

Sampling artefacts, concentration and chemical composition of fine water-soluble organic carbon and humic-like substances in a continental urban atmospheric environment

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Abstract

Water-soluble organic carbon (WSOC) and atmospheric humic-like substances (HULIS) were investigated for urban PM_{2.5}-fraction aerosol samples, which were collected with the tandem filter method on quartz fibre filters over a non-heating spring season. Sampling artefacts were of importance for all organic chemical fractions, and the back-to-front-filter concentration ratios were on average 28% for WSOC and 17% for HULIS and organic carbon (OC). The difference in the ratios indicates that the water-soluble organics play a more important role in adsorptive artefacts than the organic matter (OM) in general. The results emphasize the need for an appropriate sampling and/or correction method for measuring particulate organic substances in urban environments. The corrected atmospheric concentration of HULIS, obtained by subtracting the back-filter from the front-filter data, was on average $2 \mu\text{g m}^{-3}$; which represented 6% of the mean PM_{2.5} particulate mass, and it made up 45% of the secondary OC. The HULIS carbon accounted for 20% of the OC and 62% of the WSOC, while WSOC made up 32% of OC. The major element composition of HULIS, expressed in molar ratios, was C:H:O:N = 22:32:10:1. The molar H/C ratio of 1.49 implies the presence of unsaturated organic compounds, although these were depleted in comparison with rural aerosol or standard fulvic acids. The molar O/C ratio of 0.47 indicates the existence of oxygenated functional groups; comparison to rural aerosol suggests that the (fresh) urban-type aerosol is less oxidized (and, therefore, less water soluble as well) than the rural one. The OM/OC mass conversion factor for the isolated (water-soluble) HULIS was derived to be 1.81. It was inferred from comparisons with published data that there are substantial differences in abundance and chemical composition of HULIS for different environments.

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1. Introduction

It is increasingly recognized that atmospheric humic-like substances (HULIS) play an important

role in the atmospheric system (Gelencsér et al., 2004; Baltensperger et al., 2005; Sun and Ariya, 2006; Kanakidou et al., 2005). They are present ubiquitously in the continental atmospheric aerosol, and they make up a major fraction of the continental fine-fraction water-soluble organic compounds (references in Table 2). They exhibit strong surface activity

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(Facchini et al., 1999a, 2000; Mircea et al., 2002; Kiss et al., 2005; Dinar et al., 2006; Salma et al., 2006a) by which they influence the properties of the gas–liquid interface of droplets, and the multiphase or liquid-phase water chemistry. Consequently, they alter cloud droplet nucleation, growth, and critical super saturation, which influence substantially the indirect climate forcing of atmospheric aerosol (Facchini et al., 1999a), and the hydrological cycle (Ramanathan et al., 2001). HULIS are regarded to be an atmospheric polymeric material with strong polar and weak (poly)acidic, and chromophoric properties, and which are comprised primarily of a complex multi-component mixture of aromatic compounds that bear aliphatic chains with carboxyl, hydroxyl, carbonyl, methyl or phenol terminal groups (Decesari et al., 2000; Krivácsy et al., 2000; Kiss et al., 2002; Graham et al., 2002; Cappiello et al., 2003; Gelencsér, 2004). They are usually defined operationally by class separation based on their solubility, polarity or acidic properties. The fractions isolated by the different methods partially overlap, which is characteristic of other natural humic substances as well. The existing isolation protocols, even those that are based on water extraction (Decesari et al., 2000; Krivácsy et al., 2001; Varga et al., 2001; Duarte and Duarte, 2005; Limbeck et al., 2005; Dinar et al., 2006), unfortunately, have not been compared yet, but they are believed to target broadly the same generic class of water-soluble compounds. Characterization of HULIS has indeed been performed most frequently on the aqueous aerosol extracts since it is this chemical fraction that is of global importance due to its climatic and environmental impacts. Nevertheless, a subset of HULIS does remain in the fraction that is not extractable in water (Mukai and Ambe, 1986; Havers et al., 1998; Mayol-Bracero et al., 2002). Furthermore, there is no evidence that water-soluble HULIS isolated from aerosol samples collected in different environments of the world or seasons are actually the same class of compounds, and generalization of the results obtained for one environment to the other ones should be considered with caution. Several sources of HULIS were detected in the ambient atmosphere and smog chamber experiments, including irreversible secondary reactions or multiphase cloud processes of precursors from biogenic sources (e.g., isoprene and terpenes, Jang and Kamens, 2001; Gelencsér et al., 2002, 2004; Limbeck et al., 2003; Iinuma et al., 2004; Kalberer et al., 2004; Baltensperger et al., 2005), from biomass burning emissions (Mayol-Bracero et al., 2002; Samburova

et al., 2005b), and from anthropogenic emissions in polluted environments (mainly aromatic precursors and oxidation products of soot with ozone (Decesari et al., 2001)). Nevertheless, the chemical mechanisms of their formation (e.g., by oligomerization, polymerization or polyaddition) are poorly understood and still debated (Gelencsér, 2004; Baltensperger, 2005). In addition, the chemical composition, physico-chemical properties of HULIS for specific environments, and their worldwide distribution are often poorly characterized by the existing data sets or they are lacking, and the field is still subject to conceptual and experimental uncertainties (Fuzzi et al., 2001; Graber and Rudich, 2006).

