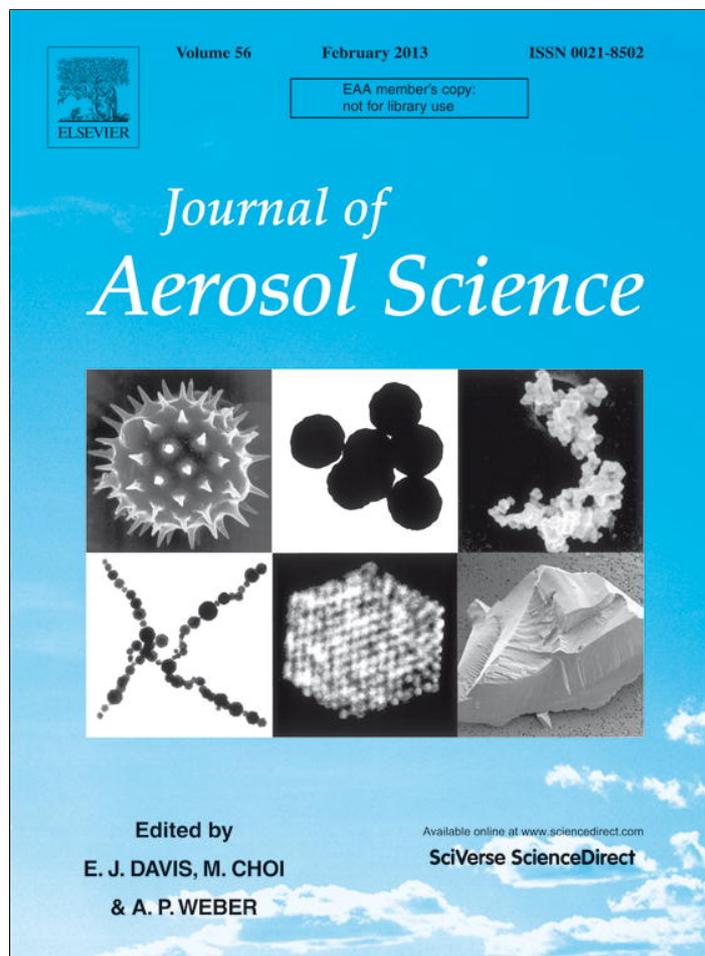


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# Mass size distribution of carbon in atmospheric humic-like substances and water soluble organic carbon for an urban environment

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## ABSTRACT

Aerosol samples were collected with a micro-orifice uniform deposit impactor in an aerodynamic diameter (AD) range of 0.5–10  $\mu\text{m}$  in central Budapest, Hungary for 12 days. Aqueous aerosol extracts and atmospheric humic-like substances (HULIS) were obtained from the combined aerosol samples for each impactor stage. Water-soluble organic carbon (WSOC) and carbon in HULIS (HULIS-C) were measured in the samples with a total organic carbon analyzer. The analytical data were inverted into semi-smooth mass size distributions, and modal parameters were derived. The size distributions for both WSOC and HULIS-C consisted of three peaks: a coarse mode and two accumulation submodes. The geometric mean AD for the coarse mode was 6.4  $\mu\text{m}$  for both WSOC and HULIS-C. Contribution of the coarse mode to the total concentration of WSOC and HULIS-C were substantial and similar for both components, i.e., approximately 20%. The splitting of the accumulation mode into condensation and droplet submodes was explained by water processing of aerosol particles in the air. The geometric mean ADs of the condensation submode for the WSOC and HULIS-C were 0.37 and 0.31  $\mu\text{m}$ , respectively, and the droplet submode appeared at 1.72 and 1.22  $\mu\text{m}$ , respectively. The condensation submode was larger than the droplet submode by similar ratios of 1.7–1.8 for both WSOC and HULIS-C. The relative concentrations of the two submodes were likely influenced by local meteorology, in particular by relative humidity, pollutant gases, and water uptake properties and aging of fine particles.

