

CHEMICAL MASS SIZE DISTRIBUTIONS OF ATMOSPHERIC AEROSOLS OVER THE ATLANTIC OCEAN BETWEEN EUROPE AND ANTARCTICA

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Keywords: ATMOSPHERIC AEROSOLS, CHEMICAL COMPOSITION

INTRODUCTION

Physical properties and chemical composition of atmospheric aerosol were measured in November - December 1999 over the Atlantic Ocean from the English Channel to the Antarctic coast, and in January 2000 at the Finnish Antarctic research station Aboa (73°03'S, 13°25'W, 470 m a.s.l.). Koponen *et al.* (2002) presented number size distributions during the cruise and Virkkula *et al.* (2002) presented some results of the chemical analyses of the filter samples during the expedition. In addition to filter samples the size-segregated chemical composition of aerosol was studied using multi-stage impactors. The chemical mass size distributions of aerosols measured both on the cruise and at Aboa are presented.

MEASUREMENTS

Aerosol samples were collected using a high-volume sampler (HV), a virtual impactor (VI) that divides the sample in sub- and supermicron fractions, a 12-stage small-deposit-area low-pressure impactor (SDI) and at Aboa also a 9-stage micro-orifice uniform deposition impactor (MOUDI). During the cruise the SDI and the VI had a common inlet with a cutoff approximately at 10 µm in particle aerodynamic diameter. At Aboa the VI and the SDI used a common inlet that had particle cutoff diameter larger than 15 µm. The filter and impactor samples were analyzed for major water-soluble inorganic ions and organic acids using a Dionex DX500 ion chromatograph. The HV samples were in addition analysed for elementary and organic carbon. In this paper the results from the SDI measurements are discussed.

The SDI flow rate was 11 LPM. The sampling durations of the SDI varied during the cruise. When the ship was in the area where more pollution was expected a 24-h sampling time was considered sufficient for getting samples above detection limit on all stages. In the cleaner areas the sampling time was doubled to get enough mass on all stages. The aerodynamic D₅₀ values of the SDI stages are 0.045, 0.086, 0.15, 0.23, 0.34, 0.59, 0.80, 1.06, 1.66, 2.68, 4.08, and 8.5 µm. In the SDI polycarbonate films were used as particle impaction substrates (Nuclepore, poreless, 10 µm thick), the films were coated with Apiezon L vacuum grease in order to reduce bounce-off of particles. The samples were analyzed for inorganic ions and organic acids. Continuous chemical mass size distributions of the SDI data were obtained using the MICRON inversion code. The size distributions were further analyzed for lognormal modes using a fitting routine.

RESULTS

The concentrations of anthropogenic compounds decreased during the cruise from north to south. For nitrate the north-south decrease was very clear down to the packed ice of the Weddell Sea. However, nitrate concentration was somewhat higher at Aboa than in the last sample over the pack-ice (Figure 1). A possible coarse particle nitrate source at Aboa is re-emission of nitrate which was originally deposited onto the ground surface in the form of nitrate or nitric acid.

Over the ocean the nitrate size distribution was mainly bimodal. Typically the two supermicron mode diameters were smaller than those of sea salt (Figure 1). The mass mean diameter of nitrate was close to the surface area mean diameter of sea salt in most samples, which indicates formation of nitrate via the interaction of gaseous nitric acid or some other reactive nitrogen compound with sea-salt particles. In one ocean sample and in most samples at Aboa also a coarse nitrate mode, $D_g > 5 \mu\text{m}$, was present. At Aboa also non-seasalt calcium has a coarse mode. This suggests that this nitrate mode is likely formed by surface reactions of gaseous nitrogen compounds with the wind-blown dust from the surface of the snow-free mountain top on which the station is located.

