U.P.B. Sci. Bull., Series B, Vol. 71, Iss. 1, 2009 ISSN 1454-2331

SHORT REMARQUE ON THE PROVENIENCE OF NANOPARTICLES IN ENVIRONMENTAL SAMPLES

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În această lucrare au fost studiate probe de aerosoli colectate în timpul unei campanii de vară din anul 2003. S-a urmărit analiza chimică a unor compuşi organici polari ca: mono- şi polioli, acizi dicarboxilici şi compuşi zaharidici. Aerosoli cu dimensiuni mici de particule au fost colectaţi pe filtre de cuarţ şi extraşi cu un amestec de solvenţi organici. Extractul derivatizat a fost analizat prin cromatografie de gaze cuplată cu spectrometrie de masă (GC/MS), conform unor proceduri prezentate în lucrări anterioare. Lucrarea prezintă o interpretare diferită a unor rezultate obţinute de autori.

In this work, some background aerosols, which were collected during a summer field campaign in 2003 were examined. Emphasis was given to the chemical analysis of polar organic compounds, i.e., polyols, mono-, dihydroxydicarboxylic acids and saccharidic compounds. Fine size aerosols collected on quartz fibre filters were extracted with an organic solvent mixture. The derivatised extract was analysed by gas chromatography/mass spectrometry (GC/MS), according to previously developed analytical procedures. The paper presents a different interpretation of some previously results of the authors.

Keywords: natural nanoparticles, aerosols, GC/MS method

1. Introduction

Nanotechnology is concerned with development and utilization of structures and devices with organizational features at the intermediate scale between individual molecules and about 100 nm where novel properties occur as compared to bulk materials [1]. From a chemistry and a material science perspective, the development of new products is exciting because, for a given particle-type, as the particle size is decreased within the nanoscale range, fundamental physical and chemical properties appear to change, yielding completely new and different physical/chemical properties [2].

Particle surface and interfaces are important components of nanoscale materials. As the particle size is reduced, the proportion of atoms found at the surface is enhanced relative to the proportion inside its volume, this resulting in

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nanoscale particles more reactive. Changes in surface chemistry forming the shell on a core nanoparticle (NP) may be important and relevant for health effects.

Murdock et al. [3] have focused on the importance of developing adequate physico-chemical characterization of nanomaterials prior to any kind of experiment. Indeed, in the absence of a careful and complete description of the nanoparticle-type being evaluated the results of any experiments will have limited value of significance. Moreover, the results of reported studies will not be comparable with other studies conducted with similar nanomaterials types [4].

Nanoparticles are unintentionally and intentional produced [5]. Regulation concerns especially particulate matter < 10µm in diameter (PM_{10}) in the atmosphere, the fine particle fraction defined as having diameter < 2.5 µm ($PM_{2.5}$) and ultrafine particles (UFPs) whose diameters < 0.1 µm is consistent with nanoparticle definition. UFPs dominate the number concentration of the ambient particle cloud, but represent only a small fraction of the total mass concentration. The major source of primary UFPs was road transport (60%), followed by combustion process (23%). Particles in the atmosphere are defined as either primary or secondary particles: primary particles are emitted directly from sources or processes, which might be natural (fires, volcanoes, sea spray, erosion) or anthropogenic (traffic industry) and secondary particles which are formed in the atmosphere by gas-to-particle conversions.

The largest database on the toxicity of NP has originated from the PM_{10} literature where the NP hypothesis has proved to be a powerful force for research. The idea is that combustion-derived NPs are important components that drive the adverse effects of environmental particulate air pollution on PM_{10} from several sources [6]. NPs in PM_{10} are mainly produced as a by-product of combustion and in conurbations predominantly emanate from traffic vehicles. Fly ash from the burning of pulverised coal contains a NPs fraction [7] may impact on PM_{10} effects locally. Even though combustion of coal and oil also produces NP-sized particles [8] . In addition, it needs to be mentioned that secondary UFPs do contribute to ambient UFPs exposure and the solubility of these UFPs is greater than for primary combustion derived UFPs [9] .