Within an urban aerosol research project, aerosol samples were collected with several filter-based devices and cascade impactors, and some in situ aerosol measurements were performed in downtown Budapest, Hungary, in spring 2002, mainly to accomplish a comprehensive characterization of carbonaceous constituents (Salma et al., 2004, 2006a), and to arrive at aerosol chemical mass closure (Maenhaut et al., 2005). The median mass concentrations of the particulate matter (PM) were 30 and $20 \mu\text{g m}^{-3}$ for the PM_{10–2.0} and PM_{2.0} size fractions, respectively. On average, 43% of the PM_{2.0} mass was attributed to organic matter (OM, $\text{OM} = 1.4\text{OC}$, where OC is organic carbon, and 1.4 is the OM-to-OC mass conversion factor, see later), 21% to elemental carbon (EC), 14% to crustal matter, 13% to sulphate, 6% to nitrate, and 6% to ammonium (Maenhaut et al., 2005). The mean contribution and associated standard deviation of the secondary organic aerosol (SOA) to the OM in the PM_{2.5} size fraction over daylight periods were derived to be $(37 \pm 18)\%$ (Salma et al., 2004). The main objectives of the present paper are to reveal and discuss the sampling artefacts of water-soluble organic carbon (WSOC) and HULIS in the urban environment, to report the carbon mass balance, and, in particular, the atmospheric concentration for WSOC and HULIS, to interpret the abundance of WSOC and HULIS, to present the main element composition of HULIS, and to discuss its structural consequences.

2. Methods

2.1. Collection of aerosol samples

The aerosol samples were obtained at a kerbside site within a street canyon at a height of about 7.5 m above the street level in downtown Budapest,

Hungary (5, Rákoczi Street, latitude 47°29'37"N, longitude 19°03'38"E, altitude 111 m above the mean sea level) during an intensive field campaign from 23 April to 5 May 2002 in the non-heating season. The mean number of motor vehicles passing the street in both directions per 15 min was obtained on line from loop counting, and ranged from 86 to 766 with an overall mean of 513. Several aerosol samplers and in situ instruments were deployed in the campaign. For the purposes of the present study, PM_{2.5}-fraction aerosol samples taken by a high-volume dichotomous virtual impactor (HiVol) sampler (Solomon et al., 1983) in the high-air-flow sampling line were used. The samples were collected by the tandem filter method, i.e. on sets of two (front and back) Gelman Pallflex quartz fibre filters type 2500QAT-UP of the same lot number in series directly on top of each other (Fitz, 1990; Kirchstetter et al., 2001) in order to study and correct for the sampling artefacts for organic constituents. The filters had been pre-baked at 550 °C for 24 h prior to sampling to remove possible organic contaminants. The exposed area of the filters was 61.5 cm², and the mean air flow rate was 308 l min⁻¹ (thus, the average air face velocity was 83 cm s⁻¹). A total of 11 filter pairs for daytime periods (from about 7:00 to 19:00 local daylight saving time) and 12 filter pairs for nights (from about 19:30 to 6:30), together with six field blanks, were obtained. The samples were placed in pre-baked aluminium foils, and were frozen during transport and storage. More information on the collections, samples, meteorological conditions, analyses, aerosol properties, source types and their relationships can be found elsewhere (Salma et al., 2004, 2005, 2006; Salma and Maenhaut, 2006b; Maenhaut et al., 2005).

2.2. Isolation of water-soluble HULIS

The HULIS samples were isolated by a modified one-step version of a solid-phase extraction (SPE) protocol based on molecular interactions of non-dissociated species (Varga et al., 2001; Kiss et al., 2002). Half sections of the filters were cut into pieces, the pieces from the daytime and night samples of each 24-h period were combined and extracted jointly by high-purity reagent Milli-Q water for about 36 h. The ratio of filter sample area to water volume was about 1.5 cm² ml⁻¹. Removal of water-soluble OC from the filters was checked occasionally by an additional sequential extraction and analyses, and it was found to be quantitative.

