ABSTRACT

Atmospheric aerosols are of importance for a wide range of geophysical and environmental problems ranging from local issues to global scale. Carbonaceous aerosols, i.e., organic carbon (OC) and elemental carbon (EC), make up a large fraction of the (fine) aerosol, often up to 50% or more, and are thought to play a major role in the climatic and health effects of aerosols. Yet, our knowledge about them is very deficient. This is to a large extent due to their complexity and to problems associated with their collection. In this project we investigated improved collection procedures, whereby the sampling artifacts are better controlled or can be corrected for. These procedures included the use of tandem quartz fibre filter set-ups (with front and back filters, Q1Q2), of a two-port sampling train (with parallel deployment of a quartz fibre filter holder, Q1, and of a sampler with sequential front Teflon filter and back-up quartz fibre filter, TQ3), and of a tandem quartz fibre filter set-up that was preceded with a diffusion denuder for volatile organic compounds (VOCs) and important gaseous inorganic oxidants (O_3, NO_2), DQ1Q2. From the simultaneous deployment of the DQ1Q2 and Q1Q2 set-ups at several urban and rural locations in Europe, it could be concluded that positive sampling artifacts (i.e., the adsorption of VOCs by the quartz fibre filters) prevail in a Q1Q2 set-up and that negative artifacts (i.e., the loss of semivolatile OC from the particulate phase) prevail in a DQ1Q2 set-up and that the same particulate phase OC data are generally obtained by subtracting the back filter OC from the front filter OC in a Q1Q2 set-up as found by adding the front and back filter OC in a DQ1Q2 set-up. It is therefore suggested that the rather simple Q1Q2 set-up and subtraction of front and back filter OC can generally be deployed to obtain reliable particulate phase OC data. It was also found that the percentage of the OC on the back-up filter (Q2) of a Q1Q2 set-up was higher during summer than winter and that there was a tendency for higher percentages at locations with warmer ambient temperatures than at colder locations. The highest percentages of OC on the back filter relative to the front filter that were obtained with our Q1Q2 set-ups at our various sampling sites were around 16-17%.

Secondly, we developed improved methods for the characterisation of the carbonaceous atmospheric aerosol, going from (a) a better discrimination between EC and OC over (b) separation into a number of main classes, for which the major functional groups are characterised, to (c) a more complete molecular characterisation, whereby special attention was given to high-molecular weight organics and highly polar compounds. Extensive work was done on the appropriate discrimination between EC and OC by thermal-optical analysis. It appeared that the results depend to a large extent on the temperature program used, particulary on the maximum temperature in the first stage (in pure He) of the analysis. Higher EC/TC

ratios (with TC = OC + EC) were obtained at lower maximum temperatures in the first stage. It was also found that the composition of the carbonaceous aerosol plays an important role in the EC/OC split point setting. Very serious discrepancies were observed between the EC (or black carbon (BC)) of different techniques for samples with large amounts of biomass burning (or brown carbon) aerosol. A very recent study to which the UGent team contributed shed some light on this issue. As to the separation into main classes, the UGent team developed a method for measuring water-soluble OC (WSOC) and applied it to samples from various sites. The largest WSOC percentages (expressed as % of the OC) were observed for rural and biomass burning sites, where they were in the range of 60-70%; at urban sites the WSOC percentages were in the range of 35-43%. This indicates that the OC at the rural and biomass burning sites is more oxygenated than at the urban sites. It also implies that the multiplication factor to convert OC data into data for organic matter (OM) should be higher for the rural and biomass burning sites than for urban sites. With regard to the more complete molecular characterisation, extensive work was done by the UA team. Methods, involving derivatisation of extracts from quartz fibre filter samples or aluminium cascade impactor foils and analysis by gas chromatography with flame ionisation detection (GC-FID) or by capillary GC/mass spectrometry (GC/MS), were developed for a variety of polar compounds, including saccharidic compounds, other polyols, and several organic acids.

