Determination of water and alkaline extractable atmospheric humic-like substances with the TU Vienna HULIS analyzer in samples from six background sites in Europe

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[1] With a newly developed method based on the combination of two separation steps (by polarity and by acidity) with a universal detector for organic carbon, efficient isolation of humic-like substances (HULIS) from the matrix and quantitative determination of the isolated organic carbon is achieved. This new method was applied to determine the water extractable (HULISWS) and, in sequence, the 0.1 M NaOH alkaline extractable HULIS (HULISAS) fractions in aerosol from six sites situated at a transect from west to east across Europe. The sum of the two HULIS fractions is here defined as total HULIS (HULIST). The lowest 12-month average concentrations of HULIST ranged from 0.075 μgC/m3 at the Azores (Portugal) to 1.7 μgC/m3 at the continental background site K-puszta (Hungary). On the continent, the HULIST concentration decreases exponentially with elevation. The relative amounts of water extractable and alkaline soluble HULIS were relatively similar at the six sites. Dramatic differences were observed for the seasonal variations of the HULIS fractions at the different sites. At the Azores, as well as at the higher mountain sites (1450 and 3100 m), a summer maximum of the HULIST concentration was observed, while at the continental low-level sites (Aveiro and K-puszta), winter maxima dominated the seasonal variation. The summer/winter ratio of the HULIST concentration varied from 7.1 at Sonnblick to 0.36 at Aveiro. The seasonal variation at the two continental lower-level sites with winter maxima might be explained by overlapping of a weaker summer source and a stronger winter source.


1. Introduction

[2] The composition of the organic part of the atmospheric aerosol and the respective source contributions are far less known than those of the inorganic part. In the last years it was shown that polymeric (by other authors also referred to macromolecular) species are important contributors to the mass of organic compounds in rural and urban aerosol. Cellulose as a constituent of plant debris [Kunit and Puxbaum, 1996; Puxbaum and Tenze-Kunit, 2003], as well as fungal spores [Bauer et al., 2002] constitute several per cent of the organic compounds as primary organic aerosol. The largest contribution, however, was found to be formed from a group of substances, with considerable similarities in structural properties to humic and fulvic acids [e.g., Havers et al., 1998a; Zappoli et al., 1999; Kiss et al., 2002; Mayol-Bracero et al., 2002]. A significant part of the humic-like substances (HULIS) is water-soluble and was recognized in precipitation [Spokes et al., 1996], fog water [Krivácsy et al., 2000] and aqueous extracts of fine aerosol [Zappoli et al., 1999]. This implies that HULIS influence the hygroscopicity and likely the CCN forming ability, thus the optical properties of the aerosol particles containing these species [Facchini et al., 1999].

[3] The atmospheric humic-like substances were characterized by several analytical methods such as capillary electrophoresis [Krivácsy et al., 2000], voltammetry [Gelencsér et al., 2000a], pyrolysis gas chromatography coupled with mass spectrometry [Gelencsér et al., 2000b], elemental analysis [Kiss et al., 2002] and different spectroscopic (UV, IR, NMR, ESI/MS, MS/MS, fluorescence) techniques [Havers et al., 1998b; De Cesari et al., 2000;
These investigations confirmed that the structural units of these compounds were very similar to natural humic and fulvic acids. As it was mentioned previously, one part of HULIS is soluble in water. This fraction is composed of mainly fulvic acids. On the other hand, a significant fraction of humic acids, having a more hydrophobic and acidic character and higher molecular weight, can be dissolved in alkaline medium like 0.1 M NaOH [Havers et al., 1998a], nevertheless this part of HULIS has not got much attention in previous studies. According to Havers et al. [1998a] a further fraction (“HUMIN”) may be obtained by hydrolysis in 0.5 M NaOH at 100°C and 24 h reaction time.

The current situation of the research of atmospheric HULIS is reflected by the lack of a sensitive method for the analysis of atmospheric HULIS. Therefore the data set of atmospheric HULIS is small and time series are not available until now. The problem of a sensitivity lacking determination method was resolved recently by Limbeck et al. [2005] introducing a “HULIS analyzer” based on a flow injection system coupled to a dissolved organic carbon detector. Here we apply the new method to investigate the temporal and regional variation of two HULIS fractions, namely the water-soluble fraction and a fraction soluble in 0.1 M NaOH. Thus the HULIS carbon content was determined not only of the water-soluble fraction, but also of the NaOH extract of the aerosol following the water extract. The HULIS concentrations were determined for six background sites located on a west-east transect across Europe. The contribution of HULIS is related to the organic carbon and other aerosol constituents obtained by classical methods. The six background sites were aerosol sampling sites of the EU project CARBOSOL.