Nucleation has long been known as a process that results in the formation of ultrafine paticles in the atmosphere [10], the key species being sulfuric acid, nitric acid and organic gases. The lifetime of ultrafine particles in the atmosphere is typically short [11], but they become fine particles that can be transported over long distances adding regional air quality degradation [12]. In recent research [13], [14], [15], emphasis has been given to the chemical characterization and the quantitative determination of polar water-soluble organic compounds in the fine size fraction (<2.5 µm) of natural aerosols [16]. Two novel previously unidentified polar organic compounds could be characterized as the diastereoisomeric 2-methyltetrols, 2-methylthreitol and 2-methylerythritol. The

2-methyltetrols have retained the isoprene skeleton and can be explained by photo-oxidation of isoprene which is emitted in large quantities by the rain forest vegetation. Other polar organic compounds identified in rural aerosols included mono- and dihydroxydicarboxylic acids, as malic acid and 2,3-dihydroxymethacrylic acid.

In the present work, we examined some background aerosols, which were collected during a summer field campaign in 2003. Emphasis was given to the chemical analysis of polar organic compounds, i.e., polyols, mono- and dihydroxydicarboxylic acids and saccharidic compounds. Valuable information could be obtained on SOA components as well as on primary organic aerosol components. Fine size aerosols collected on quartz fibre filters were extracted with an organic solvent mixture. The extract was derivatised into trimethylsilyl derivatives and analysed by and gas chromatography/mass spectrometry (GC/MS), according to previously developed analytical procedures [17], [18].

2. Experimental

2.1. Aerosol collections and analyses and analyses for organic compounds

The collection devices included a total filter sampler, several Gent PM10 stacked filters unit (SFU) samplers and different types of cascade impactors [19] following a protocol previously established [20], [21], [22].

2.2. Reagents and apparatus

Samples were analyzed using a Polaris Q GC/ ion trap MS instrument, equipped with an external ionization source (ThermoFinnigan, San Jose, CA, USA). X-calibur version 1.2 software was used for data acquisition and processing. The chromatographic system consisted of a deactivated fused-silica precolumn (2 m x 0.25 mm i.d.) (Alltech) and a low-bleed Rtx-5MS(crossbond 5% diphenyl-95% dimethyl polysiloxane) fused-silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness) (Restek, USA).

For quantitative analysis, calibration curves were constructed by analyzing aliquots of stock solutions of standards that have been evaporated and derivatized in the fashion described above. All glassware was deactivated with 5% DMDCS in toluene (Sylon CT). All reported concentrations are corrected for procedural blanks.

The filters were extracted three times, each time for 30 minutes with 20 mL of methanol under ultrasonic agitation. Like in previous work [23], CH_3OH was always used as extraction solvent for these samples.

The quantification of 2-methyltetrols, levoglucosan, arabitol and mannitol as well as that of malic acid was based on an internal standard calibration procedure employing methyl-β-D-xylopyranoside (internal standard for 2-methyltetrols, levoglucosan, arabitol and mannitol) and deuterated malic acid (

internal standard for malic acid), whereas that of 2,3-dihydroxymethacrylic acid was based on the use of the response factor of malic acid relative to deuterated malic acid.

Dichloromethane (SupraSolv grade) was supplied by Merck and methanol (Super grade) by Lab-Scan (Dublin, Ireland).

3. Results and discussion

The sources of nanoparticles are numerous, these being directly emitted from combustion processes. The aerosol size distribution can be characterized from the point of view of emissions sources like: industrial, boilers, fireplaces, automobiles, diesel trucks and meat-cooking operations, the predominant peak in the mass distribution being observed at or below 200 nm. Examining the number distribution, many of these sources have the predominant peak much below 100 nm.

Using our GC/MS technique we were able to identify and quantify a range of sugars, sugar alcohols, anhydrosugars and carboxylic acids in the samples: the 2-methyltetrols, 2-methylthreitol and 2-methylerythritol (ratio 1:3), which are unique molecular markers for the photo-oxidation of isoprene; the hydroxydicarboxylic acid, malic acid, which has been proposed to be a late product in the photochemistry of unsaturated fatty acids [24]; levoglucosan, which is a marker for biomass smoke [25]; the sugar alcohols, arabitol and mannitol, which are markers for fungal spores [26]; the monosaccharides, glucose and fructose, which are due to plant pollen [27]; the mono- and dihydroxydicarboxylic acids: malic acid and 2,3-dihydroxymethacrylic acid.

The number concentration of ultrafine particles and $PM_{2.5}$ mass concentration are not correlated, $PM_{2.5}$ mass concentration not being a consistent surrogate for health effect end points that are associated with number concentration.