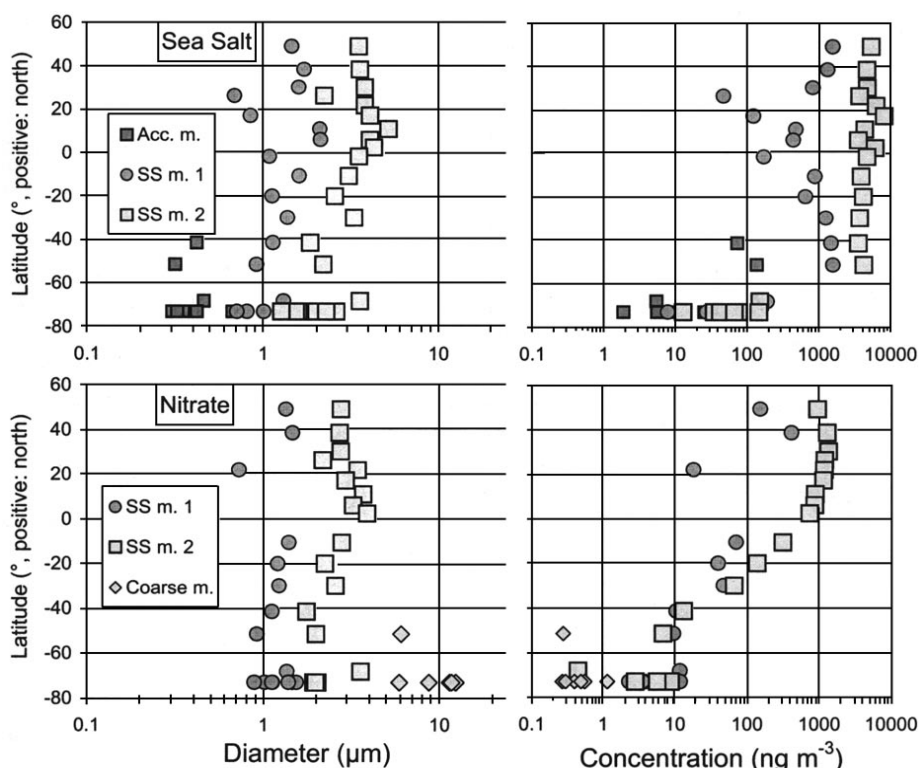


Figure 1. Diameters and concentrations of the modes of sea salt and nitrate mass size distributions. (Acc. m = accumulation mode, SS m. = Sea Salt mode)

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DIFFERENCES AMONG THERMAL/OPTICAL ORGANIC AND ELEMENTAL CARBON ANALYSIS METHODS FOR AMBIENT AEROSOLS

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Keywords: Atmospheric Aerosols, Black Carbon, Visibility, PM_{2.5}

INTRODUCTION

This presentation assembles and critically reviews existing knowledge related to the following questions about OC and EC: 1) what are elemental carbon (EC) and organic carbon (OC)?; 2) what are different OC and EC measurement methods?; 3) how do the different measurements compare?; 4) what substances might interfere with OC and EC measurements?; 5) how do OC and EC affect regional haze and the earth's radiation balance?; and 6) what should be done to resolve outstanding measurement issues? This review summarizes and adds to recently published comparisons and reviews (Chow et al., 2001, Chow and Watson, 2002, Currie et al., 2002, Watson and Chow, 2002). Atmospheric EC particles are commonly considered to be the product of incomplete combustion of carbon-containing fuels in an oxygen-starved environment. This soot contains randomly oriented three-bond carbon crystals 2 to 3 nm in diameter with a graphite-like structure, interspersed with other elements and organic compounds. EC and soot are often characterized as black carbon (BC) by light reflectance or transmittance, but some forms of EC are blacker than others. Diamonds are not black, even though they are composed of nearly pure elemental carbon. Crystalline graphite reflects ten times the visible light of synthetic black carbon and more than twice that of coal and tar. For practical purposes, EC is defined as the fraction that evolves under defined combustion conditions.