2. Experimental Section

2.1. Sampling

Aerosol samples were collected at six sites along an east-west transect across Europe. These sites from west to east are: Azores (Terceira Islands, Portugal, 50 m asl, oceanic conditions), acronym AZO, Aveiro (Portugal, 40 m asl, with rural and coastal conditions; AVE), Puy de Dome (France, 1450 m asl, highlands; PDD), Schauinsland (Germany, 1205 m asl, highlands with continental forest; SIL), Sonnblick (Austria, 3106 m asl, mountain peak in the central Alps; SBO) and K-pusztas (Hungary, 136 m asl, located in the Great Hungarian Plain surrounded by continental forest; KPZ). Aerosol sampling on quartz fiber filters was carried out with high-volume samplers with a flow rate of 30–60 m³/h for a period of 24 month on each sampling site in the period between September 2002 and May 2004. Sampling periods were generally 7 days. Sampling instruments were used were high-volume samplers, at AZO, AVE and KPZ home built instruments; at PDD, SIL and SBO manually operated Digitel’s DH77. The cutoff diameters of the sampler’s inlet systems were 2.5 μm at AZO, AVE, SBO and KPZ. At PDD and SIL an elutriating inlet was used. For this work the time periods analyzed at the sites were around 12 months. For a map and details of the sites and sampling see Pio et al. [2007].

2.2. Analysis

For determining the HULIS carbon content of atmospheric samples we used a recently developed method [Handler, 2003; Limbeck et al., 2005]. The whole HULIS determination procedure involves (1) aqueous and alkaline extraction of analytes from quartz fiber filters, (2) off-line sample preparation on a C18 SPE cartridge, and (3) HULIS determination with the FIA-SAX-DOC “HULIS analyzer” (flow injection–strong anion exchange resin–dissolved organic carbon “HULIS analyzer”). This analyzer is in the following text referred as to “TU Vienna HULIS analyzer.”

The TU Vienna “HULIS analyzer” was constructed on the basis of a flow injection system incorporating a SAX ion exchanger column coupled to a continuous flow DOC instrument. The DOC determination is based on combustion in a catalyst oven and nondispersive infrared sensing of CO₂.

2.2.1. Filter Extraction

Aliquots from high-volume quartz filters (2–20 cm²) were extracted in 7 mL MilliQ water for 2 hours while regularly shaking. After decanting the supernatant into another test tube, 2 mL MilliQ water was added to the decanted filter followed by another extraction for 10 min. Then, the liquid phase was added to the first extract constituting the solution of the water soluble HULIS fraction (HULISw). For dissolving the alkaline soluble fraction (HULISa) the same procedure (7 ml for 2 hrs; 2 mL for 10 min) was carried out with the water treated filter but with 0.1 M NaOH. Total HULIS (HULIS₅) was defined as the sum of water soluble and alkaline soluble fraction of HULIS. A direct extraction with 0.1 M NaOH for total HULIS in a single step was not performed in this study, but is expected to yield HULIS₅.

2.2.2. HULIS Sample Preparation

As sample preparation step a solid phase extraction (SPE) procedure was performed on a C18 column. By this procedure HULIS is retained on the C18 column together with other substances of lower polarity, while highly polar substances (e.g., dicarboxylic acids, sugars) elute. HULIS and weaker polar substances of lower molecular weight are then eluted from the column by methanol. This sample is then introduced into the “HULIS analyzer.”