Third, we identified new organic compounds in continental aerosols that can be used as markers for specific sources, source types or processes, and/or atmospheric processes. A major achievement was the discovery of the 2-methyltetrols in aerosol samples from the Amazon basin. These compounds were attributed to secondary organic aerosol (SOA) formation from the photo-oxidation of isoprene. The discovery was published in the scientific top journal Science. Although isoprene is emitted in very large quantities by the terrestrial vegetation, it was up to our finding not considered to give rise to SOA in the ambient air. The 2-methyltetrols were subsequently also found to be present in aerosols from a number of forested locations in Europe and, in addition, other SOA products from isoprene were discovered, such as 2-methylglyceric acid. The formation of the SOA products from isoprene was confirmed by smog chamber experiments, which were carried out in co-operation with the U.S. Environmental Protection Agency.

Fourth, our already existing and newly developed samplers and analytical methods were used for detailed carbonaceous aerosol characterisation studies at various sites in Europe, in part within the framework of the EUROTRAC-2 AEROSOL subproject. Extensive collections and measurements were performed for urban background sites (Ghent and Uccle), a kerbside (Budapest), a rural background site (Melpitz, Germany), and the forested site of K-puszta in Hungary, whereas less extensive work was done for the urban background site of Barcelona, a traffic site in Amsterdam, forested sites in Finland and Germany, and some other European sites. For Ghent and especially K-puszta, detailed molecular characterisation work was carried out. For Ghent, large concentrations of the wood-burning indicator levoglucosan were found in winter samples, whereas in summer sugars and sugar alcohols were present, which are indicators for natural primary emissions from the vegetation. The samples at K-puszta had been collected during a hot 2003 summer campaign and substantial concentrations of isoprene SOA compounds and sugar alcohols were observed. Diel patterns, with highest concentrations and highest percentage contributions to the OC during day-time, were observed for the 2-methyltetrols, which can be regarded as supporting evidence for their fast photochemical formation from isoprene that is locally emitted during the day-time. Similar diel patterns were noted for the sugar alcohols (which are markers for fungal spores), suggesting that the release of fungal fragments is enhanced during the day-time.

Our existing and improved methods for aerosol collection and chemical analysis were also used for studies in tropical and equatorial regions (South America, southern Africa, South-east Asia, North-west Australia). The measurements in South America and South Africa were conducted within large international field campaigns that were organised under the auspices of IGBP-IGAC activities, such as those of the Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA). Several campaigns were conducted in Amazonia, but the UGent and UA teams were especially active in the work of the ground-based field campaign that took place in 2002 at a pasture site in the state of Rondônia, Brazil, within the EU project “Smoke Aerosols, Clouds, Rainfall and Climate: Aerosols from Biomass Burning Perturb Global and Regional Climate” (SMOCC). The UGent team deployed several aerosol collectors at the site from early September until mid-November. These 2.5 months encompassed a dry period, with intensive biomass burning and very high levels (often more than 100 $\mu g/m^3$) of PM2.5 (particulate matter smaller than 2.5 µm), a transition period with intermediate levels, and a wet period with PM2.5 mass levels below 5 $\mu g/m^3$. Extensive chemical analyses were performed on the UGent samples from this campaign, not only by our own teams, but also by other SMOCC partners. Significant variations in the aerosol composition and concentrations were observed within each period, which can be classified into two categories: a) diurnal oscillations, caused by the diurnal cycle of the boundary layer and the different combustion phase active during day (flaming) or night (smouldering); b) day-to-day variations, due to alternating phases of relatively wet and dry conditions. There were large differences in the composition of the total identified organic compound fraction of the PM2.5 aerosol between the three periods. The relative contribution of the biomass burning products (i.e., the anhydrosugars, which include levoglucosan, and the aromatic acids and aldehydes) decreased from the dry to the wet period (with percentage contributions of 55, 33, and 16% for the dry, transition, and wet periods, respectively), while this of the biogenic and biological aerosol products, including the 2-methyltetrols, the sugar alcohols, and the sugars, showed an opposite pattern (with average percentage contributions of 5.6, 11, and 36%). Whereas the concentration of the PM2.5 aerosol mass varied over about 2 orders of magnitude over the course of the campaign, that of the coarse (2.5-10 µm) aerosol varied over less than one order of magnitude, pointing to a fairly constant emission of coarse particles from the natural background. As a consequence, the PM2.5/PM10 percentage ratio for the aerosol mass was substantially lower during the wet period (i.e., on average, 42%) than during the transition period (69%) and dry period (84%). Extensive aerosol collections and chemical analyses were also made for the ground-based field component of the final dry season (biomass burning) campaign in August-September 2000 of the “Southern African Regional Science Initiative” (SAFARI 2000). The field work for this took place at Skukuza in the Kruger National Park. Levoglucosan and oxalic acid were the dominant organic species measured, they accounted for 2.5% and 1.25% of the PM10 OC; the dicarboxylic (and other organic) acids accounted, on average, for 2.5% of the PM10 OC and the saccharidic compounds accounted for 4.9% of the PM10 OC. It can thus be concluded that the bulk of the WSOC eluded analysis by our techniques; this may be predominantly high molecular weight in nature.

