

Study of water-soluble atmospheric humic matter in urban and marine environments

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Abstract

Recently, atmospheric humic matter or humic-like substances (HULIS) have been found in the water-soluble fraction of atmospheric aerosol sampled at different locations. Most of these locations were continental, non-urban sites. Therefore, in this work HULIS was studied in urban and marine environments. The atmospheric concentration varied over a wide range from 0.40 to 5.44 $\mu\text{g m}^{-3}$, from the clean marine air (Mace Head, Ireland) to the heavily polluted winter urban atmosphere (Christchurch, New Zealand). In terms of carbon, ratio of HULIS was 19–51% of water-soluble organic carbon, and 10–22% of total carbon. Different spectroscopic techniques were applied for the physico-chemical characterisation of HULIS including relative aromaticity and molecular weight. Specific absorbance was observed to be much less variable than specific fluorescence, and consequently UV-VIS spectroscopy at $\lambda > 330$ nm was recommended for rapid, semi-quantitative determination of HULIS in the water extracts of atmospheric aerosol. Application of a dual filter sampling system at one of the sampling sites has revealed a significant positive sampling artefact which calls for further systematic studies on this subject, and also supports the idea of a secondary organic aerosol formation mechanism of HULIS.

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1. Introduction

During the last decade the approach to characterise the organic composition of atmospheric aerosol has considerably evolved. Classical methodology using solvent extraction and GC-MS analysis was only

capable of identifying a minor fraction (5–15%) of the organic compounds (e.g. Rogge et al., 1993). However, recent studies involving aqueous extraction and other analytical techniques (e.g. HPLC) have revealed that a significant portion (30–80%) of the organic carbon is water-soluble (Zappoli et al., 1999; Decesari et al., 2001; Krivácsy et al., 2001a; Temesi et al., 2003), and furthermore, polymer-type substances of higher molecular weight, both water-soluble and solvent extractable,

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are present. For example, proteins (Zhang et al., 2002), cellulose (Puxbaum and Tenze-Kunit, 2003), long-chain wax esters (Elias et al., 1999) have been found, but the most “mysterious” organic aerosol components discovered were probably compounds of (poly)acidic nature, chromophoric and fluorescence character and a high (~39 m/m%) oxygen content. The separation and identification of individual species have failed (Krivácsy et al., 2000), and the group of these compounds resembling natural humic matter in their physico-chemical behaviour has been called “humic-like substances” (HULIS). A brief history of the studies of HULIS in atmospheric aerosol can be seen in Table 1.

In 1986 Mukai and Ambe already mentioned a “humic acid-like brown substance”. But the discovery of atmospheric HULIS can be attributed to studies in the late 1990s (Havers et al., 1998; Zappoli et al., 1999). It was a turning point when HULIS were identified in large quantities in the water-soluble fraction of atmospheric aerosol. Since then research has been focused almost exclusively on this fraction, although a portion of HULIS is known to be water insoluble and extractable only with alkaline solution (Kiss et al., 2002). First, HULIS were thought to be macromolecules (Zappoli et al., 1999). However, comprehensive work on the

estimation of their molecular size has later shown that their molecular weights are most likely in the range 200–500 Da (Kiss et al., 2003). So, atmospheric HULIS are not macromolecules in general which explains their water solubility, and also why the first studies (Mukai and Ambe, 1986; Havers et al., 1998) following the protocol of soil humic acid quantification concluded that the atmospheric aerosol had a relatively low HULIS content.

The water solubility of HULIS has raised the question as to whether these organic molecules may influence cloud condensation. Facchini et al. (1999) pointed out that up to 50% of the polyacids were transferred from the aerosol to the liquid phase during fog events. More recently it has been shown that the high surface activity of HULIS might have a significant effect on the critical droplet size and supersaturation through the Kelvin term in the Köhler equation (Facchini et al., 2000; Mircea et al., 2002; Kiss et al., 2005). These findings indicate that HULIS may play a global role in the atmosphere by influencing indirect aerosol climate forcing.

Another exciting question is addressed to the origin of HULIS. Since during the first studies HULIS were observed in total suspended matter, soil dispersion could