The solid phase extraction step for sample preparation was performed on a C18 (EC) cartridge (Isolute Art.Nr: 221-0020-H). The solid phase extraction started with the conditioning of the adsorbent bed with HNO₃ (pH3), with the eluent (methanol) and with water. After conditioning the sample solution was introduced on the cartridge. The pH of the approximately 9 mL water solution was adjusted to 3 by nitric acid before the SPE, while the NaOH extract was introduced into another cartridge without any pH adjustment. After loading the cartridges the liquid phases were removed by applying a vacuum. The cartridges, containing the water soluble components, were rinsed with 1 mL MilliQ water to elute the weakly retained compounds such as oxalic acid without dissolving the sample components of interest out of the adsorbent bed. Then, the liquid phases were removed by applying a vacuum. Finally, the specific elution of the analytes was implemented by 400 μl methanol in two steps, in both using 200 μl solvent.
The SPE cartridges were originally recommended for one use by the producing company. However, multiple use is possible by careful cleaning and conditioning after every use. When the cartridges were contaminated, the resistance of them increased, and the liquid became more difficult to be removed by vacuum. Observable enlargement of resistance implied the change of cartridge. For cleaning, 3 mL methanol was used. Then, the adsorbent was washed with 10 mL MilliQ water to remove the methanol and to condition the C18 layer for the next sample. Also, at the beginning of every working day this washing procedure was twice carried out to remove possible contaminants.

[Krivácsy et al. [2001] claimed, on the basis of a range of analytical investigations, that the organic matter isolated by octadecyl-silica (C18) SPE columns is composed to a large extent of humic-like substances.]

[Handler [2003] and Limbeck et al. [2005] showed, however, that a number of substances coelute with the HULIS fraction and used a second isolation step with an ion exchanger column to increase the selectivity for the HULIS determination. An isolation of HULIS based on ion exchange was performed by Havers et al. [1998a], and a fractionation on an ion exchange HPLC column was reported by Decesari et al. [2000]. Here we use it in a combined way with a separation on C18 before.]

2.2.3. TU Vienna “HULIS Analyzer”

2.2.3.1. FIA System: Preparation and Conditioning of a SAX Microcolumn

[The task of the FIA system is to incorporate a second sample preprocessing step. In this step methanol is removed from the analyte and other weakly polar compounds with less acidity are separated from the HULIS fraction. The FIA system contained a micro-SAX column, which was prepared as follows: SAX ion exchanger material was taken from a commercial SAX SPE cartridge (silica adsorbent with quaternary amine phase having a chloride counter ion, Isolute Art.Nr.: 500-0020-H) and filled in a thin Teflon tube (1.5 mm ID and 20 mm length). This column was incorporated in the FIA part of the “HULIS analyzer.”]

[The SAX material is a strong anion exchanger. The conditioning of the SAX-SPE material was carried out in the original SPE cartridge, to remove organic contamination: Before the first use it was washed with 3 mL MeOH and rinsed with 10 mL MilliQ water, and this was repeated 5–10 times (according to the performance of blank tests with the DOC instrument). Then, 10 mL nitric acid solution with a pH of 3, containing 5% methanol was added. In the next step the cartridge was washed with 6 mL 12.5% ammonium hydroxide, which was then flushed with 10 mL MilliQ water. At the end of the conditioning the cartridge was washed with 25 mL NaOH (pH 8) to have a slightly alkaline milieu in the adsorbent bed. From this conditioned cartridge small amounts were used to fill the microcolumn.]

2.2.3.2. Operation of the “TU Vienna HULIS Analyzer”

[After isolating the HULIS fraction by the FIA-SAX system, the HULIS carbon content of the samples was determined with a DOC analyzer for low concentrations of carbon in aqueous samples, by a modified GOTO/C100 (Grüger & Obst) instrument. The modifications were made to lower the dead volume of the gas flow, and to operate the instrument in a flow injection mode.

[The effluent from the sample preparation step (C18–SPE column) containing the HULIS in 400 μL methanol was diluted to a volume of 2 mL by a solution composed of NaOH (pH 9) and nitric acid (pH 0) 5:1 to obtain an approximate pH of 3. Then, 700 μL of this solution was sucked into the FIA system, where the further steps of the procedure were completely automated. The solution containing the analyte was directed on the SAX column through an electronic valve, where the HULIS content of the sample was bound on the adsorbent, while methanol and other possible constituents were washed out by 0.01 M nitric acid solution. The HULIS were eluted from the adsorbent with 5% ammonium hydroxide solution and introduced into the DOC analyzer. There, the analyte is dropped into a vertical oven, filled with an oxidation catalyst, where the water evaporates and the organic carbon is burnt at 800°C to obtain carbon dioxide. The evolving gas from the oven is carried through a gas cooler, an acid filter and a particle filter into the detector by cleaned CO2 free air. The CO2 concentration is determined by a nondispersive infrared photometer (NDIR) Siemens ULTRAMAT 5E.]

