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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

SYNTHESIS OF THE FINAL INTEGRATED SCIENTIFIC REPORT

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

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 EURO-TRAC-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 and elemental carbon 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 organic carbon and elemental carbon. We improved and evaluated methods for extracting organic compounds from aerosols for subsequent detailed analysis by capillary gas chromatography - flame ionisation detection and gas chromatography/mass spectrometry. 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 gas chromatography/mass spectrometry for the characterisation and structure elucidation of unknown compounds that were present in notable concentrations in urban and tropical aerosols. 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.

Our contribution to the EUROTRAC-2 AEROSOL subproject includes the development, evaluation and application of analytical methods for organic carbon and elemental carbon 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 was determined for all filters by weighing, and all quartz fibre filters were subjected to analyses for organic carbon and elemental carbon; selected filters from one sampler were analysed for detailed organic compounds by capillary gas chromatography - flame ionisation detection and gas chromatography/mass spectrometry. 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 (that is the sum of organic carbon plus elemental carbon) was responsible for around one quarter of the aerosol mass and elemental carbon represented about 25% of total carbon. Considering that the organic aerosol also contains other atoms (such as hydrogen, oxygen, nitrogen) besides carbon, the organic carbon data have to be multiplied by a conversion factor in order to obtain organic aerosol mass. 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 organic aerosol plus elemental carbon) of one third of the particulate mass. 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 organic aerosol, 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 organic carbon, elemental carbon, and detailed organic compounds, our contribution to the AEROSOL subproject includes the intercomparison and evaluation of methods for measuring important aerosol parameters, such as the particulate mass and

carbon, the determination of the detailed mass size distribution for the particulate mass, organic carbon, elemental carbon 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 PM_{2.5} 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 particulate mass and a Magee Scientific aethalometer for black carbon. 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 particulate mass determinations were also done with filter holders that used different types of filters. It was found that the fine particulate mass 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 particulate mass, organic carbon, elemental carbon, 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) elemental carbon, (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 particulate mass), ammonium sulphate (27%) and elemental carbon (10%). In the supermicrometer size range, organic aerosol (28% of the particulate mass) and crustal material (24%) prevailed; ammonium sulphate and sea salt were responsible for about 10% each. On average, 74% of the gravimetric particulate mass was accounted for by the aerosol types considered. The unexplained mass is likely attributable to ammonium nitrate and water.

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 cooperation 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 particulate mass, black

carbon, 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 the vertical column-integrated aerosol optical depth and other 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 were used for measuring the aerosol chemical, physical, and optical (radiative) properties and for measuring selected atmospheric trace gases (CO, CO₂, SO₂, O₃). 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 one of these yielded an all-sky radiative forcing of -2.5 and -4.9 Watt per square meter 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 a 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 hectoPascal), 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 hectoPascal 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 vanadium and fine nickel (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 zinc. Coarse calcium, 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 particulate mass, is much less straightforward than usually thought. The measurement of the particulate mass 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.