The extracts were filtered through a syringe PVDF membrane filter with a pore size of 0.22 μm to remove the filter debris and suspended insoluble particles. The solution pH was measured and was adjusted to 2.0 by hydrochloric acid, and the solution was passed through a pre-conditioned SPE column (Oasis HLB, hydrophilic-lipophilic-balanced water-wettable copolymer, packing mass 200 mg, Waters Inc., USA). Hydrophilic organic compounds with acidic functional groups that are protonated at pH = 2 are retained by the column, while the inorganic species and organic compounds that are very hydrophilic due to the presence of strong polar functional groups (like oxalic acid) pass into the effluent. A yellowish band appeared at the top of the column while the colour of the remaining stationary phase was unaltered indicating that the analyte was efficiently retained in the first part. The isolation method was optimized to separate the fraction that exhibits the key spectral properties of the total WSOC fraction, i.e. more than 90% of the fluorescence activity, and 70% of the UV activity of natural humic and fulvic acids (Varga et al., 2001). The exposed column was rinsed with water to remove residues of inorganic constituents, and it was dried by nitrogen stream. The retained organics were eluted by 6 ml methanol yielding a markedly coloured yellow liquid that contained the HULIS. Disadvantage of the protocol is that some fatty acids, long-chain monocarboxylic acids, and aromatic alcohols could possibly remain in the isolated chemical fraction. The eluates from all front filters were joined into a pooled sample, which was divided into several aliquots (for different types of measurements), and they were finally evaporated to dryness by a gentle nitrogen stream. The drying resulted in marked dark yellow or brownish matter/pulp (brown carbon, Andreae and Gelencsér, 2006). The eluates from all back filters were also joined into a pooled sample, which was divided into two aliquots and was also evaporated to dryness. One aliquot for the front filters and one for the back filters were utilized to determine the main element composition of HULIS; other aliquots for the front and back filters were subjected to total organic carbon (TOC) analysis.

2.3. Chemical analyses

OC and WSOC contents of the aerosol samples were derived from the remaining half sections of the original front and back filters. One or two punches

with an area of 1.5 cm² each of the filter was analysed by a thermal-optical transmission (TOT) method (Birch and Cary, 1996) with a Sunset Lab (USA) instrument for OC (and EC), using the same temperature programme as adopted for the Schmid et al. (2001). The relative uncertainty of the analytical results is about 5% according to the manufacturer. The split between EC and OC in TOT depends upon the temperature programme used in the analysis (Schauer et al., 2003), and higher ratios of EC/TC (with total carbon TC = OC + EC) than ours are obtained when lower temperatures are employed in the first phase of the analysis (in pure He). Other punches of the original filters were extracted by 5 ml water each with manual shaking for about 5 min after which it was allowed to stand for 30 min. The extract was filtered through the syringe filter, and the WSOC was measured by a TOC analyzer (Shimadzu TOC-V CPH, Japan) in two steps as the difference between the total carbon and total inorganic carbon. The injection volume for both steps was 150 µl which were repeated three times each, and the mean of the results was further utilized in evaluations. The relative uncertainty of the actual measurements was estimated to be less than 3%. Carbon content of the HULIS solutions (HULIS-C) obtained for the front and back filters was measured by the TOC analyzer in a way similar to that with filter extracts. TOC content for a joint eluate from three SPE columns that were not exposed to aerosol water extract (thus, without WSOC and HULIS) was determined, and was used as column blank value for correcting the HULIS-C for the actual samples. The column blank was less than about 8% for the front filters, and it was about 20% for the back filters.

The main element composition of HULIS was measured by an elemental analyzer (Carlo Erba, model EA 1108, Italy) that was configured to detect C, H, N and S simultaneously. The HULIS samples were dissolved in acetone, and three aliquots containing about 500 µg HULIS were transferred into Sn capsules of known mass. They were thoroughly dried and then weighed by an ultra-micro-balance (precision 0.1 µg). The samples and capsules are burned in oxygen in a combustion reactor at 1 020 °C, and the products are catalytically transformed by an oxidation and a reduction catalyst to CO₂, H₂, N₂, and H₂S. The gas-phase products travel with He carrier gas into a packed chromatographic column which separates the components specified, and finally, they are detected

and quantified by a thermal conductivity detector. Calibration of the analyser was performed by sulfanil-amid standard provided by Carlo Erba. Inductively coupled plasma mass spectrometry (ICP-MS, Thermo Element 2, USA) was utilized in low-resolution mode for semi-quantitative analysis to determine or exclude some other possible major elements in the HULIS sample for the front filters.

3. Results and discussion

3.1. Sampling artefacts

The collection of organic aerosol species by quartz fibre filters is subject to sampling artefacts. On the one side, the collection process alters the gas–particle equilibrium of a number of condensable constituents of the aerosol (like semi-volatile organics) which leads to negative (evaporative) bias and, on the other side, adsorption of some gaseous compounds (mainly volatile organics) by the collection substrate can occur, resulting in positive (adsorptive) bias (Jacobson et al., 2000; Turpin et al., 2000; Kirchstetter et al., 2001). It is generally assumed that the positive sampling artefacts prevail in collections with quartz fibre filters (Turpin et al., 2000; Viidanoja et al., 2002; Mader et al., 2003; Salma et al., 2004), and as a consequence, sampling-artefact-corrected concentrations are calculated as the difference between the front and back filter data. Concentrations of OC, WSOC and HULIS-C for the front and back filters, together with the mean and standard deviation of the back-to-front-filter concentration ratios, are presented in Table 1. The mean back-to-front ratio and standard deviation for OC are somewhat larger than the mean data of (10 ± 2)% obtained for a different type of quartz fibre filter (Whatman QM-A) in a low-volume (LoVol) aerosol sampler (characterized by an air flow rate of 16.7 l min⁻¹, and an average face velocity of 19 cm s⁻¹) deployed in parallel with the HiVol sampler, and by using identical chemical analysis (Salma et al., 2004). The difference is likely attributable to the difference in filter type. The air face velocity may also play a role; however since the HiVol sampler operated at four times higher face velocity than the LoVol sampler, one would expect less instead of more OC on its back filter (Turpin et al., 2000). With regard to the WSOC, the mean back-to-front ratio is significantly larger than that for OC. It means that the organic compounds that