2.2.4. Calibration

[For calibration of the system, a standard solution was prepared using the humic acid standard of Fluka (Art.Nr.: 53680). 50 mg solid humic standard was dissolved in 100 mL MilliQ water and then it was placed in the ultrasonic bath for 30 min. The humic acid standard is not soluble completely in water, thus the concentration of its solution was determined from time to time. It was measured by a home built total carbon analyzer (for solid samples), where the sample is burnt at 1000°C in oxygen and the evolving CO2 is determined with a NDIR photometer (MAIHAK Sifor 200) [Bauer et al., 2002]. In addition to the standard solution of humic acid, another of glucose was made by dissolving 60 mg solid glucose in 250 mL MilliQ water. The glucose standard was used as primary standard to determine the carbon content of the dissolved humic acid solution.]

[Before burning the standards in the TOC analyzer small boats (cups of approximately 8 mm diameter) were prepared from aluminum foil. These boats were put into a muffle oven to clean from organic contaminations at 450°C. After cleaning the boats were kept in a desiccator. For calibration 5 different amounts of glucose and filtered (over Whatman Anotop25, 2.5 μm) humic acid standards each, as well as a blank solution (MilliQ water) were injected in boats, and then they were dried at 105°C. For analysis they were introduced into the vertical tube of the TOC analyzer one by one, and the detected peaks were evaluated by the ATS WinChrom/32 (Version 1.91) program. The calibration line was obtained from the glucose standard. By comparing with the signals of the humic acid standard the carbon content of the humic acid standard could be derived.]

[After the calibration of the humic acid standard solution, the calibration line of the procedure of the HULIS analysis was determined. A 5:1 mixture of sodium hydroxide (pH = 9) and nitric acid (pH = 0) was added to 0, 200, 400, 600, 800 μL filtered and calibrated humic acid standard to obtain each solution with a pH of 3 in the same volume (~10 mL). With these standard solutions, solid phase extraction was carried out on the C18 cartridge with 400 μL methanol (see section 2.2.2) and the procedure...
as described in section 2.2.3 was performed. The calibration was excellently reproducible, nevertheless it was repeated at the beginning of every working day, as the multiple use of cartridges influenced the blank value significantly. The calibration curves were always linear in the measuring range and this range was chosen to involve the sample values in all of the cases.

3. Operational Definition of the “HULIS Signal”

[21] Humic substances are formed in soil and watersheds by decomposition processes of biomass [Stevenson, 1994]. Their analytical determination is based on standardized procedures, by which the quantitative determinations are performed. The definition of the humic substances in an analytical sense is, thus, purely operational. A major reason for this is, that no authentic standard with a known composition is available, as humic substances from different sites within a “type of origin” such as river water, lake water, wastewater, soil, etc. exhibit a different composition even in elemental analysis (carbon, nitrogen, sulphur) [Abbt-Braun et al., 1990]. Atmospheric HULIS appear to form rather by synthetic processes from smaller molecules [e.g., Gelencsér, 2004]. However, they are a chemical group exhibiting quite a range of similarities to humic substances, in particular to the fractions of fulvic and humic acids [Havers et al., 1998a]. The separation methods used so far are operational and consider water soluble extracts of the HULIS [Varga et al., 2001; Decesari et al., 2001; Müller et al., 2000; Specht and Frimmel, 2000; Kenevsey, 2002].

[22] The most promising procedure to isolate HULIS appeared to us to apply a purification step with C18 SPE and separate on an ion exchanger from remaining smaller molecules.

[23] A further matter of debate is the detection method for the quantification of HULIS after the separation step(s) [Havers et al., 1998a; Krivácsy et al., 2000; Decesari et al., 2001; Zappoli et al., 1999].

[24] In our work we decided to use a “compound-independent” signal. This is achieved by burning the isolates from the ion exchanger in an oven and determine the achieved CO₂ with a nondispersive IR gas analyzer [Frimmel et al., 1992].