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## 1. Introduction and objectives

Water-soluble chemical compounds including both inorganic and organic constituents in fine-sized atmospheric aerosol particles play an important role in the biogeochemical cycling of water and other substances (Ramanathan, Crutzen, Kiehl, & Rosenfeld, 2001; Mahowald, 2011), climate (Facchini, Mircea, Fuzzi, & Charlson, 1999), and several other environmental processes (Fuzzi et al., 2006). The effects of inorganic salts are well documented, while the organic compounds still represent a challenge. This is caused by the large number (up to several thousands), structural complexity and similarity of the molecules involved, and by the difficulties associated with the collection, separation and analytical methods available. Instead of the quantification at the molecular level, the organic matter is usually divided into groups

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which are subsequently utilized to characterize the bulk organic material or its specific chemical fractions. Organic carbon (OC) and elemental carbon (EC) are the main groups. The former is frequently divided further into water-soluble and water-insoluble chemical fractions. The water-soluble organic fraction is usually quantified by water-soluble organic carbon (WSOC). Some water-soluble organics have unique features with respect to inorganic salts, e.g., they can substantially influence the surface tension of the gas-liquid interface of solution droplets in the air. It is a crucial property in cloud droplet formation and water uptake. One of the most important atmospheric surfactants are humic-like substances (HULIS; for a review, see [Graber & Rudich, 2006](#)). They are defined operationally as a subgroup of water-soluble organic matter. HULIS are regarded to be polymeric material comprised of aromatic compounds that have aliphatic chains with oxygenated functional groups. Formation mechanisms, physicochemical properties and chemical composition of HULIS and water-soluble organic matter are being studied increasingly (e.g., [Decesari, Facchini, Fuzzi, & Tagliavini, 2000](#); [Decesari et al., 2001](#); [Decesari et al., 2006](#); [Kiss et al., 2003](#); [Samburova, Zenobi, & Kalberer, 2005](#); [Tagliavini et al., 2005](#); [Salma, Ocskay, Chi, & Maenhaut, 2007](#); [Salma, Ocskay, & Láng, 2008](#); [Salma et al., 2010](#); [Ziese et al., 2008](#); [Claeys et al., 2012](#)).

Size distributions belong to the key properties of ambient aerosol particles. They provide valuable information on emission sources, formation and transformation processes in the air, dry deposition, atmospheric residence times, and some surface-related properties. Mass size distribution of WSOC was studied in different environments ([Decesari et al., 2001](#); [Matta et al., 2003](#); [Yu, Yang, Zhang, & Lau, 2004](#); [Huang, Yu, He, & Yuan, 2006](#); [Timonen et al., 2008](#); [Agarwal, Aggarwal, Okuzawa, & Kawamura, 2010](#); [Lin, Huang, He, & Yu, 2010](#)), while there is very limited information on the size distribution of HULIS ([Lin et al., 2010](#)). To follow up and complement these studies, mass size distributions of WSOC and HULIS-C were determined as semi-smooth curves in an aerodynamic diameter (AD) range of 0.5–10  $\mu\text{m}$  for an urban environment (central Budapest, Hungary), their fine structure were identified, the modal parameters were derived, and the identified modes were related to production and transformation processes.

## 2. Methods

### 2.1. Collection of aerosol samples

An aerosol sample collection and measurement campaign was conducted in central Budapest (5, Rákóczi Street, latitude 47°29'37" N, longitude 19°03'38" E, altitude 111 m above the mean sea level) at a kerbside site within a street canyon from 23 April through 5 May 2002 ([Salma et al., 2004, 2005](#)). Mean traffic flow of motor vehicles in both directions at the site (obtained from loop counting) over the campaign was  $2.0 \times 10^3 \text{ h}^{-1}$ . The samplings and measurements were performed at a height of about 7.5 m above the street level. The location and time period were characterized by median concentrations of particulate matter (PM) mass, OC and EC of 53, 10.6 and 3.5  $\mu\text{g m}^{-3}$ , respectively in the  $\text{PM}_{10}$  size fraction. The corresponding median concentrations for the  $\text{PM}_{2.5}$  size fraction were 22, 6.9 and 3.3  $\mu\text{g m}^{-3}$ , respectively.