Table 1
Summary of the study of HULIS in atmospheric aerosol

Site and date	Environment	Type of sample	Analytical method	Contribution to carbon content ^a	Reference
Tsukuba, Japan September 1983–September 1984	rural	total aerosol	solvent and alkaline extraction; isolation by acid precipitation; carbon measurement	0.6–3% of TC	Mukai and Ambe (1986)
Sauerland, Germany Dortmund, Germany spring and summer 1995–1996	rural urban (industrial)	total aerosol (dust)	alkaline extraction; isolation on anion exchange column; carbon measurement	1.8–1.9% of TC	Havers et al. (1998)
Po Valley, Italy	rural (polluted)	PM1.5	water extraction; size exclusion chromatography with UV-VIS detection	21–55% of WSOC	Zappoli et al. (1999)
K-pusztá, Hungary June–September 1996	rural (background)	PM1.5	water extraction; size exclusion chromatography with UV-VIS detect	40–67% of WSOC	Facchini et al. (1999)
Po Valley, Italy November 1996–March 1997	rural (polluted)	PM1.5 (interstitial)	water extraction; isolation by solid-phase extraction; carbon measurement	54% of WSOC	Krivácsy et al. (2001b)
Jungfrauoch, Switzerland summer 1998	high-alpine	PM2.5	water extraction; isolation by ion exchange chromatography; carbon measurement	40% of WSOC	Decesari et al. (2001)
Po Valley, Italy January 1998–May 1999	rural (polluted)	PM1.5	water extraction; isolation by ion exchange chromatography; carbon measurement	26% of WSOC	Mayol-Bracero et al. (2002)
Amazon region, Brazil October 1999	rural (burning season)	PM2.5	water extraction; isolation by ion exchange chromatography; carbon measurement	38–72% of WSOC	Kiss et al. (2002)
K-pusztá, Hungary January–September 2000	rural (background)	PM1.5	water and alkaline extraction; isolation by solid-phase extraction; carbon measurement	22% of WSOC and 27% of WSOC	Cavalli et al. (2004)
Mace Head, Ireland April–June and late September–October 2002	marine	PM1.5 and >PM1.5	water extraction; isolation by ion exchange chromatography; carbon measurement		

TC — total carbon, WSOC — water-soluble organic carbon.

^a Single figure means the average value.

have been assumed as a potential source. But later works, which were restricted to the fine aerosol fraction, called for other explanations. Mukai and Ambe (1986) already mentioned biomass burning which was later proven to be one of the established and significant sources of HULIS (Mayol-Bracero et al., 2002; Blazsó et al., 2003). Gelencsér et al. (2003) and Hoffer et al. (2004) verified by model experiments that HULIS may be produced in cloud droplets from aromatic acid precursors which may originate, for example, from biomass burning. However, Gelencsér et al. (2000) found HULIS earlier at a rural continental background site during summer, where and when the effect of biomass burning was almost negligible. This led the authors later on to work out a hypothesis about a biogenic origin of precursor substances (Gelencsér et al., 2002). Other possible, and at least partially natural ways of producing HULIS may be the heterogeneous reaction of dienes (e.g. isoprene) on sulphuric acid clusters (Limbeck et al., 2003), and polymerisation of semi-volatile oxidation products in the aerosol phase (Kalberer et al., 2004).

In summary we can conclude that HULIS are very likely of global importance in the atmosphere, but we still suffer from the lack of comprehensive knowledge about their effects, origins, and even their worldwide distribution. As can be seen in Table 1 studies so far have been mostly undertaken at rural continental sites. Therefore the main goal of our work was to study HULIS under urban and marine conditions. Samples from four locations were analysed: Budapest, Hungary as a continental urban site, Auckland and Christchurch, New Zealand as marine urban sites, and Mace Head, Ireland (with sector-controlled sampling) as a pristine oceanic site. We must add that recently, Cavalli et al. (2004) have identified a polyacidic fraction in the Mace Head aerosol during the phytoplankton bloom periods. However, our sampling was out of the time of phytoplankton blooming and can complete those results.

2. Experimental

2.1. Aerosol sampling

Auckland and Christchurch. The samples were collected in residential areas for 12 or 24 h on Whatman quartz fibre filters by using two high-volume PM₁₀ samplers (Graseby Anderson/GMW) with flow rates of 68 m³ h⁻¹. The summer campaign was run in January and February 2001, the winter campaign in June and July 2001. Pieces of several samples from each site and season were combined. *Budapest.* Sampling took place

in April–May 2002, i.e. in the non-heating season, at an urban canyon site in the downtown at a height of about 7.5 m above the street level. A high volume dichotomous virtual impactor was used to separate fine (<2.5 μm) and coarse (>2.5 μm) particles. Tandem quartz fibre filter set-ups were used for correction of the positive sampling artefact. The samples collected during daytime on the 25th of April (sampling time about 12 h) were selected for this study. More details of the sampling site and conditions can be found elsewhere (Salma et al., 2004). *Mace Head.* Samples were collected at the atmospheric research station on the west coast of Ireland on Whatman quartz filters and substrates by Anderson Instruments GMW PM₁₀ High Volume air sampler, equipped with high volume cascade impactor at a flow rate of 60 m³ h⁻¹. High volume cascade impactor was used with a cutpoint of 1.5 μm, and the PM_{1.5} fraction was studied. HiVol sampler was located about 80 m from the shoreline at high tide. Sampling was performed from 13.08.2001 to 05.09.2001 using a computer controlled sampling system, which ensured sampling only of air reaching the site from an oceanic clean sector between 190° and 300°, and with a total particle concentration ($d_{50\%} = 14$ nm) below 900 cm⁻³. Previous analysis has shown that, in general, air masses meeting such criteria can typically be regarded as clean marine air masses having passed over thousands of km of open sea, free from the influence of major anthropogenic sources (Cooke et al., 1997).