METHODS AND FINDINGS

More than a dozen thermal methods have been applied to measure different carbon fractions. The following thermal/optical analysis protocols will be applied with the same instrument, procedures, and standardization: 1) Oregon Graduate Institute thermal optical reflectance (TOR); 2) Interagency Monitoring of Protected Visual Environments (IMPROVE) TOR and thermal optical transmittance (TOT); 3) National Institute of Occupational Safety and Health (NIOSH) TOT; 4) Speciation Trends Network (STN) TOT; 5) Aerosol Characterization Experiments in Asia (ACE-Asia); 6) Hong Kong University of Science and Technology UST-3; 7) Meteorological Service of Canada's MSC1 TOT; 8) General Motors Research Laboratory two temperature; 9) Brookhaven National Laboratory two temperature; 10) Japanese two temperature; 11) thermal manganese oxidation; 12) Rupprecht & Patashnick two temperature; 13) Lawrence Berkeley Laboratory continuous temperature ramp; 14) French pure oxygen combustion; 15) German Verein Deutscher Ingenieure (VDI) extraction/combustion. These methods differ from each other with respect to: 1) combustion atmospheres; 2) temperature ramping rates; 3) temperature plateaus; 4) residence time at each plateau; 5) optical monitoring configuration and wavelength; 6) standardization; 7) sample aliquot and size; 8) evolved carbon detection method; 9) carrier gas flow through or across the sample; and 10) location of the temperature monitor relative to the sample. These differences are not completely documented in the published descriptions, although they may make a difference in the comparability of the measured carbon fractions. Thermal/optical methods (Chow et al., 2001) monitor darkening of the filter as organic carbon chars in the absence of oxygen. After oxygen is added to the carrier air, the original and newly pyrolyzed carbon burn off, and the portion that evolves before the optical detection attains its original value (OP) is classified as OC. The IMPROVE method is often called thermal optical reflectance (TOR) because it monitors charring by reflectance while the STN method monitors it by transmittance. This is a secondary cause of OC and EC differences between the two methods. The high temperature (900 °C) achieved by the STN method during the non-oxidizing step burns off some of the elemental carbon, as evident from the change in reflectance and transmittance. The

eight fractions identified by the IMPROVE method are included in the IMPROVE database and form the basis for calculating the OC and EC contributions to light extinction that is used to track progress toward natural visibility conditions (Watson, 2002, Chow et al., 2002).

Within a given thermal/optical protocol, allocation of total carbon to OC and EC fractions by thermal/optical methods depends on: 1) filter loading, initial and final blackness; 2) presence of catalyzing substances (e.g., NaCl) for EC; 3) liberation of oxygen by minerals present in the sample; 4) presence of carbonates that decompose with OC and EC; 5) light absorbing properties of non-carbonaceous minerals; 6) pyrolysis of organic gases adsorbed throughout the filter; and 7) changes in particle composition that affect transmittance and reflectance efficiencies during thermal evolution. These sample-to-sample variables have not been adequately studied, except for carbonate interferences. Carbonates have been thought to interfere with OC and EC measurements. This might be the case for thermal evolution methods that achieve temperatures greater than the decomposition temperature of calcium carbonate, which is reported to range from 825 °C to more than 1000 °C. Owing to weathering of surface soils, carbonates are not common interferences in ambient aerosol samples. When they are, they can be simply removed by slightly acidifying samples prior to analysis.

CONCLUSIONS

Systematic research is not being executed to resolve discrepancies among thermal/optical OC and EC analysis methods. Such research should include: 1) documentation of the method applied, especially for thermal evolution methods with different combustion temperatures, residence times, ramp rates, and optical pyrolysis corrections; 2) review and evaluation of the published carbon literature, much of which is not in the common air quality journals; 3) optical modeling of changes in absorption properties of particles on and within a filter relative to those suspended in air; 4) preparation of standards representing different black carbon sources (e.g., diesel, wood burning, tar, gasoline engine) on different filter media (e.g., Teflon membrane, quartz fiber) at different deposit levels (light, medium, and dark appearances) while measuring absolute absorption with a photoacoustic spectrometer (Moosmüller et al., 1998); 4) experimentally examine distribution of particles and pyrolysis artifact within filter; 5) experimentally evaluate effects of non-absorbing particles, transmittance wavelengths, initial darkness, carbonate deposits, and oxygen-supplying minerals; and 6) optimize fractions to identify source contributions.

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CHARACTERIZATION OF SEMI-VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR PARTICULATE MATTER (PM_{2.5}) BY DIRECT THERMAL DESORPTION - GAS CHROMATOGRAPHY - TIME-OF-FLIGHT MASS SPECTROMETRY

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Keywords: SVOC, PM_{2.5}, ENVIRONMENTAL PARTICLES, MEASUREMENTS.

INTRODUCTION

Several epidemiological studies have investigated the relevance of ambient particles (mass or number) on health effects. Investigations of the influence of individual, particle bound chemical pollutants were done only for few inorganic species. In particular the role of transition metals (Fe, V, Zn) for acute reactions is under discussion. The influence of organic substances was evaluated by measurement of the concentration of elementary and organic carbon (EC/OC) (Tolbert, 2000). Particle toxicity and carcinogenicity is enhanced by numerous organic constituents e.g. polycyclic aromatic hydrocarbons (PAH) and oxy-PAH (Li, 2000, Nielsen, 1999). But so far the association of individual specific organic pollutants or groups of pollutants with health effects, occurring in the fine dust, was not examined in epidemiological studies. As a new analytical approach, recently the thermal desorption has been employed for extracting semi volatile species from ambient particulate matter (Falkowich, 2001, Waterman, 2000).

