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**Chirality and origin of  
atmospheric  
humic-like  
substances**

I. Salma et al.

# Chirality and origin of atmospheric humic-like substances

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## Abstract

Aerosol water extracts and atmospheric humic-like substances (HULIS) obtained from  $PM_{2.5}$ -fraction aerosol samples collected in a rural/continental background environment and in an urban environment in spring and summer, and at a tropical site that was heavily impacted by biomass burning were studied. Mean organic matter-to-organic carbon mass conversion factor and standard deviation of  $2.04 \pm 0.06$  were derived for HULIS from biomass burning. Mean atmospheric concentrations of HULIS for the rural and urban environments, and for the biomass burning during daylight periods and nights were 1.65, 2.2, 43, and  $60 \mu\text{g m}^{-3}$ , respectively. This indicates that intense emission sources and/or formation mechanisms of HULIS operate in biomass burning. Mean contributions of C in HULIS (HULIS-C) to water-soluble organic carbon (WSOC) were 35, 48, 63, and 76%, respectively, for the sample set listed. The data suggest that HULIS-C is the major component of the WSOC in tropical biomass burning, and that HULIS most likely do not share common origin in the three environments studied. Differentiation among the possible formation processes was attempted by investigating the optical activity of HULIS through their (electronic and vibrational) circular dichroism properties. The urban HULIS did not show optical activity, which is in line with the concept of their major airborne formation from anthropogenic aromatics. The rural HULIS revealed weak optical activity, which may be associated with one of their important formation pathways by photo-oxidation and oligomerisation, i.e., with the formation from chiral biogenic precursors with one of the enantiomers slightly enriched. The biomass burning HULIS exhibited strong effect in the vibrational circular dichroism as a clear distinction from the other two types. This was related to the contribution of the thermal degradation products of lignins and cellulose. The biomass burning HULIS resemble Suwannee River Fulvic Acid standard more closely in some aspects than the urban and rural types of HULIS, which may be related to their common origin from plant material.

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## 1 Introduction

Aerosol particles containing atmospheric HUmic-Like Substances (HULIS) can play an important role in continental environments (Fuzzi et al., 2006). They act as cloud condensation nuclei since HULIS make up a major mass fraction of the continental fine-sized water-soluble organic compounds (Salma et al., 2007 and references therein). HULIS also influence the formation, water activation or equilibrium of cloud or fog droplets in the air (McFiggans et al., 2006; Dinar et al., 2006; Asa-Awuku et al., 2007; Wex et al., 2007; Ziese et al., 2008) by affecting their surface tension (Facchini et al., 1999; Kiss et al., 2005; Salma et al., 2006; Topping et al., 2007) and water activity of the droplets (Varga et al., 2007). In addition, HULIS are coloured and interact directly with the sunlight (Dinar et al., 2008). Furthermore, their amphiphilic properties cause aggregation above a critical concentration leading to solubilisation of other aerosol constituents (Tabazadeh, 2005; Salma et al., 2008) including some trace elements with biological role.

Atmospheric humic-like substances are regarded to be a supramolecular system of multi-component organic compounds and oligomers that exhibits many properties similar to those of humic matter (Graber and Rudich, 2006 and references therein). They contain aromatic rings and aliphatic lateral chains with carboxyl, hydroxyl, carbonyl or methoxy terminal groups. They are defined operationally; and are sometimes called organic macromolecules (Zappoli et al., 1999; Samburova et al., 2005b) or macromolecular polycarboxylic acids (PA) (Decesari et al., 2000). The existing isolation or separation methods are believed to yield largely overlapping generic classes of compounds. Nevertheless, HULIS isolated from aerosol samples collected in diverse environments of the world or seasons exhibit somewhat different properties (Blazsó et al., 2003; Kiss et al., 2005). Furthermore, spontaneous change in the aggregation and conformational states of HULIS can take place under changing solution conditions, and, therefore, uniform properties for such a complex mixture cannot always be expected (Salma and Láng, 2008). These conceptual and experimental disadvantages

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largely complicate their study.

Despite their potential importance, our knowledge on the formation of the fine-sized HULIS is still deficient. Several formation processes were proposed on the basis of atmospheric and smog chamber experiments. They include both primary emissions and chemical reaction pathways in gaseous and/or condensed phases. Biomass burning was recognized as a major primary source of HULIS via incomplete breakdown of polymeric plant matter, or recombination and direct condensation of low-molecular-mass primary combustion products (Zappoli et al., 1999; Facchini et al., 2000; Graham et al., 2002; Mayol-Bracero et al., 2002). About 33% of all plant matter is made of cellulose; wood as an important form of biomass is composed of cellulose (40–50% of dry mass), hemicelluloses (20–30% of dry mass), lignins (20–30% dry mass) and extraneous matter (extractives and ash, 4–10% of dry mass, Simoneit et al., 1999). Cellulose occurs as polysaccharide macromolecules consisting of a long linear chain of several hundred to over ten thousand linked  $C_6H_{10}O_5$  units. Hemicelluloses are mixtures of polysaccharides with much shorter and branching chains, and are less structured. Lignins are phenolic polymers produced primarily from hydroxycinnamyl alcohols, e.g., *p*-coumaryl, coniferyl and sinapyl alcohols. During the wood combustion, cellulose decomposes in two alternative ways. The first pathway (flaming combustion) occurs at temperatures  $>300^\circ C$ , and it is related to bond cleavage by transglycosylation, fission and disproportionation reactions resulting in tarry anhydro-sugars and volatile products which are rapidly oxidized in the flame. The second pathway (smouldering combustion) dominates at temperatures  $<300^\circ C$ , and it involves depolymerisation, water elimination, fragmentation and oxidation, and leads to char formation and emits large amounts of incompletely oxidised pyrolysis products with low vapour pressure. Cellulose has chirality which means that its molecules can theoretically exist in two distinct forms (mirror images which are referred to as enantiomers) that are distinguishable by their interaction with polarized light. Cellulose produced by biosynthesis is only built up from  $\beta$ -D-glucopyranose units, which endows the natural cellulose and its derivatives with very strong optical activity. HULIS formed via the thermal degradation of cellulose