The samples dealt with in the present study were collected with a micro-orifice uniform deposit cascade impactor (MOUDI, [Marple, Rubow, & Behm, 1991](#)). It has 11 impaction stages and a backup filter stage. The cut-off ADs for the impaction stages are 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.603, 0.301, 0.164, 0.094 and 0.053  $\mu\text{m}$ . The device operates at a flow rate of 30  $\text{L min}^{-1}$ . It had no additional inlet, and was operated with its inlet facing up. The samples were collected on ungreased 37-mm diameter Al foils (4  $\text{mg cm}^{-2}$ ) for the impaction stages, and on Whatman QM-A quartz fibre backup filters. The foils and filters were pre-heated at 550 °C for 24 h to remove organic contaminants prior to sampling. The samples were collected separately over daytime periods (from about 7:00 to 19:00 local daylight saving time, UTC+2) and nights (from about 19:30 to 6:30). A total of 11 samples for daytime periods and 12 samples for nights together with 6 field blank samples were obtained. The samples were placed into polycarbonate Petri-slide dishes, and were transported and stored in a freezer. Use is also made of some complementary atmospheric concentrations for comparative purposes that were obtained from collections in parallel with the MOUDI samples by a high volume (HiVol) sampler on pre-heated Pallflex quartz fibre filters. More information on the location, campaign and actual collections can be found in [Salma et al. \(2004, 2005, 2007\)](#) and [Maenhaut et al. \(2005\)](#).

### 2.2. Sample treatment and chemical analysis

The aerosol samples obtained on the backup filter and on the first impaction stage (with the largest cut-off diameter) were not treated because of the undefined size interval for these two stages, and large relative uncertainty due to sampling artifacts, in particular for the quartz fibre filters. The first impaction stage served as an inlet with a well-defined cut-off value. The aerosol samples collected on the other ten impaction stages were processed. Aerosol mass was obtained by weighing each impaction foil before and after sampling with a microbalance with a sensitivity of 1  $\mu\text{g}$ . The substrates were pre-equilibrated before actual weighing at a temperature of 20 °C and relative humidity of 50% for at least 24 h. Half sections of each foil were treated. The further procedure was performed eight years after their collection. It is expected that the samples can be kept in freezer for many years without substantial changes in their major properties since, e.g., HULIS belong to the most stable organic constituents of aerosol particles due to their aromaticity ([Salma et al., 2008](#)). There were 23 sections that corresponded to identical stage numbers. These sections were combined and processed together in order to increase the absolute amount of carbonaceous species of interest for sample treatment and chemical

analysis. The foils were cut into pieces, and these were extracted jointly in two steps with approximately 20 mL of high-purity reagent Milli-Q water with occasional stirring and hand-shaking at room temperature for 36 h. The foil-water systems were allowed to stand for 30 min at the end of the extraction procedure. The extracts were filtered through a syringe PVDF membrane filter (Millipore, USA) with a pore size of 0.22  $\mu\text{m}$  to remove the suspended insoluble particles. A volume of 2.5 mL was taken out from each aqueous solution to determine its WSOC content. The remaining solution was utilized to separate HULIS by a one-step extraction method (Varga, Kiss, Ganszky, Gelencsér, & Krivácsy, 2001; Kiss et al., 2002; Salma et al., 2007, 2008) on pre-conditioned solid-phase extraction cartridges (hydrophilic-lipophilic balanced water-wettable copolymer columns, Oasis, packing mass 200 mg, Waters, USA). The isolation method was optimized to separate the fraction that exhibits the key spectral properties of HULIS, i.e., more than 90% of the fluorescence activity and 70% of the UV activity for humic and fulvic acids (Varga et al., 2001; Lin et al., 2010). The pH of the filtrates was adjusted to 2 with HCl. Organic compounds with acidic functional groups that are protonated at this pH (including most aromatic acids, phenols, organic nitrates, aliphatic mono-, di- or tricarboxylic acids with more than 4–5 C atoms) are retained by the column, while the inorganic ions and the organic compounds that are very hydrophilic due to the presence of strong polar functional groups (including saccharides, amines, aliphatic mono-, di- or tricarboxylic acids with less than 3–4 C atoms) pass into the effluent. The exposed column was rinsed with water to remove the remaining inorganic species and dried with nitrogen gas stream. The retained organics were eluted with methanol, and the eluents were evaporated to dryness with gentle nitrogen stream. The mass of the resulting HULIS samples was not measurable by gravimetry. The HULIS samples were kept in a refrigerator until dissolution.