METHODS

PM_{2.5} is sampled on a daily time basis in Augsburg, Germany on glass fibre filters. Daily sampling started in spring 2002 and most likely will be continued till spring 2005 or longer. The samples are analysed for SVOC by direct thermal desorption - gas chromatography - time-of-flight mass spectrometry (DTD-GC-TOFMS). The a novel DTD interface is used in this study. In detail, the liner of the GC injection interface (DTD-liner) is used as a sample container for the PM_{2.5} filter aliquots. Inserting of the DTD-liner in the injector is automated. The analytes are thermally desorbed from the DTD-liner directly onto the capillary GC column. For analysis the filters are cut into pieces, each representing a PM_{2.5} aliquot of 1 m³ sampled ambient air. One to four of these pieces are placed into the DTD-liner. Isotope labeled reference compounds are added for quantification. Desorption temperature is 350°C for 15 Minutes. During desorption the SVOC are focused on a retention gap at 40°C oven temperature.

RESULTS

In the PM_{2.5} samples besides others (n-)alkanes, long chain carboxylic acids, long chain alkyl nitriles,

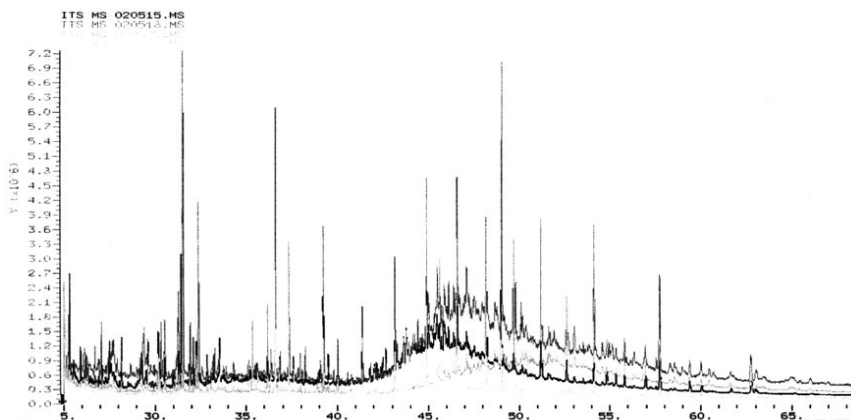


Figure 1: Total ion current (TIC) chromatograms of some filter samples (15.-28.05.02)

esters, terpenes, steranes, hopanes, substituted aromatics, PAH, oxy-PAH, heterocyclic aromatic compounds have been identified and partly quantified. Further effort for identification of unknown compounds using comprehensive two-dimensional gas chromatography - time-of-flight mass spectrometry

(GCxGC-TOFMS) and numerical peak deconvolution techniques is under way. The question, whether the detected long chain alkyl nitriles are build from the analog acids in presence of an ammonium source (e.g. NH_4NO_3) during the thermal desorption (Waterman 2001) or they are useful tracers for biomass burning (Simoneit 2003) has to be investigated in detail. As shown in figure 1 the differences in the total ion current (TIC) chromatograms are pronounced. In figure 2 and 3 examples for day-to-day fluctuations of the concentrations of some n-alkanes (Figure 2) and PAH (Figure 3) in the time 15th to 29th February 2002 are shown. The carbon preference index (CPI) indicates a slight increased contribution of anthropogenic emissions on the 22nd May only. The concentrations of all alkanes were increased on this particular day. Some PAH (e.g. chrysene and benzo[ghi]perylene) exhibit increased concentrations on the same day, whereas most of the other PAH (e.g. benzo[a]anthracene, pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene) show a maximum in concentration on two consecutive days. Long term monitoring and data analysis will give information about the variability of the organic chemical inventory of urban ambient fine particles (PM_{2.5}). It is also foreseen to include the obtained data in epidemiological studies, in order to elucidate the health relevance of SVOC in PM_{2.5}.