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in biomass burning are expected to maintain this chirality and to show optical activity. Burning of lignins produces breakdown products such as acid, aldehyde, ketone and alkyl derivatives of the phenols into the smoke. Lignins are considered to be not optically active (Ralph et al., 1999), and, therefore, their derivatives produced by burning are also not expected to exhibit substantial optical activity.

Formation mechanism of secondary organic aerosol (SOA) implicitly including HULIS as one of its major component (see below) involves generally photochemical reactions of volatile organic compounds (VOCs) in the gas phase followed by oligomerisation of some low volatile products (Claeys et al., 2004a, 2004b; Kroll and Seinfeld, 2008). There is also evidence for their formation by heterogeneous reactions of unsaturated gas-phase compounds on particle surfaces in the presence of acids (Jang et al., 2002; Limbeck et al., 2003; Gao et al., 2004), or by in-cloud processing (Gelencsér et al., 2003; Hoffer et al., 2004). Compounds that contribute to the oligomerisation can originate from both biogenic and anthropogenic sources (Gao et al., 2004; Iinuma et al., 2004; Kalberer et al., 2004; Baltensperger et al., 2005). In forested areas, isoprene, monoterpenes, and sesquiterpenes are the most abundant biogenic VOCs (they make up 55% of the biogenic VOCs emitted into the global atmosphere; Guenther et al., 1995). The two latter compound classes have large aerosol yield, and, hence, they are important precursors of the oligomerisation (Hoffmann and Warnke, 2007) leading to secondary HULIS as well. Isoprene has no chirality, while many of the relevant monoterpenes are chiral compounds. The (–)-form of the dominant monoterpene,  $\alpha$ -pinene (accounting for approximately 50% of all monoterpenes) was measured in large excess in relation to its (+)-form over and within a tropical forest, while the reverse was observed over a boreal forest consisting primarily of Scots pine (Williams et al., 2007). The relative enrichment for one of the two enantiomer precursors could be reflected in the optical activity of secondary HULIS as well since both enantiomers react with OH radical and O<sub>3</sub> at the same reaction rate (Nunes et al., 2005).

In cities, it is vehicles that contribute notably to the atmospheric concentrations of VOCs. Road traffic mainly emits ethane, propane and aromatics (e.g., benzene,

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toluene, ethyl benzene, and xylenes). The latter group of compounds contains important or possibly the dominant precursors of SOA (Atkinson, 2000; Hoffmann and Warnke, 2007) including secondary HULIS as a major component. Acid catalysed reactions of aldehydes or ketones on the surfaces of or inside the particles are also able to form oligomers (Hoffmann and Warnke, 2007). These concepts are also backed by ambient/field observations. It was estimated, e.g., that HULIS contributed up to 55% of SOA in the PM<sub>2.5</sub>-size fraction in an urban environment in spring, and a positive sampling artifact of 17% derived for urban HULIS also indicates that the secondary formation pathways are considerable in cities (Salma et al., 2007). Significant correlation between photochemical activity and atmospheric HULIS concentration in summer also confirms their secondary formation (Limbeck and Puxbaum, 1999; Samburova et al., 2005b). Atmospheric oxidation of soot particles with O<sub>3</sub> also produces HULIS (Decesari et al., 2002). The latter formation can only account for a certain part of HULIS since the products did not resemble the whole variety of the properties reported for atmospheric HULIS. It is expected that urban HULIS do not show substantial optical activity since their major precursors are not chiral, and even if some of the precursors are optically active, the chemical reactions (especially the radical-assisted reactions, which are typical) in the air yield racemic mixtures with no optical activity.

All emission and formation processes overviewed above can be operative in an environment but their intensity and extent can vary for different environments or different seasons. Secondary HULIS generated in the gas phase usually condense onto existing aerosol particles which include particles containing primary HULIS and HULIS from heterogeneous mechanisms and chemical aging as well, and, therefore, the emission sources and various formation processes become difficult to recognize and quantify separately. Comparative study on the optical activity through the circular dichroism of HULIS isolated from aerosol samples collected in rather different environments including a rural/continental background site, an urban environment and a tropical site heavily impacted by biomass burning, can, however, provide new information on their origin, and can give us further clues for identifying the major emission sources types

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and for understanding the basic formation processes of HULIS.