The nucleation mode particles can follow regular diurnal patterns with peak production around noon when the sunlight is intense, both from traffic emissions and from stationary sources [28]. Such production of small nanoparticles has also been reported during mornings instead of noons in Finland [29].

In particular, the mass concentration of aerosol with AD< 2.5 μm (fine fraction) was found to be consistently higher during days than during nights. Organic carbon (OC) measurements performed on the Hi-Vol filters indicated that organic matter accounted for only 3.2% of the OC. SOA formed via the gas-to-particle conversion of biogenic gases from the rainforest would be also expected to have made a sizeable contribution to the fine OC concentration.

Geographic locations seem to have a strong influence on the observed particle formation patterns.The formation of nucleation mode particles also occurs during atmospheric perturbations as removal of pre-existing aerosol or addition of gas-phase reactants from a surface source. Fig. 1 shows a typical GC/MS total ion chromatogram obtained for the trimethylsilylated extract of the fine size fraction of a day time and a night time aerosol sample and major peaks in the chromatogram correspond to the 2-metyhltetrols, 2-metylthreitol (3) and 2-methylerythritol (4). These polyols have been reported for the first time in forest aerosols and have been explained by gas-phase photo-oxidation of isoprene.

The nucleation occured in cold and humid weather and followed a diurnal pattern with the peak in the early morning hours, but these studies did not target the nucleation mode of the ultrafine particles because instrumental limitations. The time trends for the PM_2 particulate mass (PM derived from a separate filter sample) and for $PM_{2.5}$ OC, malic acid, the tetrols sum and the sugar alcohol mannitol show more variation in the time for the tetrols, for these compounds appearing clearly a tendency for higher concentrations during the day than during the night. From Table 1 it could be noticed that the contribution of the 2-metyltetrols to the $PM_{2.5}$ OC is on average 1% which is half that found for other natural aerosols. The tetrols and 2,3-dihydroxymethacrylic acid accounted, on average 2 times more to the OC during the day than during the night.

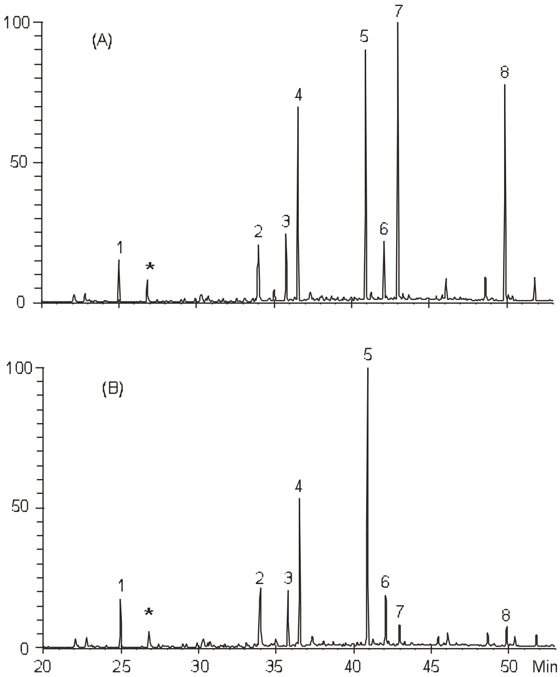

Fig.1. GC/MS TIC obtained for (A) a day- and (b) night time fine aerosol sample; **1**, 2,3-dihydroxymethacrylic acid; **2**, malic acid (+D_3-malic acid); **3**, 2-methylthreitol; **4**, methylerythritol; **5**, methylxylopyranoside; **6**, levoglucosan; **7**, arabitol; **8**, mannitol.

Table 1

Median concentrations and concentrations ranges, as derived from the $PM_{2.5}$ Hi-Vol samples, 2003 (n=25). Data for PM, OC, WSOC and EC are in $\mu g.m^{-3}$, for all other species in $ng.m^{-3}$[30]

Species	Median conc.	**Conc. Range**
OC ($\mu g.m^{-3}$)	4.2	1.94 – 6.8
WSOC	2.6	0.98 – 4.7
EC	0.20	0.077 – 0.59
Malic acid ($ng.m^{-3}$)	38	11.5 – 79
Levoglucosan	12.3	3.5 – 95
Arabitol	4.8	0.69 – 25
Mannitol	5.3	0.62 – 29
2-methylthreitol	7.5	0.79 – 34
2-methylerythritol	21	1.03 – 85
2,3-dihydroxymethacrylic acid	7.6	2.2 – 18.3

Sugars and sugar alcohols of the various compounds identified the sugars (glucose and fructose) and sugar alcohols (arabitol and mannitol) were found. Fungal fragments may also contribute to the fine aerosol fraction. In natural aerosols the sugar alcohols (arabitol and mannitol) accounted on average 4 times more to the OC during the day than during the night.