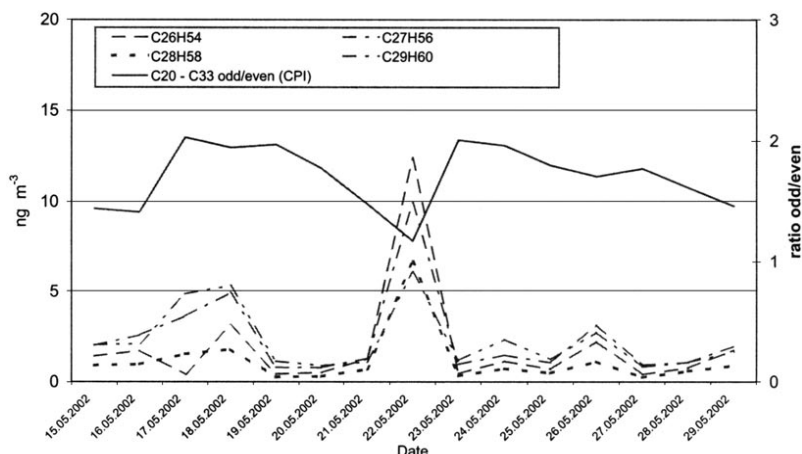


Figure 2: Day-to-day changes in concentrations of some n-alkanes in PM_{2.5}

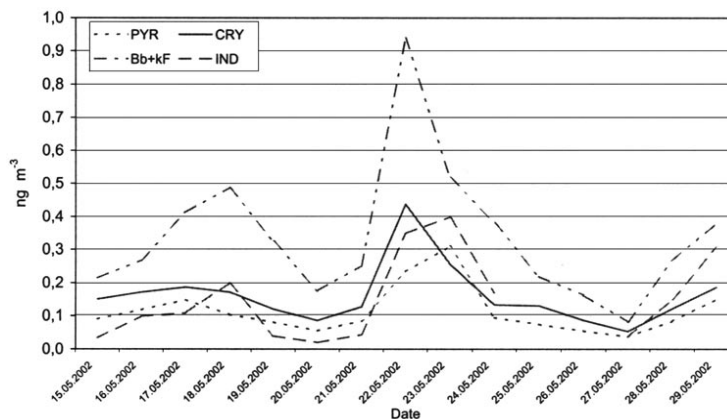


Figure 3: Day-to-day changes in concentrations of some PAH in PM_{2.5}

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Size Distributions and Spatial and Temporal Patterns of Particulate Carbon in Vancouver, British Columbia

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Keywords: atmospheric aerosols, organic carbon, black carbon, Vancouver

INTRODUCTION

Atmospheric PM is an area of extensive research due to impacts on human health, the environment, visibility and climate. In August 2001 an intensive field study (Pacific 2001) was carried out in the Lower Fraser Valley (LFV) of British Columbia (Vancouver) to study the sources and processes influencing PM in this region. As in many places, carbonaceous compounds contribute significantly to the PM mass. In Vancouver, the contribution to fine particle mass (PM_{2.5}) is, on average, 63%. This is quite large, relative to many parts of North America, and thus, there was considerable emphasis on carbonaceous PM during Pacific 2001. This includes extensive measurements of total organic (OC) and black carbon (BC), total semi-volatile (SVOC) and non-volatile OC (NVOC) and chemical speciation of OC. This presentation will focus on the OC, BC, SVOC and NVOC, including spatial and temporal patterns in the LFV and OC and BC size distributions measured at the urban location.

METHODS

Three measurement sites in the LFV were operated for ~20 days to study the spatial and temporal variation in OC and BC. The Slocan Park (SP) site was in the city of Vancouver; the Langley (LY) site was in a rural area on the outskirts of suburban Vancouver, ~30 km southeast of SP; the Sumas Mountain (SM) site was ~25 km northeast of LY at an elevation of 300 meters with a small city to the west and agricultural land in the surrounding area. At each of these sites five pre-fired quartz filter samples were collected per day, with four hour durations during the day, starting at 0600 LDT, and an eight hour duration sample overnight from 2200-0600 LDT. A cyclone was attached to the filterpack (FP) to prevent particles greater than 2.5 µm from being collected. At SP, a Micro-Orifice Uniform Deposition Impactor (MOUDI; 1992) was used with pre-fired quartz filters to measure OC/BC size distributions from 1000-1000 each day. An Integrated Organic Gas and Particle Sampler (IOGAPS) was also operated at SP on several days to determine NVOC and SVOC using methods described by Fan et al. (2003). All quartz filter samples (FP, MOUDI and IOGAPS) were analyzed using a Sunset Labs Thermal Optical Transmission Instrument. Concentrations were determined from the NIOSH 5040 method (Birch and Cary, 1996) with slight modifications as described in Sharma et al. (2002) and Fan et al. (2003).