## 2 Experimental

### 2.1 Samples and sample treatment

The rural/continental background aerosol samples were collected at K-pusztá (latitude 46°58' N, longitude 19°35' E, altitude 125 m above mean sea level, m.s.l.) on the Great Hungarian Plain approximately 80 km southeast from Budapest, and 15 km northwest from the nearest town Kecskemét. The site is located on a clearing within a mixed forest (62% coniferous and 28% deciduous trees) including 10% grassland. Two daily collections were conducted on 4 May and 6 May 2008 with a KS-300 high volume aerosol sampler equipped with a PM<sub>2.5</sub> pre-separator (Kalman System, Hungary) and operated at an air flow rate of 530 l min<sup>-1</sup>. Whatman QM-A quartz fibre filters pre-baked at 650°C for 8 h before sampling in order to remove possible organic contaminants were used as collection substrate. The exposed area of the filters was 154 cm<sup>2</sup>.

The urban aerosol sample was collected in central Budapest (at Széna Square, latitude 47°37.4' N, longitude 19°1.7' E, altitude 114 m above m.s.l.) from 3 till 10 June 2008 for one week. The site is heavily influenced by vehicular traffic. The aerosol sample and a field blank filter were taken with a DHA-80 high-volume aerosol sampler equipped with a PM<sub>2.5</sub> pre-separator (Digitel Elektronik, Switzerland) and operated at an air flow rate of 500 l min<sup>-1</sup>. Whatman QM-A quartz fibre filters were used as collection substrate. The filters had been pre-baked at 550°C for 12 h before sampling. The exposed area of the filters was 154 cm<sup>2</sup>.

The biomass burning aerosol samples were collected on a pasture site (latitude 10°45.7' S, longitude 62°21.5' E, altitude 315 m above m.s.l.) in the Amazon Rainforest, state of Rondônia, Brazil, during the LBA-SMOCC field campaign (e.g., Decesari et al., 2006). The samples that are dealt with in the present study were taken from 18 till 22 September 2002 separately over daylight periods (from about 07:45 through 17:45

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local time, LT, UTC-4) and night (from about 18:30 through 07:00 LT). The biomass burning activity was reported to be the most intensive during this period of the campaign (Decesari et al., 2006). The samples were collected with a high-volume dichotomous virtual impactor on Gelman Pallflex front and back quartz fibre filters in series.

5 The filters had been pre-baked at 550°C for 24 h prior to sampling. The exposed area of the filters was 61.5 cm<sup>2</sup>. PM<sub>2.5</sub>-size fraction aerosol samples collected on the front filters in the high-flow air stream at a flow rate of 300 l min<sup>-1</sup> were used for the present research. Altogether five samples for the daylight periods, five samples for nights, and two field blank filters were obtained during the days specified above.

10 The aerosol samples were placed in pre-baked Al foils, and were kept in the freezer until further treatment. The two samples collected at the rural site were treated together. Of the aerosol samples collected at the biomass burning impacted site, one quarter of each filter was processed for the present study. The filter sections for the daylight periods were treated together, and the filter sections for the nights were also processed together. The samples were utilized for isolation of pure HULIS by a one-step solid-phase extraction (SPE) method (Varga et al., 2001; Kiss et al., 2002; Salma et al., 2008). In short, the filters were cut into pieces and extraction was carried out with high-purity reagent Milli-Q water for 36 h. The water extracts were filtered through a 0.22 µm syringe PVDF membrane filter (Millipore, USA) to remove the filter debris and suspended insoluble particles. The pH of the filtrates was adjusted to 2 with HCl, and HULIS were separated by pre-conditioned SPE columns (Oasis HLB, Waters, USA). The retained organics were eluted with methanol, and the eluents were subdivided into several aliquots, which were evaporated to dryness with nitrogen stream. The mass of the resulting pure HULIS aliquot samples was measured by gravimetry, and the weighing was repeated one day later after the samples had been placed into a drying chamber with a temperature of 40°C for 1 h. The samples were kept in the refrigerator until further dissolution.

25 Some aliquots of the HULIS samples were dissolved in Milli-Q water, and the solutions were utilised for electronic circular dichroism (ECD) spectrometry and UV ab-



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sorbance measurement without any treatment. Other HULIS aliquots were dissolved in acetone with a volume of 150–500  $\mu\text{l}$ , and the solutions were utilised to prepare thin films for vibrational circular dichroism (VCD) spectrometry and IR absorbance measurement. Approximately 20  $\mu\text{l}$  of the HULIS solution in acetone was carried on a window plate made of  $\text{CaF}_2$  as a droplet, it was dried at room temperature, and the procedure was repeated two or three times at the same location of the plate in order to reach reasonable absorbance values. Spots with a typical diameter of 5–7 mm were obtained in this way. Of the biomass burning HULIS samples, two aliquots obtained for the daylight periods only were investigated by ECD and VCD methods. Suwannee River Fulvic Acid (SRFA, code 2S101F, International Humics Substances Society, based in USA) standard was used for comparative purposes since several previous studies referred to it as representative of atmospheric HULIS. The SRFA standard was dissolved in Milli-Q water and was measured without any treatment, or it was dissolved in acetone to prepare a thin film.