2.2. Sample pre-treatment

The aim of the sample pre-treatment was the isolation of water-soluble HULIS for physico-chemical investigations and quantification. The methodology of the whole isolation procedure was published by Varga et al., 2001. In summary, it included the overnight soaking of the exposed (front and back in Budapest) and blank quartz fibre filters in a closed beaker with ultra-pure water applying a water volume [cm³] and filter surface [cm²] ratio of about 2. Then the pH of the water extracts was adjusted to 2 with HCl. Isolation of HULIS was carried out by a solid phase extraction method using Oasis HLB cartridges (Waters). In the acidified solution, HULIS were retained on the cartridge stationary phase, while other organics and inorganic ions passed through the cartridge. Then HULIS were eluted by methanol from the cartridge. Inert atmosphere was not applied to this point of the sample preparation. The methanol solution was shared for the different studies, and the solvent was evaporated under ambient conditions with the help of a gentle nitrogen flow. Later, when needed, HULIS was re-dissolved in ultra-pure water.

2.3. Analysis

Carbon analysis of the original filters, water extracts and re-dissolved HULIS solutions was performed with a Zellweger Astro 2100 TOC analyser by catalytic burning of the samples in oxygen at 680 °C, and measuring the quantity of the evolved CO₂ with a non-dispersive infrared detector. These analyses provided results for total carbon (TC) and water-soluble organic carbon (WSOC). Elemental analysis of the New Zealand samples was carried out by a Carlo Erba CHNS-O 1108 elemental analyser. The method is based on catalytic burning in oxygen at 1020 °C followed by gas chromatographic separation of the products. The precision of the carbon analysis by either the TOC or elemental analyser was about 5%. The mass of the samples burnt was measured with a Sartorius microbalance (resolution of 0.1 µg). Both the UV-VIS measurements and fluorescence measurements with 235 nm excitation wavelength were carried out by two different analytical systems. The UV-VIS and fluorescence studies of the New Zealand samples were accomplished with a Waters 490E UV-VIS and a Waters 470 fluorescence liquid chromatographic detector, respectively. In case of the Budapest and the Mace Head samples the UV-VIS spectra were recorded by a Waters

996 diode array detector. Here, absolute absorbance was not available because of the lack of an appropriate voltage/absorbance conversion factor. Due to the application of two different analytical systems, and the lack of the absolute absorbance values for the Budapest and Mace Head samples, neither the fluorescence nor the absorbance spectra recorded by the two separate systems are comparable on a quantitative basis. Mass spectral analysis was carried out with a Micromass Quattro II tandem quadrupole mass spectrometer equipped with an atmospheric pressure ion source. Electrospray ionisation in negative ion mode was applied. With this soft ionisation technique deprotonated molecular ions can mostly be produced (Kebarle and Ho, 1997).

3. Results and discussion

3.1. Verifying the presence of HULIS

HULIS can be well characterised by UV-VIS and fluorescence spectroscopy. The UV-VIS spectra show a continuous decrease of the absorptivity with increasing wavelength, but still have a well-defined absorption in the visible region, as well. Fluorescence emission spectra can be described as a broad emission band between 300 and 500 nm with a peak maximum at