Table 1

Range and median atmospheric concentrations for PM_{2.5}-fraction OC, WSOC and HULIS carbon (HULIS-C) in $\mu\text{g m}^{-3}$, as obtained by the tandem filter method for the front and back Pallflex quartz fibre HiVol filter samples, and the mean back-to-front-filter concentration ratio and standard deviation (both in %) for 23 urban-type aerosol samples collected in the non-heating spring season

Concentration/constituent	Front filter		Back filter		Back-to-front ratio
	Range	Median	Range	Median	
OC	2.8–13.3	6.4	0.58–1.79	1.03	17 ± 3
WSOC	1.21–4.2	2.4	0.42–0.85	0.60	28 ± 7
HULIS-C	—	1.30 ^a	—	0.22 ^a	17 ^a

^aFor the pooled HULIS sample of all 23 filters.

are mainly responsible for the adsorptive sampling artefacts seem to be more water soluble, thus they possibly contain more polar functional groups or they may be more oxidized than the OM in general. This is in agreement with the expectation that quartz fibre filters primarily adsorb polar (thus more water soluble) organic molecules, while the volatile or semi-volatile organic compounds are often non-polar. The back-to-front ratios for the WSOC were strongly and negatively correlated with the WSOC concentration, PM_{2.5} mass concentration and ambient temperature, while their correlations with OC, PM_{2.0}-fraction S, CO, and relative humidity were not significant ($|R| < 0.57$). As a consequence, the importance of the sampling correction decreases with increasing aerosol mass or WSOC concentrations, as has also been observed for the back-to-front ratio for OC at different study sites in the US (Turpin et al., 2000). In our case, the correlation coefficient for the back-to-front ratio for OC and OC concentration was $R = -0.712$ with a p -value of 0.00012. The scatter plot of the back-to-front ratio for WSOC versus the amount of WSOC is displayed in Fig. 1 as example. It can be estimated from the regression analysis that the correction factor is less than 5% for WSOC levels above about $5 \mu\text{g m}^{-3}$ assuming similar sampling conditions. This is typically the case in studies on tropical biomass burning aerosol, when WSOC concentrations larger than about $15 \mu\text{g m}^{-3}$ are often reported. The back-to-front ratio for HULIS was also significant (equal to that for OC), which was somewhat unexpected. In test experiments for collecting PM₁₀-fraction HULIS at an urban background site in Zurich, Switzerland, a much smaller back-to-front ratio (about 3%) was observed, and, therefore, the artefact was neglected there (Samburova et al., 2005b). Direct adsorption of HULIS being a polymer-type material in

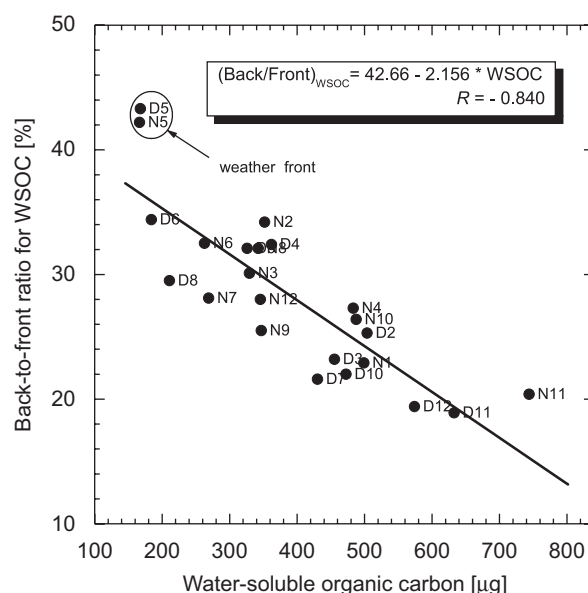


Fig. 1. Scatter plot of the back-to-front-filter concentration ratio for WSOC versus the amount of WSOC sucked through the filter for the PM_{2.5}-size-fraction urban-type atmospheric aerosol collected on Pallflex tandem quartz fibre filters in the non-heating spring season. Samples for the daylight periods (D) and nights (N) are also indicated.

