinguish between CuCl and $CuCl_2$) by ratio-ing adduct ions. The speciation of individual compounds in multi-component systems can, however, be inherently limited by the occurrence of “cross contamination” (e.g., a neutral from component A combines with an ion of component B). It was therefore necessary to expand the work to mixtures of two pure compounds before addressing speciation analysis in real atmospheric samples. Applications of the method on atmospheric particles sampled near a smelter in Genoa are given in Van Ham et al. [2001]. In this work, S-SIMS supplemented work obtained by micro-PIXE. Measurements were also made for the characterisation of these aerosols on pure Si wafers. Fourier transform laser microprobe mass spectrometry relying on the “selvedge” ionisation appeared to be a valuable technique for the validation of some of the results obtained [Van Vaeck et al., 1998a, 1998b]. An application of the latter technique was the analysis of polycyclic hydrocarbons (PAHs) adsorbed on soot particles. The variation of PAH patterns at different positions in the combustion chamber of an incineration plant was investigated [Zimmermann et al., 2000].

4 AEROSOL RESEARCH IN ARCTIC AND SUB-ARCTIC AREAS

Research was done within the framework of the Arctic Ocean Expedition 1996 (AOE-96), for Summit (72°34'N, 37°38'W, 3170 m asl) in Greenland, at the Zeppelin mountain station (78°54'N, 11°53'E, 474 m asl) in Ny Ålesund, Spitsbergen, at Sevettijärvi (69°35'N, 28° 50'E, 130 m asl) in Finnish Lapland, and for two sites in southern Norway, i.e., Birkenes (58° 23' N, 8°15' E, 190 m asl) and Skreådalen (58°49' N, 6°43' E, 465 m asl).

AOE-96 took place in summer 1996. Aerosol filter and cascade impactor samples were collected for chemical analysis by us onboard the Swedish icebreaker *Oden* during Leg-1 of the expedition, i.e. from 20 July to 24 August and between 75°N and 87°N. About 5 days were spent in the open waters between Norway and the ice edge (at about 60°E and 80°N), and the rest of the time was spent in the permanent pack ice of the Nansen and Amundsen basins. Our samplers were a PM10 Teflon filter unit (TF), a Gent PM10 SFU sampler, which provided two size fractions (coarse: 2-10 µm EAD; fine <2 µm EAD) on Nuclepore polycarbonate filters, and a 12-stage small deposit area low pressure impactor (SDI). Particulate matter (PM) was determined for the filters from the TF and SFU devices by weighing at 20°C and 50% RH. All samples were subjected to multi-elemental analysis by PIXE and INAA (for the SDI samples only by PIXE) and the TF samples were also analysed for major anions (methanesulphonate (MSA$^-$), SO_4^{2-}, Cl^-, Br^-, NO_3^-, NO_2^-) and cations (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) by IC. The results indicated that the atmospheric concentrations of the continental aerosol species (or elements) were substantially lower during AOE-96 than during the 1991 International Arctic Ocean Expedition (IAOE-91). The data from the TF and SFU samplers were used to assess which fraction of the experimentally determined aerosol mass could be reconstituted on the basis of the measured species and elements, and thus aerosol chemical mass closure could be obtained. The dry reconstituted mass was estimated as follows:

$$\begin{aligned}(\text{dry PM}) = {} & \text{Sea salt} + \text{Crustal matter} + \text{Sum [nss/ncr-elements(INAA/PIXE)]} \\ & + \text{MSA}^- + \text{nss-SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ \end{aligned} \qquad (1)$$

with nss standing for non-sea-salt and ncr for noncrustal. Sea salt was estimated from Na and Cl using the approach of Virkkula et al. [1999] and crustal matter was estimated from a number of crustal elements, as done by Cahill et al. [1989] and Chan et al. [1997], so that equation (1) became:

$$\begin{aligned}(\text{dry PM}) = {} & [\text{Cl} + 1.4486\ \text{Na}] + [1.16\ (1.90\ \text{Al} + 2.15\ \text{Si} + 1.41\ \text{nss-Ca} + 1.67\ \text{Ti} \\ & + 2.09\ \text{Fe})] + \text{Sum [nss/ncr-elements(INAA/PIXE)]} \\ & + \text{MSA}^- + \text{nss-SO}_4^{2-} + \text{NO}_3^- + \text{NH}_4^+ \end{aligned} \qquad (2)$$

One aerosol constituent not considered so far is water, so that the reconstituted PM is actually the dry PM, as indicated. Since the gravimetric PM was determined at 50% RH and the aerosol samples contained large proportions of hygroscopic components, such as sea salt and sulphate, water cannot be neglected. It was estimated from the composition of the samples using a thermodynamic model described by Clegg et al. [1998]. Water estimated in this way should be considered as an upper limit (maximum value) for the actual water mass in the samples. The difference between the gravimetric PM and the sum of (dry PM) + water (at 50% RH) varied from +23 to -6% for the TF samples, but it was only significant (and positive) for two of the eight samples, so that it was concluded that other aerosol types or species than those considered provided a significant contribution to the gravimetric PM in those two samples. A plausible candidate for the missing aerosol type is the carbonaceous aerosol (including so-called biological aerosols). Bigg and Leck [2001] examined individual particles collected during AOE-96 by transmission electron microscopy and found that particles larger than 100 nm contained significant organic material. This was even the case for most sea-salt particles. In addition to organic compounds, bacteria and diatoms were observed. The volume or mass contribution of the organics to the aerosol was not quantified by Bigg and Leck [2001], however, and it is also unclear which variability one may expect in the levels of the organic/biological PM when considering long collection periods, such as those used for the TF samples. It is noteworthy that the two TF samples with significant unexplained PM are among the three TF samples with lowest gravimetric PM levels. This suggests that closure was obtained for the other samples because the relative contribution from the organic and biological aerosols became less important. The missing PM (± 1s) was 46 ± 20 ng m^{-3} and 85 ± 20 ng m^{-3} in the two TF samples. These data represent rough first estimates of the organic/biological aerosol PM10 level in the high Arctic during summer. Clearly, they should be confirmed by actual OC/EC measurements in future expeditions. The data indicated that sea salt was normally the dominant aerosol type, followed by water, and then nss-sulphate. When averaging the percentage contributions over all 8 samples, the following results were obtained: 45% for sea-salt, 27% for water, 10% for nss-sulphate, 6% for crustal matter, 2.8% for MSA, 2.3% for NH_4^+, 1.5% for NO_3^-, and 0.4% for the nss/ncr-elements. For the SFU samples, separate mass closure calculations were performed for the fine (<2 µm EAD) size fraction, the coarse fraction (2-10 µm EAD), and the sum of both (SFU-sum). The results of the chemical mass closure calculations for the sum of the fine and coarse filters agreed overall quite well with the results for the TF filters. The separate data for the coarse and fine SFU filters indicated that there was only missing mass for two fine filters. Considering that we attributed the missing mass essentially to organic/biological aerosols, it is tentatively concluded that these aerosols are mainly present in the fine (<2 µm EAD) size fraction. When averaging the percentage contribution of the various aerosol types and species to the gravimetric SFU fine PM over all 8 samples, the results were as follows: 38% for sea-salt, 27% for water, 18% for nss-sulphate, 3.5% for crustal matter, 3.1% for MSA, 3.3% for NH_4^+, 1.5% for NO_3^-, and 0.4% for the nss/ncr-elements. Compared to the PM10 aerosol, sea-salt is less important in the fine aerosol, but is on average still the main contributor to the fine PM. The contribution of nss-sulphate to the fine PM is substantially larger than that to the total PM (on average 18% versus 10%), and for three of the eight sampling periods, fine nss-sulphate was more important than fine sea-salt.

During AOE-96 SDI samples had also been taken by the Finnish Meteorological Institute (FMI) and analysed for anionic and cationic species by IC. The data set obtained was combined with the PIXE data of our SDI samples. Continuous particle size spectra were extracted from the raw data using a data inversion method. Log-normal size distribution modes were fitted to the continuous spectra. Clear and varying modal structures for aerosols consisting of primary sea salt particles or of secondary particles related to dimethylsulphide emissions were found. The concentration levels of all modes decreased rapidly when the distance from open sea increased. The major ions in the submicrometer size range were MSA, sulphate, and ammonium. They had most of the time a clear Aitken mode and one or two accumulation modes, with aerodynamic mass median diameters around 0.1 µm, 0.3 µm, and between 0.5-1.0 µm, respectively. Primary sea-salt particles formed a mode with an aerodynamic mass median diameter around 2 µm. The observed modal structure of the submicron SO_4^{2-}, MSA, and NH_4^+ mass size distributions was consistent with the mass size distribution derived from the number size distribution measured with a differential mobility particle sizer. More details on this SDI work are given by Hillamo et al. [2001].

With regard to the aerosol research at Summit, we refer to three published papers [Maenhaut et al., 1997c; Jaffrezo et al., 1998; Kerminen et al., 1998]. Notable was that biomass burning plumes from forest fires in Canada could be detected on top of the Greenland Ice Sheet [Jaffrezo et al., 1998].

For the Zeppelin station at Ny Ålesund, we combined our long-term aerosol composition data sets with aerosol light scattering data sets from the Department of Meteorology of the University of Stockholm (MISU), and studied the interrelations between the chemical composition and light scattering. It was found that fine non-sea-salt sulphate provided the largest contribution to the total light scattering coefficient. More details on this study can be found elsewhere [Maenhaut et al., 1999e].

From July 1992 until January 1996 atmospheric aerosol samples had been collected nearly continuously in two size fractions at Sevettijärvi in northern Finland. The samples were analysed for the PM, BC, major anions and cations (by IC), and up to 46 elements (by a combination of INAA and PIXE). The fine fraction data set was subjected to absolute principal component analysis (APCA) [Maenhaut and Cafmeyer, 1987] in order to examine the interrelations between the various chemical species and elements, and to identify the major aerosol components and/or source types. Furthermore, trajectory statistics [Stohl, 1996] was employed to identify the major source regions of sulphate and of selected elements and heavy metals. The trajectories used were 3-dimensional 96-hour back-trajectories arriving at 950 hPa. Six components were identified by APCA. The first component had high loadings (of 0.7 to 0.9) for S, K, V, Mn, Zn, ammonium, BC, and the PM; it represents a general pollution component. The second component was highly loaded with Cu and Ni (loadings of 0.9) and is most likely mainly due to the Cu-Ni smelters of Nikel and Zapolyarni on the Kola peninsula, at about 60 km to the east of Sevettijärvi. The third component was a crustal component (with Al, Si, and Fe); the fourth component sea salt (Na, Cl). The fifth component was mostly loaded with As, and to a lesser extent also with Se and Sb. And the sixth component was a nearly pure nitrate component. The air trajectories indicated that there was no predominant pathway for air mass transport to the Sevettijärvi site. The air masses came from all directions, but there was some preference for transport from over the sea. The trajectory statistics analysis showed that the highest levels of fine S at the site were observed for air masses that had passed over Ukraine and European Russia. The maps for K, ammonium, and the PM were rather similar to that for S. Also those for BC, V, Mn, Zn, Sb, and Pb showed some resemblance to that of S, but European Russia was much more important than Ukraine as potential source region for these species and metals. It is noteworthy that most of these species (and metals) which have Ukraine and European Russia as potential source region were also highly correlated with the APCA component 1. This strongly suggests that this component also had the same source regions. The maps for Cu and Ni suggested that these elements had source regions in the Kola peninsula, but also (and even more important ones) in northern Siberia. However, only few trajectories had passed over the latter region, so that the attribution to this region should be considered with caution. The map for As clearly indicated that the Kola peninsula was the most important source area for this element. An article about this study has been published [Maenhaut et al., 1999f]. Other features about our long-term research at Sevettijärvi, including results from chemical mass closure work, were described by Virkkula et al. [1999].

Further with regard to Sevettijärvi, we contributed to the work of the three intensive field campaigns of the European Arctic Aerosol Study (EAAS). These campaigns took place in summer 1997, winter 1998, and summer 1998. Results from this research are described elsewhere [Hillamo et al., 1999; Maenhaut et al., 1999b; Ricard et al., 2001].

As to Birkenes and Skreådalen in southern Norway, we examined the data sets from our 5-year aerosol study. From 29 January 1991 to 6 March 1996, Gent PM10 SFU samplers had been deployed at the two sites for continuous collections in parallel according to a 2-2-3 day schedule. The coarse and fine filters of the nearly 800 SFU samples from each site were analysed for the PM, BC, and over 40 elements. APCA was used to identify the major source types, and chemical mass closure calculations were performed using an approach described by Chan et al. [1997]. The concentrations of PM, BC and the sea-salt elements were very similar at the two sites; the S levels at Skreådalen were 80% of those at Birkenes, and for the crustal elements and anthropogenic metals, the Skreådalen/Birkenes concentration ratio was around 0.6. Scatter plots and time trends indicated that the fine PM and the anthropogenic species (e.g., BC, non-sea-salt (nss) S, noncrustal V) were generally well correlated between the two sites, thus strongly suggesting that their atmospheric levels in southern Norway are mainly due to long-range transport. There was quite some variability in the concentrations from sample to sample, which presumably resulted mainly from variations in meteorological conditions and in air mass origin [Maenhaut et al., 1997b]. Nevertheless, clear seasonal variations were observed for several elements (species). The crustal elements exhibited highest levels during spring and summer (especially during May). This was also observed by Amundsen et al. [1992] in their study on the total aerosol at Birkenes. Fine iodine showed a maximum in spring and BC was most elevated during the winter months. APCA on the fine data set from Birkenes (with 27 variables included) resulted in five components, i.e., a general pollution component (with loadings in the range 0.7-0.9 for PM, BC, S, K, V, Ni, Cu, Zn, As, Se, Br, In, Sb, I, and Pb), a crustal component (with loadings around 0.9 for Al, Si, Ca, Sc, Ti, Fe, La, and Sm), sea salt (with Na, Mg, and Cl), a weak residual oil burning component (loadings of 0.5 for V and of 0.4 for Ni and S), and a nearly pure Mn component. This last component originates from local Mn sources in southern Norway [Pakkanen et al., 1996; Maenhaut et al., 1997b]. For the chemical mass closure calculations 5 aerosol types were considered, i.e., crustal matter, sea salt, BC, smoke (actually noncrustal K = K - 0.6 Fe), and ammonium sulphate. The 5 aerosol types explained, on average, 70% of the experimental fine PM, and there was no seasonal variation in this percentage. For the coarse size fraction at Birkenes, 63% of the experimental PM was, on average, attributed to the 5 aerosol types, but this percentage exhibited a clear seasonality, and was around 50% in summer versus 70% in winter. The results for Skreådalen were similar to these for Birkenes, but the mass closure was somewhat poorer at that site. The unexplained mass is thought to be mostly attributable to organic aerosol (i.e., to mainly secondary organic particles in the fine size fraction and to primary organic aerosol (including biological aerosol particles) in the coarse fraction) and to a lesser extent to nitrate. Two articles about this work have been published [Hanssen et al., 2000; Maenhaut et al., 2000c]

5 RESEARCH WITHIN THE FRAMEWORK OF THE EUROTRAC-2 AEROSOL SUBPROJECT

Our contribution to the AEROSOL subproject includes the development of analytical methods for OC and EC and for detailed organic compounds, described above in subsections 3.1 and 3.2. During 1998 the methods were evaluated and applied to aerosol samples collected in Gent, during two different seasons (winter and summer). In both seasons, daily samples were taken with three types of collection devices, each with 47-mm diameter filters. Sampler #1 was a Gent PM10 SFU sampler [Maenhaut et al., 1994b], in which the coarse size fraction (2-10 µm EAD) was collected on a Nuclepore polycarbonate filter and the fine size fraction (further denoted as PM2) on a Whatman quartz fibre filter (type QM-A). Sampler #2 was similar to #1, but contained only a single Whatman QM-A filter which collected the PM10 aerosol. Sampler #3 was a “total” filter sampler (Qtot); it also used a Whatman QM-A filter; the particles collected by it are further denoted as PMtot aerosol. Samplers #1 and #2 operated at 17 L/min, sampler #3 at 150 L/min. Particle mass (PM) was determined for all filters; and all quartz filters were subjected to OC/EC analysis with the TOT technique. Selected filters from sampler #3 were also analysed for detailed organic compounds by GC-FID and GC/MS.

The average aerosol mass concentrations, and the TC/(particle mass) and EC/TC ratios (with TC = OC + EC) for the 1998 winter and summer seasons, as derived from each of the three collection devices, are presented in Table I. For sampler #3 (Qtot), the EC/TC data were recalculated with manual “split point” setting, as described in subsection 3.1. The average PM2/PM10 mass ratio and associated standard deviation (sampler #1) were 0.69 ± 0.10 (N: 34) during winter and 0.67± 0.07 (N: 51) during summer. Clearly, most of the aerosol mass was contained in the fine (<2 µm EAD) size fraction at Gent during the sampling campaigns. PMtot is, on average, very similar to PM10, indicating that there was either relatively little aerosol mass in the size fraction above 10 µm EAD or that this size fraction was not efficiently collected by our “total” aerosol sampler. The mean levels of PM2, PM10 and PMtot for the summer campaign are only 50% of the respective levels during the winter campaign. This difference is mainly attributed to the frequent occurrence of surface inversions during the winter campaign. During both winter and summer, TC was responsible for around one quarter of the aerosol mass, with somewhat higher percentages for the PM2 aerosol than for the PM10 aerosol. EC represented about 25% of TC and was slightly more pronounced in the PM2 aerosol. As already indicated in subsection 3.1, the organic aerosol also contains other atoms (such as H, O, N) besides C, so that the OC data have to be multiplied by a conversion factor in order to obtain organic aerosol mass (organic matter, OM). Using a multiplication factor of 1.4, as is commonly used for urban aerosols [Seinfeld and Pandis, 1998; Turpin et al., 2000], one arrives at a percentage of carbonaceous aerosol (that is the sum of OM plus EC) of one third of the particle mass.

Table I: Average aerosol mass concentrations, (TC/particle mass) ratios, and EC/TC ratios at the Gent sampling site during the 1998 winter and summer sampling campaigns.