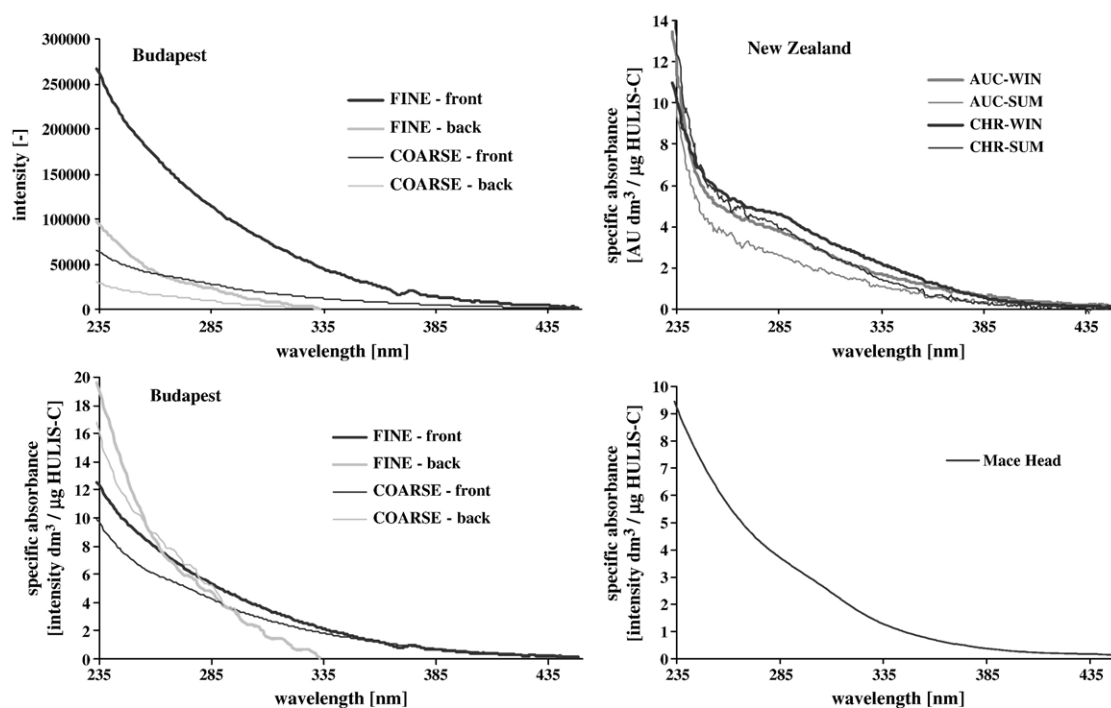


Fig. 1. UV-VIS spectra typical of HULIS isolated from the water-soluble fraction of atmospheric aerosol samples. Specific absorbance means the measured value divided by the concentration of HULIS carbon in the solution tested.

around 400 nm, when a relatively short (e.g., 235 nm) excitation wavelength is applied. These phenomena have been observed previously in the water-soluble fractions of all aerosol samples independent of sampling site and origin (see references in Table 1).

Every sample investigated in this work also showed the same UV-VIS (Fig. 1) and fluorescence character (Fig. 2). Based on this finding we can conclude that every aerosol sample studied here contained atmospheric humic matter. In addition, it must be emphasised that HULIS was also identified on the back filters in Budapest. This unexpected observation raises questions about sampling artefact and atmospheric synthesis of HULIS which are addressed in Section 3.4.

3.2. Physical and chemical characterisation

UV-VIS and fluorescence spectroscopy are the two major and relatively simple analytical tools to characterise natural humic matter both in terrestrial (Alberts and Takács, 2004; Trubetskaya et al., 2002) and aquatic environments (Peuravuori and Pihlaja, 1997; Hautala et al., 2000; Thomsen et al., 2002; Clark et al., 2002; Chen et al., 2002, 2003; Goslan et al., 2004). The different features of the UV-VIS and fluorescence spectra are related to the physical and chemical properties of humic substances. Fluorescence and absorption are usually affected in the opposite way; fluorescence is reduced but absorbance is enhanced with

increasing molecular weight (MW) and aromatic content (Chen et al., 1977; Stewart and Wetzel, 1980).

Although these techniques cannot yield detailed information about the chemical structure of humic substances they are routinely applied because of widespread availability, relative simplicity, and the ability to provide results for comparative studies of different humic acid fractions, as well as similar fractions from different environments. Therefore we think that UV-VIS spectroscopy and fluorescence spectrometry are useful for the quick, screening-like characterisation of HULIS, as well.

Chen et al. (2003) revealed that a fluorescence peak with a maximum at about 400 nm can be attributed to phenolic-type fluorophores. The separation of the fulvic acid fraction of aquatic natural organic matter resulted in a polyphenolic fraction being rich in aromatic moieties (Chen et al., 2002). Senesi et al. (1991) have also suggested that benzoic derivatives can significantly contribute to the fluorescence of fulvic and humic acids. We may therefore conclude that HULIS are of relatively high aromatic content, and the benzoic-phenolic sub-units are mainly responsible for the intensive fluorescence both in the aerosol samples and in atmospheric humic matter in general. Results obtained previously by pyrolysis-GC-MS studies on rural, continental samples (Gelencsér et al., 2000) and biomass burning aerosol (Blazsó et al., 2003) also support this idea, as among the pyrolysis products many hydroxy benzoic and hydroxy

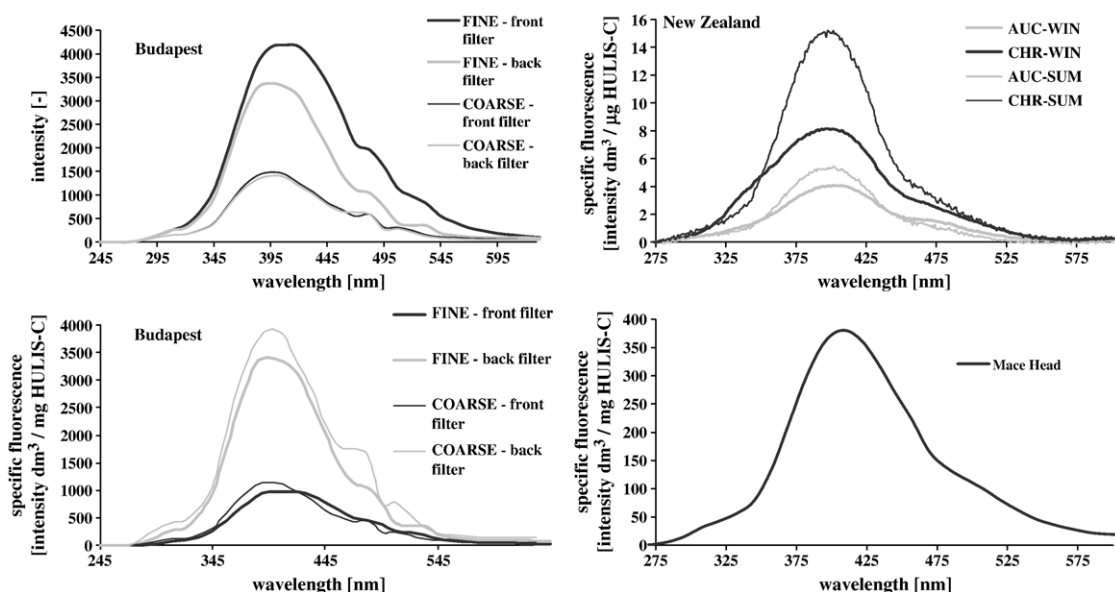


Fig. 2. Fluorescence spectra typical of HULIS isolated from the water-soluble fraction of atmospheric aerosol samples. Specific fluorescence means the measured value divided by the concentration of HULIS carbon in the solution tested.