[25] The combination of two separation steps (one by polarity, the other by acidity) with a universal detector for organic carbon allows efficient isolation of HULIS from the matrix and quantitative determination of the isolated organic carbon.

[26] The HULIS data in recent reports, obtained by quite different analytical methods are operationally defined “proxy” signals, depending on the types of separation/isolation and detection methods achieved. It will be the task of inter comparison studies to obtain insight into the band width of the methods achieved and to evaluate the methods in use. The current method is advanced in the sense, that isolation of the HULIS fraction is performed with high effectiveness because of application of two separation principles, and quantification is performed with an absolute method, independent of the organic compound.

[27] Havers et al. [1998a] performed the first thorough investigation of HULIS in atmospheric particulate matter. In their study they applied classical methods from aquatic chemistry to isolate the fulvic and humic acids fractions from particulate matter samples. They find that airborne HULIS differ in their spectroscopic properties from those of aquatic and soil origin and resemble mostly fulvic acids with molecular weights below 1 kDa. In the isolation procedure used by Havers et al. [1998a] samples are exposed to 0.1M NaOH and the sum of humic and fulvic acids is isolated by precipitation after acidification of the extract. Authors of more recent papers, however, derived “HULIS” only from aqueous extracts to investigate organic material of potentially cloud forming activity [e.g., Zappoli et al., 1999; Decesari et al., 2001]. As we investigate the contributions of different species or groups of organic compounds to the organic material (OM) mass balance, we were interested, in addition to the water soluble part, also in the part soluble in alkaline media. Thus we decided after the aqueous extraction step of the sample to add a second extraction step with 0.1M NaOH. The material extracted in the second, alkaline extraction step may be of higher molecular weight than those material extracted with water, or of lower acidity. Our method does not allow to derive the molecular weight fraction of the alkaline extracted material, however, it delivers a notable amount of material with general properties of “HULIS.”

4. Results and Discussion

4.1. HULIS Annual Averages at the CARBOSOL Sites

[28] The humic-like substances’ content of the atmospheric aerosol was determined with our method in samples from 6 different sites located on a west-east transect across Europe. The determination of HULIS for each site was carried out for a period of around 12 months within the time frame of June 2002 to February 2004, because of the fact that sampling periods were not identical throughout the study. As we described in section 2, the water soluble fraction (HULIS_WS) and the alkaline soluble fraction (HULIS_AS) of the humic-like substances were analyzed separately. The annual average concentration of black carbon, organic carbon and HULIS fractions considering several aspects are summarized in Table 1. Note that the HULIS concentration is expressed as carbon concentration.

[29] The six sites can be divided into following designations. Azores (AZO) is an oceanic background site, Puy de Dome (PDD) and Schauinssel (SIL) are located on highlands at comparable elevation, while Sonnblick (SBO) is a high alpine summit at the Central Alps. Aveiro (AVE) and K-puszta (KPZ) are continental sites: Aveiro a small coastal city, where sampling was performed outside of the settled area, and K-puszta a background site in Central Europe. The HULIS concentrations reflect this spatial distribution: the oceanic concentration (AZO) was found to be smaller than that of the high alpine site (SBO) by a factor of almost 2. The HULIS concentrations at the two lower mountain sites were quite similar and compared to Sonnblick more than a factor of 2 higher. Finally, the concentration at the lower-level central European site KPZ was higher than at the west European continental site AVE, and it exceeded the concentrations of the lower mountain sites approximately 5 times, respectively, and the concentration at the high mountain site more than a factor of 10. A factor of 10 between low-level sites in Austria and the SBO
was also observed for sulphate and ammonium concentrations [Kasper and Puxbaum, 1998]. On the continent the annual average of the HULIS\textsubscript{T} concentration appears to decrease with elevation exponentially (Figure 1). However, it must be taken into consideration that the seasonal variations differ considerably among sites. [30] HULIS accounted for 15–26% of the particulate organic carbon; it was more abundant at the rural sites and less in the mountains. The relative fraction of HULIS carbon in organic aerosol carbon was very similar at the three mountain sites (15.4–15.8%) and at the two rural sites (23.2 and 26.2%), respectively (Table 1). The fraction of water soluble HULIS relative to total humic-like substances was quite similar and varied between 44 and 57%. At five sites the fraction of the HULIS\textsubscript{WS} was in the range of 51–57%; only in Aveiro the alkaline fraction was more abundant than the water soluble part. The fraction of water soluble HULIS in relation to WSOC was in the range of 9–24%, lowest at the high alpine site. The concentration of the alkaline soluble fraction was very similar at the two rural sites, and the significance of this fact is enhanced considering that this similarity can be found in every season. [31] The similarity between the HULIS\textsubscript{T} concentration and the BC levels at the investigated sites (Table 1) allows to derive information about the atmospheric formation rate: The formation in the atmosphere of Europe occurs apparently with a source strength in the order of the BC emissions in Europe, which is in the order of 500 Gg/yr [Bond et al., 2004]. This is a conservative assumption, as life time of HULIS in the atmosphere will be equal or rather lower than BC, because of potential decomposition processes, e.g., via UV radiation, which do not affect BC [Allard et al., 1994; Corin et al., 1996].