The aerosol aqueous extracts were diluted to 5 mL, and the HULIS samples were dissolved in 1.7 mL of Milli-Q water. The solutions were subjected to total organic carbon (TOC) analysis using Multi N/C 2100S TOC analyzer (Analytik Jena, Germany). The TOC in the aerosol aqueous extracts was determined in two steps as the difference between the total carbon and inorganic carbon, while the TOC in the HULIS solutions was derived as the total carbon. The negligible amount of inorganic carbon in the HULIS solutions relative to the inorganic carbon in the added water was checked and confirmed occasionally. The injections for TOC analysis were repeated 3 times with a volume of 500  $\mu\text{L}$  each, and their mean concentration was further utilized in the evaluations. The relative uncertainty of the mean was estimated to be less than 3%. The TOC for the aerosol aqueous extracts represented the WSOC, while the TOC for the HULIS solutions represented the HULIS-C. The blank foils were treated and analysed identically to the sample foils, and the results obtained were used as blank values for WSOC and HULIS-C. The analytical results were expressed in atmospheric concentrations (in  $\mu\text{g m}^{-3}$ ).

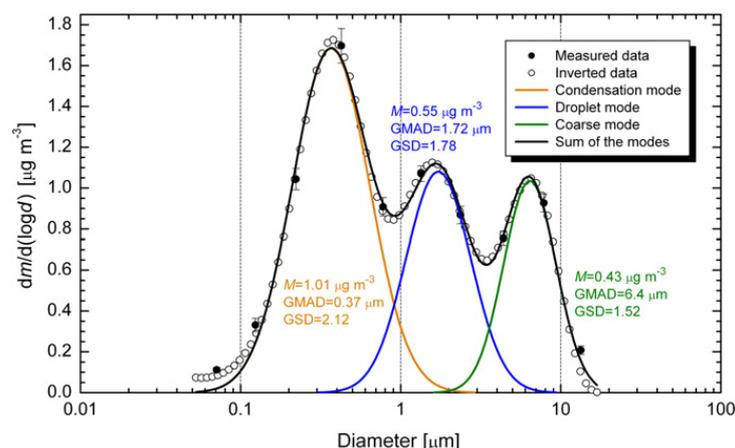
### 2.3. Evaluation of analytical results

It was estimated earlier that the relative uncertainty of concentrations due to sampling by cascade impactors is 10–15% (Maenhaut, Ptasiński, & Cafmeyer, 1999). These values were combined according to the propagation of uncertainty with the standard deviation of the analytical concentrations in order to obtain more realistic overall uncertainties. The combined values were utilized as standard deviation of the concentrations. The experimental data were subjected to mathematical inversion by the computer program MICRON (Winklmayr, Wang, & John, 1990; Wolfenbarger & Seinfeld, 1990). The program makes use of the actual collection efficiency curves of the individual impactor stages to construct response functions for the stages. The collection efficiency curves utilised were supplied by the manufacturer, but they were fine-tuned according to their experimentally determined 50% cut-off values. The inversion is based on constrained regularisation, and produces a semi-smooth size distribution, i.e., 80 data points. Finally, the inverted data were fitted by log-normal functions, and the concentrations, geometric mean ADs (GMADs) and geometric standard deviations (GSDs) of the contributing modes were derived.