benzoic acid derivatives were identified. The same conclusions have been drawn for the New Zealand winter samples (Krivácsy et al., 2006).

Peuravuori and Pihlaja (1997) studied the UV-VIS behaviour of aquatic humic substances and found that the absorptivity ratios between 250 and 340 nm (E_2/E_3) anti-correlated strongly with the total aromaticity. The application of intensity ratios is very useful because it makes the comparison of the data very simple without the need of molar absorptivity calculation, and it is even possible in a case such as ours where exact absorbance values are missing (Mace Head and Budapest samples). If we look at the E_2/E_3 values related to our samples (Table 2) a certain differentiation can be made. Ratios of the New Zealand winter samples are the smallest, the ratio for Mace Head is twice as large, with the rest of the values being in between. This means that the aromatic content of HULIS probably reduces if we move from a polluted urban site to a clean marine environment. This seems to be confirmed by the same ratios calculated for aerosol samples from a high-alpine site, Jungfrauoch, Switzerland (Krivácsy et al., 2001b), and a rural continental site, K-pusztá, Hungary (Kiss et al., 2002). It is known that combustion processes release aromatics at high concentration into the atmosphere (Simoneit et al., 1993), what is the most probable source of HULIS in New Zealand cities during winter (for more details see Section 3.4). On the other hand, HULIS of biogenic or natural origin may be more aliphatic (Cavalli et al., 2004). The question may arise if the aromatic content of HULIS, which on a relative scale can easily be estimated from UV absorption, can be useful as a indicator of the origin of HULIS. Further studies on more samples collected in different environments, and including the application of independent analytical techniques for the determination of the aromatic content, must certainly be done to answer this question.

Considerable variation of the specific absorbance and fluorescence (detector signal normalised to the carbon content of the solution tested) (Figs. 1 and 2) reveals the diversity of the chemical structure of HULIS according

to different sources and atmospheric conditions. This is true despite the fact that, due to the technical circumstances (see details in Experimental), the specific values can only be compared in two groups (New Zealand samples in one group, Budapest and Mace Head samples in the other group), separately. Variation in specific fluorescence is about twice that of absorbance indicating that fluorescence of HULIS is more sensitive to the structure of the molecules, and also their molecular environment and conditions. (For quantitative details see Section 3.3).

As has already been mentioned, intense fluorescence of HULIS may indicate a fulvic acid character of lower MW. Our results (Budapest and Mace Head) obtained by mass spectrometry (MS) with electrospray ionisation (Fig. 3) correlate well with this consideration. As can be seen, the mass-to-charge ratios (m/z) of the ions were less than 1000 Da. It should be added that this MS method has been used earlier for rural continental aerosol samples, and proved to be reliable in comparison with the results of vapour pressure osmometry (Kiss et al., 2003). This means that electrospray ionisation mainly produces deprotonated, monovalent molecular ions from acidic compounds in this MW range. So, the m/z distribution of the “humps” in the MS spectra can be assumed to reflect the MW distribution of HULIS. The distributions at the two sites are very similar. The primary maximum is at about 250 Da, but two other local maxima can also be observed at around 350 and 500 Da. This latter maximum is more obvious for the Mace Head aerosol. The higher average MW of HULIS in the Mace Head aerosol is in a good agreement with findings of Chen et al. (2003) who demonstrated that the fluorescence peak emission wavelength of aquatic natural organic matter sub-fractions was shifted to greater values with increasing MW. The fluorescence peak emission wavelength of the Mace Head aerosol was the highest (409 nm) of all the values. The other peak emission wavelengths varied between 399 and 405 nm, and it was 403 nm for the Budapest samples.

The mass spectra are also characterised by individual peaks superimposed on the “hump” of ions. In the Mace Head sample the intense individual peaks around $m/z=200$ are members of primarily three series of ions with $\Delta m/z=14$, and starting at $m/z=143$, 159 and 189 which might be fatty acid derivatives or decomposition products thereof. This periodicity can be observed throughout the spectrum and may indicate the presence of members of aliphatic homologues. On the other hand, this series of ions are less typical of the Budapest aerosol. This supports the idea that HULIS is more aliphatic in the Mace Head than Budapest aerosol.