Size fraction (sampler)	part. mass (µg m^{-3})	TC/(part. mass)	EC/TC
Winter [a]			
PM2 (sampler #1)	41 ± 20	0.28 ± 0.07	0.25 ± 0.04
PM10 (sampler #1)	58 ± 28		
PM10 (sampler #2)	60 ± 30	0.24 ± 0.05	0.23 ± 0.03
PMtot (sampler #3)	58 ± 32	0.24 ± 0.05	0.24 ± 0.03
Summer [b]			
PM2 (sampler #1)	20 ± 9	0.26 ± 0.06	0.28 ± 0.05
PM10 (sampler #1)	29 ± 12		
PM10 (sampler #2)	30 ± 13	0.23 ± 0.04	0.25 ± 0.04
PMtot (sampler #3)	29 ± 13	0.23 ± 0.03	0.23 ± 0.03

[a] Winter: period 12 January - 11 March 1998 (number of samples N: 34)
[b] Summer: period 12 June - 21 August 1998 (number of samples N: 51)

The detailed analyses for organic compounds enabled us to construct organic aerosol apportionments. The average apportionments for the winter and summer samples are shown in Figure 1. The extractable and elutable organic matter (EEOM) fraction, which is determined as the sum of resolved and unresolved mass, corresponded on average to 19(± 7)% and 15(± 3)% of the OM for the winter and summer samples, respectively. The unresolved complex mixture (UCM) was the major part of the EEOM and corresponded to 75% and 65% of it for winter and summer samples, respectively. The UCM consists mainly of branched and cyclic hydrocarbons and originates from car exhaust [Simoneit, 1984; Rogge et al., 1993b]. For urban aerosols, large percentages of UCM are quite typical. In the resolved OM, over 100 compounds belonging to different classes could be identified. *n*-Alkanes and fatty acids were the prevailing resolved organic compounds in both seasons, but the distribution patterns of individual components within each class showed seasonal differences. The *n*-alkane pattern for summer aerosols was clearly affected by emissions from

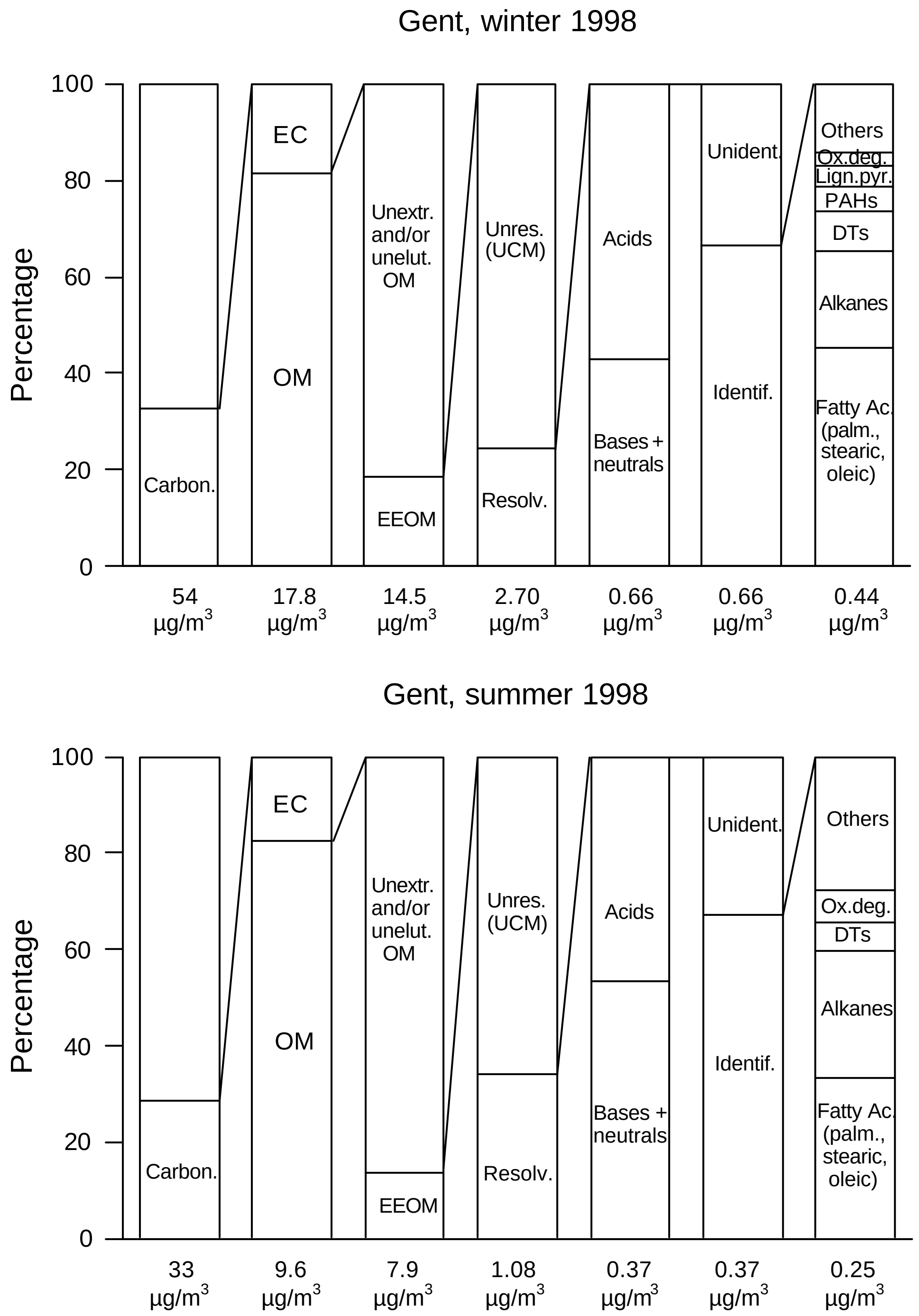


Figure1: Percentage contributions of different carbonaceous and organic compound classes in winter and summer 1998 “total” filter samples from Gent, Belgium (based on 22 samples from each season). The first column represents the contributions of the carbonaceous (OM + EC) and the inorganic aerosol to the particulate mass (PM). The atmospheric concentrations under the columns indicate the average concentration for the sum of the species in the column. Thus, the concentration under the first column indicates the average PM, that under the last column the average concentration of the sum of identified organic compounds.

the vegetation, while that of fatty acids revealed a lower relative abundance of unsaturated fatty acids in summer than winter, that can be related to more extensive atmospheric oxidation of unsaturated fatty acids during summer. Concentrations of dicarboxylic acids and related products (Ox. deg.) that are believed to be oxidation products of hydrocarbons and fatty acids were highest in summer aerosols. Some individual compounds in the latter class could only be detected in summer samples and showed the highest concentrations on hot summer days that were characterised by maximum temperatures above 25°C and increased ozone concentrations. The latter compounds included novel, recently identified glutaric acid derivatives, namely, 3-isopropyl and 3-acetyl pentanedioic acid, likely originating from atmospheric oxidation of reactive mono- or sesquiterpene precursors that still need to be identified. Two other novel compounds were 3-acetyl hexanedioic acid, and, interestingly, a tricarboxylic acid, 3-carboxy heptanedioic acid. Several compounds were found that are markers of wood combustion, including diterpenoic acids (DTs), lignin pyrolysis products, and levoglucosan. The quantitative results obtained for diterpenoic acids and lignin pyrolysis products indicated that contributions from wood combustion are more important in winter than in summer. There was evidence that both soft and hard wood burning contribute to the organic aerosol, but that hard wood burning prevails during winter. Polyaromatic hydrocarbons (PAHs) were also more prevalent in winter than in summer. More details about this study are given by Claeys et al. [1999] and Kubátová et al. [1999, 2001a, 2001b].

Besides work on OC, EC, and detailed organic compounds, our contribution to the AEROSOL subproject includes intercomparison and evaluation of methods for measuring important aerosol parameters such as the PM and carbon, determination of the detailed mass size distribution for PM, OC, EC and other important aerosol species, chemical mass closure work, and source (type) apportionment.

During 1999 and 2000, intercomparisons were made at Gent of filter collections and in-situ measurements for the aerosol particle mass and elemental/black carbon. The filter collections (of typically 24 hours) were performed with a PM2.5 sampler, using a Whatman QM-A quartz fibre filter, and the samples were analysed for the PM by weighing (at 20°C and 50% relative humidity) and for OC and EC by the TOT technique (see subsection 3.1). In parallel with the filter collections, the PM and BC in the PM2.5 size fraction were measured in-situ and in real time with a Rupprecht and Patashnick tapered element oscillating microbalance (TEOM, model 1400A) and a Magee Scientific aethalometer (tape-feeder model AE-14U), respectively. Both instruments were operated with 5 min time resolution, but the results were averaged for each filter collection period. During 1999 and 2000, the TEOM values were on average 77 (± 13) % [N = 64] and 59 (± 11) % [N = 85], respectively, of the gravimetric mass derived from the quartz fibre filters. Discrepancies between TEOM and gravimetric aerosol data have been observed by others [e.g., Ayers et al., 1999] and are attributed to the heating to 50°C (and loss of semi-volatile aerosol) in the TEOM. The comparison of the aethalometer BC data with the EC results from the PM2.5 filter sampler showed that good agreement between both could be obtained when the original BC data were subjected to an empirical correction, as used by Reid et al. [1998]. The average ratios (corrected BC)/EC and associated standard deviations were 0.96 ± 0.08 [N = 65] and 0.88 ± 0.13 [N = 83] for 1999 and 2000, respectively. The average ratios (uncorrected BC)/EC for

1999 and 2000 were 1.38 ± 0.12 [N = 65] and 1.28 ± 0.19 [N = 83]. The results from the study during 1999 are discussed in more detail by Maenhaut et al. [2001a].

Weighing of aerosol filter samples at a specified temperature and relative humidity (normally 20°C and 50% relative humidity) is the reference method for PM determination. However, during the actual filter collection, various artifacts can occur, which may depend upon the type of filter material used. We examined the importance of such artifacts for the fine aerosol at Gent. In January-February 2000, aerosol collections (of typically 24 hours) were done with 3 different Gent PM10 SFU samplers, operating in parallel. The coarse filter was always an Apiezon-coated 8-µm pore size Nuclepore polycarbonate filter, but as fine filter (which collects the <2-µm EAD size fraction), we used a 0.4-µm pore size Nuclepore polycarbonate filter in the first SFU sampler, a Gelman Teflo filter (pore size 2 µm) in the second, and a Whatman QM-A quartz fibre filter in the third. The PM was determined for all filters by weighing at 20°C and 50% relative humidity. It was found that the Nuclepore polycarbonate filters and the Teflo filters collected on average only 74 (± 12) % [N = 37] and 73 (± 10) % [N = 26] of the PM2 PM derived from the quartz fibre filters. The difference may be due to the loss of semi-volatile aerosol for the Nuclepore and Teflo filters or to the collection of gaseous species by the quartz filters or to a combination of both. Further investigations should clarify this.

In September-October 1999, we examined the detailed mass size distribution of the PM, OC, EC, and various elements at Gent, and used the data for aerosol chemical mass closure calculations as a function of particle size. The aerosol collections were done with a 10-stage rotating microorifice uniform deposit impactor (MOUDI) and a 12-stage small deposit area low pressure impactor (SDI). The collection surfaces in the MOUDI consisted of pre-baked aluminium foils, whereas thin polycarbonate films were used in the SDI. Thirty-four parallel samples (of typically 24 hours) were collected. The MOUDI samples were analysed for the PM and for OC and EC. The SDI samples were analysed for up to 27 elements by PIXE. Examples of mass size distributions are shown in Figure 2, which presents the results for PM, OC, EC, and several elements for the samplings of 5-6 October 1999. From looking at the entire data set, it could be concluded that PM and OC exhibited typically a rather similar bimodal size distribution, with most of their mass in the submicrometer size range. EC was predominantly associated with fine particles, with maximum typically at around 0.2 µm EAD. EC is expected to have a large contribution from traffic (mainly heavy duty vehicles) at the sampling site. Sulphur was also mainly in the fine size range, but with maximum at 0.5 µm EAD. Other elements with mainly a fine mode were V and Ni (both are excellent indicators of residual oil combustion), As, Se, and Pb. The crustal elements (Al, Si, Ti, Fe, Zr) exhibited mostly a unimodal coarse mode size distribution, with maximum at about 4 µm EAD. Soil dust, road dust, and coal fly ash all contribute to the concentrations of these elements. Other elements with mainly a coarse mode were Na, Mg, P, Ca, Cr, Mn, Cu, Ga, and Sr. The element K was generally bimodal. Its fine mode is most likely predominantly due to emissions from biomass burning and waste burning (incinerators). Also Zn and Rb were mostly bimodal.

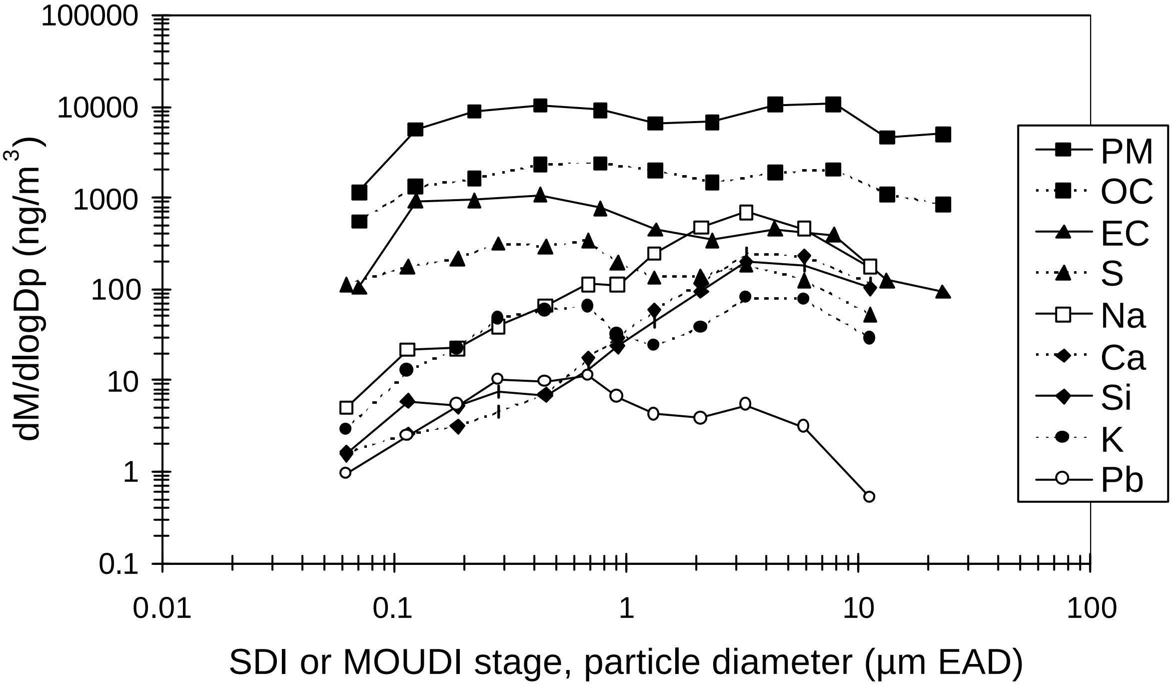


Figure 2: Mass size distributions for PM, OC, EC, and several elements for the sampling period of 5-6 October 1999. The data for PM, OC, and EC were derived from the MOUDI sample, those for the elements from the SDI sample collected in parallel.

Mass closure calculations were performed in a similar way as done by Chan et al. [1997]. Six aerosol types were considered: (1) organic aerosol, which was estimated as 1.4 OC, (2) EC, (3) ammonium sulphate, (4) sea salt, (5) crustal matter, and (6) smoke (actually, noncrustal K = K - 0.6 Fe). The average percentage (averaged over all samples) of the gravimetric PM attributed to each of the six aerosol types as a function of particle size in shown in Figure 3. As expected, crustal matter and sea salt provide a larger contribution in the supermicrometer size range than they do in the submicrometer size range. The opposite is noticed for ammonium sulphate and EC. The percentage contribution from organic aerosol to the gravimetric PM is rather constant in the size range from 8 µm EAD down to 0.2 µm EAD, but increases clearly with decreasing particle size below 0.2 µm EAD. The very fine organic aerosol consists undoubtedly predominantly of secondary organic aerosol (SOA) and emissions from traffic are expected to provide the largest contribution to it. Average percentage attributions of the gravimetric PM to each of the 6 aerosol types were calculated for the submicrometer (<1 µm EAD) and supermicrometer (1-10 µm EAD) size ranges. The major aerosol types in the submicrometer fraction are organic aerosol (on average responsible for 32% of the PM), ammonium sulphate (27%) and EC (10%). In the supermicrometer size range, organic aerosol (28% of the PM) and crustal material (24%) prevail; ammonium sulphate and sea salt are responsible for about 10% each. On average, 74% of the gravimetric PM is accounted for by the aerosol types considered. The unexplained mass is likely attributable to ammonium nitrate and water. The percentage of organic aerosol, obtained in this study in fall 1999, is quite similar to that derived from the filter collections in winter and

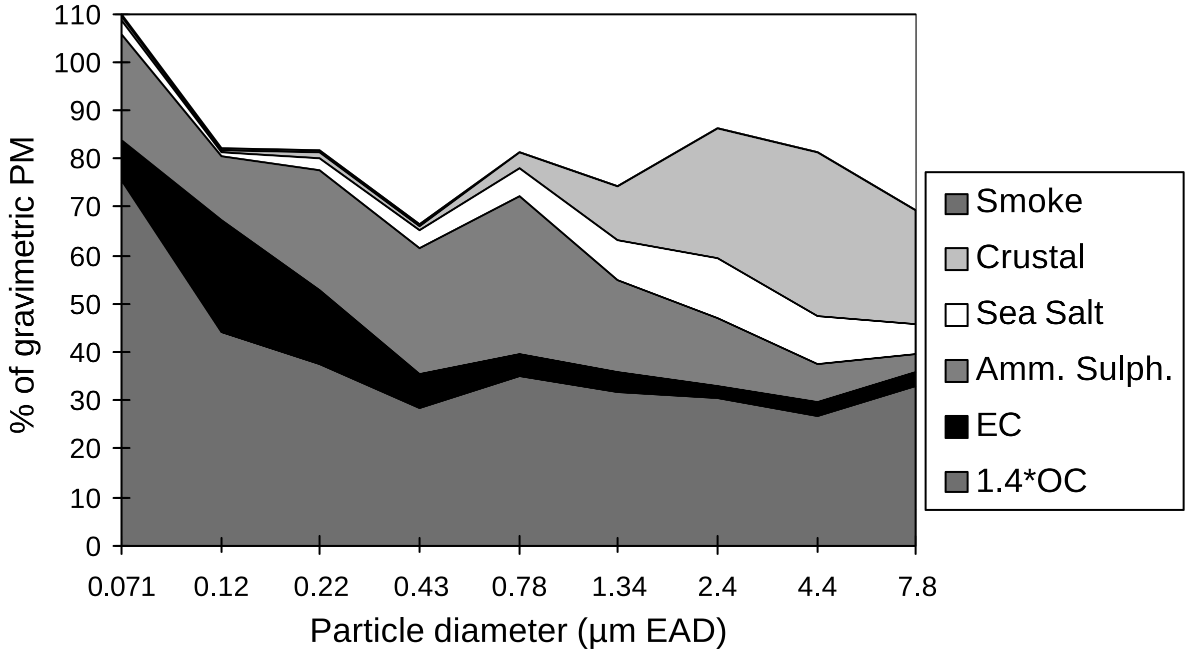


Figure 3: Average percentage attribution of the gravimetric aerosol mass (PM) to 6 aerosol types as a function of particle size during fall 1999 at Gent (based on 34 samples).

summer 1998. The fall 1999 study is described in more detail by Maenhaut et al. [2001b, 2001c].