### 4.2. Seasonal Variation of the HULIS Concentration

[32] Seasonal average values of the concentrations for the total HULIS, water soluble as well as alkaline soluble HULIS fractions (Table 2) were calculated from the individual measurements (see auxiliary material\textsuperscript{1}) for all six sites. The seasonal trends of HULIS\textsubscript{T} and HULIS\textsubscript{WS} are shown in Figure 2. In this graph the dramatic differences of the seasonal variation among the sites studied are evident. Summer maxima are occurring at Azores and Sonnblick, however at a relatively low level, and at Puy de Dome. At the continental lower-level sites Aveiro and K-pusztá pronounced winter maxima are found at relatively high concentrations. The different seasonality between elevated and low-level continental sites is a result of emission and transport. At ground the source strength of HULIS precursors is apparently higher in winter, leading to the winter maxima; however also lower mixing layer heights in the cold season increase concentrations compared to the warm season. At elevated sites, however, the upward transport is hampered during the cold season as a consequence of stable conditions with frequent inversion layers well below the elevated sites. [33] A special case is the oceanic site Azores. Because of the far distances to the North American and European borders they resemble a remote site with the lowest concentrations and a seasonality more similar to the high-elevation sites than the low-level continental sites. The sources for the occurrence of HULIS at the Azores are potentially long-range transport, maritime emissions [O’Dowd et al., 2004] and some local influence. Seasonality at Azores showed the smallest variance in time, with HULIS\textsubscript{T} concentrations about twice higher in summer (0.12 µg m\textsuperscript{-3}) than during the other seasons. The HULIS\textsubscript{WS} fraction was also almost constant (approximately 0.03 µg m\textsuperscript{-3}) during the year except for the summer with 0.06 µg m\textsuperscript{-3}. The concentration of HULIS\textsubscript{AS} showed a very similar temporal tendency to that of the HULIS\textsubscript{WS} fraction, however, in winter it dropped to a minimum value of 0.017 µg m\textsuperscript{-3} (Table 2).

[34] Particularly strong seasonalities of HULIS\textsubscript{AS} concentrations were observed at the mountain sites Puy de Dome and Sonnblick (Figure 2). Expressed as a summer/winter ratio (ratio of the summer and winter quarters) the summer-time concentration of HULIS\textsubscript{AS} at Puy de Dome was 2.8 times higher than in winter; for Sonnblick it was even 7.1 times higher in summer than in winter (Table 3). A summer/winter ratio of 11 was reported for Sonnblick for the sulphate concentration, measurements performed 1991/1992 [Kasper and Puxbaum, 1994]. The large differences of summer vs. winter concentrations at an elevated site was explained by the effective decoupling of the lower air masses and the midtroposphere in winter, while thermal mixing as well as cloud venting appear to be effective mixers for lifting the mixed layers up to high elevations in the warm season [Kasper and Puxbaum, 1994, 1998; Tscherwenka et al., 1998].