Table 2
Absorbance ratio at 250 vs. 365 nm wavelengths (E_2/E_3) of aqueous solutions of HULIS isolated from aerosol samples

Sample	E_2/E_3
AUC-WIN	5.6
CHR-WIN	5.7
AUC-SUM	7.3
CHR-SUM	9.7
BP-fine	9.6
Mace Head	11.4
Jungfrauoch summer (Krivácsy et al., 2001a,b)	9.3
K-pusztá (Kiss et al., 2002)	8.0

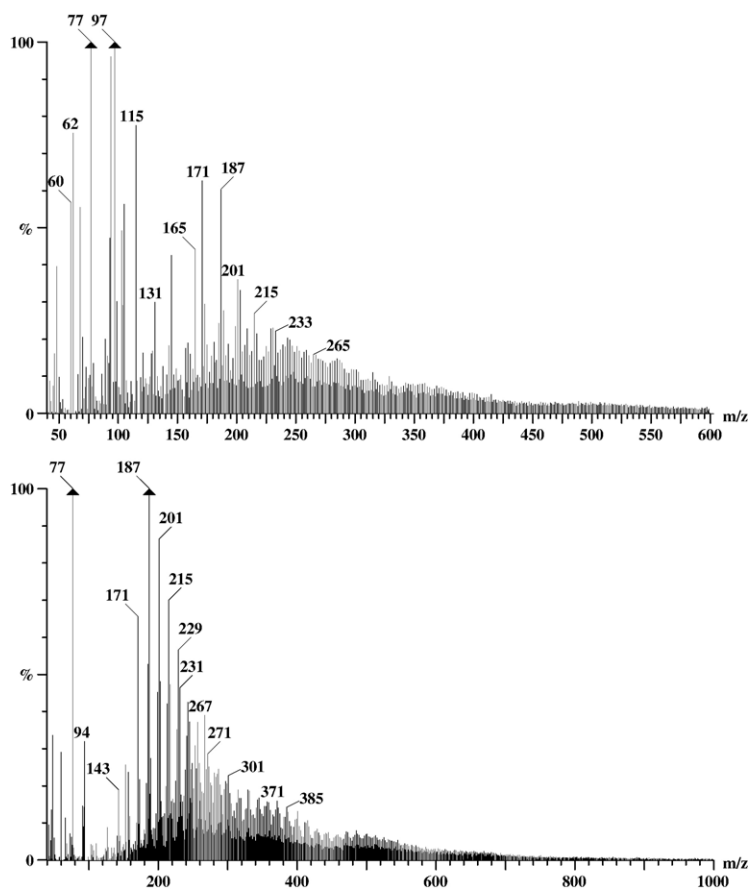


Fig. 3. Mass spectra of the HULIS fractions of Budapest (upper trace) and Mace Head (lower trace) aerosol. (Note that mass spectrum for Budapest was only recorded up to $m/z=600$ Da).

Unfortunately MS results for the New Zealand samples are not available, but elemental analysis for the winter samples was carried out. The elemental composition was almost the same at the two sites: 58–60 m/m% carbon, 6 m/m% hydrogen, 2% m/m% nitrogen and 32–34 m/m% oxygen (calculated by subtraction). This result is very close to those obtained for HULIS in other places, and in a humic substance reference material (Krivácsy et al., 2001b; Kiss et al., 2002).

3.3. Atmospheric concentrations

Based on the isolation procedure followed by carbon analysis, atmospheric concentrations of water-soluble HULIS and their contributions to WSOC and TC fractions were determined (Table 3). For comparison the same results obtained by the same procedure from the study of aerosol samples collected at continental background sites (Jungfraujoch and K-pusztza) are also listed. As seen in Table 3, the absolute concentrations vary within two

orders of magnitude. The high winter concentrations in the New Zealand cities and also in K-pusztza were determined by anthropogenic sources, most likely biomass burning (see Section 3.4). The relatively low

Table 3
Concentration of water-soluble HULIS carbon (HULIS-C), and its contribution to WSOC and TC aerosol fractions

Sample	HULIS-C [$\mu\text{g m}^{-3}$]	HULIS-C/ WSOC [%]	HULIS-C/ TC [%]
Mace Head	0.04	19	12
AUC-SUM	0.35	51	22
CHR-SUM	0.24	34	17
AUC-WIN	2.11	47	21
CHR-WIN	5.44	45	15
BP-fine	0.90	25	10
BP-fine-back	0.22	14	10
Jungfraujoch summer (Krivácsy et al., 2001a,b)	0.46	54	34
K-pusztza winter (Kiss et al., 2002)	2.32	55	36
K-pusztza summer (Kiss et al., 2002)	1.68	58	40

concentration in Budapest can be explained by the fact that sampling was performed in the non-heating season. The much greater summer concentrations in the New Zealand cities vs. Mace Head are likely due to the contribution by anthropogenic influence and the different aerosol size range (PM₁₀ vs. PM_{1.5}). The concentration in Mace Head (0.04 µg m⁻³) obtained by us was very close to the average value (0.055 µg m⁻³) found by Cavalli et al. (2004) for the same size fraction. The percentages of HULIS in the WSOC and TC fractions were in general lower at the urban and marine sites than in the continental background locations. Nevertheless, their contributions were still quite significant indicating the global importance of HULIS in controlling the mass concentration and physico-chemical behaviour of organic and, in certain cases, even the total atmospheric aerosol.