During 2000 we participated in the INTERCOMP 2000 experiment of the EUROTRAC-2 AEROSOL subproject. The field work for INTERCOMP 2000 took place from 4 to 14 April 2000 at the Institute for Tropospheric Research (IfT) research station Melpitz, about 50 km north-east of Leipzig, Germany. Eight European research groups participated in the field work, and 6 other groups received samples for analysis. The objectives of the experiment were (1) to intercompare instruments and methods for measuring the particulate mass (PM) and various aerosol types (e.g., crustal matter, nitrate, carbonaceous aerosols), (2) to assess to which extent the gravimetric particulate mass could be reconstituted on the basis of the various aerosol types (or components) measured, and thus aerosol chemical mass closure could be obtained for the site, and (3) to identify the source categories of the aerosol particles and to apportion the PM and the major aerosol types to these categories. We participated in the field work of the experiment and deployed various filter collectors, two cascade impactors, and two in-situ instruments at the site. Most of our analyses were completed before the end of the OSTC project, but the intercomparisons of our data with the data from the other groups and the chemical mass closure work were started in 2001.

In preparation for the EC-EUROTRAC aerosol phenomenology workshop at Ispra in January 2001, we started doing chemical mass closure calculations for our various long-term aerosol data sets for European sites. These sites are (1) Sevettijärvi (69°35'N, 28°50'E, 130 m asl) in northern Finland (data set for the period from 27 October 1993 to 14 December 1994 and from 4 March 1995 to 15 January 1996); (2) Birkenes (58°23' N, 8°15' E, 190 m asl) and (3) Skreådalen (58°49' N, 6°43' E, 465 m asl) in southern Norway (data sets from 29 January 1991 to 6 March 1996); (4) Gent (51°01' N, 3°44' E, 10 m asl) in Belgium (data set from 26 May 1993 to 14 July 1994); and (5) Waasmunster (51°07' N, 4°05' E, 20 m asl) in Belgium (data set from 16 July 1994 to 23 November 1995). The results from the chemical mass closure calculations for the two sites in southern Norway (Birkenes and Skreådalen) were partially discussed in Section 4.

6 COMPREHENSIVE STUDIES ON CHEMICAL, PHYSICAL, AND OPTICAL AEROSOL PROPERTIES IN THE MEDITERRANEAN AND ASSESSMENT OF THE DIRECT RADIATIVE FORCING BY AEROSOLS

These studies are performed in close co-operation with foreign research groups, especially with the Biogeochemistry Department (director: Prof. Dr. M.O. Andreae) of the Max Planck Institute for Chemistry (MPIC), Mainz, Germany, and the Ben Gurion University (BGU) of the Negev, Israel (Dr. A. Karnieli), and in part also with the Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki (AUTH), Greece (Prof. Dr. C. Zerefos).

Both long-term and intensive chemical, physical, and optical (radiative) aerosol measurements were conducted at Sde Boker (30°51'N, 34°47'E, 470 m asl), Israel. The long-term measurements started in January 1995 and are still going on. The intensive measurements were conducted during two campaigns (of about 4 weeks each), the first one, called ARACHNE-96, in June-July 1996, the other, ARACHNE-97, in February-March 1997.

In the long-term measurements, aerosol samples are collected with a Gent PM10 SFU sampler according to a 2-2-3-day schedule and analysed for the PM, BC, and over 40 elements. From December 1995 through September 1997, an integrating nephelometer (TSI 3563) was used for the continuous measurement of the aerosol scattering and backscattering coefficients at 3 wavelengths (450, 550, and 700 nm), and it was then replaced by a Radiance Research unit which only measures the scattering at 550 nm. Furthermore, measurements of vertical column-integrated aerosol optical depth and aerosol properties are conducted at the site on a nearly continuous basis with an automatic tracking combined sunphotometer/sky radiometer (CIMEL Electronique 318A).

During the intensive campaigns, a wide array of instruments was used for measuring the aerosol chemical, physical, and optical (radiative) properties and for measuring selected atmospheric trace gases (CO, CO_2, SO_2, O_3). Details on most of the instruments used can be found in publications by Maenhaut et al. [1999d], Ichoku et al. [1999], and Formenti et al. [2001b].

A comprehensive article on the physical and chemical aerosol characteristics and their interrelation for ARACHNE-96 was written by Formenti et al. [2001b]. In brief, fine non-sea-salt (nss)-SO_4^{2-} averaged 9 ± 3 µg m^{-3} and fine black carbon averaged 1.4 ± 0.5 µg m^{-3}, comparable to values observed off the east coast of the United States. Optical parameters relevant for radiative forcing calculations were determined. The backscatter ratio was β = 0.13 ± 0.01. The mass absorption efficiency for fine black carbon ($\alpha_{a,BCEf}$) was estimated as

8.9 ± 1.3 m^2 g^{-1} at 550 nm, while the mass scattering efficiency for fine nss-SO_4^{2-} ($\alpha_{s,nss\text{-}SO_4^{2-}f}$) was 7.4 ± 2.0 m^2 g^{-1}. The average dry single scattering albedo (ω_0) characterising polluted conditions was 0.89, whereas during "clean" periods ω_0 was 0.94. The direct radiative effect of the pollution aerosols was estimated to be cooling. At low altitudes (below 800 hPa), the area was generally impacted by air masses travelling over the Balkan region, Greece, and Turkey. Additional pollution was often added to these air masses along the Israeli Mediterranean coast, where population and industrial centres are concentrated. At higher levels (700 and 500 hPa), air masses came either from eastern Europe or from North Africa (Algerian or Egyptian deserts). The combination of measurements of SO_2, CO, condensation nuclei (CN), and accumulation mode particles allowed us to characterise the air masses impacting the site in terms of a mixture of local and long-range transported pollution. In particular, the lack of correlation between SO_2 and nss-SO_4^{2-} indicated that the conversion of regional SO_2 into the particulate phase is not an efficient process in summer and that aged pollution dominates the accumulation mode particle concentrations. The elemental mass size distributions, as derived from cascade impactor samplings during ARACHNE-96, were also examined. Details on this work are given by Maenhaut et al. [1999d].

Also for ARACHNE-97 we examined interrelationships between aerosol characteristics and light scattering [Ichoku et al., 1999]. During this campaign, average background scattering coefficients were about 25 Mm^{-1} at 550 nm wavelength, but strong dust events caused this parameter to rise up to about 800 Mm^{-1}. Backscattering fractions did not depend on aerosol loading, and generally fell in the range of 0.1 to 0.25, comparable to values reported for marine and Arctic environments. Chemical analysis of the aerosol revealed that, in the coarse size range (2-10 µm EAD), Ca was by far the most abundant element followed by Si, both of which are indicators for mineral dust. In the fine size fraction (<2 µm EAD), S generally was the dominant element, except during high dust episodes when Ca and Si were again the most abundant. A preview of the short-term effect of aerosol loading on radiative forcing was provided by measurements of global and diffuse solar radiation, which showed that during high turbidity periods (strong dust events), almost all of the solar radiation reaching the area was scattered or absorbed.

During ARACHNE-97, samples had also been collected for OC/EC analysis and for the determination of detailed organic compounds. The mean ratio of OC to the particulate mass (PM) in the fine size fraction was 0.120 ± 0.046 [N = 25], and the mean ratio EC/PM in the same size fraction: 0.022 ± 0.012 [N=25]. As to the detailed organic compounds, a series of higher alkanes with uneven C-number (range: C_{25}-C_{35}) originating from waxes of higher plants were found in samples taken during intense dust storm episodes.

With regard to the long-term measurements, the data from the TSI 3563 nephelometer and the Gent PM10 SFU sampler were interrelated. This was done for the period December 1995 through September 1997 [Andreae et al., 2001]. The total scattering coefficient at 550 nm showed a median of 66.7 Mm^{-1} (mean value 75.2 Mm^{-1}, std. dev. 41.7 Mm^{-1}) typical of moderately polluted continental air masses. Values of 1000 Mm^{-1} and higher were encountered during severe dust storm events. During the study period, 31 such dust events were detected, which were characterised by a sharp drop in the Ångström coefficient (i.e., the spectral dispersion of the light scattering) to values near zero. When considering the full data set, there was a clear linear relationship between the Ångström coefficient and the log of the (coarse PM/fine PM) ratio, with values around 2 when the (coarse PM/fine PM) ratio was below 1 to values around zero during dust storms, in good agreement with the behaviour expected from Mie theory [Seinfeld and Pandis, 1998]. Mass scattering efficiencies were obtained by multivariate regression of the scattering coefficients on dust, sulphate, and residual components. Various multiple linear regressions (MLRs) were performed [Maenhaut et al., 1997a; Andreae et al., 2001], including MLRs according to the following equation:

$$\sigma_{sp,\lambda} = k + \alpha_{\lambda,CPM}\,[CPM] + \alpha_{\lambda,Fsulphate}\,[Fsulphate] + \alpha_{\lambda,Fres}\,[Fres] \qquad (3)$$

with $\sigma_{sp,\lambda}$: scattering coefficient, in Mm^{-1}, at wavelength λ (450, 550 or 700 nm)
α: mass scattering efficiency (MSE), in $m^2\ g^{-1}$
in brackets: aerosol type concentration, in $\mu g\ m^{-3}$
CPM: Coarse (2-10 µm EAD) PM
Fsulphate: Fine (<2 µm EAD) sulphate
Fres: Fine residual PM = Fine PM - Fsulphate

For comparison with the literature, we have also computed this regression without the Fres term, which provides information on the scattering efficiency of the combination of fine sulphate itself and the other components associated with it (termed $\alpha_{\lambda,Fsulphate+}$ in Table II).

In Table II we compare our mass scattering efficiencies for 550 nm, as obtained from the above and other MLRs, to values found in the literature. It is important to note, that due to differences in the sampling and analysis regimes, such as the size cut-off for the fine and coarse mode, humidity of the sampled air, and chemical apportionment of the aerosols, the calculated α values are not always directly comparable. Our sulphate scattering efficiency, $\alpha_{550,Fsulphate}$ falls within the range reported for low-humidity conditions by other authors, and coincides with the theoretically predicted value for sulphate particles with a diameter of 0.4-0.5 µm [Charlson et al., 1999]. In contrast, our mass scattering efficiency of 5.2 $m^2\ g^{-1}$ for total FPM, $\alpha_{550,FPM}$, is above the range of literature values (2.4 to 4.7 $m^2\ g^{-1}$). This discrepancy may be partially due to differences in cut-off size, since the frequently used cut-off at 2.5 µm would result in more dust aerosol being included, and therefore a lower α. Another factor is the fact that the fine aerosol at Sde Boker, because of its aged character, is relatively large, with a sulphate mass median diameter around 0.4-0.5 µm [Maenhaut et al., 1999d], and therefore near the maximum in the scattering efficiency/size relationship [Charlson et al., 1999]. In studies conducted in or near urban regions, such as those by Dzubay et al. [1982], White et al. [1994], or Hegg et al. [1995], the effective fine aerosol diameter is often only about half that typical of our region. Finally, since sulphate dominates the composition of the fine aerosol at Sde Boker, it is to be expected that sulphate and fine-mass α have similar values.

Table II: Estimates of mass scattering efficiencies for four categories of aerosol. Fsulphate+ refers to the scattering from fine SO_4^{2-} and other, correlated aerosol ingredients present in the sampled air.

General Location	Date	Altitude	α_{550} ($m^2 g^{-1}$)				Reference
			Fine	Coarse	fine SO_4^{2-}	Fsulphate+	
Southern Sweden	1973-74	Aircraft	--	--	--	5±2 (450 nm)	[Waggoner et al., 1976]
New York City, U.S.A.	1976-77	Surface	--	--	8.8±0.5	--	[Leaderer et al., 1981]
--	--	--	3.1±0.2	--	--	--	[Waggoner et al., 1981]
Houston, U.S.A.	--	Surface	3.5	--	--	--	[Dzubay et al., 1982]
Canadian Arctic	1979-84	Surface	--	--	10.9±1.1	--	[Barrie and Hoff, 1985]
Maryland, Long Island, U.S.A.	1980-83	Aircraft	--	--	--	12.0±1.4	[ten Brink et al., 1987]
Eastern U.S.A.	--	Surface	--	--	5	--	[White, 1990]
--	--	--	--	--	5	8.5	[Charlson et al., 1991, 1992]
NE Atlantic, Azores Islands	1992	0-2.7 km	--	--	2.8±0.14	2-26.3	[Hegg et al., 1993]
Southwest U.S.A.	1989	Surface	2.4-2.5	0.34-0.45	--	--	[White et al., 1994]
Northeastern Atlantic Seaboard	1993	0.3-2 km	3.2	--	2.2±0.4	2.1±0.8	[Hegg et al., 1995]
Pacific Ocean	1991-92	Surface	--	--	3.6±1.1	--	[Quinn et al., 1995]
NE Atlantic (ASTEX)	--	0-3 km	4±0.7	1.1±0.2	~5	5-16	[Clarke et al., 1996]
Barbados	1994	Surface	--	0.83±0.4	--	--	[Li et al., 1996]
Pacific Ocean	1993-94	Surface	--	--	4.3-7.5	--	[Quinn et al., 1996]
North Sea, Netherlands	1993	Surface	--	--	--	20	[ten Brink et al., 1996]
mid Atlantic coast, U.S.A.	1996	0-4 km	2.8	--	2.7±1.3	--	[Hegg et al., 1997]
Hungary, rural winter	1994-95	Surface	--	--	8.3	--	[Meszaros et al., 1998]
Hungary, rural summer	1995	Surface	--	--	5.9±2	--	[Meszaros et al., 1998]
Negev Desert, Israel, winter	1997	Surface	3.7±0.6	0.12±0.05	--	--	[Ichoku et al., 1999]
Negev Desert, Israel, summer	1996	Surface	--	--	7.4±2.0	--	[Formenti et al., 2001b]
Negev Desert, Israel	1995-97	Surface	5.2±0.2	0.31±0.03	5.5±0.4	7.9±0.5	This work

An analysis of the contributions of the various aerosol components to the total scattering observed showed that anthropogenic aerosol accounted for about 70% of scattering. The rest was dominated by the effect of the large dust events mentioned above, and of small dust episodes typically occurring during mid-afternoon.

To obtain an initial, rough estimate of the radiative forcing by anthropogenic aerosols in the study region, we estimated the radiative forcing efficiency (RFE) at the top of the atmosphere (TOA), i.e., the amount of radiative forcing corresponding to a unity increase in aerosol optical thickness using an equation given by Anderson et al. [1999], based on the analysis of Haywood and Shine [1995]. In this estimation we used the average dry single scattering albedo (ω_0) of 0.92 ± 0.03 obtained during ARACHNE-96 [Formenti et al., 2001b]. We obtained a RFE of -12.8 W m^{-2} over land and -55.2 W m^{-2} over the sea. Using the long-term average aerosol optical thickness (AOT) at 670 nm measured at Sde Boker of 0.16 [Holben et al., 2001] and a 70% anthropogenic contribution to AOT based on the 70% anthropogenic contribution to total scattering, we obtained TOA forcing estimates of -1.4 and -6.2 W m^{-2} over land and sea, respectively. As an alternative to this rough estimate of radiative forcing, we computed the TOA forcing due to the anthropogenic aerosol using the Streamer radiative code [Key and Schweiger, 1998] for the same aerosol optical depth and the aerosol optical properties derived from our measurements. This yielded an annually averaged clear-sky radiative forcing of -3.5 and -6.9 W m^{-2} over desert and ocean surfaces, respectively. Assuming a negligible aerosol direct effect in cloudy sky and using the climatological mean cloud cover of 29%, this translates into an all-sky radiative forcing of -2.5 and -4.9 W m^{-2} over desert and ocean surfaces, respectively. Both our crude estimate, based on the formula by Anderson et al. [1999], and the detailed radiative transfer calculation are in good agreement with predictions from global models of aerosol radiative forcing. For example, Haywood and Shine [1995] predicted a TOA forcing of -2 to -3 W m^{-2} for our study region (without explicitly distinguishing between land and sea areas).

For further comparison with model predictions of forcing, we estimated the sulphate forcing alone and obtained values of -2.3 and -4.7 W m^{-2} over land and sea, respectively. These values are in good agreement with the model predictions for climate forcing due to sulphate in our region, which fall in the range of -2 to -5 W m^{-2} [Charlson et al., 1991; Boucher and Anderson, 1995; Feichter et al., 1997; Langmann et al., 1998; Penner et al., 1998]. Overall, we conclude that our data provide strong support for a negative radiative forcing due to anthropogenic aerosols in the eastern Mediterranean region, and that the magnitude of this forcing is in good agreement with current model predictions.

For the long-term fine and coarse aerosol chemical data sets, covering the 4year period from January 1995 through November 1998, it was examined to which extent the experimental PM could be explained by the sea salt, mineral dust, and nss-sulphate aerosol types (which were derived on the basis of the PIXE/INAA elemental data) and by some additional components, such as nitrate, ammonium, OC and EC (these additional components were only measured in a limited number of samples). This work involved a combination of chemical mass balance (CMB) and pure chemical mass closure calculations.