[35] The seasonal variation of HULIS at the site Schauinsland situated at 1205 m elevation was distinctly different to that at Puy de Dome (elevation 1450 m)
exhibiting a summer minimum (HULIS$_T$ 0.24 $\mu$g m$^{-3}$) and an autumn maximum (Figure 2; HULIS$_T$ 0.46 $\mu$g m$^{-3}$). A possible explanation is the lower elevation than at Puy de Dome and the vicinity of the densely populated Rhine valley, which is a large source region. The HULIS$_{WS}$ and HULIS$_{AS}$ fractions at the mountainous sites exhibited a similar seasonal trend at Sonnblick, both with a summer maximum (Table 2). At Puy de Dome the HULIS$_{WS}$ fraction showed a spring maximum concentration (0.29 $\mu$g m$^{-3}$), while HULIS$_{AS}$ had a summer maximum as observed at Sonnblick. In Schauinsland both HULIS$_{WS}$ and HULIS$_{AS}$ were at peak levels in autumn.

[36] Very similar seasonal trends of the HULIS concentrations (both for HULIS$_{WS}$ and HULIS$_{AS}$) were observed at the continental rural sites at low elevation (Figure 2 and Table 2) though their geographical distance and different exposure type: Aveiro close to the west coast of Europe; K-puszta at a big plain in central Europe. The HULIS$_T$ concentrations, as well as concentrations of both fractions, exhibited summer minima and winter maxima with peak levels of 2.18 $\mu$g m$^{-3}$ HULIS$_T$ at Aveiro and 3.00 $\mu$g m$^{-3}$ HULIS$_T$ at K-puszta (Figure 2). The summer/winter ratio for HULIS$_T$ was 0.36 at Aveiro and 0.33 at K-puszta (Table 3). The seasonality at the low-level continental sites reflects the regional source strength of the HULIS fractions. As discussed in the introduction, according to current knowledge, major precursor emission sources for HULIS in winter (cold season) are biomass combustion for space heating and to some extent anthropogenic emissions. At the low-level sites HULIS$_{WS}$ and HULIS$_{AS}$ concentrations are well correlated with the wood combustion tracer levoglucosan (Table 4). At elevated sites, however, this correlation becomes weak, possibly indicating that for those sites other sources may be more important than wood combustion.

[37] Nothing is known about possible differences of the relative source strength of HULIS$_{WS}$ and HULIS$_{AS}$. The relationship between HULIS$_{WS}$ and HULIS$_{AS}$ at the two low-level continental sites was relatively constant (Table 2), however the relative fraction of HULIS$_{WS}$ compared to HULIS$_T$ was in Aveiro in winter with 40% rather lower, while with 59% at K-puszta rather higher (Table 2).

[38] Still, there is no clear differentiation of HULIS$_{WS}$ and HULIS$_{AS}$ between the seasons as seen from Table 2. The relationship between HULIS$_{WS}$ and HULIS$_{AS}$ is close to 1, with rather small differences between sites and seasons. Also the correlation with biomass combustion tracers (levoglucosan and fine K, Table 4) indicates a similar behavior of the two HULIS fractions. The non uniform correlation of fine K with HULIS fractions, as well as the HULIS fractions and levoglucosan at the different sites is not clear and may indicate different main sources of fine K and levoglucosan at the sites investigated.

5. Conclusions

[39] 1. The recently developed TU Vienna HULIS analyzer has been applied to determine two HULIS fractions, water extractable, and, in sequence 0.1 M NaOH extractable HULIS in background particulate matter from six European background sites.

[40] 2. The concentration of HULIS$_T$ at a continental midtropospheric observatory (Sonnblick) was only a factor of 1.7 higher than at the Atlantic background site Azores, but a factor of 13 lower than at K-puszta (low level central European background). On the continent, the HULIS$_T$ concentration decreases exponentially with elevation.

[41] 3. The relative amounts of water extractable and alkaline soluble HULIS were relatively similar at the six investigated sites, with a range of 44–57% of HULIS$_{WS}$ in relation to HULIS$_T$ for the long-term average.

[42] 4. Seasonal variations of the HULIS fractions exhibited considerable differences at the different sites. At

![Figure 1](image-url) Fig 1. Yearly average of the total HULIS-C concentration ($\mu$g/m$^3$ C) versus elevation (m). Note the similar concentration of the maritime and high alpine background.