considerable amounts on the (back) filters is rather unlikely due to their low volatility (Gelencsér et al., 2000). Therefore, it is thought that HULIS on the back filters were formed during the sampling process by adsorption of volatile (aromatic) gaseous precursors on the filter surface, and by heterogeneous reactions with oxidants, which was followed by their formation processes (e.g., polymerization) similar to their formation paths in the atmosphere. This can also explain the difference in the extent of the observed sampling artefacts; formation of HULIS is known to be significantly enhanced on/with acidic seeds (e.g., sulphuric or nitric acid

droplets), which could be present in a larger amount in downtown Budapest than in the urban background of Zurich. The difference in the sampling artefact also points to the importance of some catalyst air pollutants together with the precursors in the HULIS formation. It is estimated in Section 3.2 that a very large fraction of the SOA consisted of HULIS, which is in line with the explanation as well. Moreover, preliminary experiments show that the HULIS concentration for the back filter in the high-air-flow sampling line was similar to that in the low-air-flow sampling line, which indicates that the formation process was independent of the aerosol size fraction (and chemical composition). At the same time, some differences in the UV–VIS spectra of HULIS derived for the front and back filters were observed. Absorption of HULIS obtained from the back filters was very small above 330 nm—similar to the HULIS synthesized in model cloud water from a single aromatic acid precursor (Hoffer et al., 2004). A simple explanation for the spectral differences between the front and back filters can be that HULIS on the back filter have somewhat smaller average molar mass in comparison for the front filters, which also suggests that HULIS on the back filter was still in the phase of polymerization. The hypothesis is consistent with the understanding of the main formation routes via precursor gases from both anthropogenic (including road traffic) and biogenic emission sources. The effect also implies that the formation rate of HULIS on the filter surface was quite high, and, therefore, saturation concentration values could be achieved even for 12-h sampling times (Kirchstetter et al., 2001). The results emphasize the importance of and need for an appropriate sampling and correction methods for organic chemical fractions in downtown urban environments.

3.2. Atmospheric concentrations

Sampling-artefact-corrected atmospheric concentrations of OC, WSOC and HULIS-C were calculated, and used for further evaluation. Concentrations of OC varied from 2.2 to $12.6 \mu\text{g m}^{-3}$ with a median of $5.6 \mu\text{g m}^{-3}$. The individual data were compared to the corrected concentrations obtained for the LoVol aerosol sampler deployed in parallel. The correlation coefficient between HiVol and LoVol concentrations was $R = 0.971$ (with a p -value of <0.001), and the mean LoVol/HiVol concentration ratio and standard deviation

were 1.26 ± 0.15 . A LoVol/HiVol ratio of somewhat higher than 1.0 was also observed in other studies with the same samplers (Decesari et al., 2006) and was attributed to a systematic overestimation in the air volume for the HiVol sampler. Concentrations of WSOC ranged from 0.74 to $3.3 \mu\text{g m}^{-3}$ with a median of $1.60 \mu\text{g m}^{-3}$. Temporal variability of PM_{2.5}-fraction mass, OC and WSOC over the sampling campaign is displayed in Fig. 2. No significant difference between the daytime periods and nights for both OC and WSOC data could be identified in accordance with the previous observations regarding the PM_{2.5} size fraction (Salma et al., 2004). Temporal variability of several aerosol constituents were interpreted in detail by Salma et al. (2004), Salma and Maenhaut (2006b), and it was concluded that the local emission sources dominated over the polluted time periods, while the smaller atmospheric concentrations were related to long-range transport of air masses and local meteorology. The WSOC was strongly correlated with the PM_{2.5} mass and OC (with coefficients $R > 0.83$, $p < 0.01$) but the WSOC/OC ratio was changing irregularly over the sampling campaign, or even irrespective of the relative source intensities, as can be seen in Fig. 2. In addition, the correlation between the WSOC/OC ratios and the PM_{2.5}/PM₁₀ ratios for OC was not significant, which all indicate that the WSOC takes part in a complex system in the atmosphere as far as its actual concentration and formation are concerned, and it needs further investigations. The average atmospheric concentration of HULIS was $1.96 \mu\text{g m}^{-3}$ (when using a carbon content of HULIS of 55%, see carbon-to-organic aerosol mass conversion factor in Section 3.3). The unrecoverable water-soluble HULIS from the separation column and the water-insoluble fraction of HULIS were hereby not taken into account yet, and, therefore, the concentration is to be strictly regarded as a lower estimate. The mass balance for the carbonaceous species is summarized in Fig. 3. It is noted that HULIS represent about 6% of the mean particulate mass obtained for the quartz fibre filter in the PM_{2.5} size fraction. The atmospheric concentration of HULIS was comparable for other continental aerosol samples (Zappoli et al., 1999; Samburova et al., 2005a,b) in spite of the fact that the WSOC concentrations can vary quite substantially for different regions and with season.

On average, WSOC accounted for $(32 \pm 8)\%$ of the OC on a sample-by-sample basis under the