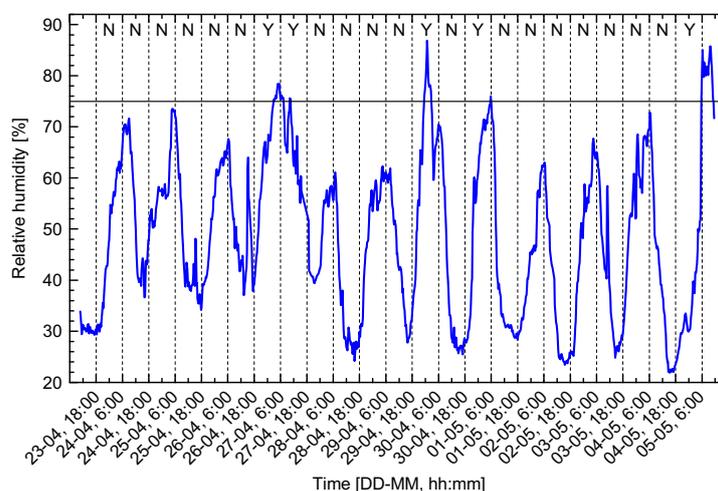
## 3. Results and discussion

### 3.1. Mass size distribution of WSOC

The mass size distribution of WSOC obtained from the combined impactor stages is shown in Fig. 1. It represents the average size distribution for 12 days. The distribution consists of three modes. The coarse mode has a GMAD of 6.4  $\mu\text{m}$ , and its concentration represents 21% of the total WSOC concentration. This relative contribution is considerable. The WSOC-containing coarse particles are usually associated with mechanical disintegration processes such as soil erosion and dispersion, and resuspension. In cities, both natural and anthropogenic processes promote these emission sources. The coarse particles are mostly of local origin. The accumulation mode consists of a well developed doublet: a condensation submode and a droplet submode. The splitting of the accumulation mode into two submodes was observed and explained earlier for the major inorganic ions (Hering & Friedlander, 1982; John, Wall, Ondo, & Winklmayr, 1990; Hering et al., 1997) and some chemical elements (Salma et al., 2005). In short, it is caused by water activation of condensation mode particles under high relative humidity (RH) conditions to form cloud droplets, followed by dissolution of some atmospheric gases (e.g.,  $\text{SO}_2$ ) into the droplets, and by aqueous-phase chemical reactions leading to non- or less-volatile products. If the ambient RH decreases at a later time and the droplets evaporate, the remaining solid particles will have slightly larger diameters than the original dry particles (Meng & Seinfeld, 1994; Kerminen & Wexler, 1995). The GMADs for the condensation and droplet submodes are 0.37  $\mu\text{m}$  and 1.72  $\mu\text{m}$ , respectively, and 51% and 28% of the total WSOC



**Fig. 1.** Mass size distribution of water-soluble organic carbon (WSOC) for a kerbside site in Budapest in springtime. Mass concentration ( $M$ ), geometric mean aerodynamic diameter (GMAD) and geometric standard deviation (GSD) for the condensation, droplet and coarse modes are also indicated. The error bars indicate one standard deviation.



**Fig. 2.** Time variation of relative humidity over the sampling period. Relative humidity of 75% is indicated by a horizontal line. The half-day time periods that correspond to the individual sampling intervals were classified as no water processing (N) and possible water processing (Y).

concentration are associated with the condensation and droplet submodes. The structure of the present mass size distribution of WSOC is in line with earlier results (e.g., Timonen et al., 2008; Lin et al., 2010). It has to be mentioned that the earlier distributions were mostly presented as column graphs, and, therefore, splitting of the accumulation mode and in particular, the relative concentrations of the submodes can only be assessed by visual inspection. The absolute modal concentrations depended sensitively on the actual type of the sampling environment (Salma et al., 2007, 2010).

