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Atmospheric
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Discussions

Interactive comment on "Chirality and origin of atmospheric humic-like substances" *by* I. Salma et al.

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The authors thank Referee #2 for his/her exceptionally detailed and precious comments for further improving and clarifying the ACPD paper. The comments attracted our attention to important details and questions that were not fully explained or dealt with satisfactorily in the MS. We have considered all recommendations, and made the alterations according to our best. Our responses to the comments are as follows.

Response to the Specific Comments

Response to Comments 1 and 2

Circular dichroism spectrometry primarily investigates the steric structure of chiral molecules, and it is not a quantitative analytical method in the classical sense. Exact critical and detection limits can only be determined for structurally well characterised pure compounds. These conditions obviously do not hold for HULIS. However, the substantial absorbance values observed in the UV and IR ranges indicate that amount of HULIS that was present in the samples would be sufficient for observing the CD effect. In the VCD spectrometry, the solid films resulted in absorbance values which were within the recommended range (approximately from 0.3 to 1.0). Intensity of the VCD signal is usually between 10ˆ-5-10ˆ-4 of the IR absorbance, which means that the differential absorbance is expected to be above the noise level and baseline uncertainty of ca. 5 10ˆ-6. Actual concentrations of HULIS solutions investigated were documented on page 19951, line 27 - page 19952, line 1. The upper concentration range is also limited by the colloidal properties of HULIS. HULIS can form aggregates in water solutions with concentrations above approximately 1 g Lˆ–1 (Tabazadeh, 2005; Salma et al., 2008), which are undesirable in the ECD spectrometry. The uncertainty interval of the baselines in both ECD and VCD methods were estimated for each sample, and were shown in Figures 2 and 4. In order to clarify that the total amount of HULIS examined was sufficient for observing the CD effect, we added a brief note, and also discussed the possibility of the negative effect due to small concentration and/or weak optical activity of some individual chiral components present in the mixture.

Response to Comments 3

The urban and rural aerosol samples dealt with in the present paper were completely used up to measure WSOC concentrations and to isolate HULIS from them, and we did not determine levoglucosan at that step of the research. The aerosol composition in the rural and urban sites is definitely influenced by biomass burning in the region, nevertheless, its contribution and importance cannot be compared to those for the samples collected directly at biomass burning. It is 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. Aerosol water extract samples and HULIS aqueous samples obtained from similar urban and rural aerosol samples (and from aerosol samples heavily impacted by biomass burning as well) have been investigated in detail by LC-MS with photo diode array detection as next step of the research, and a separate MS dealing with the compounds identified is in preparation. See also Response to Comment 5.

Response to Comment 4

Reasons and implications for the operational definition of HULIS were discussed in Sect. 1 Introduction (page 19941, line 19 - page 19942, line 1). The isolation protocol actually applied was briefly described in Sect. 2.1 Samples and sample treatment (page 19946, lines 15-22), and three references which contain much more information on the process and sample types that are obtained were cited. To the request of the Referee, we also made now an explicit and brief expression in the Abstract on the type of the extraction, isolation and analysis protocol applied.

Response to Comment 5

HULIS are extremely complex multi-component mixture of compounds, and we are aware of the limitations and weakness imposed by their operationally defined character. The isolation procedure applied was optimized to separate the fraction that exhibits the key spectral properties of HULIS, i.e., more than 90% of the fluorescence activity and 70% of the UV activity for humic and fulvic acids (Varga et al., 2001). There can indeed be some compounds that show up in the HULIS-containing eluent. As far as oxalic acid (listed by the Referee) is concerned, it is not protonated at pH=2, and, therefore, it does not appear in the eluated fraction, which is in line with our laboratory experience and other results (Limbeck et al., 2005; Emmenegger et al., 2007). Some other compounds listed by the Referee (e.g., trifluoroacetic acid) cannot be present in the HULIS fraction in a substantial amount because their corresponding absorption bands were not detected in the IR spectra. Some other compounds have been investigated in detail in urban, rural and biomass burning HULIS and corresponding

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aerosol water extracts by LC-MS with photo diode array detection. The preliminary results show that identification and quantification of the accompanying compounds and HULIS substituents are rather complicated, and the topic is to be dealt with in a separate manuscript, but these compounds don't seem to influence substantially the bulk OM/OC and HULIS-C/WSOC ratios. More importantly, their impact on the HULIS optical activity is negligible as explained in Response to Comment 24. We extended the text with several sentences to discuss the effect and importance of the positive biases associated with the HULIS isolation method, and added some new citations.

Response to Comment 6

We think that the discussion of the HULIS-C/WSOC ratios in the context of the historical records in ice core samples is beyond the goals of the present paper.