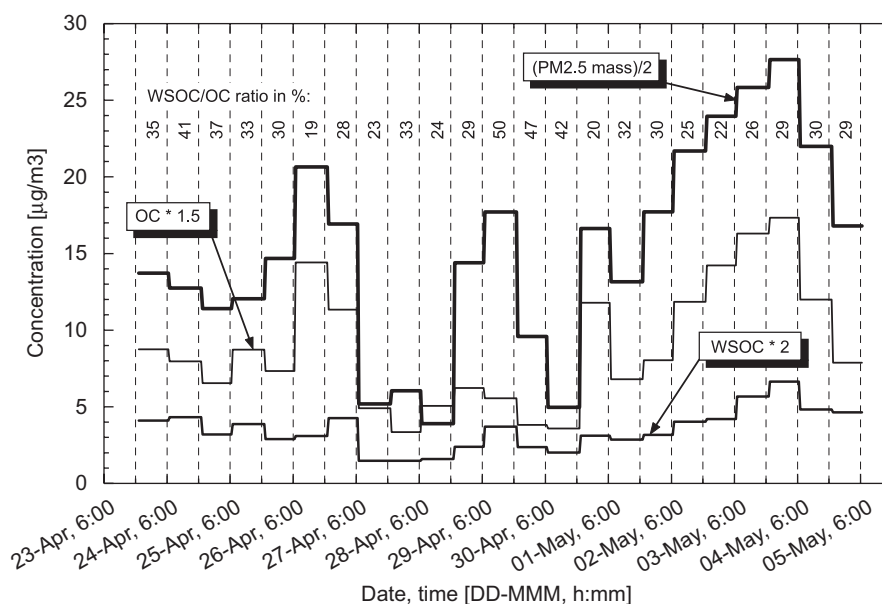


Fig. 2. Temporal variability of the PM_{2.5}-fraction mass, OC, and WSOC concentrations over daytime periods and nights, together with the numeric WSOC/OC concentration ratios for each sample.

assumption of completely insoluble EC. The assumption was supported by the weak correlation between WSOC and EC (and BC measured by an aethalometer) of $R = 0.462$. In an earlier study in Budapest, contribution of WSOC to OC was found to be increasing from 20% (for a road tunnel) to 49% (for the urban background), and a range of 27–34% was derived for the downtown (Salma et al., 2001). The present contribution fits very well to the interval; furthermore, it is within the range of data reported for other urban or traffic-influenced locations (Ruellan and Cachier, 2001; Chi and Maenhaut, 2004; Viana et al., 2006a, b). It is, however, substantially less than for the aerosol that originated from main sources other than road traffic. The mean WSOC/OC concentration ratio for rural/continental background sites, e.g. for K-puszta, Hungary is between 60% and 70% (Kiss et al., 2002; Chi and Maenhaut, 2004), and for tropical biomass burning aerosol (e.g., LBA-EU-STACH, SAFARI2000 and SMOCC2002), the ratios were up to about 75% (Mayol-Bracero et al., 2002; Chi and Maenhaut, 2004; Decesari et al., 2006). The explanation for the differences involves most likely the small share of oxygenated organics (low WSOC level) in vehicle emissions, the time required for transformation of organic aerosol species into more oxidized (more polar, and thus more water soluble) forms and for formation of PM

from precursor gases, and diversity of the combustion sources and formation paths in these environments. The correlation coefficients between WSOC and PM_{2.5} mass, TC, and OC in our study, were 0.848, 0.711, and 0.827, respectively, which indicate that the concentrations of these constituents varied in a coherent manner. It should be remembered that concentrations of WSOC (and OC) are somewhat method dependent. As far as the HULIS are concerned, 20% of the OC and 62% of the WSOC were attributed to HULIS carbon. These results are comparable to the data for other environments, although the value for WSOC is at the upper end of the reported contributions as summarized in Table 2. It should be mentioned here, however, that the sampling artefact for WSOC was either derived to be within the experimental uncertainty of the carbon analysis for the front filters, and, therefore, was neglected (Mayol-Bracero et al., 2002), or was not taken into account in the earlier studies. It can be seen from Table 2 that the reported HULIS contributions to WSOC vary from low level (10%) to high level (72%) implying that HULIS do not share common origin and formation paths in different environments and seasons. HULIS in the papers specified in Table 2 were represented by partially overlapping chemical fractions as water-soluble macromolecular compounds, polycarboxylic acids, with molecular mass > 500 Da by

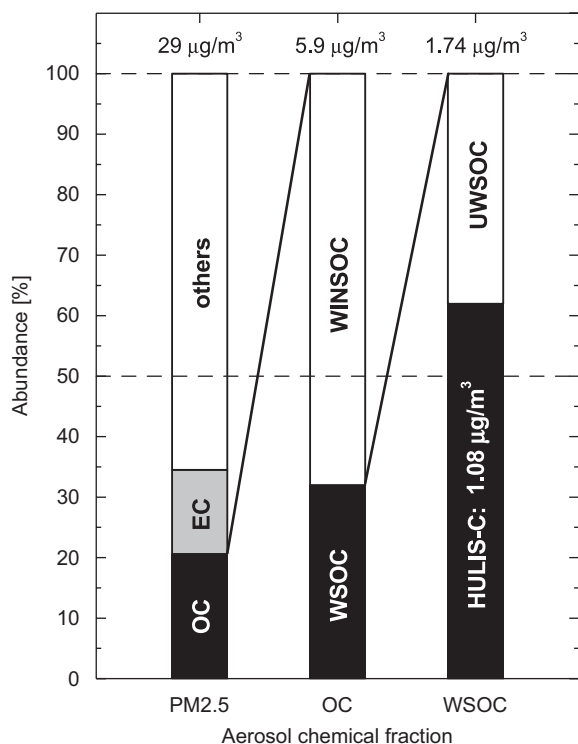


Fig. 3. Mean atmospheric concentrations and mean apportionment of the carbonaceous aerosol species for the PM_{2.5}-size-fraction urban-type atmospheric aerosol collected on quartz fibre filter in the non-heating spring season. OC: organic carbon, EC: elemental carbon, WSOC: water-soluble organic carbon, WINSOC: water-insoluble organic carbon, UWSOC: unresolved water-soluble organic carbon including unrecoverable WSOC from the separation column, HULIS-C: carbon content in humic-like substances.