## 2.2 Measuring methods and data treatment

The ECD spectra and UV absorbance were recorded with a Jasco J-810 spectropolarimeter (Japan) in the wavelength interval from 200 to 280 nm and from 260 to 400 nm in a nitrogen atmosphere. Cuvettes made of quartz windows, and with path lengths of  $d=0.2$ , 0.1 or 0.02 cm were used. Baseline correction for the ECD was achieved by subtracting the spectrum recorded for the solvent under the identical experimental conditions. The ECD data were recorded in ellipticity ( $\theta$ ) which were converted to molar circular dichroism ( $\Delta\varepsilon$ ) defined as the differential molar extinction coefficient for the left-handed circularly polarized light ( $\varepsilon_L$ ) and for the right-handed circularly polarized light ( $\varepsilon_R$ ) according to the equation:

$$\Delta\varepsilon \equiv \varepsilon_L - \varepsilon_R = \frac{1}{cd} (A_L - A_R) = \frac{\theta}{cd k}, \quad (1)$$

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where  $c$  is the molar concentration,  $A_L$  and  $A_R$  are the absorbance for the left- and right-handed circularly polarized light, and  $k$  is an aggregate numerical conversion factor, which is  $k=32\,982$  mdeg when  $\theta$  is expressed in unit of mdeg,  $d$  in cm and  $c$  in  $\text{mol dm}^{-3}$ . The molecular mass of HULIS was assumed to be  $280$  g/mol (Kiss et al., 2003; Salma and Láng, 2008), while for the SRFA standard, it was approximated by  $836$  g/mol (Salma et al., 2008).

The VCD spectra (difference in the absorbance for the left-handed circularly polarized light and for the right-handed circularly polarized light as function of wavenumber) and IR absorbance were measured with a Bruker Equinox55 and PMA37 system (Germany) in a nitrogen atmosphere using a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector. An optical filter with a transmission range of  $1800\text{--}800$   $\text{cm}^{-1}$  was applied to optimize the sensitivity of the instrument in the carbonyl and fingerprint regions. The samples were investigated by VCD spectrometry as solid thin films to avoid the strong absorption band of water at a wavenumber of  $1650$   $\text{cm}^{-1}$ . The measurements were performed in two perpendicular orientations of the window plate for 7 h each. If the two corresponding spectra were identical to each other within the experimental uncertainty, then the individual spectra were averaged, and the resulting spectrum was used in further evaluations. Baseline correction for the VCD was adopted by subtracting the spectrum recorded for the clear window plate under the identical experimental conditions.

Concentration of organic carbon (OC) in the liquid HULIS samples and filtered aerosol water extracts were measured with a Multi N/C 2100S total organic carbon (TOC) analyzer (Analytik Jena, Germany) in two steps as the difference between total carbon and inorganic carbon. The injection volume was  $500$   $\mu\text{l}$  for both steps, and three replicate injections were carried out. The measured concentration levels were at least two orders above the detection limit for OC, and the relative uncertainty of the mean OC value calculated from the three individual data was less than 2%. Organic carbon in the liquid HULIS samples represents carbon in HULIS (HULIS-C), while OC in the aerosol water extracts corresponds to water-soluble organic carbon (WSOC). No

correction was applied for sampling artifacts in the present study.

### 3 Results and discussion

#### 3.1 OM/OC conversion factor for HULIS from tropical biomass burning

The OM/OC mass ratio for HULIS is of importance since it can be used for converting HULIS-C data experimentally obtained by the TOC method into HULIS mass concentrations. The conversion factor is also a major source of uncertainty in aerosol chemical mass closure calculations involving organics. Conversion factors between 1.2 and 1.6 were proposed for fine atmospheric aerosol in oxidizing (urban) environments, and a factor of  $2.1 \pm 0.2$  was suggested for aged (non-urban) aerosol (Turpin and Lim, 2001). For rural and urban environments, OM/OC mass conversion factors specifically for HULIS were determined earlier; they are  $1.93 \pm 0.04$  and 1.81, respectively (Kiss et al., 2002; Salma et al., 2007). For biomass burning, the conversion factor was not known. The mass of the pure HULIS samples from biomass burning was large enough even in the aliquot samples (typically between 2 and 3 mg) as to be weighted with a relative uncertainty below approximately 10% and with a sufficient reproducibility. Hence, the OM/OC conversion factors for HULIS from tropical biomass burning was estimated by dividing the gravimetric mass by the corresponding HULIS-C data obtained with the TOC method. Mean OM/OC ratio and standard deviation of  $2.04 \pm 0.06$  was derived for both daylight periods and nights based on altogether four sample pairs. The difference between the ratios indicates that the contribution of C to the HULIS mass changes with the HULIS type, and is likely associated with the different formation processes involved in these environments, chemical aging, and the time that is needed for atmospheric (oxidation) reactions to take place.