In the light of this it would be desirable to standardise an analytical method that could be easily and routinely used for HULIS concentration determination in a large number of samples. The isolation procedure used by us is quite reliable but it is laborious and time-consuming. So, there is a need to find a simple method that may be directly applied to the aqueous aerosol extract without the requirements of any further sample preparation.

UV-VIS spectroscopy and fluorescence spectrometry are often used for quantitative determination of humic substances in soil and water (Hautala et al., 2000; Goslan et al., 2004). As fluorescence may be extremely sensitive to the different environmental factors (e.g., chemical composition, ionic strength, pH of the solution) (Senesi, 1990) UV-VIS spectroscopy is usually preferred. Quite a few different wavelengths in both the UV and VIS regions have been suggested (Hautala et al., 2000, and references in Table 1 of this paper). The specific absorptivities at the wavelengths recommended, as well as specific peak fluorescence of the aerosol samples are summarised in Table 4. Data for Budapest and Mace Head, and those for New Zealand can only be compared separately because of the technical reasons mentioned above. Nevertheless it is obvious that the variation of specific fluorescence is at

least about double that of specific absorbance. This indicates, as it might be expected, that UV-VIS spectroscopy is better as a proxy screening method for quantification of water-soluble HULIS. Variation at shorter wavelengths (e.g. 250 and 285 nm) was smaller. But other organic substances can also absorb in this region, and if we are going to use the method without isolation of HULIS they will interfere to a variable and unknown extent. In order to avoid the possible interference longer wavelengths (at or above 330 nm) may be preferred. Furthermore, studies on a larger number of samples from the same sites are highly recommended to investigate whether site- and probably season-specific absorptivities do exist, which has also been observed in the case of black carbon (soot) particles (Liousse et al., 1993).

3.4. Sources

Biomass burning is thought to be one of the major sources of HULIS (Mayol-Bracero et al., 2002). Primarily, wood combustion was also the origin of HULIS in the New Zealand cities during winter. This has been proved by the identification of biomass burning tracers such as levoglucosan and dehydroabietic acid in relatively large amounts. More details about this study can be found elsewhere (Krivácsy et al., 2006). Dehydroabietic acid was also detected both in Auckland and Christchurch during summer. So, a contribution of biomass burning to the HULIS formation even in summer cannot be excluded.

However, the summer concentration of the biomass tracer was only about 1% of that in winter. We should assume another and likely biogenic source which at least partly determines the atmospheric concentration of HULIS during summer in the sea-shore New Zealand cities. Low- and moderate-molecular-weight fulvic acids comprise more than 98% of the humic substances in ocean water (Malcolm, 1990). These compounds may be transported from the liquid to the gas (air) phase by bubble bursting, and become attached to sea-salt

Table 4

Specific absorbance ([AU dm³/µg HULIS-carbon] for New Zealand samples; [intensity dm³/µg HULIS-carbon] for Budapest and Mace Head) at certain wavelengths, and specific fluorescence [intensity dm³/µg HULIS-carbon] at maximum emission wavelength

Sample	Specific UV-VIS absorbance					Specific fluorescence
	250 nm	285 nm	330 nm	350 nm	400 nm	
Budapest- fine	9.23	5.34	2.38	1.48	0.42	980
Mace Head	6.84	4.00	1.46	0.89	0.27	380
AUC-WIN	5.58	3.80	1.79	1.29	0.45	4.1
AUC-SUM	4.36	2.63	1.10	0.78	0.30	5.3
CHR-WIN	6.25	4.58	2.41	1.64	0.34	8.1
CHR-SUM	5.92	3.93	1.69	1.04	0.24	15.2

particles. Recently, O'Dowd et al. (2004) have already linked dominant contribution of organic matter in clean marine air masses to biogenic processes in oceanic surface waters of North Atlantic. We believe that this primary source of HULIS in the marine environment might be relevant. The size distribution of organic carbon in marine aerosol may support this idea as a significant fraction of organic carbon can be found in the coarse particles (Neusüss et al., 2002; Cavalli et al., 2004). Furthermore, in the supermicron ($>1.5 \mu\text{m}$) size range a concentration of water-soluble HULIS carbon ($0.046 \mu\text{g m}^{-3}$) comparable to that in submicron ($<1.5 \mu\text{m}$) size range ($0.055 \mu\text{g m}^{-3}$) was measured (Cavalli et al., 2004).