	OC			BC			OC/BC (when BC>0.1)		
	SP	LY	SM	SP	LY	SM	SP	LY	SM
N	67	60	59	67	60	59	34	34	29
AVE	3.0	2.2	1.9	0.37	0.14	0.11	10.4	12.6	11.1
MED	2.7	1.7	1.9	0.33	0.11	0.08	9.4	12.2	11.0
MAX	7.1	12.1	4.3	1.70	0.69	0.52	24.6	28.0	27.0

Table 1. Comparison in OC and BC concentrations (µg m⁻³) and their ratio among sites.

RESULTS

The urban site had the highest concentrations (Table 1). From this site to the rural areas BC decreased more on a percent basis than did OC. This suggests additional sources of OC such as secondary production and natural emissions. The OC/BC ratio was greatest at LY, which is consistent with its location, and suggests that this site experienced the most 'aged' carbonaceous aerosols. IOGAPS measurements collected on 15 separate 12 hr periods showed that the FP measurements of OC (as in Table 1 - SP) were, on average, 30% greater than 'true' OC. This latter measurement represents OC corrected for positive and negative artefacts, which is expected to be a better representation of particle OC in atmosphere. A size distribution for a day with large OC is shown in Figure 1. BC was highest in

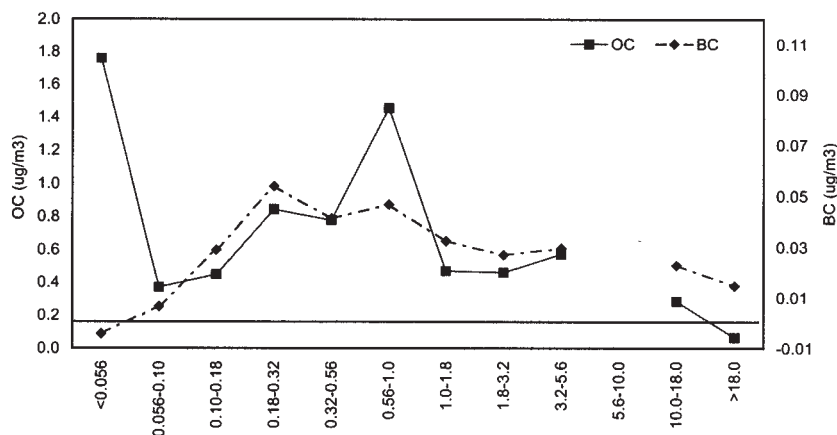


Figure 1. Vancouver, BC, (SP) MOUDI size distribution of OC and BC for Aug. 26, 2001.

the 0.18-0.32 µm size range, but there was a considerable amount of BC in particles from 0.32-1.0 µm. On most other days the 0.18-0.32 µm peak in BC was more pronounced suggesting fresher emissions. The larger sized BC particles and the pronounced OC peak at 0.56-1.0 µm suggests that on the 26th the carbonaceous particles had experienced greater atmospheric processing compared to other days. The higher overall OC concentration and the fact that the OC/BC ratio was 22.6 during the afternoon of the 26th is consistent with more processing and also suggests more secondary organic aerosol formation.

CONCLUSIONS

- The urban area of Vancouver, BC, is influenced more by fresh emissions. Within 50 km, in rural areas, the carbonaceous aerosol has undergone a detectable amount of atmospheric processing leading to greater influence of secondary organics. However, such conditions can also be detected in the urban area. In the city sampling artifacts from collection using a simple PM_{2.5} cyclone and filterpack with a quartz filter lead to, on average, a 30% over-estimation in OC.

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MEASUREMENT OF ORGANIC ACIDS USING A WET EFFLUENT DIFFUSION DENUDER / AEROSOL (WEDD/AC) COLLECTOR IN THE ZURICH AREA

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Keywords: Organic acids, diffusion denuder, aerosol, Zurich.