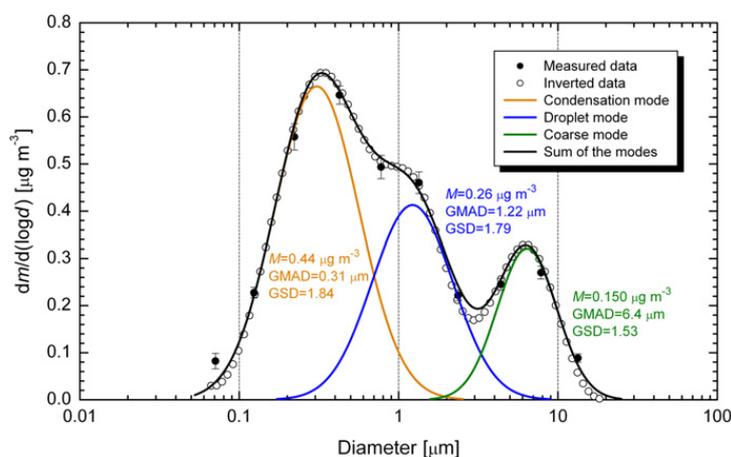
The appearance of the droplet submode is related to high ambient RHs and water uptake properties of accumulation-mode particles. The time variation of the RH as 15-min averages over the time period studied is shown in Fig. 2. The sampling interval can be divided into two major parts from the meteorological point of view (Salma et al., 2004). The first 5 days were characterised by changing, cloudy and wet weather conditions which were finished by a cold front that passed the city on 27 April. Over the last 7 days, the weather was generally more stable, dry and warm with clear sky. It was only disturbed by a fast-moving cold front with rain showers that passed the city during the night of 29 April. At the end of the campaign, it was raining again. Half-day time periods (from 6:00 to 18:00 and from 18:00 to 6:00, which correspond to the aerosol sampling intervals) with high RHs were classified and counted. Relative humidity of 75% was selected as a lower estimate of the critical value for water uptake (Ziese et al., 2008). Similarly, half-day time periods with RHs below this value were also counted. The number of the latter half-days, thus probably with no water processing was 18, while the number of periods with high RHs, thus with expected water processing was 5. The relative WSOC concentration for the non-processing periods to the overall WSOC concentration was approximately 85%. The individual WSOC concentrations used here were derived from the HiVol aerosol samples collected in parallel with the MOUDI samples, and were obtained by TOC analysis (Salma et al., 2007). The relative WSOC concentration obtained in this way (as a lower estimate) is substantially larger than the contribution of the condensation submode, which was 51%. This can indicate indirectly that the water processing actually activated a smaller part of fine aerosol particles. Water uptake is also influenced by other

aerosol constituents and mixing state of the particles (Burkhart et al. 2012), which can be unfavourable for urban aerosol (see section 3.3.). Another possibility that the water processing took place from smaller RHs than 75% is not probable.

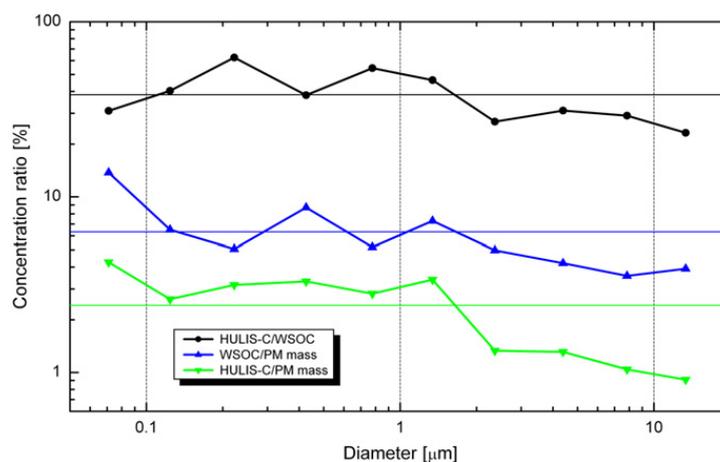
### 3.2. Mass size distribution of HULIS-C

The mass size distribution of HULIS-C derived from the combined impactor stages is shown in Fig. 3. It represents the average size distribution for 12 days in spring. The structure of the distribution is similar to that for the WSOC. This is expected since HULIS was shown to make up the major mass fraction of the water soluble organic matter (e.g., Salma et al., 2007 and references therein). The distribution consists of three modes. The GMAD for the coarse mode is identical to that of the WSOC; it is 6.4  $\mu\text{m}$ . This mode contained 18% of the total water-soluble HULIS-C concentration. It implies that the coarse-mode HULIS definitely represent a non-negligible and important share of atmospheric HULIS in cities. A simple explanation of their major sources is that they were emitted directly by mechanical disintegration processes such as soil erosion and dispersion, and resuspension. It remains, however, an open question whether the coarse-mode HULIS indeed exhibit the same or very similar optical and thermal properties, and mass spectrum as the humic matter present in the soil and waters. The amount of the size-fractionated HULIS samples left, unfortunately, did not make it feasible to accomplish the necessary experiments to find an explicit answer, and further studies are desired. The coarse-mode contributions for the WSOC and HULIS-C agree within the uncertainty interval of 5–10%. The accumulation mode is split into a condensation and a droplet submode similarly to WSOC. The GMADs for the two submodes are 0.31  $\mu\text{m}$  and 1.22  $\mu\text{m}$ , respectively, and the submodes make up 51% and 31%, respectively of the total water-soluble HULIS-C concentration. Several formation mechanisms were proposed for the fine-sized HULIS. They include both high-temperature primary emissions and chemical reaction pathways in the air. Incomplete breakdown of polymeric plant matter in biomass burning contributes to the former possibility (Mayol-Bracero et al., 2002). Secondary HULIS can be formed by photochemical reactions of precursor volatile organic compounds (VOCs) followed by oligomerisation of the products (Claeys et al., 2004; Gelencsér et al., 2004; Kroll & Seinfeld, 2008). Isoprene, monoterpenes and sesquiterpenes are the most abundant relevant biogenic VOCs in forested areas. In cities, road traffic is thought to contribute notably to the production of secondary HULIS by emitting precursor VOCs such as aromatics, e.g., benzene, toluene, ethyl benzene and xylenes (Hoffmann & Warnke, 2007). All the processes listed above together with the long-range transport produced (at least) approximately 80% of the total water-soluble HULIS concentration in central Budapest.