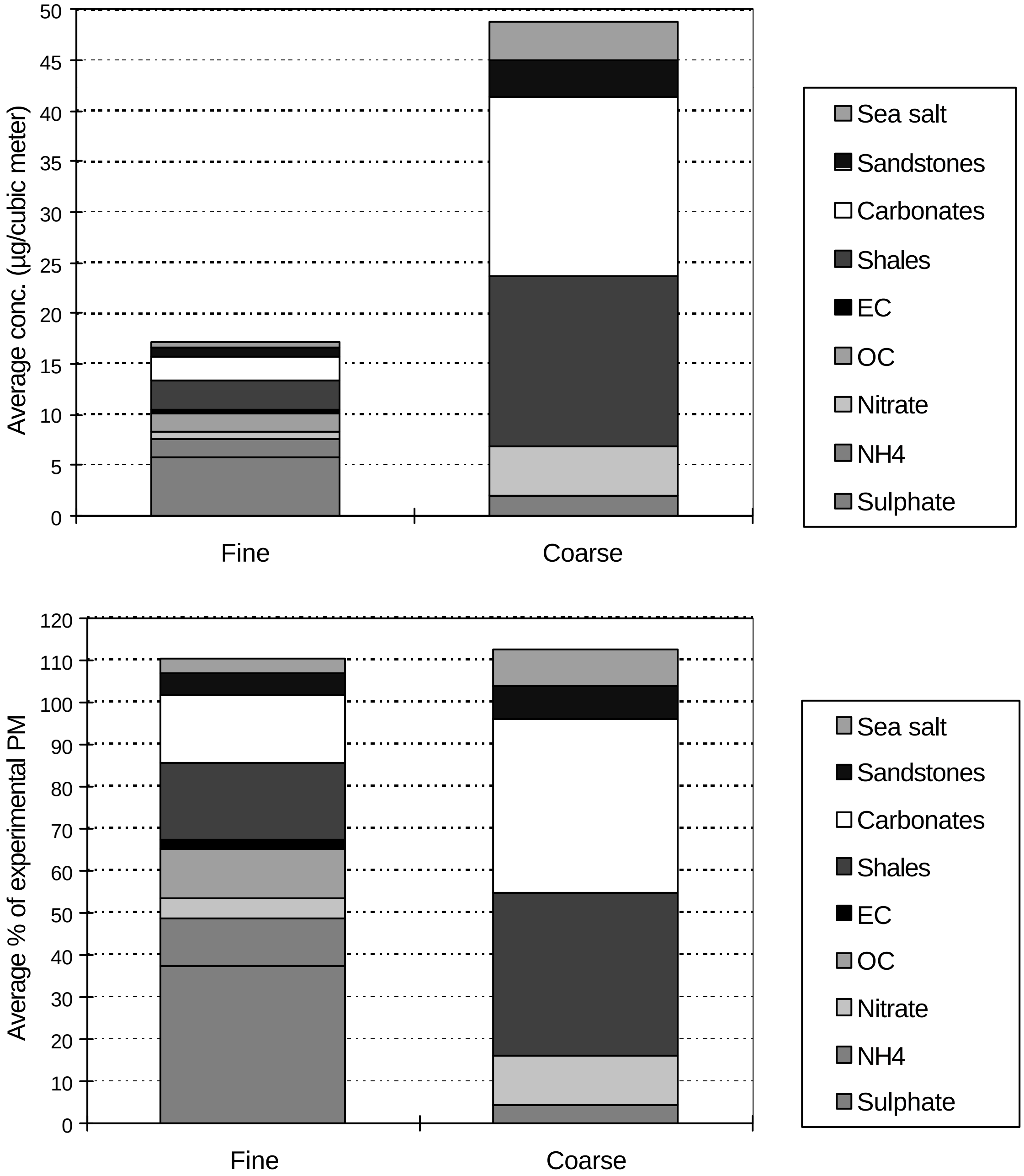
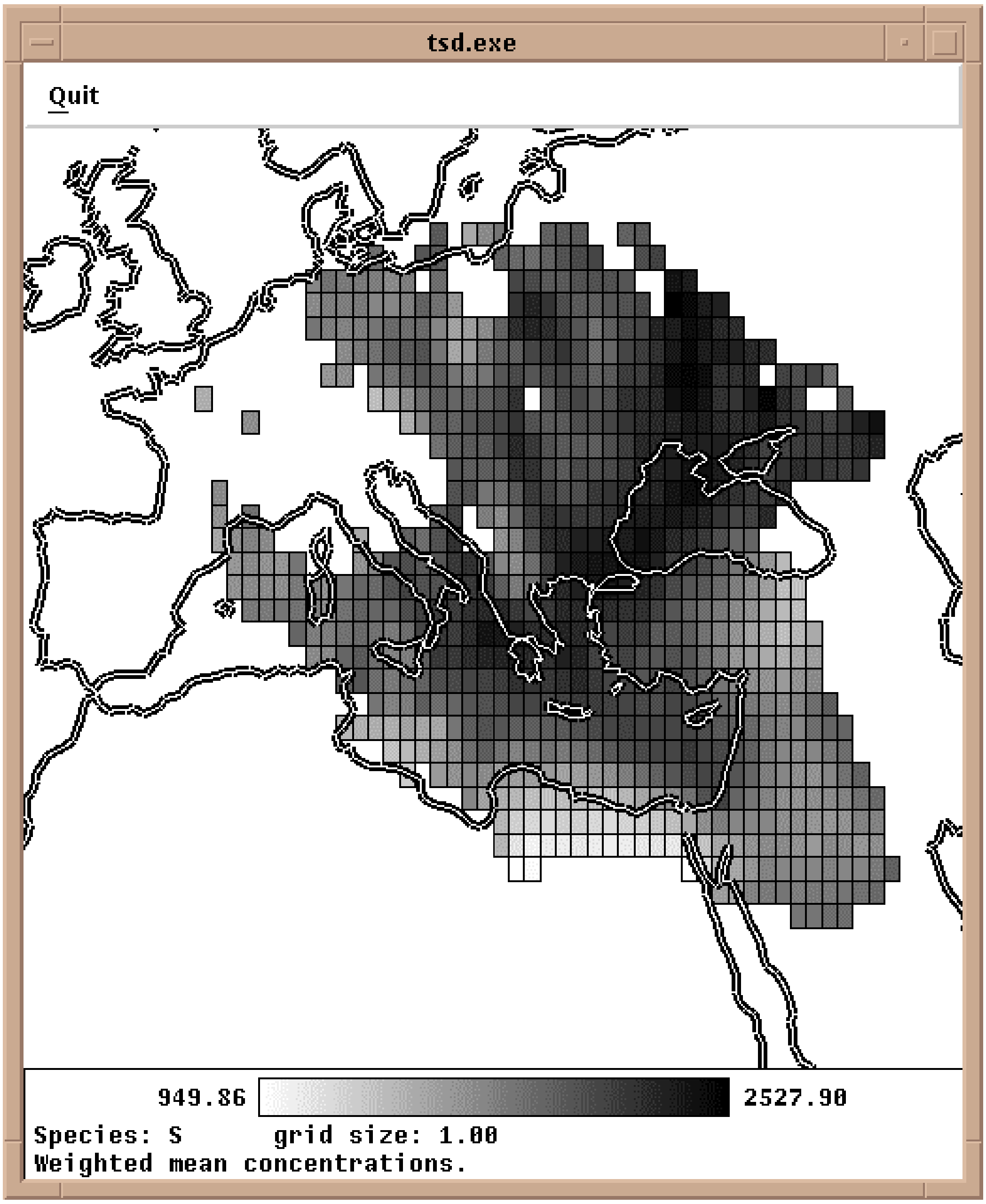


Figure 4: Average absolute (top) and percentage (bottom) apportionment of the gravimetric aerosol mass (PM) to various aerosol types and components in the fine and coarse size fractions at Sde Boker (4-year period, Jan. 1995 through Nov. 1998, 622 SFU samples).

In the CMB calculation, three different mineral dust profiles were included, i.e., shales, carbonates, and sandstones. The average apportionments (averaged over all samples) of the gravimetric PM to the various aerosol types and components in the fine and coarse size fractions are shown in Figure 4. Both absolute apportionments (average atmospheric concentrations of the various components) and percentage apportionments (average percentages of the aerosol types/components relative to the gravimetric aerosol mass (PM)) are shown. In both size fractions very good mass closure was obtained. On average, nss-sulphate contributed for 38% to the fine PM, ammonium for 11%, and mineral dust for 39%.

Further with regard to the long-term collections, we applied trajectory statistics in order to assess the source regions of some important aerosol constituents [Ptasinski et al, 1998]. The SFU data set for the 3-year period from 1995 through 1997 (493 samples in total) was used for this purpose. The air masses, which arrived at Sde Boker slightly above ground (i.e., at a level corresponding to 950/960 hPa), originated mainly from the north-west, and



```
949.86                                  2527.90
Species: S      grid size: 1.00
Weighted mean concentrations.
```

Figure 5: Concentration field for fine S for the Sde Boker receptor site, as computed using trajectory statistics (see text for details). The grey scale indicates the S concentration in ng m^{-3}.

had remained in the atmospheric boundary layer (below 2000 meters) during the 5 days preceding their arrival. The same was true for the 900 hPa arrival level. Using trajectory statistics, concentration fields were calculated for several fine and coarse species and elements. The concentration field for fine S (obtained by subdividing the domain of interest in grid cells of 1° x 1°) is shown in Figure 5. The concentration in each grid cell indicates the average concentration obtained at the receptor site (i.e., Sde Boker) when the air masses passed over that cell. Figure 5 shows that the highest levels of fine S were associated with air masses that originated in the North; the dominant source region appeared to be Ukraine, followed by the West coast of the Black Sea, and Greece. In contrast, fine V and fine Ni (two indicators of residual fuel burning) were from local/regional origin, including from the power plants along the Israeli coast. Russia seemed to be the major source area of fine Zn. Coarse Ca, an indicator for the carbonate mineral dust, was highest for air masses coming from the south-east and west, consistent with the location of the desert source regions.

Selected SFU filter samples from both ARACHNE-96 (summer) and ARACHNE-97 (winter) were subjected to automated scanning electron microscopy (SEM) with X-ray micro-analysis (EPXMA). All together, about 20,000 individual particles were examined. Hierarchical cluster analysis was performed to interpret the data on the basis of particle diameter and composition. Eleven particle classes (groups) were identified and these provided clues on the sources and/or formation processes of the particles. These 11 particle classes were (1) alumino-silicates, (2) $CaCO_3$ particles, (3) $CaSO_4$ particles, (4) other mineral dust particles, (5) sea-salt particles, (6) aged sea salt, (7) transformed mineral dust, (8) pure S particles (which actually consist of ammonium sulphate, ammonium bisulphate or sulphuric acid), (9) industrial particles, (10) P-rich particles, and (11) a particle group with composition that differed from that of the other 10 particle groups. The average contribution, as a function of particle size, of the 11 particle types to the summer and winter samples is shown in Figure 6. This figure shows that there were substantial differences between the two campaigns. The summer samples were enriched in sulphates and mineral dusts, while the winter samples contain more sea salts, aged sea salts, and industrial particles. As expected, mineral dust and sea salt particles become relatively more abundant with increasing particle size, while sulphates and other sulphur containing particles are more pronounced with decreasing particle size. The fine size fraction is enriched in secondary particles, largely below 1 µm diameter, and it showed evidence of chemical processing in the atmosphere. The secondary sulphate particles were mainly attributed to long-range transport. Regional conversion from calcite to sulphate occurred during summer. Industrial particles originating from local pollution sources were present during winter. More details about this study can be found in a submitted manuscript (S. Sobanska, C. Coeur, W. Maenhaut and F. Adams, SEM-EDX characterization of tropospheric aerosols in the Negev desert (Israel), 2001).

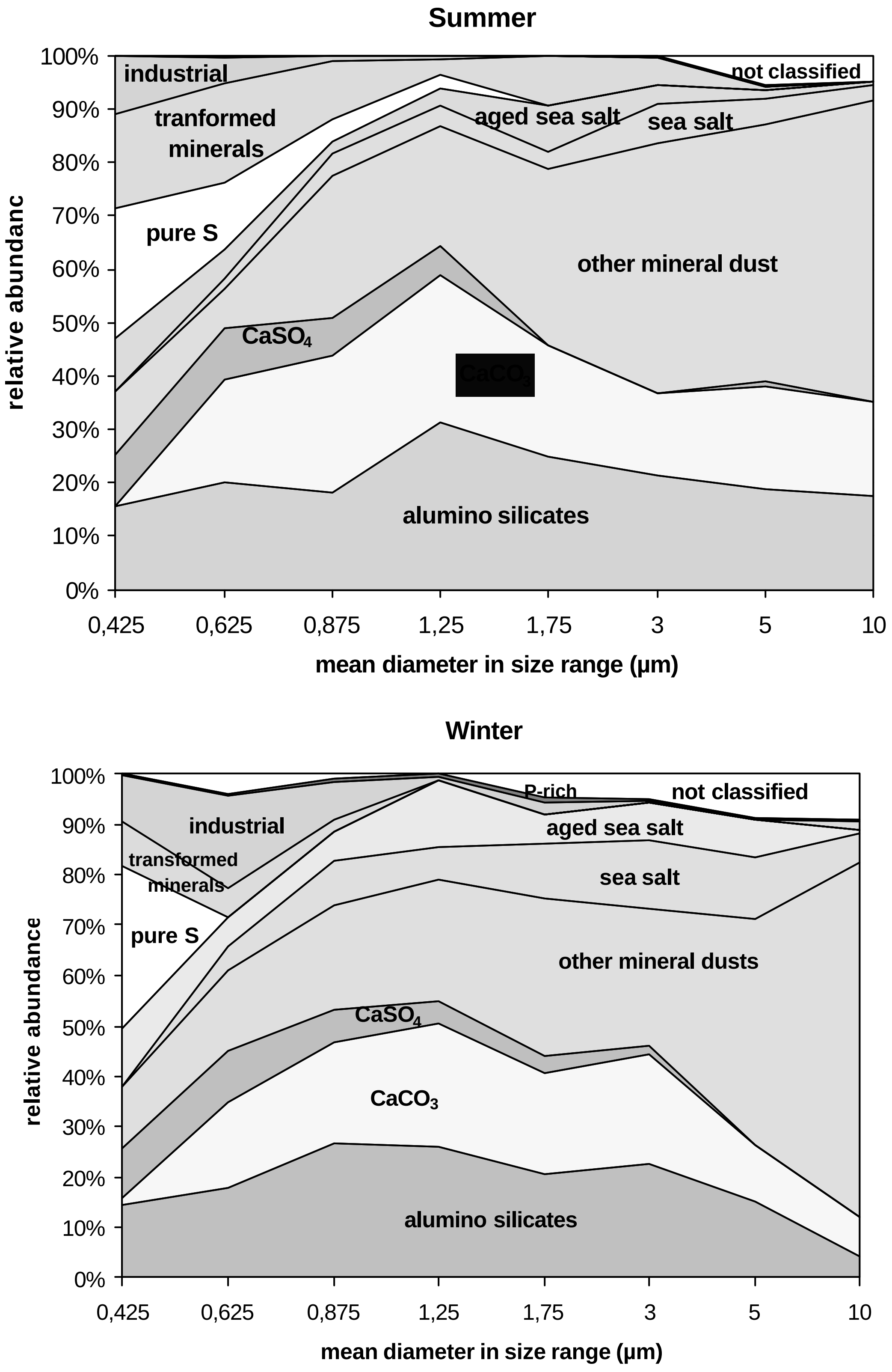


Figure 6: Average contribution, as a function of particle size, of 11 particle types to the aerosol samples from the 1996 summer and 1997 winter campaigns at Sde Boker.

During the two campaigns, samples had also been collected on Cu-grids for analysis by transmission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDX), and selected area electron diffraction (SAED). In the summer samples several types of S-containing particle types could be distinguished, including acidic sulphates and ammonium sulphates, and particles that contained soot, K, Na, and/or Ca in addition to S. Among the soot-containing particles, both internal and external mixtures of soot and sulphate were discerned. Examples of the two different soot-containing particle types and of pure ammonium sulphate particles are shown in Figure 7.

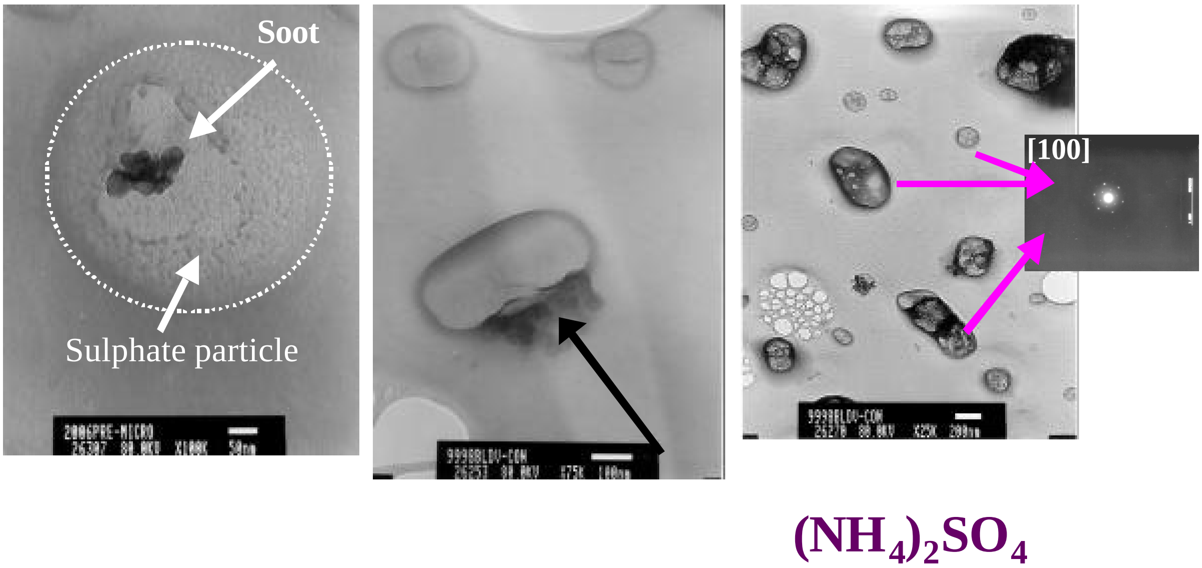


Figure 7: Examples of internally-mixed (left) and externally mixed (center) soot-containing sulphate particles and of pure ammonium sulphate particles (right), as identified by TEM/EDX/SAED of samples collected during the 1996 summer campaign at Sde Boker.