INTRODUCTION

A wet effluent diffusion denuder/ aerosol collector (WEDD/AC) coupled to ion chromatography has been being used for measurement of gaseous compounds and aerosol in the atmosphere (Simon and Dasgupta, 1995; Löflund *et al.*, 2001; Zellweger *et al.*, 1999). This method allows an automated quasi-continuous measurement of the gaseous compounds and aerosols separately with higher time resolution. So far the WEDD/AC was mainly used for the determination of water-soluble inorganic anions however, with the use of appropriate columns and gradient technology in ion chromatography, it is also possible to measure the concentration of water-soluble organic acids from the atmosphere. Sampling of individual acids separately for both the gaseous compounds and aerosols was also made possible by connecting a fraction collector to the effluent of the IC.

METHODS

The WEDD/AC has a denuder (a flattened, approximately rectangular glass tube), which was sand blasted in order to increase the wettability of the denuder, and an aerosol collector, which is connected to the top of the denuder. A detailed description of the instrument is found in Zellweger *et al.* (1999) and Löflund *et al.* (2001). The collecting efficiency of the denuder was measured for gaseous acetic and formic acid to be at least 85% and 75%, respectively. The effluents from the denuder and aerosol collector were passed through concentrator traps and then analysed using ion chromatography (IC). The IC system was calibrated using a standard solution of 12 anions, including 7 organic acids in order to quantify the atmospheric concentrations of the respective gas and particle phase. The system also contains a fraction collector for sampling the IC effluent for stable isotope analysis with isotope ratio mass spectrometry (IRMS).

The instrument was tested in a first field campaign in Zurich in summer 2002. In this field measurement, a few organic acids were identified including acetic, formic, oxalic, propanoic, malonic and succinic acid. Acetic acid, formic acid and oxalic acid were observed above the detection limit in both the gas and aerosol phase throughout the whole period of measurement. For a few days, propanoic acid was also measured above the detection limit in the gas phase. The concentrations of acetic and formic acid were found to be higher in the gas phase than in the aerosol phase, whereas oxalic acid was exclusively found in the aerosol phase. The inorganic anions appear to be higher in the aerosol collector than in the denuder except fluoride, which is below the detection limit in the aerosol collector. The concentration of sulphate was higher than any other anion in the aerosol phase, and SO₂ (measured as sulphite) exhibited the highest concentration in the gas phase. Nitrate, nitrite, fluoride, and chloride were also measured in the atmosphere, and their respective concentrations are given in Table 1.

Table 1. Detection limits and one-day average concentrations of the identified peaks in the air samples from Zurich Kaserne.

Peak no.	Compound	Aerosol		Gas	
		Det. limit (pptv)	Mixing ratio (pptv)	Det. limit (pptv)	Mixing ratio (pptv)
1	Fluoride	50	-	50	70
2	Acetate	100	40	100	590
3	Formate	50	60	50	425
4	Chloride	50	165	50	340
5	Nitrite	50	-	50	-
6	Nitrate	100	540	100	310
9	Sulphate	20	800	20	1760(SO ₂)
10	Oxalate	20	25	20	-

CONCLUSIONS

The possibility of sampling both the gas and aerosol phase simultaneously makes this method a preferred choice for sampling water soluble organic acids than the traditional filter sampling which has more positive and negative artifacts (Baltensperger, 2001). In addition to this, the extension of the fraction collector allows us to collect the organic acids separately for stable isotope analysis of individual organic acids. Though optimizing the method for the conversion of small quantities of organic acids to CO₂ is pending, taking individual samples with a fraction collector is the preferred way of sampling organic acids for stable isotope analysis rather than taking bulk samples using filters. Further work will focus on the development of the IRMS analysis.

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DETAILED CHEMICAL CHARACTERIZATION OF AEROSOLS FROM THE COMBUSTION OF BIOMASS INDIGENOUS TO SOUTH-ASIA

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INTRODUCTION

Throughout South-Asia biomass is commonly used as a fuel source for cooking and heating homes. The smoke from domestic use of these fuels is expected to be a major source of atmospheric particulate matter in the region and needs to be characterized for input in regional source apportionment models and global climate models.