According to our knowledge, there is only one article presenting explicit mass size distributions of HULIS (Lin et al., 2010). They were obtained in agricultural areas in time periods with visible presence of biomass burning aerosol, which originated from direct crop residue burning emissions in southern China. Those distributions consisted of condensation, droplet and coarse modes - similarly to our curve - with GMADs between 0.23–0.28  $\mu\text{m}$ , 0.63–0.87  $\mu\text{m}$  and 4.0–5.7  $\mu\text{m}$ , respectively. Our GMADs for the modes are near the higher limit of the intervals. Considering that size distributions have a logarithmic diameter scale, a factor of (at most) two does not really mean a huge difference. There can be several effects and local or regional circumstances influencing this shift. Modal concentrations for the Chinese samples were substantially larger than our values since biomass burning is known to emit large amounts of HULIS (Salma et al., 2010). It is more relevant, therefore, to compare relative modal concentrations. Our contribution of the coarse mode (18%) is larger than the Chinese mean values of 7% (Lin et al., 2010). The difference can be explained by the expectation that biomass burning conducted on a cement threshing floor remobilizes a smaller portion of soil particles than the portion which is generally present in cities. The largest distinction between the two distributions is that for the Chinese samples, the droplet submode dominated the size distributions with 81% of the total concentration, and the contribution of the condensation



**Fig. 3.** Mass size distribution of carbon in water-soluble atmospheric humic-like substances (HULIS-C) for a kerbside site in Budapest in springtime. Mass concentration ( $M$ ), geometric mean aerodynamic diameter (GMAD) and geometric standard deviation (GSD) for the condensation, droplet and coarse modes are also indicated. The error bars indicate one standard deviation.



**Fig. 4.** Concentration ratios of HULIS-C to WSOC, HULIS-C to PM mass, and WSOC to PM mass for MOUDI impactor stages. The mean ratios over all stages (for the PM<sub>13</sub> size fraction) of 38%, 6.3% and 2.4%, respectively are indicated by thin horizontal lines.

mode was minor, 12%. Larger SO<sub>2</sub> concentrations are expected in Southern China than in Hungary, which in combination with typically larger RHs (see section 3.1) add to the explanation of the different relative contributions of the condensation and droplet submodes for the two environments.

### 3.3. Atmospheric concentrations and abundances of WSOC and HULIS-C

The individual concentrations summed over all impactor stages represent atmospheric concentrations for the PM<sub>13</sub> size fraction, while the sums over the last seven impactor stages express concentrations for the PM<sub>2.4</sub> size fraction. For the PM<sub>2.4</sub>-fraction WSOC, an atmospheric concentration of 1.68 μg m<sup>-3</sup> was derived in this way. The value agrees reasonably well with the mean PM<sub>2.5</sub>-fraction WSOC concentration of 2.3 μg m<sup>-3</sup> obtained for HiVol samples collected in parallel with the cascade impactor samples. The atmospheric concentration of the PM<sub>2.4</sub>-fraction HULIS-C was calculated similarly, and the sum was converted to HULIS concentration by an organic matter-to-organic carbon mass ratio of 1.81 derived specifically for PM<sub>2.5</sub>-sized urban-type HULIS (Salma et al., 2007). An atmospheric concentration for the PM<sub>2.4</sub>-fraction HULIS of 1.31 μg m<sup>-3</sup> was obtained in this way. The result is comparable but somewhat smaller than the range of ordinary HULIS concentrations of 2.2–4.7 μg m<sup>-3</sup> determined earlier for central Budapest (Salma et al., 2007, 2008, 2010). It is also worth noting that the mean PM mass concentrations for the PM<sub>13</sub> and PM<sub>2.4</sub> size fractions were 41 and 25 μg m<sup>-3</sup>, respectively, which agree well with the filter-based results (cf. section 2.1.).