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## 3.2 Atmospheric concentration and abundance

Mean atmospheric concentrations of WSOC, HULIS-C and HULIS for rural and urban environments, and for biomass burning during the daylight periods and nights are given in Table 1. The concentrations for the rural and urban HULIS are based on the TOC measurements, and the HULIS masses for the biomass burning were derived from gravimetry. All data for the rural and urban sites, and the WSOC values for the biomass burning are in line with the previous corresponding results (Zappoli et al., 1999; Graham et al., 2002; Kiss et al., 2002; Mayol-Bracero et al., 2002; Samburova et al., 2005a, 2005b; Salma et al., 2007, 2008; Maenhaut et al., 2008). The daily mean HULIS-C concentration for biomass burning of  $24 \mu\text{g m}^{-3}$  is substantially larger than for the mean value for the PA chemical fraction of  $6 \pm 5 \mu\text{g C m}^{-3}$  (Mayol-Bracero et al., 2002) and approximately  $4.4 \mu\text{g C m}^{-3}$  (Decesari et al., 2006) derived for the same sampling site during the dry season in 1999 and 2002, respectively. The difference is explained by the occurrence of the maximum burning activity over the period represented by the selected samples and by the possible differences in the separation protocols applied. Mean concentration of HULIS increases from the rural environment to the urban environment by a factor of 1.4, while the daily mean concentration of HULIS for the biomass burning impacted site was approximately 30- and 20-times larger than for rural and urban environments, respectively. This unambiguously indicates that biomass burning is a rather intense and important emission source of or formation mechanism for HULIS with respect to rural and urban environments. The mean concentration of WSOC for the biomass burning site was larger by a factor of approximately 13 than for the other two environments. The night-to-daylight period concentration ratios for OC, WSOC and HULIS-C at the biomass burning site were 1.49, 1.15, and 1.40, respectively. The larger concentrations during nights were primarily caused by the smaller mixing height of the tropical continental boundary layer which undergoes a diurnal cycle and shows a clear minimum during the night under high pressure meteorological conditions. Mean contributions of HULIS-C to WSOC

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are also shown in Table 1. They were calculated as mean values of the concentrations ratios for the individual sample pairs. The corresponding ratios obtained via the mean gravimetric HULIS mass and mean WSOC value are 72 and 70% for the biomass burning during the daylight periods and nights, respectively. This all implies that HULIS for tropical biomass burning represents the major chemical fraction of WSOC, and the increasing tendency of the HULIS-C/WSOC ratio suggests that basic properties of HULIS from various environments are influenced demonstrably by the differences in their major formation processes. It is also worth noting that OC concentration and standard deviation for the biomass burning samples during the daylight periods and nights measured by the thermal-optical transmission method were  $45\pm 1$  and  $66\pm 2 \mu\text{g m}^{-3}$ , respectively, and, hence, mean HULIS-C makes up 45 and 43% of the OC for these samples, respectively. The OC values and the last two WSOC data for the biomass burning site in Table 1 were extracted and adopted from a more extensive data set (cf. Decesari et al., 2006).

### 3.3 Electronic circular dichroism

Absorbance spectra in the UV/Vis and IR ranges for HULIS were presented, analysed, and discussed earlier (e.g., Zappoli et al., 1999; Krivácsy et al., 2001; Kiss et al., 2002; Duarte et al., 2005) mainly with the purpose of comparing HULIS to humic or fulvic acids, or for identifying some chemical functional groups within HULIS. In the present work, relevant parts of the spectra are shown for different types of HULIS primarily to examine their variance, and to discuss its consequences for optical activity and chromophores. The absorbance spectra of HULIS obtained from biomass burning over daylight periods, rural and urban aerosols, and of the SRFA standard in the UV wavelength interval of 200–280 and 260–400 nm are shown in Fig. 1a and b, respectively. The spectra for HULIS on Panel a were measured in a cuvette with a path length of 0.02 cm, while the curves on Panel b were obtained in a cuvette with a path length of 0.2 cm. The dissolved concentrations were approximately 0.4, 0.5;  $0.4 \text{ g l}^{-1}$ , respectively. For the SRFA standard, a cuvette with a path length of 0.2 cm was only used,

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and the dissolved concentrations on Panels a and b were  $0.17$  and  $0.3 \text{ g l}^{-1}$ , respectively. It is seen that the spectra of HULIS are rather similar to each other in the whole region; in particular, the curves for the biomass burning and rural HULIS are close to each other. The UV absorbance spectra essentially have a featureless shape, and are also similar to those observed earlier. The curves exhibit a maximum at the far end of the wavelength interval, and they are shifted toward larger wavelength values in the order of the samples: urban, rural, biomass burning HULIS, and SRFA. The intensity in the curves decreases almost monotonically with wavelength. There is only a small shoulder on the curves in the region of 245–275 nm, which is also shifted to larger wavelength values in the order of the sample set listed above. The maxima in both regions are explained by the absorption of the aromatic rings, and the (red) shift can be caused by increasing abundance of polar (oxygenated) substituents on the aromatic rings with respect to non-polar substituents, which is inferred from the increasing molar O/C and WSOC/OC ratios derived for this sample set (Kiss et al., 2002; Mayol-Bracero et al., 2002; Salma et al., 2004; see also Sect. 3.4), and from the concept of aerosol aging (Fuzzi et al., 2006).