METHODS

Biomass fuel samples including coconut leaves, rice straw, jackfruit branches, dried cowdung patties, and biomass briquettes manufactured from compressed biomass material were obtained from Bangladesh. The fuel samples were burned in a wood stove and the smoke was collected in a dilution source sampler. Fine particulate matter (less than 2.5 μm) was collected on pre-baked 47 mm quartz filters in order to characterize the emissions. The sampling trains contain a combination of Teflon and quartz filters for particle collection followed by polyurethane foam (PUF) for organic vapor absorption. The Teflon filters were used for gravimetric mass determination, trace metals, and ionic species. The quartz filters were used for elemental and organic carbon analysis and detailed organic analysis of extracts by gas chromatography-mass spectrometry (GC-MS) using previously developed methods (Schauer, Kleeman, Cass and Simoneit 2002). Elemental and organic carbon fractions were determined using the NIOSH 5040 method of thermal evolution and combustion (Birch and Cary 1996). Ionic species including sulfate, nitrate, and chloride were determined by ion chromatography. Ammonium was determined by indophenol colorimetric procedure using an Alpkem rapid flow analyzer. Trace metal concentrations were determined by instrumental neutron activation analysis (INAA).

CONCLUSIONS

The bulk chemical composition including total organic and elemental carbon, sulfate, nitrate, ammonium and chloride ions, and bulk elements such as potassium and sodium did not show conclusive differences among the biomass samples tested. Unique features, however, exist in the detailed organic characterization of the combustion smoke from the different sources. The organic compound fingerprints of the particulate matter are shown to be distinct from one another and distinct from North American wood fuels. Fecal stanols including 5 β -stigmastanol,

coprostanol, and cholestanol are found to be good molecular markers for the combustion of cowdung. Additionally, the patterns of methoxyphenols and plant sterols provide a unique signature for each biomass sample and are conducive as source apportionment tracers. Figure 1 shows the molecular markers in black and illustrates the unique profile of each biomass smoke sample.

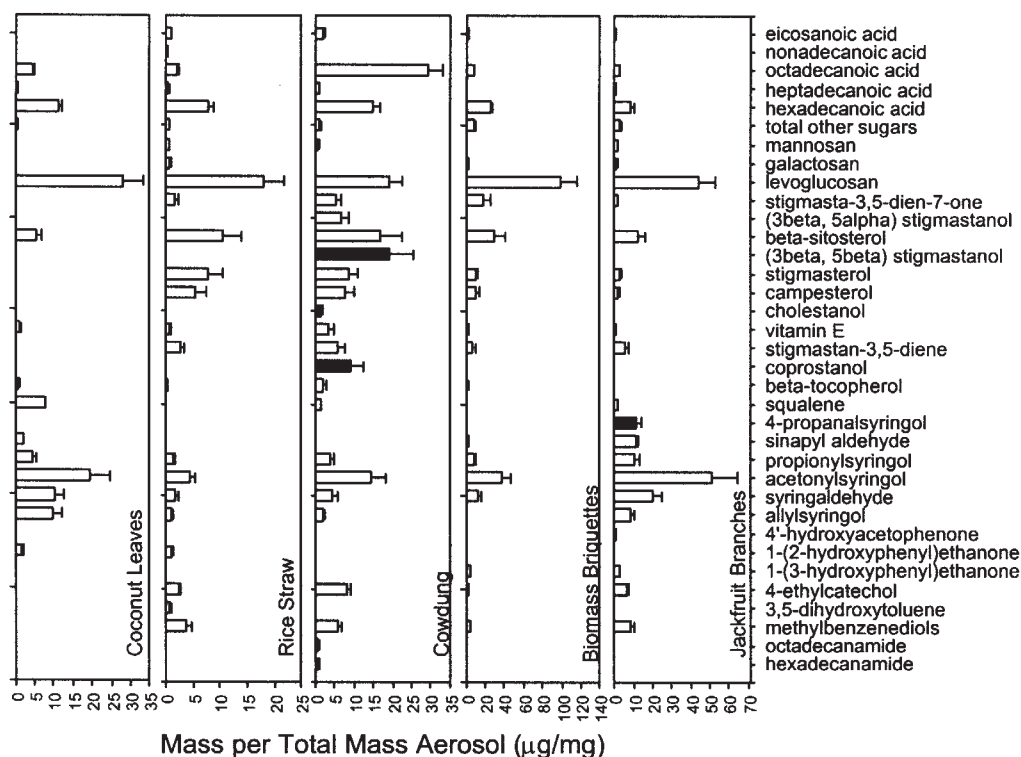


Figure 1. Source profile of select organic compounds for South-Asia biomass smoke.

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