Besides the work at the Sde Boker site, work was done at Ouranoupolis (40°23'N, 23° 57'E), a site near Mount Athos in Greece. The research at this site is essentially an effort of the MPIC and AUTH teams, with whom we co-operate. At the Mount Athos site, an integrating nephelometer (TSI 3563) and an automatic tracking combined sunphotometer/sky radiometer (CIMEL Electronique 318A) are continuously operated since fall 1997. From these instruments spectral measurements of the aerosol particle scattering coefficient s_s and the aerosol optical depth t_a are obtained. For the period between June and September 1998, such spectral measurements were conducted simultaneously at the Mount Athos and Sde Boker sites. The data were related to 5-day three-dimensional back trajectories at 950, 850, and 550 hPa calculated daily, to assess the influence of long-range transport from particular source regions to the aerosol load at the two sites. It appeared that the eastern Mediterranean basin is severely polluted during summer. Daily average s_s values at 550 nm were typically in the range of 30-200 Mm^{-1} at both sites. The range obtained for the summer regional aerosol optical depth t_a was 0.03-0.52 at 500 nm. Enhanced aerosol extinction was related to transport of polluted air masses from western and eastern Europe. High-altitude transport of mineral dust from northern Africa was observed at both sites, particularly in Israel. For further details on this study, see Formenti et al. [2001a].

7 AEROSOL RESEARCH IN TROPICAL AND SUBTROPICAL REGIONS

This research was conducted in Africa (the Republic of Congo, Zimbabwe, South Africa), the Brazilian Amazon region, northern Australia, and Indonesia. It was done in close co-operation with several foreign research groups, in particular with the Biogeochemistry Department (director: Prof. Dr. M.O. Andreae) of the Max Planck Institute for Chemistry (MPIC), Mainz, Germany, the School of Geosciences of the University of the Witwatersrand, Johannesburg, South Africa (Prof. Dr. H.J. Annegarn), the Institute of Physics of the University of Sao Paulo (USPIF), Brazil (Prof. Dr. P. Artaxo), and the School of Applied Science, Monash University, Churchill, Australia (Prof. Dr. M.A. Hooper). The studies involved both long-term and campaign-type measurements. The emphasis in the studies was placed on the impact of biomass burning and of natural biogenic emissions on the climatically active fine aerosol.

During the Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO-96), SFU samples had been collected during the dry season (in November and December 1996) at a ground site in the tropical rain forest at the N'doki National Park (NNP) in the Republic of Congo. The samples were analysed for up to 26 elements by PIXE. Elements related to mineral dust and pyrogenic aerosol exhibited greater concentrations during the daytime, while aerosol produced by the rain forest exhibited higher concentrations at night. Samples were also collected at two levels on a tower, above and below the canopy, to characterise vegetation sources. APCA identified three major aerosol source types in both the fine and coarse fractions. The fine size fraction contained mineral dust (Al, Si, Ca, Ti, and Fe), pyrogenic (black carbon, K, and Zn), and marine/anthropogenic sulphur components. The coarse size fraction included a mineral dust (Al, Si, Ca, Ti, Mn, and Fe) and two primary biogenic components consisting of K, P, Zn, and S. Absolute principal component scores were calculated for the components of APCA, and temporal trends were compared to 7-day isopycnic backward trajectories. Consistent relationships between the temporal trends of the fine fraction aerosol components and meteorological patterns were observed. Trade wind air masses transported biomass burning and mineral dust aerosol to NNP during the first half of the experiment. The fine fraction sulphur component correlated well with the pyrogenic activity before the change in meteorological patterns halfway through the experiment. The fine and coarse sulphur concentrations nearly doubled in the latter part of the experiment as a monsoon circulation brought sulphur-enriched aerosol from the Atlantic Ocean. Various industrial activities on the coast of Cameroon and Gabon probably contributed to the high sulphur concentrations as well. This study is described in detail by Roberts et al. [1998, 2001].

Since September 1994, a long-term aerosol study is being performed at Rukomechi (16 °S, 29°30' E, 500 m asl), a site at 70 km to the ENE of lake Kariba in Zimbabwe [Maenhaut et al., 2000a]. The aerosols are collected with a Gent PM10 SFU sampler. The coarse and fine filters are analysed for PM, BC, and over 40 elements (from Na upward). The results for the period September 1994 through March 1998 (334 SFU samples) covering several transitions from dry to wet season, were examined by APCA and chemical mass balance (CMB) receptor modelling techniques in order to identify the major aerosol components and/or source types in each of the two size fractions and to apportion the PM and the various aerosol constituents to the aerosol components or source types. By APCA on the fine size fraction data set, 5 components were identified, viz., mineral dust, sea salt, and biomass burning (pyrogenic), pollution, and sulphate components. For the CMB calculations on this fine data set we used 4 source profiles, one for mineral dust, one for sea salt, one for pyrogenic aerosol [Maenhaut et al., 1996d], and a pure $(NH_4)_2SO_4$ profile. The pyrogenic component was the dominant contributor to the total CMB-modelled fine PM during the dry season (period July-November), see Figure 8. During the wet season, sulphate was the dominant aerosol type. The sulphate is thought to originate mainly from fossil fuel burning and industrial activities in sub-equatorial Africa. The 4 profiles reproduced the experimental fine PM rather well during the dry season, but during the wet season about 50% of the experimental fine PM remained unaccounted. Presumably, the unexplained fine PM consists mainly of organic matter from natural origin. For the CMB on the coarse data set 3 source profiles were used (i.e., the same ones as for the fine data with the exception of the pyrogenic profile). The 3-source solution reproduced the experimental coarse PM well during the period April-October. In the other months, and especially during December-January, a large fraction (up to 70% or more) of the coarse PM remained unexplained. This fraction consisted most likely mainly of organic matter from the vegetation.

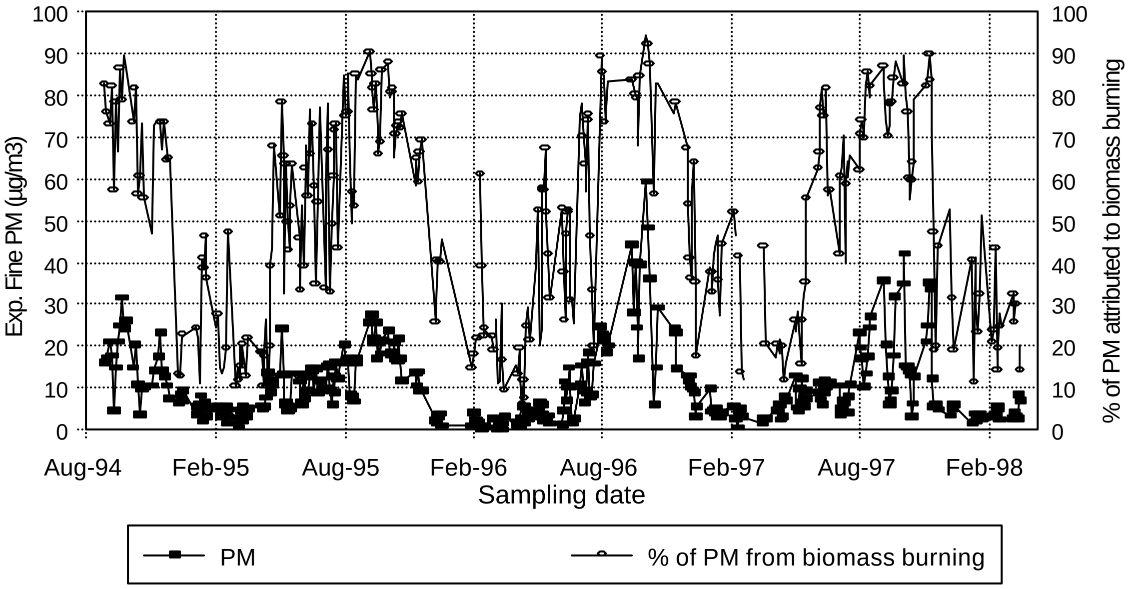


Figure 8: Time trend of the fine (<2 µm EAD) PM at Rukomechi and percentage contribution of the pyrogenic aerosol to the total CMB-modelled fine PM.

With regard to the aerosol research in South Africa, we completed an EPXMA study on aerosol samples that had been taken during SAFARI-92 [Liu et al., 1998, 2000a, 2000b], and we finished some other studies that resulted in publications [Andreae et al., 1998; Piketh et al., 1998].

In August-September 2000, we participated in the field work of the final dry season campaign of the Southern African Regional Science Initiative (SAFARI 2000). SAFARI 2000 is an international science initiative aimed at developing a better understanding of the southern African earth-atmosphere-human system (see at: http://safari.gecp.virginia.edu/ for details). Particular emphasis is placed upon biogenic, pyrogenic and anthropogenic emissions, their characterisation and quantification, their transport and transformations in the atmosphere, their influence on regional climate and meteorology, their eventual deposition, and the effects of this deposition on ecosystems. We contributed to SAFARI 2000 by performing various types of aerosol collections and measurements at Skukuza airport (25°01'S, 31°35'E, 260 m asl), in the Kruger National Park, South Africa. An aerosol collector was also deployed for us at Mongu, a site in Zambia. Some of our analyses were completed before the end of the OSTC project, but other analyses and the data interpretation were only started in 2001.

With regard to our research in Brazil, we contributed to the Smoke, Clouds, Aerosols and Radiation - Brazil (SCAR-B) Experiment, for which the field work took place in 1995, and to various activities of the “Large Scale Biosphere-Atmosphere Experiment in Amazonia” (LBA), and more specifically in its “Atmospheric Chemistry Component” (ACC). Furthermore, we were involved in several long-term studies. For the work within SCAR-B and in the long-term studies we refer to a number of publications [Artaxo et al., 1996, 1998, 2000; Echalar et al., 1998; Maenhaut et al. 1999a, 2001d, 2001e].

As to our work within LBA, in March-April 1998, we participated in a large international measuring campaign, which was named LBA-CLAIRE-98 (CLAIRE = Cooperative LBA Airborne Regional Experiment). The field work for it took place in Brazil and Surinam, during the wet season. We participated in the ground component of the campaign, and especially in the component at Balbina (1°55'S, 59°24'W, 130 km North of Manaus), Brazil. At this site aerosol samples were taken from 23 March until 15 April 1998 (23 days) with various types of filter samplers and cascade impactors. The bulk analyses on the filter samples included measurements of PM, BC, OC/EC, up to 50 elements, and detailed organic compounds. The cascade impactor samples, in contrast, were only analysed for elements (by PIXE). PM, OC and most elements were predominantly associated with the coarse (supermicrometer-sized) particles. During the first 6 days (23-29 March), mineral dust was elevated and responsible for the bulk of the PM. The dust appeared to have been advected by long-range transport from northern Africa, as explained in some detail below. During the second part of the campaign (from 30 March to 15 April), PM was much reduced (coarse PM: 5 µg m^{-3}, fine PM: 1.6 µg m^{-3}) and the organic aerosol became the dominant aerosol type; it was responsible for about two thirds of the PM10 aerosol mass. From separate day and night SFU collections, it appeared that, during the second part of the campaign, there was a substantial difference between day and night in the concentrations of coarse PM and of the elements that were associated with the coarse organic aerosol (P, S, K, Zn, (Ca, Mn)). The average coarse PM level was 8.7 µg m^{-3} during the night versus 2.4 µg m^{-3} during the day. This difference is probably due to increased atmospheric stability and reduced vertical mixing during the night, so that the organic aerosol which is produced from the regional forest cannot be transported aloft. From the detailed analyses for organic compounds, it appeared that 4% of the OM was extractable and elutable (EEOM), and that the fatty acids (palmitic (C_{16}), stearic (C_{18}), and oleic ($C_{18:1}$) acid) were the major identified compounds in the EEOM. A number of dicarboxylic acids, indicative of atmospheric oxidation processes, could also be detected. The EEOM appeared mostly associated with the fine size fraction. The bulk of the organic aerosol is undoubtedly attributable to natural emissions from the vegetation, but its composition remains largely unknown. The following elements were associated with the coarse organic aerosol: P, K, and Zn, and to a lesser extent also S, Ca, Mn, Cl, Br, and I. On the basis of the cascade impactor measurements it was found that the mineral dust and sea-salt elements exhibited essentially a broad unimodal size distribution with geometric mean aerodynamic diameter of 2-3 µm. Also the biogenic elements were only (P) or mainly (K, Zn) present in a coarse mode. Of the elements from Na upward, S was the only one with elevated concentrations in a submicrometer-sized fine mode. The fine S is presumably present as sulphate and it is expected to be a major contributor to the climatic effects of the Amazonian aerosol during the wet season. Using the size distribution data in combination with enrichment factors and time trends, it is suggested that the fine S was mainly from marine origin.

As indicated above, the detailed organic analyses of the aerosol samples from Balbina indicated that a number dicarboxylic acids were present. Special emphasis was placed on the characterisation and identification of several novel unknown dicarboxylic acids and related oxidative degradation products. This class of acidic products was enriched in the fine size fraction, suggesting that they were secondary organic aerosol products formed by gas-to-particle conversion. Some of the unknowns contributed more to the class of dicarboxylic acids than the major known compound, nonadioic acid (azelaic acid). The same unknowns were also observed in urban aerosol samples collected on hot summer days in Gent (see Section 5). Four unknowns were identified. The most abundant were two derivatives of glutaric acid, 3-isopropyl pentanedioic acid and 3-acetyl pentanedioic acid. The other two identified unknowns were another oxo homologue, 3-acetyl hexanedioic acid, and 3-carboxy heptanedioic acid. The biogenic precursors of the novel identified compounds could not be pinpointed, but most likely include monoterpenes and fatty acids. For further details on this study we refer to Kubátová et al. [2000].

Several SFU samples that we had collected at Balbina were provided to the research group of Prof. Dr. R. Van Grieken at the University of Antwerp for individual particle analysis by EPXMA. The EPXMA data sets were analysed by cluster analysis and around 10 clusters (particle types) were observed in each individual sample. During the first 6 days of the campaign (23-29 March), mineral dust particles dominated, but later on (from 30 March to 15 April) biogenic and organic particles became the most prominent ones. These results are consistent with those from the bulk analyses discussed above.

Further with regard to LBA-CLAIRE-98, the chemical and optical measurements during March 1998 in Brazil and Surinam were related to a large-scale outbreak of Saharan dust [Formenti et al., 2001c]. The observations in South America were supported by measurements in Israel and Tenerife (Canary Islands), where the dust outbreaks were also detected.

In Brazil, the dust outbreak produced an increase of a factor of 3 in the daily mean mass concentration (up to 26 ± 7 µg m^{-3}) of particles smaller than 10 µm EAD, and in the daily mean aerosol particle scattering coefficient s_S (up to 26 ± 8 Mm^{-1} STP, ambient humidity). Background levels of aerosol scattering (ambient) were s_S ~ 10 Mm^{-1}.

During 1999 two new large international campaigns took place in Brazil within the framework of LBA, this time in the state of Rondônia. Two sites were used, i.e., a “primary rain forest site” (Biological Reserve Jaru) and a “pasture site” (“Fazenda Nossa Senhora”). In the latter area, tropical forest had been converted to pasture for cattle. The first of the two campaigns took place during the wet season and the subsequent transition to dry season (February through May 1999), the second campaign occurred during the transition from dry to wet season (September-October 1999). Through co-operations with USPIF and MPIC, we obtained samples from both campaigns for analysis for OC and EC and detailed organic compounds. Two articles about this work have been published [Zdráhal et al., 2001a, 2001b], but the work on these samples is continued in 2001.

With regard to our aerosol research in northern Australia, the samplings for it took place at Jabiru (12°40' S, 132°53' E, at sea level) and some articles about this work were published [Vanderzalm et al. 1998a, 1998b; Maenhaut et al., 2000b]. As to Indonesia, we started long-term studies at two sites [i.e., at Bukit Tinggi (0°18'S, 100°20'E, 864 m asl) in Sumatra and at Pontianak (0°5'S, 109°16'E) in Kalimantan]. The work at these Indonesian sites is still ongoing.

8 OTHER AEROSOL-RELATED STUDIES

Besides the research described so far, we performed a number of other aerosol-related studies, which resulted in papers that were published or are in press. The Gent PM10 sampler was further characterised [Hopke et al., 1997]; work was done on the applicability of XRF with capillary optics for analysing aerosol samples [Holynska et al., 1997], and on the use of the NMP for individual particle analysis [Maenhaut et al., 1997d]. The elemental mass size distributions, as derived from cascade impactor measurements, were examined for a site near Rome [Maenhaut et al., 1999c] and the long-term data set from SFU samplings on the Antarctic Peninsula was analysed [Correia et al., 1998]. The aerosol composition and deposition were examined in eastern Germany [Matschullat et al., 2000]. Urban aerosols were studied in Cracow, Poland [Wróbel et al., 1999, 2000], in Helsinki, Finland [Pakkanen et al., 1999, 2000, 2001a, 2001b, 2001c], and in Budapest, Hungary [Salma et al., 2000a, 2000b, 2000c, 2001a, 2001b, 2001c]. These urban studies were to some extent linked to the EUROTRAC-2 AEROSOL subproject. Furthermore, the work in Helsinki fitted within the EUROTRAC-2 project SATURN.

9 VALORISATION POTENTIAL OF THE RESULTS

With regard to the valorisation of our results, this is in part done through traditional channels, such as publications in international journals and presentations at international conferences. For our research that is done within intensive campaigns and/or in co-operation with other groups, we also relate our data with results of the other participants, which leads to joint publications and presentations. Several articles about our project have already been published and more are planned. The articles are published in peer-reviewed journals with high impact factor and/or broad distribution within the fields of atmospheric and environmental sciences, such as Atmospheric Environment, Journal of Geophysical Research, Journal of Atmospheric Chemistry, Environmental Science and Technology, and Journal of Aerosol Science, and also in journals that deal with analytical chemistry and/or with instrumental techniques and methods.

The presentations at the international level are done at scientific conferences, symposia, workshops, and meetings, such as the EUROTRAC-2 Symposia, International Global Atmospheric Chemistry (IGAC) Conferences, the European Aerosol Conference, the General Assembly of the European Geophysical Society, and workshops of the EUROTRAC-2 AEROSOL subproject.