Concentration ratios of HULIS-C/WSOC, WSOC/PM mass and HULIS-C/PM mass for all impactor stages are shown in Fig. 4. It is seen that HULIS-C has the largest contribution of 63% to the WSOC in the peak region of the condensation mode, while its share is the smallest, i.e., about 31% for the coarse particles. This is in line with the formation concept of HULIS and water-soluble organic matter. The mean HULIS-C/WSOC, WSOC/PM mass and HULIS-C/PM mass ratios over all impactor stages were 38%, 6.3% and 2.4%, respectively, while the mean ratios for the PM<sub>2.4</sub> size fraction were 43%, 7.4% and 3.0%, respectively. The former HULIS-C/WSOC data (43%) agrees well with the available earlier ratios of approximately 47% derived for the PM<sub>2.5</sub>-fraction filter based samples collected at the same location (Salma et al., 2007, 2008), and it is substantially smaller than for typical biomass burning of 60% (Lin et al., 2010), and 63–76% (Salma et al., 2010). The difference can be explained by different formation processes of HULIS and water-soluble organic matter in urban and biomass burning environments. In Budapest, the contribution of WSOC to the OC mass for the PM<sub>2.5</sub> size fraction was found to have an increasing tendency from 20% (for a road tunnel) to 49% (for a near-city background), with a range of 27–34% derived for the central urban part (Salma et al., 2001). The small share of WSOC seems to be a typical urban feature. For example, Viana et al. (2007) similarly found for PM<sub>2.5</sub> size fraction in Amsterdam (The Netherlands), Ghent (Belgium) and Barcelona (Spain) average WSOC/OC ratios of 33%–40% in winter, and of 34%–43% in summer. Favez et al. (2008) obtained a yearly average WSOC/OC ratio of 33% for total suspended particulates in Cairo megacity (Egypt). At Dar es Salaam (Tanzania), mean WSOC/OC ratios of 29% and 35% were obtained in PM<sub>10</sub> and PM<sub>2.5</sub> size fractions, respectively, during dry and wet season campaigns (Mkoma et al., 2010).

## 4. Conclusions

The mass size distributions of WSOC and water-soluble HULIS-C for an urban environment in springtime contained three modes. About 80% of both the WSOC and HULIS-C concentrations were apportioned to fine particles. The accumulation mode was split into two submodes due to water processing, similarly for major ionic constituents. Abundances of the submodes likely depend on ambient RHs, water uptake properties and age of particles, and on pollutant gases. Therefore, the extent of the environmental and climate importance of water-soluble organic aerosol and

water-soluble HULIS may be influenced by location, type of the environment and season since it is the fine size fraction that contains effective cloud condensation nuclei.

The contribution of coarse particles to the total atmospheric concentrations for both WSOC and HULIS-C was considerable. Research interests in atmospheric HULIS (and partly in WSOC) have focused on fine-fraction bulk matter because it is this size fraction that is expected to have larger relevance. Previous studies documented both remarkable similarities and differences between the fine-sized HULIS on one side, and terrestrial and aquatic humic and fulvic acids on the other side. It was demonstrated for instance that the fine-sized HULIS have much smaller average molecular mass, different spectroscopic (mainly UV absorption and fluorescence) properties and thermal behaviour than humic or fulvic acids of terrestrial and aquatic origin. For the time being, there is no information available on the properties of coarse-fraction HULIS, but they can be discrepant from the fine-sized HULIS since their formation procedures differ from each other. Further studies are required, however, to investigate the similarities and differences between the coarse-fraction HULIS and terrestrial or aquatic humic matter. It is also realised that the smaller atmospheric residence time and less intense optical interactions of coarse particles can limit their atmospheric relevance.

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