Figure 2a and b shows the ECD spectra in the wavelength ranges of 200–280 and 260–400 nm, respectively for HULIS obtained from the biomass burning over daylight periods (Panels a), rural (Panels b) and urban aerosols (Panels c), and for the SRFA standard (Panels d). The thinner lines represent the measured data, and the thicker lines were obtained by 10-nm smoothing. The experimental uncertainty interval for the baseline of the differential molar extinction coefficient depends on the actual measurement setup of the instrument, cuvette characteristics, and on the optical properties of the sample measured. The yellow colour of the solutions further hindered the adjustment of the optimal signal-to-noise ratio. The uncertainty interval of the baseline was estimated for each measurement, and it is also shown in the panels by the grey area. All measured and smoothed curves in Fig. 2a lay within the uncertainty interval of the baseline; moreover, the smoothed curves show no tendency. The curves in Fig. 2b also fall within the experimental uncertainty interval of the baseline except for the rural

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HULIS (Panel b in Fig. 2b) which is just above the limit. Moreover, the spectrum for the rural HULIS differs from all the other curves in that it seems to reveal some regular change, an ECD band in the interval of 300–335 nm. The available spare amount of the rural HULIS, unfortunately, did not make it feasible to prepare a more concentrated solution to examine the concentration dependence on the band. We could only record another spectrum for the same solution in a cuvette with a smaller path length of 0.1 cm. The two corresponding smoothed curves showed a similar shape with an amplitude in the specified interval that was smaller for the smaller cuvette. Therefore, it cannot be excluded that the spectra for rural HULIS reveal chirality. The (other) spectra do not necessary mean that HULIS from all investigated environments and the SRFA are achiral. To be optically active, a molecule must be structurally asymmetric and exhibit absorbance. It is possible that the chiral centres associated with HULIS do not exhibit substantial absorbance in the studied range, and, therefore, other aliquots of the samples were investigated further by a complementary, VCD method. In this regard, it is also worth mentioning that levoglucosan as the major single product of the cellulose thermal degradation is chiral; however, it lacks chromophores, and, therefore, it does not generate ECD bands, and also, it is not expected to appear in the isolated chemical fraction.

### 3.4 Vibrational circular dichroism

Absorbance of HULIS obtained from biomass burning over daylight periods, rural and urban aerosols, and the SRFA standard in the IR range for the wavenumber interval from 1800 to 1000  $\text{cm}^{-1}$  that is covered by the VCD spectrometry is shown in Fig. 3. The spectra exhibit relatively few, broad bands, and are comparable to those observed earlier (see Refs. in Sect. 3.3). The curves are also similar to each other for the various HULIS types. The similarity between the rural and urban HULIS is larger than between them and biomass burning HULIS. Some apparent differences are the following: 1) The absorption band near 1730  $\text{cm}^{-1}$  (attributed to C=O stretching for carboxylic acid) is larger for biomass burning than for the other two environments. The larger intensity

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of the band for the biomass burning indicates a larger abundance of the carbonyl functional group, or its different position with respect to the aromatic ring(s). Interestingly, the bands for the other two types of HULIS are almost identical despite the fact that urban HULIS (with a molar O/C ratio of 0.47, Salma et al., 2007) are less oxidized than rural HULIS (with a molar O/C ratio of 0.58, Kiss et al., 2002); 2) The band in the 1600–1650  $\text{cm}^{-1}$  region appears at smaller values for biomass burning HULIS due likely to differences in chemical environment for the various types of HULIS; 3) The band at approximately 1520  $\text{cm}^{-1}$  appears in the spectrum for the biomass burning while it is missing from the other two spectra. The later two absorption bands are related to the skeletal vibrations of the aromatic rings, and are influenced by functional groups linked to the rings. Both bands appear markedly in the IR spectra of lignins and their derivatives (Petrovic et al., 2004) which suggests that lignins contribute remarkably to the HULIS formation in biomass burning; 4) The absorption band at 1280  $\text{cm}^{-1}$  (assigned to the C–O stretching of methoxy-substituted aromatic rings and/or OH bending vibrations of COOH groups) is less evident for biomass burning than for the other two environments. The IR absorption bands for biomass burning HULIS are generally broader, which indicates that biomass burning HULIS are a more complex mixture than the other two types. Interestingly, the absorbance spectrum of biomass burning HULIS agrees better with the spectrum of SRFA standard in several aspects than with that for the other two HULIS types. This might be related to the fact that both biomass burning HULIS and SRFA have common origin in the plant material though they were generated by different decomposing processes, i.e., by thermal degradation and anaerobic biodegradation (or humification), respectively.

Figure 4 shows the VCD spectra of HULIS obtained from the tropical biomass burning over daylight periods, rural and urban aerosols in the wavenumber range of 1800–1000  $\text{cm}^{-1}$ . It is seen that rural and urban HULIS showed practically no optical activity in the whole range. HULIS from biomass burning, however, shows a huge negative VCD band near 1730  $\text{cm}^{-1}$ , which is related to the large absorption band (vibration of carbonyl functional group in carboxylic acid) shown in Fig. 3. This means that the



considerable abundance of the carboxyl group in biomass burning HULIS is in chiral chemical environment, which is a clear distinction from the other two HULIS types. The chiral environment can be associated with the cellulose degradation products. Unlike the HULIS film samples, the SRFA film sample prepared for the VCD measurement formed an oriented anisotropic film which led to linear dichroism artifacts. It means that the shape of the VCD spectra recorded in two perpendicular orientations strongly differed from each other, and, therefore, valuable conclusions on the optical activity of the SRFA standard could not be drawn from the solid sample.