The results can be used and are being used in workshops, activities and reports that aim at transfer of knowledge to policy advisers, policy makers, and the general public, and this at both the national and international levels. At the national level, the valorisation can be done through activities that are being organised by, for example, the Federal Office for Scientific, Technical and Cultural Affairs (OSTC). Furthermore, the results were and will be used for contributions to Impact and Assessment , Application and other reports and publications that are prepared for policy advisers and makers by, e.g., EUROTRAC-2, IGBP-IGAC, and the Intergovernmental Panel on Climate Change (IPCC). Within EUROTRAC-2, some of our results are used for progress reports, and we will contribute to the Synthesis and Integration document, i.e., to the chapter on “Tropospheric Aerosols and Clouds”. Our long-term and other data sets with concentrations and compositions of fine atmospheric aerosols and chemical mass closure results for various European sites are being used for advice to the European Commission, in particular within work for the 2003 revision of the EU Particulate Matter Directive. Also our findings on the differences on particulate matter values obtained with filter and in-situ measurements and between different filter types are of value for this revision.

Further at the national level, the project and its results can be and are being used in university teaching and education. Undergraduate and graduate students and postdoctoral researchers are performing research that is closely related to this project, and this research enables them to write theses that lead to licentiate and doctoral degrees and to gain knowledge and experience on environmental issues, atmospheric aerosols and their impact on climate and health. The results are integrated in our course on Chemistry of the Global Atmosphere and in other courses.

The project is and will also be used to strengthen our existing co-operations with foreign research groups (of which several are of top quality, such as the Max Planck Institute for Chemistry (MPIC) in Mainz) and to initiate new co-operations with excellent European groups, and we will use the results of the project as a basis for joint applications in calls for proposals within the 6th Framework Programme of the European Union (EU). We hope to be able to contribute to the improvement of the Belgian competitiveness and participation in EU-funded projects.

10 CONCLUSIONS

As indicated in Section 1, the overall goal of the project was to contribute to the reduction of the uncertainties in our knowledge of the sources, spatial distribution, and characteristics of the tropospheric aerosols that are of importance for climate. The project definitely provided new, invaluable and important knowledge on these topics. Concentrations of climatically active aerosol types, including sulphate, carbonaceous aerosols and mineral dust, and of the aerosol mass itself were obtained at several sites in (and downwind of) Europe and at locations in tropical and subtropical regions in various continents. The relative contributions of the major aerosol types to the particulate mass were generally determined for the separate fine and coarse size fractions, and in a number of occasions also as a function of particle size down to around 50 nanometer (by using cascade impactors with 10 or more stages or size fractions). It was found and/or inferred from chemical mass closure calculations that the carbonaceous aerosol (organic aerosol and elemental carbon) is responsible for a very significant fraction (often over 30%) of the particulate mass, and this in both the coarse and fine size fractions. Valuable information was obtained on the sources, source types, and source regions of several aerosol types, acidic species and heavy metals. With regard to the organic aerosol, it is evident that this originates from natural emissions by the vegetation or biomass burning in tropical regions. However, its sources in urban areas are far less clear. Work for Gent has indicated that the contribution from car exhaust is very important, but there are also significant contributions from wood combustion and the vegetation. However, the relative contributions from these various source types and from other sources, such as meat cooking and road dust, remain rather uncertain. The detailed analyses of the organic aerosol also indicated the importance of atmospheric processing. At Gent, we observed high concentrations of dicarboxylic acids and related oxidative degradation products on hot summer days with elevated ozone levels. This has implications for the climatic effects of aerosols. By such atmospheric processing, the organic aerosol particles may become more water-soluble and/or hydrophilic, and thus become possible cloud condensation nuclei (CCN) and contribute to the *indirect* radiative aerosol forcing. While the detailed analyses of the molecular composition of the organic aerosol provided invaluable information, only a minor fraction of the organic aerosol mass (e.g., in Gent only 3%) was accounted for the various organic compounds measured. Clearly, further work on the characterisation of the organic aerosol is urgently needed. This work will lead to a better source apportionment of the carbonaceous aerosol and will provide invaluable information for assessing the effects of the carbonaceous aerosols on human health and climate.

At a number of sites, and in close co-operation with foreign research groups, our physico-chemical aerosol measurements were complemented with measurements of pure physical and optical/radiative aerosol properties. This was especially the case for our extensive research in the eastern Mediterranean. The various data were interrelated and used to asses the *direct* radiative forcing by aerosols in the region. Our estimates for the all-sky radiative forcing were -2.5 and -4.9 W m^{-2} for land and sea surfaces, respectively; more than 90% of these forcings was due to fine non-sea-salt sulphate, and most of the sulphate came from source regions in Europe. Our forcing estimates were in good agreement with current model predictions.

The intensive work by several research groups in the past few years has led to significant progress in our knowledge on the *direct* radiative aerosol forcing. However, with regard to the *indirect* radiative forcing (that is through the effects of aerosols on clouds) much work remains to be done. The *indirect* effect is receiving increasing attention nowadays. It is normally split into two components corresponding to (1) the radiative forcing due to modification of the radiative properties of clouds (cloud albedo (or Twomey) effect) and (2) the effects of anthropogenic aerosols upon the lifetime of clouds (cloud lifetime (or Albrecht) effect) [Haywood and Boucher, 2000; Penner et al., 2001; Rotstayn and Penner, 2001]. With regard to the second *indirect* effect, it has been found that warm rain processes in convective tropical clouds infected by heavy smoke from forest fires are practically shut off [Rosenfeld, 1999]. The tops of the smoke-infected clouds must exceed the freezing level, i.e., grow to altitudes colder than about -10°C, for the clouds to start precipitating. Also urban and industrial air pollution can completely shut off precipitation from clouds that have temperatures at their tops of about -10°C over large areas [Rosenfeld, 2000]. A side-effect of the production of numerous small droplets and of the suppression of the mean droplet size above polluted areas is that more cloud water can reach the mixed phase region where it is involved in the formation of precipitation and the separation of electric charge, leading to an enhancement of cloud-to-ground lightning [Orville et al., 2001]. The magnitude of the *indirect* forcing by aerosols is highly uncertain. More research on it is clearly needed. This work should include a better characterisation of the atmospheric aerosol in general and of the carbonaceous aerosol in particular.

Our project involved the development and implementation of novel methods and approaches for aerosol collection, for “bulk” and individual particle analysis, and for data interpretation and interrelation. Our work has shown that the determination of seemingly simple aerosol parameters, such as the particulate mass (PM), is much less straightforward than usually thought. Substantial differences are found between the PM data from filter and in-situ measurements and between the data from different filter types. The measurement of the PM is complicated by both positive and negative artifacts. Work on the control, elimination, and assessment of the artifacts is needed. This work will assist regulatory bodies which are setting and imposing guidelines for particulate matter. Also the important issue of the accurate differentiation between black (or elemental) carbon and organic carbon is not settled at all. And as already indicated, improved characterisation of the organic aerosol is strongly recommended. The latter work should include research on the water-soluble fraction and/or on organic aerosol components that cannot be extracted by organic solvents.

ACKNOWLEDGMENTS

This project was funded by the Belgian State - Prime Minister's Service - Federal Office for Scientific, Technical and Cultural Affairs. Financial support was also received from other sources, in particular from the “Fonds voor Wetenschappelijk Onderzoek - Vlaanderen” and the “Instituut voor Wetenschappelijk and Technologisch Onderzoek”. For the research team of W. Maenhaut, contributions were provided by K. Beyaert, J. Cafmeyer, X. Chi, D. De Ridder, S. Dubtsov, M.-T. Fernández-Jiménez, S. Mertens, I. Neefs, J. Ptasinski, I. Rajta and P. Van den Broeck. In the team of F. Adams, contributions were provided by A. Adriaens, C. Coeur, B. de la Calle, W. Dorriné, K. Janssens, F. Laturnus, S. Sobanska, R. Van Ham and H. Wille. Dr. Xiande Liu, Dr. Shuping Dong and Dr. Yuwu Li, guest scientists from the National Research Centre for Environmental Analysis and Measurements, Beijing, China, also participated in the activities. A. Kubátová, J. Jeko, J. Oliveira, H. Van den Heuvel, R. Vermeylen, V.G. Voinov and Z. Zdráhal contributed in the team of M. Claeys.

Furthermore, we benefited from co-operation with the following universities and institutes:

- Biogeochemistry Department, Max Planck Inst. for Chemistry (MPIC), Mainz, Germany: M.O. Andreae, F.X. Meixner and others;
- Institute of Physics, University of Sao Paulo, Brazil: P. Artaxo and others;
- Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE), Saint-Martin-d'Hères, France: C. Boutron and J.-L. Jaffrezo;
- Finnish Meteorological Institute (FMI), Helsinki, Finland: R. Hillamo, V.-M. Kerminen, T.A. Pakkanen and others;
- Department of Meteorology, University of Stockholm, Sweden: C. Leck and others;
- Norwegian Institute for Air Research (NILU), Kjeller, Norway: J.E. Hanssen and others;
- J. Blaustein Institute for Desert Res., Ben Gurion University of the Negev, Sde Boker, Israel: A. Karnieli and others;
- Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, Greece: C. Zerefos;
- University of the Witwatersrand, Johannesburg, South Africa: H.J. Annegarn and others;
- Tsetse Control Branch, Department of Veterinary Services, Harare, Zimbabwe: J.W. Hargrove and others;
- School of Applied Science, Monash University, Churchill, Australia: M.A. Hooper and others, and Department of Geography and Environmental Science, Monash University, Melbourne, Australia: N.J. Tapper;
- National Research Centre for Environmental Analysis and Measurements (NRCEAM), Beijing, China: X.D. Liu and others;
- Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Cracow, Poland: B. Holynska;
- Institute of Physics, Jagiellonian University, Cracow, Poland: A. Wróbel and E. Rokita;
- Department of Chemical Technology and Environmental Chemistry, L. Eötvös University, Budapest, Hungary: I. Salma;
- Interdisciplinary Environmental Research Center, Freiberg Technical University and Berg-akademie, Freiberg, Germany: J. Matschullat;
- Forestry and Renewable Natural Resources, University of Agriculture, Vienna: P. Seibert;
- Bioclimatology and Immission Research, Ludwig-Maximilians-University, Munich: A. Stohl;
- Department of Chemistry and Department of Civil & Environmental Engineering, Clarkson University, Potsdam, N.Y., U.S.A.: P.K. Hopke;
- Department of Materials, University of Oxford: G.W. Grime;
- Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, U.S.A.: J.R. Anderson;
- Department of Chemistry, University of Antwerp (UIA), Belgium: A. Worobiec, R. Van Grieken and others;

- Department of Physics, Chalmers University of Technology, Gothenburg, Sweden: A. Rindby;
- European Synchrotron Radiation Facility (ESRF), Grenoble: C. Riekel, P. Engström, A. Snigirev and I. Snigireva; and synchrotron sources in Brookhaven: K.W. Jones; and Hamburg: A. Knöchel;
- Laboratory for Analytical Chemistry, Agricultural University of Norway: B. Salbu;
- GSF-Forschungszentrum GmbH, Oberschleisheim, Germany: R. Zimmermann;
- Departimento di Fisica and Istituto Nazionale di Fisica Nucleare, Sezione di Genova, Italy: P. Prati and A. Zucchiatti.

The financial support by the funding agencies and the work and/or assistance of the internal and external contributors is very much appreciated.

REFERENCES

Adams, F., Janssens, K. and Snigirev, A. 1998. Microscopical X-ray fluorescence analysis and related methods with laboratory and synchrotron radiation sources. J. At. Anal. Spectrom. 13 : 319-331.

Amundsen, C.E., Hanssen, J.E., Semb, A. and Steinnes E. 1992. Long-range atmospheric transport of trace elements to southern Norway. Atmos. Environ. 26A : 1309-1324.

Anderson, T.L. and Ogren, J.A., Determining aerosol radiative properties using the TSI 3563 integrating nephelometer. 1998. Aerosol Sci. Technol. 29 : 57-69.

Anderson, T.L., Covert, D.S., Marshall, S.F., Laucks, M.L., Charlson, R.J., Waggoner, A.P., Ogren, J.A., Caldow, R., Holm, R.L., Quant, F.R., Sem, G.J., Wiedensohler, A., Ahlquist, N.A. and Bates, T.S. 1996. Performance characteristics of a high-sensitivity, three-wavelength, total scatter/backscatter nephelometer. J. Atmos. Ocean. Technol. 13 : 967-986.

Anderson, T.L., Covert, D.S., Wheeler, J.D., Harris, J.M., Perry, K.D., Trost, B.E., Jaffe, D.J. and Ogren, J.A. 1999. Aerosol backscatter fraction and single scattering albedo: Measured values and uncertainties at a coastal station in the Pacific Northwest. J. Geophys. Res. 104 : 26,793-26,807.

Andreae, M.O. 1995. Climatic effects of changing atmospheric aerosol levels. In: World Survey of Climatology, Volume XVI: Future Climates of the World. Henderson-Sellers, A. (Ed). Elsevier, New York: 341-392.

Andreae, M.O., Andreae, T.W., Annegarn, H., Beer, J., Cachier, H., le Canut, P., Elbert, W., Maenhaut, W., Salma, I., Wienhold, F. and Zenker, T. 1998. Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition. J. Geophys. Res. 103 : 32119-32128.

Andreae, T.W., Andreae, M.O., Ichoku, C., Maenhaut, W., Cafmeyer, J., Karnieli, A. and Orlovsky, L. 2001. Light scattering by dust and anthropogenic aerosol at a remote site in the Negev desert, Israel. J. Geophys. Res., in press.

Artaxo, P., Fernandes, E.T., Martins, J.V., Yamasoe, M.A., Longo, K.M., Hobbs, P. and Maenhaut, W. 1996. Large scale elemental composition of atmospheric aerosols measured during SCAR-B. In: SCAR-B Proceedings. Kirchhoff, V.W.J.H. (Ed). Transtec, Sao José dos Campos, SP, Brazil: 9-14.

Artaxo, P., Fernandes, E.T., Martins, J.V., Yamasoe, M.A., Hobbs, P.V., Maenhaut, W., Longo, K.M. and Castanho, A. 1998. Large scale aerosol source apportionment in Amazonia. J. Geophys. Res. 103 : 31837-31847.

Artaxo, P., de Campos, R.C., Fernandes, E.T., Martins, J.V., Zifan Xiao, Lindqvist, O., Fernández-Jiménez, M.T. and Maenhaut, W. 2000. Large scale mercury and trace elements measurements in the Amazon basin. Atmos. Environ. 34 : 4085-4096.

Ayers, G.P., Keywood, M.D. and Gras, J.L. 1999. TEOM vs. manual gravimetric methods for determination of PM2.5 aerosol mass concentrations. Atmos. Environ. 33 : 3717-3721.

Barrie, L.A. and Hoff, R.M. 1985. Five years of air chemistry observations in the Canadian Arctic. Atmos. Environ. 19 :1995-2010.

Bauman, S., Houmere, P.D. and Nelson, J.W. 1981. Cascade impactor aerosol samples for PIXE and PESA analysis. Nucl. Instr. and Meth. 181 : 499-502.

Bigg, E.K. and Leck, C. 2001. Properties of the aerosol over the central Arctic Ocean. J. Geophys. Res., in press.

Birch, M.E. and Cary, R.A. 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25 : 221-241.

Bohren, C.F. and Huffman, D.R. 1983. Absorption and Scattering of Light by Small Particles, Wiley, New York, 1983.

Boucher, O. and Anderson, T.L. 1995. General circulation model assessment of the sensitivity of direct climate forcing by anthropogenic sulfate aerosols to aerosol size and chemistry. J. Geophys. Res. 100 : 26,117-26,134.

Cahill, T.A., Eldred, R.A., Motallebi, N. and Malm, W.C. 1989. Indirect measurement of hydrocarbon aerosols across the US by nonsulphate hydrogen and remaining gravimetric mass correlations. Aerosol Sci. Technol. 10 : 421-429.

Cary, R.A. 1998. Personal communication.

Chan, Y.C., Simpson, R.W., McTainsh, G.H., Vowles, P.D., Cohen, D.D. and Bailey, G.M. 1997. Characterisation of chemical species in $PM_{2.5}$ and PM_{10} aerosols in Brisbane, Australia. Atmos. Environ. 31 : 3773-3785.

Charlson, R.J. and Heintzenberg, J. (Eds). 1995. Aerosol Forcing of Climate. Wiley, Chichester, 416 pages.

Charlson, R.J., Langner, J., Rodhe, H., Leovy, C.B. and Warren S.G. 1991. Perturbation of the northern hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols. Tellus 43AB : 152-163.

Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley, J.A., Hansen, J.E. and Hofmann, D.J. 1992. Climate forcing by anthropogenic aerosols. Science 255 : 423-430.

Charlson, R.J., Anderson, T.L. and Rodhe, H. 1999. Direct climate forcing by anthropogenic aerosols: Quantifying the link between atmospheric sulfate and radiation. Contr. Atmos. Phys. 72 : 79-94.

Claeys, M., Vermeylen, R., Kubátová, A., Cafmeyer, J. and Maenhaut, W. 1999. Characterisation of organic compounds in atmospheric aerosols. In: Proceedings of EUROTRAC Symposium '98, Transport and Chemical Transformation in the Troposphere. Volume 1, Chemical Mechanisms; Photo-Oxidants; Aerosols and Clouds; Policy Applications. Borrell, P.M. and Borrell P. (Eds). WITpress, Southampton, United Kingdom: 501-505.

Clarke, A.D., Porter, J.N., Valero, F.P.J. and Pilewskie, P. 1996. Vertical profiles, aerosol microphysics, and optical closure during the Atlantic Stratocumulus Transition Experiment: Measured and modeled column optical properties. J. Geophys. Res. 101 : 4443-4453.

Clegg, S.L., Brimblecombe, P. and Wexler, A.S. 1998. A thermodynamic model of the system H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O at 298.15 K. J. Phys. Chem. 102A : 2155-2171.

Correia, A., Artaxo, P. and Maenhaut, W. 1998. Monitoring of atmospheric aerosol particles at the Antarctic Peninsula. Annals of Glaciology 27 : 560-564.

Dockery, D.W., Pope, C.A. III, Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G. Jr. and Speizer, F.E. 1993. An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med. 329 : 1753-1759.