ultrafiltration, isolated on non-ionic resins, or resolved by positive matrix factorization. It has also to be mentioned that the contributions presented are usually much larger than the values derived for alkaline-extracted humic-like materials (Graber and Rudich, 2006).

In a previous paper (Salma et al., 2004), the amount of SOA in the PM_{2.5}-fraction aerosol collected by the LoVol sampler operated in parallel with the HiVol sampler was quantified by using EC as the tracer for the primary OC emissions. The mean SOC concentration was estimated in this way to be $2.4 \mu\text{g}/\text{m}^3$ for the daytime periods. The data can be utilized now to estimate roughly the contribution of HULIS-C to SOC, which resulted in 45%. This result emphasizes the importance of HULIS in aerosol transformation processes in cities and over continents.

It is worth noting that the mean WSOC/OC concentration ratio and standard deviation for the separate front filters were $(36 \pm 8)\%$, thus similar to the sampling-artefact-corrected WSOC/OC data, while for the separate back filters, they were much larger $(59 \pm 15)\%$. This confirms that the organic species that cause adsorptive sampling artefacts are more water soluble (more polar) than the OM in general. A similar comparison for HULIS on the separate front and back filters indicated that about 19% of the OC and about 54% of the WSOC were attributed to HULIS carbon for the front filter, while the corresponding data for the back filters were 20% and 34%, respectively. This indicates that the contribution of the compounds causing adsorptive sampling artefacts was practically identical for HULIS as for the OC in general, but the importance of HULIS among these compounds was lower for the back filters than for the front filters, since the WSOC/OC ratio increased for the back filters. It also means that it is the polar compounds that were mainly responsible for the sampling artefacts via adsorption on the active sites of the quartz fibre filter material.

3.3. Major element composition of HULIS and consequences

The mean C, H and N contents for the bulk pooled HULIS sample isolated from the front filters were 55%, 6.9% and 3.0% by mass; the standard deviations were estimated to be about 10%. The S amount was below the detection limit of about 0.1% of the mass analysed. The presence of other possible major elements (except for O), such as P, Cl, K, Mg, and Fe, was checked by ICP-MS, and their presence was excluded. Their overall mass contribution was estimated roughly to be less than 1–1.5%. The analysis for the back filters yielded mass ratios of 55%, 7.0% and 3.1% for C, H and N, respectively, which were practically identical to the data for the front filters. The HULIS samples were regarded to be made up of C, H, N, and O as major elements, and the residual mass (i.e., 35 mass%) of the isolated matter was supposed to consist primarily of oxygen. In this way, the major element composition of HULIS, expressed by molar ratios, was C:H:O:N = 22:32:10:1. The average elemental composition of HULIS for a PM_{2.5}-fraction aerosol collected at an Alpine site (Jungfrauoch, Switzerland) was reported to be 52% C, 6.7% H, 2.5% N, and 39% O (Krivácsy et al., 2001). Another average

Table 2

Contribution of atmospheric humic-like substances carbon (HULIS-C) to water-soluble organic carbon (WSOC) in % for different environments and seasons

Sample type	Location and season/period	Size fraction	HULIS-C/WSOC		References
			Range	Average	
Polluted rural aerosol	Po Valley, Italy, autumn	PM1.5	21–41	29	Zappoli et al. (1999)
Background rural aerosol	K-pusztá, Hungary, summer	PM1.5	28–55	41	
Fog water (interstitial)	Po Valley, Italy, winter-spring	—	40–67	—	Facchini et al. (1999b)
Fog water (interstitial) and polluted rural aerosol	Po Valley, Italy, n.a.	PM1.5	—	17	Decesari et al. (2000), Facchini et al. (2000)
Polluted rural aerosol	Po Valley, Italy, ca. yearly interval	PM1.5	26–44	—	Decesari et al. (2001)
Alpine aerosol	Jungfraujoch, Switzerland, summer	PM2.5	55–60	—	Krivácsy et al. (2001)
Fog water	Valley of California, USA, winter	—	27–57	—	Herckes et al. (2002)
Background rural aerosol	K-pusztá, Hungary, winter-spring-summer	PM1.5	38–72	57	Kiss et al. (2002)
Biomass burning aerosol	Amazonia, Brazil, dry-to-wet season	PM2.5	15–32	25 ± 6	Mayol-Bracero et al. (2002)
Urban aerosol	Bologna, Italy, ca. yearly interval	PM1.2	—	21	Matta et al. (2003)
Oceanic aerosol	Mace Head, Ireland, spring	PM1.5	—	22	Cavalli et al. (2004)
Atmospheric aerosol	Jeju Island, Korea, spring	PM1.5	33–40	—	Decesari et al. (2004)
Atmospheric aerosol	Hong Kong, ca. yearly interval	PM2.1	0–58	46	Yu et al. (2004)
Rural/urban aerosol	Near Aveiro, Portugal, summer-autumn	PM2.5	—	55	Duarte et al. (2005)
Urban background aerosol	Zurich, Switzerland, summer	PM10	—	10	Samburova et al. (2005a, b)
Biomass burning aerosol	Amazonia, Brazil, dry-to-wet season	PM1.2	18–31	—	Decesari et al. (2006)
Background (boreal) aerosol	Hyytiälä, Finland, spring	PM1.2	21–35	—	Cavalli et al. (2006)
Urban aerosol	Budapest, Hungary, spring	PM2.5	—	62	Present work