Response to Comment 7

All filters samples were transported and stored in the freezer. HULIS are considered to be a refractory fraction of the organic aerosol, and, therefore, their degradation and transformation are thought to be not substantial under such conditions. According to our experience, amount of HULIS extractable from different sections of an aerosol sample remains constant within the experimental uncertainties for years. It is not unexceptional to process aerosol samples that were collected some years earlier. In a very recent paper (Fors et al., 2009), a list of respected authors dealt with HULIS that were obtained from aerosol samples collected in 2001 and 2002.

Response to Comment 8

According to the Referee's recommendations, we extended the text on page 19946, lines 17-18, and lines 22-23 as follows. "In short, the filters were cut into pieces and the extraction was carried out with high-purity reagent Milli-Q water with occasional stirring and hand-shaking at room temperature for 36 hours. The filter-water system was allowed to stand for 30 min at the end of the extraction procedure." ... "The

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retained organics were eluted with methanol, and the eluents were first combined and then subdivided into several aliquots. The aliquots were evaporated to dryness with nitrogen stream."

Response to Comment 9

The gravimetrical analysis was done by weighing the HULIS samples with a microbalance at stabilized temperature (20 C) and relative humidity (50%). The samples were pre-equilibrated at these conditions for several hours. Hygroscopic uptake of water by HULIS is substantial at considerably higher relative humidities (Gysel et al., 2004; Dinar et al., 2007; Ziese et al., 2008). The text was modified to include this argument.

Response to Comment 10

Contribution of HULIS-C to WSOC for biomass burning aerosol during daylight periods and nights was derived in two different ways. In one of the methods, the HULIS-C and WSOC concentrations were measured by TOC analyzer in aqueous HULIS samples and aerosol water extracts, respectively. HULIS-C/WSOC ratios were calculated from the concentrations, and the individual ratios were averaged. The mean contributions obtained for the daylight periods and nights were 63 and 76%, respectively. (See Table 1 of the ACPD paper.) In the other method, the HULIS-C concentrations were derived from the gravimetrically measured mass of solid HULIS samples and OM/OC mass conversion factor (of 2.04), while the WSOC concentrations were directly measured by TOC analyzer in the aerosol water extracts. The mean ratios for the daylight periods and nights obtained by this method were 72 and 70%, respectively (see page 19951, lines 2-4). The corresponding data agree fairly well, and the differences between them are most likely caused by uncertainties in weighing and OM/OC ratio. Nevertheless, we decided now to remove the sentence in question to avoid any misunderstanding.

Response to Comment 11

Intensity and extent of the possible formation processes for HULIS overviewed in the

Introduction can vary significantly for rural/continental background sites, urban environments and tropical sites heavily impacted by biomass burning. Formation from aromatic or terpene precursors, or from biomass results in divers HULIS-C/WSOC ratios. The possible influence of the isolation artifacts for different types of HULIS are expected to be smaller than the effect of the different formation processes, and, therefore, the considerable range in the HULIS-C/WSOC ratios (from 35 to 76%, see Table 1 of the ACPD paper) were primarily associated with the differences in their formation processes. The text was modified now to include this assumption and explanation.

Response to Comment 12

Discussion on multiple formation processes at a given site was done in the Introduction, page 19944, lines 19-25. A reference/hint to the discussion of the various source categories was added now at the requested place.

Response to Comment 13

Organic carbon concentrations available were included in Table 1.

Response to Comment 14

A new column with the units was added to Table 1 according to the Referee's suggestion.

Response to Comment 15

We completed the text on page 19950, lines 19-21 by a sentence about the contribution of HULIS-C to OC and to PM2.5 mass for the different environments as recommended by the Referee.

Response to Comment 16

Comparison of daylight periods with nights was extended by evaluating the HULIS-C/OC and HULIS-C/WSOC ratios for daylight periods and nights as requested.

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Response to Comment 17

Unfortunately, we have no access to the individual concentrations of the PA chemical fraction derived by a different research group for the same days as considered in the present work, and, moreover, according to our knowledge, selected aerosol sample sets were only subjected to the determination of PA, and, therefore, the direct comparison of the HULIS and PA data doesn't seem to be feasible for the moment. Instead, we added a brief discussion now on the possible effects of the different separation protocols applied for HULIS and PA chemical fraction.

Response to Comment 18

We changed the upper scale of the abscissa in Figure 1 to 280 nm. At the same time, we would like to keep the lower scale at 185 nm. The maximum of the absorbance for the rural HULIS occurs approximately at 190 nm, which becomes apparent in the 185-190 nm range. We agree that it can be regarded as indication only because the measuring range of the instrument ends at 185 nm, and, therefore, increased noise levels are seen in this lower region.