## 4 Conclusions

Atmospheric concentrations and abundances of HULIS in various environments imply that important emission sources or formation mechanisms of HULIS operate in biomass burning environments when compared to rural/continental background and urban sites. Differentiation among the possible formation processes was attempted by investigating the optical activity of various HULIS types. Circular dichroism – applied, to our knowledge, for the first time in aerosol research – together with isolation methods were shown to be valuable accessory tools for investigating carbonaceous constituents. The urban HULIS did not show optical activity in both ECD and VCD spectrometry, which is in line with the concept of their airborne formation mainly from anthropogenic aromatics. The rural HULIS revealed weak optical activity in the ECD spectrometry and no effect in the VCD, which may be associated with one of their important formation pathways by photo-oxidation and oligomerisation, i.e., with the formation from chiral precursor VOCs, e.g., biogenic monoterpenes with one of their enantiomers slightly enriched. Biomass burning HULIS exhibited no activity in the ECD spectrometry and a strong VCD band, which was interpreted – together with their IR absorbance – as the contribution of thermal degradation products of lignins and possibly cellulose. It has also to be noted that the conclusions are based on a limited number of samples, and, therefore, the topic definitely needs further experimental studies. In

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addition, the achievements of the method can also be improved in the future studies by further optimising, modifying, and extending the procedures presented.

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**Table 1.** Mean atmospheric concentrations of water-soluble organic carbon (WSOC), carbon in humic-like substances (HULIS-C) and humic-like substances (HULIS) in  $\mu\text{g m}^{-3}$  for rural/continental background and urban environments and for a tropical biomass burning impacted site during daylight periods and nights, and the mean contribution of HULIS-C to WSOC in %.

HULIS type Constituent	Rural	Urban	Biomass burning	
			Daylight	Night
WSOC	2.5	2.6	32	37
HULIS-C	0.86	1.24	20	28
HULIS	1.65 <sup>a</sup>	2.2 <sup>a</sup>	43 <sup>b</sup>	60 <sup>b</sup>
HULIS-C/WSOC	35	48	63	76

<sup>a</sup> Calculated from TOC data and OM/OC conversion factors

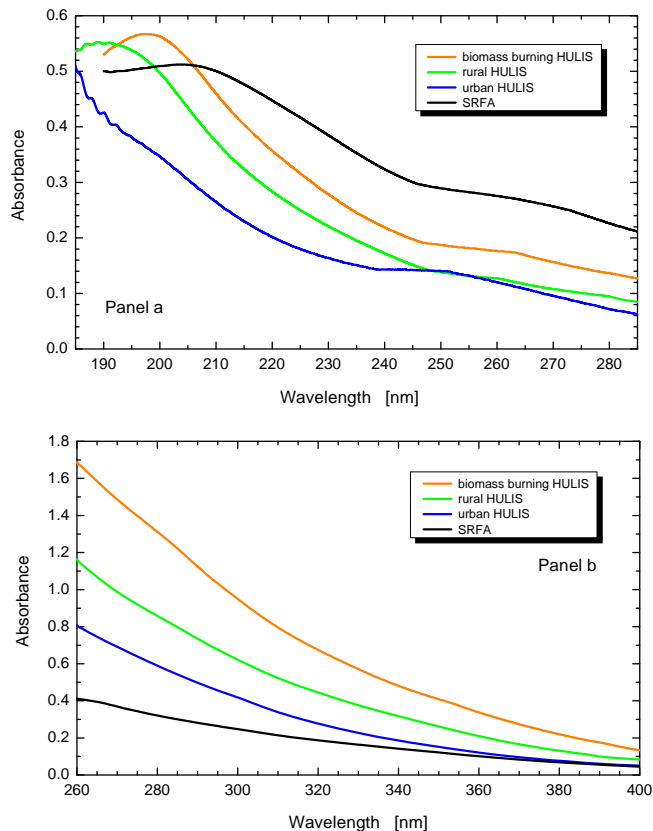
<sup>b</sup> Derived from gravimetry

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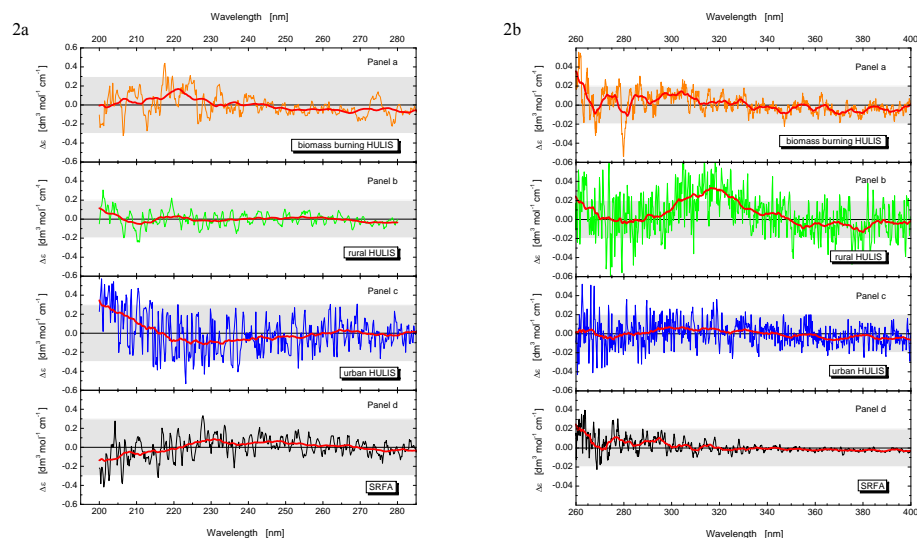
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**Fig. 1.** UV absorbance spectra for HULIS isolated from tropical biomass burning, rural and urban aerosols, and for the Suwannee River Fulvic Acid (SRFA) standard in the wavelength range of 190–280 nm **(a)** and 260–400 nm **(b)**. The HULIS concentrations and cuvette path length utilised are described in the text.