Table 2. Seasonal Concentration of Total HULIS (HULIS$_T$) and Water Soluble (HULIS$_{WS}$) Humic-Like Substances and Percentage of HULIS$_{WS}$ Related to HULIS$_T$ and to Water Soluble Organic Carbon (WSOC)$^a$

<table>
<thead>
<tr>
<th>Site and Season</th>
<th>HULIS$_{T}$ (gm C m$^{-3}$)</th>
<th>HULIS$_{WS}$ (gm C m$^{-3}$)</th>
<th>% of WSOC</th>
<th>% of HULIS$_T$</th>
<th>% of HULIS$_{WS}$</th>
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</thead>
</table>
| AZO<br>Spring  | 0.063 | 0.033 | 52 | 17 | 17<br>Summer | 0.117 | 0.064 | 55 | 32 | 32<br>Autumn | 0.064 | 0.032 | 53 | 22 | 22<br>Winter | 0.047 | 0.030 | 63 | 16 | 16<br>AVE<br>Spring | 1.14 | 0.57 | 50 | 28 | 28<br>Summer | 0.78 | 0.37 | 45 | 23 | 23<br>Autumn | 0.106 | 0.039 | 39 | 17 | 17<br>Winter | 0.218 | 0.081 | 40 | 23 | 23<br>PDD<br>Spring | 0.45 | 0.31 | 62 | 22 | 22<br>Summer | 0.54 | 0.25 | 49 | 7 | 7<br>Autumn | 0.21 | 0.10 | 46 | 15 | 15<br>Winter | 0.19 | 0.13 | 68 | 36 | 36<br>SIL<br>Spring | 0.30 | 0.18 | 59 | 40 | 40<br>Summer | 0.24 | 0.14 | 60 | 6 | 6<br>Autumn | 0.51 | 0.27 | 53 | 20 | 20<br>Winter | 0.39 | 0.24 | 56 | 20 | 20<br>SBO<br>Spring | 0.127 | 0.040 | 33 | 7 | 7<br>Summer | 0.296 | 0.087 | 29 | 13 | 13<br>Autumn | 0.070 | 0.035 | 50 | 12 | 12<br>Winter | 0.042 | 0.011 | 26 | 7 | 7<br>KPZ<br>Spring | 1.55 | 0.85 | 53 | 25 | 25<br>Summer | 1.00 | 0.55 | 54 | 20 | 20<br>Autumn | 1.33 | 0.65 | 49 | 25 | 25<br>Winter | 3.00 | 1.76 | 59 | 26 | 26

$^a$Spring, March–May; summer, June–August; autumn, September–November; winter, December–February.
the Azores, as well as at the higher mountain sites (Puy de Dome and Sonnblick) a summer maximum of the HULIS\textsubscript{T} concentration was observed, while at the continental low-level sites (Aveiro and K-puszta) winter maxima dominated the seasonal variation. The very low concentrations at the elevated sites are a result of effective decoupling of the lower layers from the elevated sites during the cold seasons.

5. Significant correlations between both HULIS fractions and biomass combustion tracers at the low-level sites AVE and KPZ support the hypothesis of biomass

<table>
<thead>
<tr>
<th>Site</th>
<th>HULIS\textsubscript{T} SU/WI Ratio</th>
<th>HULIS\textsubscript{WS} SU/WI Ratio</th>
<th>OC SU/WI Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO</td>
<td>2.5</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>AVE</td>
<td>0.36</td>
<td>0.46</td>
<td>0.38</td>
</tr>
<tr>
<td>PDD</td>
<td>2.8</td>
<td>1.9</td>
<td>6.3</td>
</tr>
<tr>
<td>SIL</td>
<td>0.62</td>
<td>0.58</td>
<td>2.4</td>
</tr>
<tr>
<td>SBO</td>
<td>7.1</td>
<td>7.9</td>
<td>17.3</td>
</tr>
<tr>
<td>KPZ</td>
<td>0.33</td>
<td>0.31</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Figure 2. Seasonal variation of water extractable HULIS\textsubscript{WS} (dotted line with diamonds) and total HULIS\textsubscript{T} (bold line with squares) at remote sites (AZO and SBO), midalpine sites (PDD and SIL) and low-level sites (AVE and KPZ).
combustion emissions as precursors for a sizable fraction of atmospheric HULIS at the low-level sites [4]. 6. The similarity of HULIS and BC concentrations at all six sites allows a first-order estimate of the source term, respectively the formation rate of HULIS in the atmosphere.

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References


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