Response to Comment 19

The absorbance curves in Figure 1 were normalized to HULIS-C concentration to facilitate their comparison, and the text was also modified accordingly as suggested by the Referee.

Response to Comment 20

Lack of optical activity for HULIS in the UV range does not necessary mean that HULIS are achiral. To be optically active, a molecule must be structurally asymmetric and exhibit absorbance. Insignificant optical activity can mean that HULIS absorb light in the UV range by chromophores that are achiral, while their chiral centra do not absorb substantially in the experimentally accessible UV range. This is an important conclusion of the paper, and we reformulated the corresponding text on page 19953, lines 9-14 to emphasize this unambiguously and avoid any misunderstanding.

Response to Comment 21

The sentence questioned was originally included to note that the extent of the optical activity of the rural HULIS sample was very small with respect to ordinary optically active compounds. It was rewritten now to express clearly this intention.

Response to Comment 22

Normalization of the absorbance spectra to HULIS-C in Figure 3 involves considerable uncertainties (unlike for Figure 1). Amount of HULIS-C in the actual solid samples were not know accurately due to the sample preparation procedure described on page 19947, lines 1-8, and it is the IR absorbance that was optimized.

Response to Comment 23

The yellowish colour of the HULIS is caused by absorbance in the violet and near UV range. Their absorption in the visible range is very small and featureless.

Response to Comment 24

All compounds mentioned by the Referee which possibly accompany the isolated HULIS fraction (oxalic, succinic, adipic, phthalic, hydroxybenzoic, trifluoroacetic acids, n-hexanoic, n-octanoic, cis-pinonic, phenylacetic, methylphthalic, cyclopentanedicarboxylic, butanedioic, heptanedioic, octanedioic, tricarballylic, benzenetricarboxylic, benzenetetracarboxylic acids, guaiacol, and lignin precursors as vanillin, acetovanillone, syringaldehyde, with the exception of lactic acid) are achiral, and, therefore, they cannot contribute the observed strong VCD band in the biomass burning HULIS. We added a sentence on this important feature of the compounds.

Response to Comment 25

We agree with the Referee that the two sentences in their original form were seemingly contradictory. The first sentence (page 19954, line 11) refers to the ECD inactivity of lignins in the UV spectral region, while the second sentence (page 19943, line 4) concerns the VCD band in the IR region. Both sentences were reformulated to prevent the confusion.

Response to Comment 26

The huge VCD band of the biomass burning HULIS at 1730 cmˆ-1 was checked in two aliquot samples, and, more importantly, it was also confirmed by using a different optical filter that optimizes the performance of the instrument in the carbonyl region. The shape and intensity of the band also indicated that it represents a real effect. A sentence was added to include this.

Response to Comment 27

The measured quantity in the VCD spectrometry is the differential absorption of the left and right circularly polarized IR light (due to vibrations of chiral or chirally perturbed functional groups). Optical rotation occurs as a result of the different refraction index for the left and right circular polarized component of a plane polarized light usually measured in the UV and visible ranges. VCD spectrometry and polarimetry are based on different physical phenomena (caused by differential absorbance and differential refraction index, respectively). Therefore, the sign of the VCD band cannot be directly related to the direction of the rotation of the plane-polarized light.

Response to Comment 28

We would like to keep “chirality and origin of HULIS” in the title of the paper because one of the main purposes of the study was to relate the optical activity of HULIS to their formation process.

Response to Technical Corrections

Technical corrections from a) through t) were accepted and adopted.

As far as Technical comment b) is concerned, we just note that according to SI, there are two official symbols for the litre: the Latin letter l in lower and upper cases. Originally, the only symbol for the litre was the lowercase letter l, following the SI convention that only those unit symbols that abbreviate the name of a person start with capital letter. Nevertheless, it is barely distinguishable from number 1, and, therefore, the uppercase letter L was adopted as an alternative symbol in 1979. The US National Institute of Standards and Technology recommends now the use of the uppercase letter L, while the traditional lowercase l is still used in many European countries.

Response to the General Comments

The present paper demonstrates the applicability, potentials and limitations of a new method, i.e., of the circular dichroism spectrometry for organic aerosol research. The achievements of the experimental procedures and methods can be improved in further studies. The ideas and experience formulated in the present paper can contribute to this progress. As far as the isolation and separation processes for HULIS and their artifacts are concerned, the existing protocols, even those that are based on water extraction, exhibit several important differences, and, unfortunately, have not been compared yet. This is definitely caused by the complexity of the subject as well. More effort should be devoted to avoid this ambiguity.

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