Dzubay, T.G., Stevens, R.K., Lewis, C.W., Hern, D.H., Courtney, W.J., Tesch, J.W. and Mason, M.A. 1982. Visibility and aerosol composition in Houston, Texas. Environ. Sci. Tech. 16 : 514-525.

Echalar, F., Artaxo, P., Martins, J.V., Yamasoe, M., Gerab, F., Maenhaut, W. and Holben, B. 1998. Long-term monitoring of atmospheric aerosols in the Amazon Basin: source identification and apportionment. J. Geophys. Res. 103 : 31849-31864.

Feichter, J., Lohmann, U. and Schult, I. 1997. The atmospheric sulfur cycle in ECHAM-4 and its impact on the shortwave radiation. Climate Dynamics 13 : 235-246.

Formenti, P., Andreae, M.O., Andreae, T.W., Galani, E., Vasaras, A., Zerefos, C., Amiridis, V., Orlovsky, L., Karnieli, A., Wendish, M., Wex, H., Holben, B.N., Maenhaut, W. and Lelieveld, J. 2001a. Aerosol optical properties and large-scale transport of air masses: observations at a coastal and a semiarid site in the eastern Mediterranean during summer 1998. J. Geophys. Res. 106 : 9807-9826.

Formenti, P., Andreae, M.O., Andreae, T.W., Ichoku, C., Schebeske, G., Kettle, A.J., Maenhaut, W., Cafmeyer, J., Ptasinsky, J., Karnieli, A. and Lelieveld, J. 2001b. Physical and chemical characteristics of aerosols over the Negev desert (Israel) during summer 1996. J. Geophys. Res. 106 : 4871-4890.

Formenti, P., Andreae, M.O., Lange, L., Roberts, G., Cafmeyer, J., Rajta, I., Maenhaut, W., Holben, B.N., Artaxo, P. and Lelieveld, J. 2001c. Saharan dust in Brazil and Suriname during the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA)- Cooperative LBA Regional Experiment (CLAIRE) in March 1998. J. Geophys. Res. 106 : 14,919-14,934.

Gordon, G.E. 1988. Receptor models. Environ. Sci. Technol. 22 : 1132-1142.

Hansen, A.D.A., Rosen, H. and Novakov, T. 1984. The aethalometer, an instrument for the real time measurement of optical absorption by aerosol particles. Sci. Total Environ. 36 : 191-196.

Hanssen, J.E., Maenhaut, W. and Semb, A. 2000. Chemical composition of PM2.5 and PM10 at Birkenes. In: EMEP/WMO Workshop on fine particles - emissions, modelling and measurements, Interlaken, Switzerland, 22-25 November 1999. Hanssen, J.E., Ballaman, R, and Gehrig R. (Eds). EMEP/CCC-Report 9/2000, O-98134: 111-116.

Harrison, L., Michalsky, J. and Berndt, J. 1994. Automated multifilter rotating shadow-band radiometer: an instrument for optical depth and radiation measurements. Appl. Opt. 22 : 5118-5125.

Haywood, J.M. and Shine, K.P. 1995. The effect of anthropogenic sulfate and soot aerosol on the clear-sky planetary radiation budget. Geophys. Res. Lett. 22 : 603-606.

Haywood, J. and Boucher O. 2000. Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review. Rev. Geophys. 38 : 513-543.

Hegg, D.A., Ferek, R.J. and Hobbs, P.V. 1993. Light scattering and cloud condensation nucleus activity of sulfate aerosol measured over the Northeast Atlantic Ocean. J. Geophys. Res. 98 : 14,887-14,894.

Hegg, D.A., Hobbs, P.V., Ferek, R.J. and Waggoner, A.P. 1995. Measurements of some aerosol properties relevent to radiative forcing on the east coast of the United States. J. Appl. Meteor. 34 : 2306-2315.

Hegg, D.A., Livingston, J., Hobbs, P.V., Novakov, T. and Russell, P. 1997. Chemical apportionment of aerosol column optical depth off the mid-Atlantic coast of the United States. J. Geophys. Res. 102 : 25,293-25,303.

Henry, R.C., Lewis, C.W., Hopke, P.K. and Williamson, H.J. 1984. Review of receptor model fundamentals. Atmos. Environ. 18 : 1507-1515.

Hillamo, R., Kerminen, V.-M., Teinilä, K., Meriläinen, J., Jaffrezo, J.-L., Cachier, H., Liousse, C., Masclet, P. and Maenhaut, W. 1999. European Arctic Aerosol Study (EAAS): Presentation and preliminary results. In: Proceedings of EUROTRAC Symposium '98, Transport and Chemical Transformation in the Troposphere. Volume 1, Chemical Mechanisms; Photo-Oxidants; Aerosols and Clouds; Policy Applications. Borrell, P.M. and Borrell, P. (Eds). WITpress, Southampton, United Kingdom: 546-549.

Hillamo, R., Kerminen, V.-M., Aurela, M., Mäkelä, T., Maenhaut, W. and Leck, C. 2001. Modal structure of chemical mass size distribution in the high Arctic aerosol. J. Geophys. Res., in press.

Holben, B.N., Tanre, D., Smirnov, A., Eck, T.F., Slutsker, I., Abuhassan, N., Newcomb, W.W., Schafer, J.S., Chatenet, B., Lavenu, F., Kaufman, Y.J., Castle, J.V., Setzer, A., Markham, B., Clark, D., Frouin, R., Halthore, R., Karneli, A., O'Neill, N.T., Pietras, C., Pinker, R.T., Voss, K. and Zibordi, G. 2001. An emerging ground-based aerosol climatology: Aerosol optical depth from AERONET. J. Geophys. Res. 106 : 12067-12097.

Holynska, B., Ptasinski, J., Maenhaut, W. and Annegarn, H.J. 1997. Energy-dispersive X-ray fluorescence spectrometer with capillary optics for the chemical analysis of atmospheric aerosols with high time resolution. J. Aerosol Sci. 228 : 1455-1463.

Hopke, P.K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P. and Cohen, D. 1997. Characterization of the Gent stacked filter unit PM10 sampler. Aerosol Sci. Technol. 27 : 726-735.

Houghton, J.T., Meira Filho, L.G., Callander, B.A., Harris, N., Kattenberg, A. and Maskell, K. (Eds). 1996. Climate Change 1995. The Science of Climate Change. Contribution of WGI to the Second Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.

Ichoku, C., Andreae, M.O., Andreae, T.W., Meixner, F.X., Schebeske, G., Formenti, P., Maenhaut, W., Cafmeyer, J., Ptasinski, J., Karnieli, A. and Orlovsky, L. 1999. Interrelationships between aerosol characteristics and light scattering during late-winter in an Eastern Mediterranean arid environment. J. Geophys. Res. 104 : 24371-24393.

IPCC (Intergovernmental Panel on Climate Change). 1994. Climate Change 1994: Radiative Forcing of Climate and an Evaluation of the IS92 Emission Scenarios. Houghton, J.T., Meira Filho, L.G., Bruce, J., Lee Hoesong, Callander, B.A., Haites, E.F., Harris, N. and Maskell, K. (Eds). Cambridge University Press, Cambridge, UK.

Jaffrezo, J.-L., Davidson, C.I., Kuhns, H.D., Bergin, M.H., Hillamo, R., Maenhaut, W., Kahl, J.W. and Harris, J.M. 1998. Biomass burning plumes over central Greenland: Sources, characteristics of the aerosol and record in the snow. J. Geophys. Res. 103 : 31067-31078.

Jonas, P.R., Charlson, R.J. and Rodhe, H. 1995. Aerosols. In: Climate Change 1994: Radiative Forcing of Climate and an Evaluation of the IS92 Emission Scenarios. Houghton, J.T., Meira Filho, L.G., Bruce, J., Lee Hoesong, Callander, B.A., Haites, E.F., Harris, N. and Maskell, K. (Eds). Cambridge University Press, Cambridge, UK: 127-162.

Kerminen, V.-M., Hillamo, R.E., Mäkelä, T., Jaffrezo, J.-L. and Maenhaut, W. 1998. The physico-chemical structure of the Greenland summer aerosol and its relation to atmospheric processes. J. Geophys. Res. 103 : 5661-5670.

Key, J. and Schweiger, A.J. 1998. Tools for atmospheric radiative transfer: Streamer and Fluxnet. Computers and Geosciences 24 : 443-451.

Kiehl, J.T. and Briegleb, B.P. 1993. The relative role of sulfate aerosols and greenhouse gases in climate forcing. Science 260 : 311-314.

Kiehl, J.T. and Rodhe, H. 1995. Modeling geographical and seasonal forcing due to aerosols. In: Aerosol Forcing of Climate. Charlson, R.J. and Heintzenberg, J. (Eds). Wiley, Chichester: 281-296.

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J. and Maenhaut, W. 1999. Carbonaceous aerosols and particulate organic compounds in Gent, Belgium, during winter and summer of 1998. J. Aerosol Sci. 30, Suppl. 1 : S905-S906.

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J., Maenhaut, W., Roberts, G. and Artaxo, P. 2000. Carbonaceous aerosol characterisation in the Amazon basin, Brazil: Novel dicarboxylic acids and related compounds. Atmos. Environ. 34 : 5037-5051.

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J. and Maenhaut, W. 2001a. Characterisation of novel dicarboxylic acids and related compounds in urban atmospheric aerosols. In: Transport and Chemical Transformation in the Troposphere. Proceedings of EUROTRAC Symposium 2000, Garmisch-Partenkirtchen, Germany, 27-31 March 2000. Midgley, P.M., Reuther, M. and Williams, M. (Eds). Springer Verlag Berlin, Heidelberg, 4 pages (published on CD-rom).

Kubátová, A., Vermeylen, R., Claeys, M., Cafmeyer, J. and Maenhaut, W. 2001b. Organic compounds in urban aerosols from Gent, Belgium: Characterization, sources, and seasonal differences. J. Geophys. Res., in press.

Langmann, B., Herzog, M. and Graf, H.F. 1998. Radiative forcing of climate by sulfate aerosols as determined by a regional circulation chemistry transport model. Atmos. Environ. 32 : 2757-2768.

Leaderer, B.P., Tanner, R.L., Lioy, P.J. and Stolwijk, J.A.J. 1981. Seasonal variations in light scattering in the New York region and their relation to sources. Atmos. Environ. 15 : 2407-2420.

Li, X., Maring, H., Savoie, D., Voss, K. and Prospero, J.M. 1996. Dominance of mineral dust in aerosol light-scattering in the North Atlantic trade winds. Nature 380 : 416-419.

Liu, X., Li, Y., Adams, F. and Maenhaut, W. 1998. Identification of particle classes in African savanna fire samples based on EPMA data. J. Aerosol Sci. 29, Suppl. 1 : S227-S228.

Liu, X.D., Dong, S.P., Van Espen, P., Adams, F., Cafmeyer, J. and Maenhaut, W. 2000a. Size and chemical characterization of atmospheric aerosol and savanna fire samples in southern Africa. J. Aerosol Sci. 31, Suppl. 1 : S186-S187.

Liu, X.D., Van Espen, P., Adams, F., Cafmeyer, J. and Maenhaut, W. 2000b. Biomass burning in Southern Africa: Individual particle characterization of atmospheric aerosols and savanna fire samples. J. Atmos. Chem. 36 : 135-155.

Lowenthal, D.H., Hanumara, R.C., Rahn, K.A. and Currie, L.A. 1987. Effects of systematic error, estimates and uncertainties in chemical mass balance apportionments: Quail Roost II revisited. Atmos. Environ. 21 : 501-510.

Maenhaut, W. 1993. Composition and origin of the regional atmospheric aerosol at great distance from anthropogenic source areas. Assessment of the extent of the anthropogenic perturbation. In: Belgian Impulse Programme “Global Change”, Symposium 17 & 18 May 1993, Proceedings, Vol. 1. Belgian Science Policy Office: 5-30.

Maenhaut, W. 1996. Composition and origin of the regional atmospheric aerosol at great distance from anthropogenic source areas. Assessment of the extent of the anthropogenic perturbation. Belgian Impulse Programme “Global Change” 1990-1996, Final Report, Federal Office for Scientific, Technical and Cultural Affairs, 105 pages [published in 1997].

Maenhaut, W. and Cafmeyer, J. 1987. Particle induced X-ray emission analysis and multivariate techniques: an application to the study of the sources of respirable atmospheric particles in Gent, Belgium. J. Trace Microprobe Techn. 5 : 135-158.

Maenhaut, W., Ducastel, G., Beyaert, K. and Hanssen, J.E. 1994a. Chemical composition of the summer aerosol at Ny Ålesund, Spitsbergen, and relative contribution of natural and anthropogenic sources to the non-sea-salt sulfate. In: The Proceedings of EUROTRAC Symposium '94. Borrell, P.M. et al. (Eds). SPB Academic Publishing bv, The Hague: 467-471.

Maenhaut, W., François, F. and Cafmeyer, J. 1994b. The “Gent” stacked filter unit (SFU) sampler for the collection of aerosols in two size fractions: Description and instructions for installation and use, In: Applied Research on Air Pollution using Nuclear-Related Analytical Techniques. NAHRES-19, IAEA, Vienna: 249-263.

Maenhaut, W., Fernández-Jiménez, M.-T., Polasek, M., Meixner, F.X., Torr, S., Hargrove, J.W., Chimanga, P. and Mlambo, J. 1996a. Long-term aerosol composition measurements at Rukomechi, Zimbabwe. Annales Geophysicae, Suppl. II to Vol. 14 : C598.

Maenhaut, W., Hillamo, R., Mäkelä, T., Jaffrezo, J.L., Bergin, M.H. and Davidson, C.I. 1996b. A new cascade impactor for aerosol sampling with subsequent PIXE analysis. Nucl. Instr. and Meth. B109/110 : 482-487.

Maenhaut, W., Koppen, G. and Artaxo, P. 1996c. Long-term atmospheric aerosol study in Cuiabá, Brazil: Multielemental composition, sources, and impact of biomass burning. In: Biomass Burning and Global Change. Volume 2: Biomass Burning in South America, Southeast Asia, and Temperate and Boreal Ecosystems, and the Oil Fires of Kuwait. Levine, J.S. (Ed). MIT Press, Cambridge, Mass., Chapter 61: 637-652.

Maenhaut, W., Salma, I., Cafmeyer, J., Annegarn, H.J. and Andreae, M.O. 1996d. Regional atmospheric aerosol composition and sources in the eastern Transvaal, South Africa, and impact of biomass burning. J. Geophys. Res. 101 : 23631-23650.

Maenhaut, W., Cafmeyer, J., Ptasinski, J., Andreae, M.O., Andreae, T.W., Elbert, W., Meixner, F.X., Karnieli, A. and Ichoku, C. 1997a. Chemical composition and light scattering of the atmospheric aerosol at a remote site in the Negev desert, Israel. J. Aerosol Sci. 28, Suppl. 1 : S73-S74.

Maenhaut, W., François, F., Cafmeyer, J., Gilot, C. and Hanssen, J.E. 1997b. Long-term aerosol study in southern Norway, and the relationship of aerosol components to source regions. In: Proceedings of EUROTRAC Symposium '96, Volume 1: Clouds, Aerosols, Modelling and Photo-oxidants. Borrell, P.M., Borrell, P., Kelly, K., Cvitas, T. and Seiler, W. Computational Mechanics Publications, Southampton, United Kingdom: 277-280.

Maenhaut, W., Hillamo, R., Mäkelä, T., Jaffrezo, J.-L., Bergin, M.H. and Davidson, C.I. 1997c. Concentrations and mass size distributions of particulate trace elements at Summit, Greenland: Impact of boreal forest fires. J. Aerosol Sci. 28, Suppl. 1 : S565-S566.

Maenhaut, W., Salomonovic, R., Ptasinski, J. and Grime, G.W. 1997d. Nuclear microprobe analysis of atmospheric aerosol samples: Comparison with bulk measurements and analyses of individual particles. Nucl. Instr. and Meth. B130 : 576-581.

Maenhaut, W., Fernández-Jiménez, M.-T. and Artaxo, P. 1999a. Long-term study of atmospheric aerosols in Cuiabá, Brazil: Multielemental composition, sources and source apportionment. J. Aerosol Sci. 30, Suppl. 1 : S259-S260.

Maenhaut, W., Jaffrezo, J.-L., Hillamo, R.E., Mäkelä, T. and Kerminen, V.-M. 1999b. Size-fractionated aerosol composition during an intensive 1997 summer field campaign in northern Finland. Nucl. Instr. and Meth. B150 : 345-349.

Maenhaut, W., Kohl, F., Hillamo, R.E. and Allegrini, I. 1999c. Detailed size distributions of aerosol species and elements during a 1995 summer field campaign near Rome, Italy. In: Proceedings of EUROTRAC Symposium '98, Transport and Chemical Transformation in the Troposphere. Volume 1, Chemical Mechanisms; Photo-Oxidants; Aerosols and Clouds; Policy Applications. Borrell, P.M. and Borrell, P. (Eds), WITpress, Southampton, United Kingdom: 490-494.

Maenhaut, W., Ptasinski, J. and Cafmeyer, J. 1999d. Detailed mass size distributions of atmospheric aerosol species in the Negev Desert, Israel, during ARACHNE-96. Nucl. Instr. and Meth. B150 : 422-427.

Maenhaut, W., Rajta, I., Beyaert, K., Leck, C., Holmen, K. and Hanssen, J.E. 1999e. Interrelations between chemical composition and light scattering of the atmospheric aerosol at Ny Ålesund, Spitsbergen. J. Aerosol Sci. 30, Suppl. 1 : S119-S120.

Maenhaut, W., Rajta, I., François, F., Aurela, M., Hillamo, R. and Virkkula, A. 1999f. Long-term atmospheric aerosol study in the Finnish Arctic: Chemical composition, source types and source regions. J. Aerosol Sci. 30, Suppl. 1 : S87-S88.

Maenhaut, W., Fernández-Jiménez, M.-T., Rajta, I., Dubtsov, S., Meixner, F.X., Andreae, M.O., Torr, S., Hargrove, J.W., Chimanga, P. and Mlambo, J. 2000a. Long-term aerosol composition measurements and source apportionment at Rukomechi, Zimbabwe. J. Aerosol Sci. 31, Suppl. 1 : S228-S229.