For additional comments see the text.

elemental composition for a rural site (K-pusztá, Hungary) was given to be 52% C, 6.2% H, 2.5% N and 39% O (Kiss et al., 2002). The results for the two background sites were obtained by the same analytical method as in the present work. The main element compositions of HULIS for the two background sites are remarkably similar to each other, but they are somewhat different from that at our urban location. The molar H/C ratio of 1.49 for our samples implies the presence of unsaturated organic compounds; it is larger than for the rural site of K-pusztá (1.42; Kiss et al., 2002) or for standard fulvic acids of the International Humic Substances Society (0.82–1.01), and shows thus an excess of saturated compounds when compared to the fulvic acids. The molar ratio O/C = 0.47 indicates the existence of oxygenated functional groups; this ratio is significantly less than for the rural site of K-pusztá (0.58)

or for the standard fulvic acids (0.61–0.68), suggesting that the (fresh) urban-type aerosol is to be regarded less oxidized (and hence, less water soluble), than the rural one. The comparisons indicate that there are certain differences in the molecular composition of HULIS for different locations.

The mass ratio between OM and OC (the organic aerosol-to-organic carbon mass conversion factor) is one of the most important factors of uncertainty in aerosol chemical mass closure calculations involving OM. It is usually estimated by indirect considerations (Russell, 2003). Mass conversion factors between 1.2 and 1.4 were estimated for fine atmospheric aerosol in mildly oxidizing environments (Gray, 1986; Turpin et al., 2000); some more recent studies suggest that a factor of 1.6 ± 0.2 describes better the oxidizing urban environment

(Turpin and Lim, 2001). The elemental composition of HULIS just determined makes possible to derive directly the partial mass conversion factor for HULIS, and it resulted in a value of 1.81. For comparison, a factor of 2.1 ± 0.2 was suggested for aged (non-urban) aerosol (Turpin and Lim, 2001). The present factor for HULIS is identical to the one reported for the rural environment of K-pusztá (Kiss et al., 2002), or that proposed for the WSOC in the PM10 size fraction for the urban area of Bologna, Italy (with the WSOC preferentially distributed in the fine size fraction, Matta et al., 2003), and with the factor for the SOA formed in smog chamber experiments (Kalberer et al., 2004).

4. Conclusions and outlook

A combination of aqueous extraction, solid-phase extraction and thermal (and thermo-optical) analytical methods is advantageous for studying the concentration and properties of the water-soluble organic chemical species, in particular of HULIS. The main disadvantage of the protocol utilized for the isolation of HULIS, and of other ones in use up to now, is that they are laborious and time consuming. A simple and standardized method for determination of the water-soluble (and water-insoluble) HULIS is highly desirable. At present, however, substantial differences in the separation, isolation or determination of water-soluble HULIS can be witnessed instead. This is definitely caused by the complexity of the subject. The available procedures exhibit several important differences, e.g., in (1) volume, duration, and intensification of the water extraction, (2) principle and actual realization of the separation or isolation, (3) presence and interference of remaining inorganic compounds or other organic chemical fractions, (4) choice and usage of the reasonable calibration standard(s) for the spectral methods, (5) handling of sampling artefacts, and (6) variable concept for the approximation of HULIS by a chemical fraction (frequently related to the separation and detection process). These diversities altogether (can) cause systematic uncertainties that are likely much larger than the analytical uncertainty of a method. It seems, therefore, difficult to compare the results and properties derived, and to determine further global or regional distributions for HULIS in a reliable and traceable way. More effort should be devoted to avoid this ambiguity.

The aerosol samples collected in downtown Budapest in spring season revealed a small WSOC/OC ratio in comparison to non-urban locations, which could be one of the particularities of continental downtown (kerbside) urban locations. Our results also indicate the need for an appropriate sampling strategy and correction for the sampling artefacts. The relative importance of the different secondary formation processes for HULIS and of the precursor emissions, together with the primary emissions from combustion in/near cities will have to be investigated in the future. The unresolved WSOC (including the unrecoverable WSOC from the separation columns) accounted for 38% of the WSOC, which indicates that there is a need for further investigations on the chemical entities of the water-soluble material, as well as on the water-insoluble organics.

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