The data sets on the carbonaceous aerosol were used in combination with data on the inorganic aerosol constituents and on the particulate mass (PM) for source (source type) identification and apportionment, for assessing the relative proportions of SOA and primary OC, and for aerosol chemical mass “closure” work (that is for examining to which extent the experimental gravimetric PM can be reconstituted on the basis of the measured aerosol types and components). Up to 8 aerosol types (components) were included in the mass closure calculations, i.e., OM, EC, ammonium, nitrate, non-sea-salt (nss-) sulphate, sea salt, crustal matter, and other elements. The aerosol composition at our Belgian sites (Ghent and Uccle) was dominated by secondary inorganic aerosol (SIA), that is the sum of ammonium, nitrate, and nss-sulphate. In winter, the sum of these 3 components accounted, on average, for 40% or more of the PM10 mass. For PM2.5 even larger percentage contributions of SIA were observed. Also a substantial fraction of the OM may consist of secondary aerosol and thus be SOA, especially in summer. The total contribution of secondary aerosol to PM10 is likely over 50% in all seasons in Belgium. Also for our other European sites (i.e., Melpitz, Budapest, and K-puszta) large percentages of SIA were observed. Quite different results, with very low SIA percentages of typically

5%, were obtained for our two sites in Tanzania. Whereas the higher temperatures may play a role for the lower nitrate percentages there, other explanations have to be invoked for the lower percentages of nss-sulphate. They indicate that the emissions of the precursor gas SO_2 on the regional scale are substantially lower for our Tanzanian sites than they are for our European sites, as is also evident from the GEIA emission inventory [see http://geiacenter.org/]. OM was clearly the dominant aerosol component in SAFARI 2000 and SMOCC 2002. It accounted for 50% of the PM10 mass during SAFARI 2000 and for about 80% of the PM10 mass during SMOCC 2002. Overall, excellent aerosol chemical mass closure was obtained for all our sites for which all important aerosol constituents (with the exception of water) were determined. The unexplained mass may be attributed to water, which may easily represent 10% or more of the gravimetric PM10 mass at 20°C and 50% relative humidity (which are the conditions at which the weighings were done). Several of our data sets were subjected to multivariate and other receptor modelling. For the combined UGent/UA data set of SMOCC 2002 seven aerosol components were identified: (1) a very important pyrogenic (biomass burning) component, which contained anhydrosugars, phenolic acids, and several other species, (2) a component with dicarboxylic and hydroxycarboxylic acids, (3) crustal matter, (4) aged sea salt, (5) isoprene SOA, with the 2-methyltetrols, (6) a primary biogenic component, and (7) a biological aerosol component with the fungal spore indicators arabitol and mannitol. Although the dicarboxylic and hydroxycarboxylic acids were on a separate component, some of these acids were also in part associated with the pyrogenic component.

In co-operation with other groups (especially within the IGBP-IGAC activities), we examined the relationships between the carbonaceous aerosol characteristics and physical and optical/radiative aerosol properties (e.g., condensation nuclei (CN) and cloud condensation nuclei (CCN) concentrations and particle number size distributions, light scattering and absorption coefficients) in order to assess the contribution of the carbonaceous aerosol to the *direct* and *indirect* effects of aerosols on climate.

Part of the work was done within International collaboration with Central European countries and with China. Special attention was given to the exploitation of the research results. This included transfer of knowledge and results from this project to policy advisers and makers, administrators, the members of the users committee and the general public.

Keywords: atmosphere, carbonaceous aerosols, organic carbon, elemental carbon, secondary organic aerosols, aerosol sources, mass closure.