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**Fig. 2.** Electronic circular dichroism spectra in the wavelength ranges of 200–280 nm (2a) and 260–400 nm (2b) for HULIS isolated from tropical biomass burning (a), rural (b) and urban (c) aerosols, and for the Suwannee River Fulvic Acid (SRFA) standard (d). The thinner lines are the measured data, and the thicker (red) lines were obtained by 10-nm smoothing. The uncertainty interval of the baseline is shown by the grey area.

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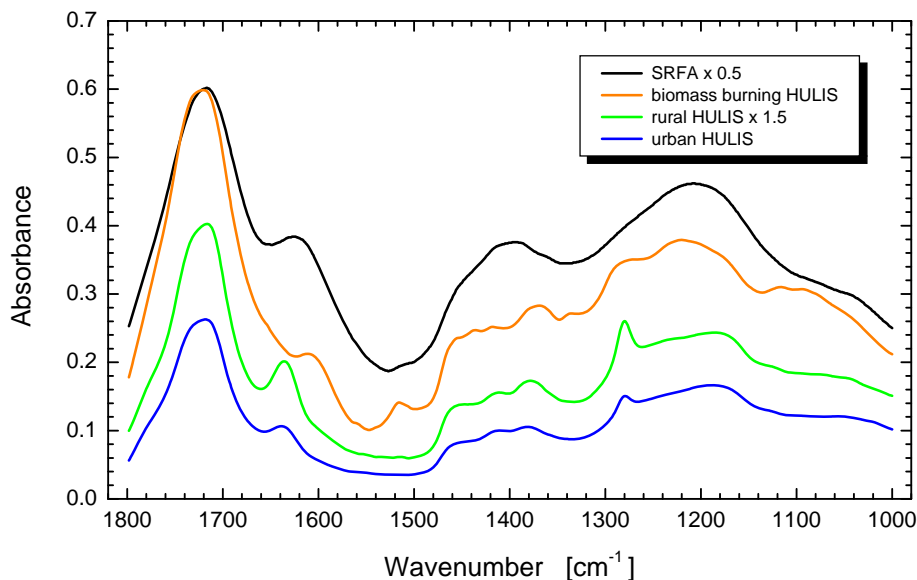
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**Fig. 3.** IR absorbance spectra for HULIS samples isolated from urban, rural and tropical biomass burning aerosols, and for the Suwannee River Fulvic Acid (SRFA) standard in the wavenumber range of 1800–1000 cm<sup>-1</sup>.

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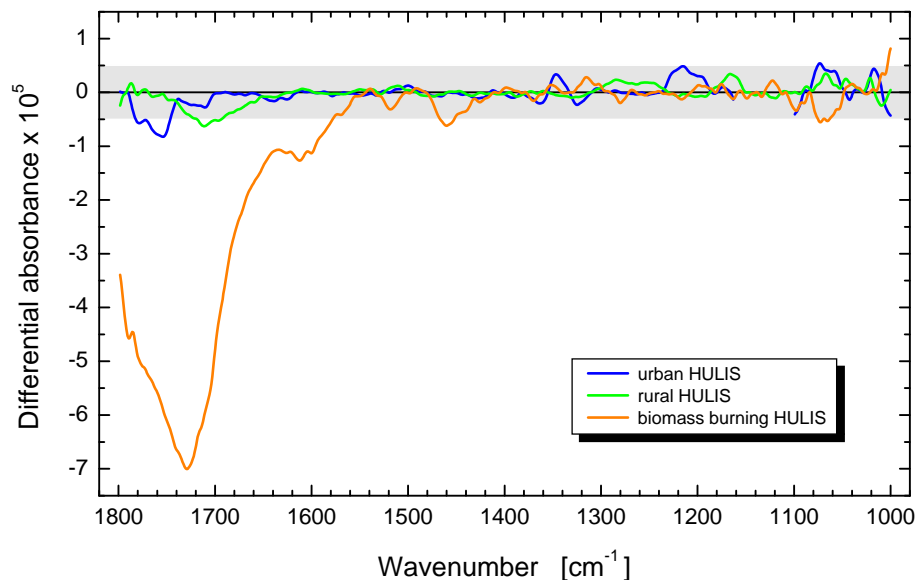
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**Fig. 4.** Vibrational circular dichroism spectra for HULIS samples isolated from urban, rural and tropical biomass burning aerosols in the wavenumber range of 1800–1000 cm<sup>-1</sup>. The uncertainty interval of the baseline is shown by the grey area.

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