Levoglucosan which is an anhydrosugar has been previously identified as a major compound of organic particulate matter in areas impacted by wood smoke and it was found in the samples, too (Table 1). This compound is a derivative of glucose and it is formed through the pyrolysis of cellulose and hemicellulose present in the biomass. A day-night variation in concentration was observed (levoglucosan accounted, on average, 2 times more to the OC during the night than during the day). The average fine-fraction concentration of levoglucosan (the major anhydrosugar) was found to be almost 0.54% of fine OC.

The dihydroxymonocarboxylic acid 2,3-dihydroxymethacrylic acid was not observed previously and it seems to be an important secondary organic aerosol component in the forest aerosol examined. This compound can be formed from methacrolein and methacrylic acid, both volatile gas-phase oxidation products of isoprene by acid-catalysed reaction with H_2O_2 in aqueous medium. Unlike malic acid (the other important acid we detected), 2,3-dihydroxymethacrylic acid has retained the key structural features of isoprene. Regarding the mean percent carbon (and associated standard deviation) of the PM2.5 OC that is attributed to WSOC and the polar organic compounds, malic acid is the dominant organic species measured and it accounts for 0.97% ± 0.49 of the OC and 2,3-dihydroxymethacrylic acid for 0.23% ± 0.15 (Table 2). The day/night difference of the organic compounds in the attribution of the OC was also examined: for malic acid there was no difference, but 2,3-dihydroxymethacrylic acid accounted on average 2 times more to the OC during the day than during the night.

Table 2

Mean percentages (and associated standard deviations) of the OC attributable to the WSOC and to the carbon in the organic compounds, as derived from the PM2.5 Hi-Vol samples, (n = 25).

Species	Mean % ± std.dev.
WSOC	61 ± 9
Malic acid	0.97 ± 0.49
Levoglucosan	0.54 ± 0.66
Arabitol	0.19 ± 0.17
Mannitol	0.21 ± 0.22
2-methylthreitol	0.28 ± 0.22
2-methylerythritol	0.76 ± 0.57
2,3-dihydroxymethacrylic acid	0.23 ± 0.15
Sum (compounds)	3.2 ± 1.6

A phenomenon which appears in atmospheric conversion is the dissapearance of nanoparticles when high concentrations of larger particles are present and this is a problem if the concentration of ultrafine particles has to be controlled. Because a major fraction of the OC is blocked in cellular structures, either as biopolymers like proteins, cellulose and other polysaccharides or as low-molecular-weight compounds inside cells, techniques as GC/MS can never be expected to explain more than a small fraction of the organic aerosol mass. Overall, the carbon content of the organic species quantified by GC/MS accounted for an average of only 3.2% of the OC in the fine aerosol fraction. However, an important majority of the remaining OC was likely in the form of complete or fragmented primary biological structures, such as spores, pollen, algae, bacteria, leaves and insect parts.

4. Conclusions

The data set presented in this paper shows that the rural background aerosols, collected during a summer field campaign in 2003 is a complex mixture of polar organic compounds, derived primarily from biomass burning. The individual compounds identified by GC/MS analysis were: malic acid (the dominant organic species measured) which accounts for 0.97% of the OC and 2-methyltetrols, whose contribution to the $PM_{2.5}$ OC is, on average 1%, which is less that found for other natural aerosols in the same group. The average night time-to-day time concentration measured for these compounds exhibited higher concentrations in the daytime samples. This indicates that the acids may have been largely associated with biogenic SOA derived from from the photo-oxidation of VOCs emitted from the forest. Enhanced daytime concentrations have been reported previously and are generally seen as evidence for a photochemical source.

Acknowledgements: This research was partial supported by the Belgian Federal Science Policy Office during a postdoctoral visiting fellowship to A.C.Ion in the Department of Pharmaceutical Science, University of Antwerp, Belgium.

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