In Budapest the separate sampling of fine and coarse particles gave the opportunity to get direct information about the size distribution of HULIS. In the coarse fraction the fluorescence spectra for the front and back filters were almost identical (Fig. 2). The UV-VIS absorption of HULIS isolated from the front filter was slightly higher than that isolated from the back filter, and a weak absorption above 330 nm was also detected (Fig. 1). In the fine mode, the differences in spectral intensities between front and back filters were much more obvious (Figs. 1 and 2). This suggests, in contrast to Mace Head, that HULIS were mostly present in the fine particles, despite the fact that the OC concentrations in the fine and coarse fractions were about the same: 6.70 and $5.33 \mu\text{g m}^{-3}$, respectively. (This is why no concentration for Budapest coarse fraction is listed in Table 4.) However, presence of HULIS in the coarse particles cannot entirely be excluded which was also shown at an urban site in the USA by fluorescence study of single particles of $3\text{--}10 \mu\text{m}$ in diameter (Pinnick et al., 2004). But it can be pointed out that in the Budapest samples the concentration of HULIS in the coarse fraction was small, at least one order of magnitude smaller than that in the fine particles. This result is in good agreement with those of previous studies at continental sites revealing that most of the carbon is in the fine particles and dispersion of the Earth's surface as the major source of atmospheric HULIS is not important (Gelencsér et al., 2000, 2002).

As has already been mentioned, the application of a dual filter sampling system in Budapest led to the observation of agents on the back filters which fluoresced similar to HULIS (Fig. 2). One of the reasons for this might be that HULIS are present in the gaseous phase in the atmosphere and can directly be adsorbed onto quartz fibre filters. We believe that this is very unlikely owing to the low volatility of HULIS (Gelencsér et al., 2000). A second and more meaningful

reason could be that gaseous precursors do adsorb on the filter surface where polymerisation reaction can take place resulting in the formation of HULIS in a similar way to that suggested e.g., by Kalberer et al. (2004). If this is true we can conclude that the production rate of HULIS is pretty high as the sampling time in this case was only 12 h.

The UV-VIS and fluorescence features of HULIS on the front and back filters were, however, not exactly the same. Unlike HULIS on the front filters, the compounds on the back filters did not absorb above 330 nm (Fig. 1). A similar phenomenon was described by Hoffer et al. (2004) during the experiment where HULIS were synthesised from a single aromatic acid precursor in model cloud water. The specific intensities also differed between front and back filters, but separately for front and back filters they were almost the same in both the fine and coarse size fractions (Figs. 1 and 2). This may indicate, on one hand, that the same HULIS production reactions occurred on both fine and coarse back filters, as might be expected, and on other hand, it reveals that HULIS was of similar physico-chemical structure independent of particle size. The specific absorbance of the back filter HULIS was greater at lower wavelengths (235–280 nm) but smaller at higher wavelengths (above 280 nm) (Fig. 1). The specific fluorescence of back filter HULIS was significantly higher than that of front filter HULIS (Fig. 2), with the maximum value being about four times larger. On the other hand the emission wavelength corresponding to maximum intensity was about 10 nm less, 395 nm compared to 405 nm typical of HULIS on front filters. We think that all these differences primarily suggest a lower MW of HULIS on the back filter in comparison to the front filter. We suggest therefore that compounds found on back filters are HULIS in a starting phase of polymerisation still having lower MW, consequently higher fluorescence but lower high wavelength absorbance.

The possibility of HULIS being formed on filters during sampling of coarse leads to a sampling artefact when studying humic matter in atmospheric aerosol. The use of a back filter is suggested during sampling to take this artefact into account. However, we believe that this artefact is probably more crucial close to the pollution sources where the atmospheric concentration of gaseous precursors can be high. This might have been the case in Budapest where about 25% of the front filter HULIS was found on the back filter (Table 4). The subtraction of the back filter value provided a more realistic HULIS concentration of $0.68 \mu\text{g m}^{-3}$ for the aerosol phase. This means that the magnitude of the

sampling artefact in terms of HULIS carbon was about +33% ($0.22 \mu\text{g m}^{-3}/0.68 \mu\text{g m}^{-3} \cdot 100\%$).

These results confirm the idea that in certain periods HULIS can be produced from gaseous precursors of both anthropogenic and biogenic origin in continental environments (Gelencsér, 2004). At urban sites the precursors probably derive first of all from anthropogenic sources. However, in Budapest sampling was accomplished in the non-heating season. So we think that other possible anthropogenic sources (e.g. fossil fuel combustion) should be taken into account.

4. Conclusions

Water-soluble HULIS was found to comprise about 20% of WSOC and 10% of TC in marine, and 25–50% of WSOC and 10–20% of TC in urban environments. Absorptivity ratios at 250 vs. 340 nm wavelengths might be useful to characterise the aromatic content of HULIS and differentiate between sources. UV-VIS absorption at $\lambda > 330 \text{ nm}$ can be recommended for the rapid, semi-quantitative analysis of HULIS directly in the water aerosol extracts. The MW was $< 1000 \text{ Da}$ revealing the fulvic-acid like character of water-soluble HULIS. Application of dual filter system for sampling in Budapest verified about 30% of positive sampling artefact which strongly suggests the need of intensive research on this topic. Certainly there are still many other questions calling for further studies on the physics, chemistry, formation and atmospheric behaviour of HULIS. We believe that, because of the universal occurrence and effects of atmospheric humic matter, these questions must be clarified for a better understanding of the global (e.g. climatic) influence of atmospheric aerosol.

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