Maenhaut, W., Fernández-Jiménez, M.-T., Vanderzalm, J.L., Hooper, B., Hooper, M.A. and Tapper, N.J. 2000b. Aerosol composition at Jabiru, Australia, and impact of biomass burning. J. Aerosol Sci. 31, Suppl. 1 : S745-S746.

Maenhaut, W., François, F., Ptasinski, J., Mertens, S.F. and Hanssen, J.E. 2000c. Five-year study of the atmospheric aerosol composition, sources and chemical mass closure at two sites in southern Norway. J. Aerosol Sci. 31, Suppl. 1 : S180-S181.

Maenhaut, W., Cafmeyer, J., Chi, X. and Dubtsov, S. 2001a. Intercomparison of filter collections and in-situ measurements for the aerosol particle mass and elemental/black carbon at Gent, Belgium. In: Transport and Chemical Transformation in the Troposphere. Proceedings of EUROTRAC Symposium 2000, Garmisch-Partenkirtchen, Germany, 27-31

March 2000. Midgley, P.M., Reuther, M. and Williams, M. (Eds). Springer Verlag Berlin, Heidelberg, 4 pages (published on CD-rom).

Maenhaut, W., Cafmeyer, J., Dubtsov, S. and Chi, X. 2001b. Detailed mass size distributions of aerosol species and elements, and aerosol chemical mass closure during fall 1999 at Gent, Belgium. In: Transport and Chemical Transformation in the Troposphere. Proceedings of EUROTRAC Symposium 2000, Garmisch-Partenkirtchen, Germany, 27-31 March 2000. Midgley, P.M., Reuther, M. and Williams, M. (Eds). Springer Verlag Berlin, Heidelberg, 4 pages (published on CD-rom).

Maenhaut, W., Cafmeyer, J., Dubtsov S. and Chi X. 2001c. Detailed mass size distributions of elements and species, and aerosol chemical mass closure during fall 1999 at Gent, Belgium. Nucl. Instr. and Meth. B, in press.

Maenhaut, W., Fernández-Jiménez, M.-T., Rajta, I. and Artaxo, P. 2001d. Two-year study of atmospheric aerosols in Alta Floresta, Brazil: Multielemental composition, sources and source apportionment. J. Aerosol Sci. 32, Suppl. 1 : S469-S470.

Maenhaut, W., Fernández-Jiménez, M.-T., Rajta, I. and Artaxo, P. 2001e. Two-year study of atmospheric aerosols in Alta Floresta, Brazil: Multielemental composition and source apportionment. Nucl. Instr. and Meth. B, in press.

Marple, V.A., Rubow, K.L. and Behm, S.M. 1991. A microorifice uniform deposit impactor (MOUDI): description, calibration and use. Aerosol Sci. Technol. 14 : 434-446.

Matschullat, J., Maenhaut, W., Zimmermann, F. and Fiebig, J. 2000. Aerosol and bulk deposition trends in the 1990's, Eastern Erzgebirge, Central Europe. Atmos. Environ. 34 : 3213-3221.

Mazurek, M.A., Simoneit, B.R.T., Cass, G.R. and Gray, H.A. 1987. Quantitative high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry analysis of carbonaceous fine aerosol particles. Int. J. Environ. Anal. Chem. 29 : 119-139.

Meszaros, E., Molnar, A. and Ogren, J. 1998. Scattering and absorption coefficients vs. Chemical composition of fine atmospheric aerosol particles under regional conditions in Hungary. J. Aerosol Sci. 29 : 1171-1178.

Novakov, T. and Penner, J.E. 1993. Large contribution of organic aerosols to cloud-condensation-nuclei concentrations. Nature 365 : 823-826.

Ogren, J.A. 1995. A systematic approach to in situ observations of aerosol properties. In: Aerosol Forcing of Climate. Charlson, R.J. and Heintzenberg, J. (Eds). Wiley, Chichester: 215-226.

Orville R.E., Huffines G., Nielsen-Gammon J., Zhang R.Y., Ely B., Steiger S., Phillips S., Allen S. and Read W. 2001. Enhancement of cloud-to-ground lightning over Houston, Texas. Geophys. Res. Lett. 28 : 2597-2600.

Pakkanen, T.A., Hillamo, R.E., Keronen, P., Maenhaut, W., Ducastel, G. and Pacyna, J.M. 1996. Sources and physico-chemical characteristics of the atmospheric aerosol in southern Norway. Atmos. Environ. 30 : 1391-1405.

Pakkanen, T., Ojanen, C., Hillamo, R., Aurela, M., Aarnio, P., Koskentalo, T. and Maenhaut, W. 1999. Mass balance of atmospheric fine particles in the Helsinki area. J. Aerosol Sci. 30, Suppl. 1 : S275-S276.

Pakkanen, T.A., Korhonen, C.H., Hillamo, R.E., Aurela, M., Aarnio, P., Koskentalo, T. and Maenhaut, W. 2000. Ultrafine particles ($PM_{0.1}$) in the Helsinki area. J. Aerosol Sci. 31, Suppl. 1 : S522-S523.

Pakkanen, T.A., Kerminen, V.-M., Korhonen, C.H., Hillamo, R.E., Aarnio, P., Koskentalo, T. and Maenhaut, W. 2001a. Urban and rural ultrafine particles ($PM_{0.1}$) in the Helsinki area. Atmos. Environ. 35 : 4593-4607.

Pakkanen, T.A., Kerminen, V.-M., Korhonen, C.H., Hillamo, R.E., Aarnio, P., Koskentalo, T. and Maenhaut, W. 2001b. Use of atmospheric elemental size distributions in estimating aerosol sources in the Helsinki area. Atmos. Environ., in press.

Pakkanen, T.A., Loukkola, K., Korhonen, C.H., Aurela, M., Mäkelä, T., Hillamo, R.E., Aarnio, P., Koskentalo, T., Kousa, A. and Maenhaut, W. 2001c. Sources and chemical composition of atmospheric fine and coarse particles in the Helsinki area. Atmos. Environ., in press.

Penner, J.E., Dickinson, R.E. and O'Neill, C.A. 1992. Effects of aerosol from biomass burning on the global radiation budget. Science 256 : 1432-1434.

Penner, J.E., Charlson, R.J., Hales, J.M., Laulainen, N.S., Leifer, R., Novakov, T., Ogren, J., Radke, L.F., Schwartz, S.E. and Travis, L. 1994. Quantifying and minimizing uncertainty of climate forcing by anthropogenic aerosols. Bull. Am. Meteorol. Soc. 75 : 375-400.

Penner, J.E., Chuang, C.C. and Grant, K. 1998. Climate forcing by carbonaceous and sulfate aerosols, Climate Dynamics 14 : 839-851.

Penner J.E., Hegg D. and Leaitch R. 2001. Unraveling the role of aerosols in climate change. Environ. Sci. Technol. 35 : 332A-340A.

Piketh, S.J., Formenti, P., Freiman, M.T., Maenhaut, W., Annegarn, H.J. and Tyson, P.D. 1998. Industrial pollutants at a remote site in South Africa. In: Papers of the 11th World Clean Air and Environment Congress, Durban, South Africa, 13-18 September 1998, Volume Six. National Association for Clean Air, Parklands, South Africa: paper # 17E-5, 6 pages.

Ptasinski, J., Maenhaut, W., Meixner, F.X. and Stohl, A. 1998. Source areas of radiatively active and anthropogenic aerosol constituents at a remote site in the Negev desert, Israel. EOS Transactions of the American Geophysical Union 79, No. 45/supplement (1998) F84.

Quinn, P.K., Marshall, S.F., Bates, T.S., Covert, D.S. and Kapustin, V.N. 1995. Comparison of measured and calculated aerosol properties relevant to the direct radiative forcing of tropospheric sulfate aerosol on climate. J. Geophys. Res. 100 : 8977-8991.

Quinn, P.K., Kapustin, V.N., Bates, T.S. and Covert, D.S. 1996. Chemical and optical properties of marine boundary layer aerosol particles of the mid-Pacific in relation to sources and meteorological transport. J. Geophys. Res. 101 : 6931-6951.

Radzi bin Abas, M. and Simoneit, B.R.T. 1996. Composition of extractable organic matter of air particulates from Malaysia: an initial study. Atmos. Environ. 30 : 2779-2793.

Reid, J.S., Hobbs, P.V., Liousse, C., Martins, J.V., Weiss, R.E. and Eck, T.F. 1998. Comparisons of techniques for measuring shortwave absorption and black carbon content of aerosols from biomass burning in Brazil. J. Geophys. Res. 103 : 32031-32040.

Ricard, V., Jaffrezo, J.-L., Kerminen, V.-M., Hillamo, R.E., Teinila, K. and Maenhaut W. 2001. Size distributions and modal parameters of aerosol constituents in Northern Finland during the European Arctic Aerosol Study. J. Geophys. Res., submitted.

Rindby, A., Engström, P. and Janssens, K. 1997. The use of a scanning X-ray microprobe for simultaneous XRF/XRD studies of fly-ash particles. J. Synchrotron Rad. 4 : 228-235.

Roberts, G., Andreae, M.O., Maenhaut, W. and Fernández-Jiménez, M.-T. 1998. Inorganic composition and sources of aerosols in a central African rainforest during the dry season. J. Aerosol Sci. 29, Suppl. 1 : S727-S728.

Roberts, G.C., Andreae, M.O., Maenhaut, W. and Fernández-Jiménez, M.-T. 2001. Composition and sources of aerosol in a Central African rainforest during the dry season. J. Geophys. Res. 106 : 14423-14434.

Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R. and Simoneit, B.R.T. 1993a. Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation. Atmos. Environ. 27A : 1309-1330

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. 1993b. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. 27 : 636-651.

Rosenfeld D. 1999. TRMM observed first direct evidence of smoke from forest fires inhibiting rainfall. Geophys. Res. Lett. 26 : 3105-3108.

Rosenfeld D. 2000. Suppression of rain and snow by urban and industrial air pollution. Science 287 : 1793-1796.

Rotstayn L.D. and Penner J.E. 2001. Indirect aerosol forcing, quasi forcing, and climate response. J. Clim. 14 : 2960-2975.

Salma, I., Maenhaut, W., Dubtsov, S., Zemplén-Papp, É. and Záray, G. 2000a. Impact of phase out of leaded gasoline on the air quality in Budapest. Microchem. J. 67 : 127-133.

Salma, I., Maenhaut, W., Weidinger, T., Záray, G. and Zemplén-Papp, É. 2000b. Elemental size distributions in the urban atmospheric aerosol. J. Aerosol Sci. 31, Suppl. 1 : S747-S748.

Salma, I., Maenhaut, W., Zemplén-Papp, É. and Bobvos, J. 2000c. Chemical characteristics and temporal variation of size-fractionated urban aerosols and trace gases in Budapest. In: Aerosol Chemical Processes in the Environment. Spurny, K.R. (Ed). CRC Press Lewis, Boca Raton: 415-430.

Salma, I., Maenhaut, W., Zemplén-Papp, É. and Záray, G. 2001a. Comprehensive characterization of atmospheric aerosols in Budapest: Physicochemical properties of inorganic species. Atmos. Environ. 35 : 4367-4378.

Salma, I., Maenhaut, W., Zemplén-Papp, É. and Záray, G. 2001b. Comparative study of elemental mass size distributions in urban atmospheric aerosols. J. Aerosol Sci., in press.

Salma, I., Weidinger, T., Maenhaut, W. and Záray, G. 2001c. Sources of atmospheric coarse and fine particles in Budapest. J. Aerosol Sci. 32, Suppl. 1 : S769-S770.

Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.M., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D. and Puxbaum, H. 2001. Results of the “carbon conference” international aerosol carbon round robin test stage I. Atmos. Environ. 35 : 2111-2121.

Seibert, P. and Jost, D.T. 1994. Investigation of potential source areas by statistical analysis of ALPTRAC aerosol measurements. EUROTRAC Newsletter no. 14 : 14-17.

Seinfeld, J.H. and Pandis, S.N. 1998. Atmospheric Chemistry and Physics: From Air pollution to Climate Change. John Wiley, New York, 1326 p.

Simoneit, B.R.T. 1984. Organic matter of the troposphere: III - characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. Atmos. Environ. 18 : 51-67.

Sobanska, S., Coeur, C., Pauwels, B., Maenhaut, W. and Adams, F. 2000. Micro-characterisation of tropospheric aerosols from the Negev desert, Israel. J. Aerosol Sci. 31, Suppl. 1 : S344-S345.

Stohl, A. 1996. Trajectory statistics - a new method to establish source-receptor relationships of air pollutants and its application to the transport of particulate sulfate in Europe. Atmos. Environ. 30 : 579-587.

Taylor, K.E. and Penner, J.E. 1994. Response of the climate system to atmospheric aerosols and greenhouse gases. Nature 369 : 734-737.

Tegen, I. and Fung, I. 1995. Contribution to the mineral aerosol load from land surface modification. J. Geophys. Res. 100 : 18707-18726.

Tegen, I., Lacis, A.A. and Fung, I. 1996. The influence on climate forcing of mineral aerosols from disturbed soils. Nature 380 : 419-422.

ten Brink, H.M., Schwartz, S.E. and Daum, P.H. 1987. Efficient scavenging of the aerosol sulfate by liquid-water clouds. Atmos. Environ. 21 : 2035-2052.

ten Brink, H.M., Veefkind, J.P., Waijers-Ijpelaan, A. and van der Hage, J.C. 1996. Aerosol light-scattering in the Netherlands. Atmos. Environ. 30 : 4251-4261.

Turpin, B.J., Saxena, P. and Andrews, E. 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos. Environ. 34 : 2983-3013.

Van Borm, W. and Adams, F. 1988. Cluster analysis of electron microprobe data for source apportionment of air particulate matter. Atmos. Environ. 22 : 2287-2307.

Vanderzalm, J.L., Hooper, M.A., Maenhaut, W. and Tapper, N.J. 1998a. Particulate air quality and polycyclic aromatic hydrocarbons in regional northwest Australia and southeast Asia. In: Proceedings 14th International Clean Air and Environment Conference, Melbourne, Australia, 18-22 October, 1998. Clean Air Society of Australia and New Zealand Inc.: 433-438.

VanderZalm, J.L., Hooper, M.A., Tapper, N.J., Maenhaut, W., Ryan, B. and Martin, P. 1998b. An aerosol study of regional haze in northwest Australia and southeast Asia: A preliminary report on methods and first results. In: Proceedings 13th Conference on Fire and Forest Meteorology, Lorne, Australia, 1996, International Association of Wildland Fire, PO Box 327, Moran, WY USA 83013: 127-131.

Van Ham, R., Adriaens, A., Prati, P., Zucchiatti, A., Van Vaeck, L. and Adams F. 2001. Static secondary ion mass spectrometry as a new analytical tool for measuring atmospheric particles on insulating substrates. Atmos. Environ., revised version submitted.

Van Vaeck, L., Adriaens, A. and Adams, F. 1998a. Microscopical speciation analysis with laser microprobe mass analysis and static secondary ion mass spectrometry. Spectrochim. Acta 53B : 367-378.

Van Vaeck, L., Cuynen, E., Van Espen, P. and Adams, F. 1998b. Microscopical speciation analysis with laser microprobe mass spectrometry and static secondary ion mass spectrometry. In: Proceedings of the Second Biennial International Conference on Chemical Measurements and Monitoring of the Environment, Ottawa, Canada, 11-14 May 1998. Clement, R. and Burk, B. (Eds). Carleton University, Ottawa, Canada: 535-540.

Vincze, L., Janssens, K., Adams, F., Rindby, A., Engström, P. and Riekel, C. 1998. Optimization of tapered capillary optics for use at the microfocus beamline (ID 13) at the European Synchrotron Radiation Facility (ESRF). Adv. X-ray Anal. 41: 252-261.

Virkkula, A., Aurela, M., Hillamo, R., Mäkelä, T., Pakkanen, T., Kerminen, V.-M., Maenhaut, W., François, F. and Cafmeyer, J. 1999. Chemical composition of atmospheric aerosol in the European subarctic: Contribution of the Kola Peninsula smelter areas, Central Europe and the Arctic Ocean. J. Geophys. Res. 104 : 23681-23696.

Waggoner, A.P., Vanderpol, A.J., Charlson, R.J., Larsen, S., Granat, L. and Tradgard, C. 1976. Sulfate light scattering ratio as an index of the role of sulfur in the tropospheric optics. Nature 261 : 120-122.

Waggoner, A.P., Weiss, R.E., Ahlquist, N.C., Covert, D.S. and Charlson, R.J. 1981. Optical characteristics of atmospheric aerosols. Atmos. Environ. 15 : 1891-1909.

White, W.H. 1990. Contributions to light extinction. In: Visibility: Existing and Historical Conditions - Causes and Effects. NAPAP Rep. 24, by Trijonis, J.C., Malm, W.C., Pitchford, M., White, W.H., Charlson, R. and Husar, R. Natl. Acid Precip. Assess. Program, Washington D.C.: 85-102.

White, W.H., Macias, E.S., Nininger, R.C. and Schorran, D. 1994. Size-resolved measurements of light scattering by ambient particles in the Southwestern USA. Atmos. Environ. 28 : 909-921.

Wróbel, A., Rokita, E. and Maenhaut, W. 1999. The influence of meteorological parameters on short range transport of aerosols. Nucl. Instr. and Meth. B150 : 403-408.

Wróbel, A., Rokita, E. and Maenhaut, W. 2000. Transport of traffic-related aerosols in urban area. Sci. Total Environ. 257 : 199-211.

Zdráhal, Z., Vermeylen, R., Claeys, M., Maenhaut, W., Guyon, P. and Artaxo, P. 2001a. Characterization of novel di- and tricarboxylic acids in fine tropical aerosols. J. Mass Spectrom. 36 : 403-416.

Zdráhal, Z., Vermeylen, R., Claeys, M. and Maenhaut, W. 2001b. Characterization of tricarboxylic acids in tropical biomass burning aerosols. In: Proceedings of the 49th ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, Illinois, May 27-31, 2001, 2 pages (published on CD-rom).

Zimmermann, R., Van Vaeck, L., Davidovic, M., Beckmann, M. and Adams, F. 2000. Analysis of polycyclic hydrocarbons (PAHs) adsorbed on soot particles by Fourier transform laser microprobe mass spectrometry (FT LMMS) : Variation of the PAH patterns at different positions in the combustion chamber of an incineration plant. Environ. Sci. Technol. 34 : 4780-4788.