

Interactive comment on “Water-soluble atmospheric HULIS in urban environments” by C. Baduel et al.

Anonymous Referee #2

Received and published: 9 December 2009

This paper reports concentrations and spectroscopic properties of aerosol water-soluble humic-like substances (HULIS) in France. HULIS account for around one third of water-soluble organic carbon (WSOC) and are therefore important constituents of the aerosol organic matter. The origin of HULIS is not clear, and in spite of the several laboratory studies showing that complex high-molecular weight organic compounds can form within secondary organic aerosols (SOA), it is not really demonstrated that SOA polymers account for ambient aerosol HULIS. The main finding of the present study is that two HULIS types can be observed in polluted continental European areas, one typical of wintertime conditions, the other of summertime, and that these two types can be discriminated based on their UV absorbance, which is related to aromaticity. I have two major comments:

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1. In this reviewer's opinion, the conclusions are oversimplified. The Authors state that the nature of HULIS is mainly a function of the period of the year, while it is largely independent of the geographical location. However, a clear seasonal cycle is provided only for the site of Grenoble, while for the other sites HULIS data are available only for one of the two seasons (warm or cold). Table 1 shows that the UV absorbance of the wintertime samples in Grenoble are similar to those measured in the same periods at the northern French sites, and that the absorbance of Grenoble summertime samples are similar to those of HULIS in southern French cities in the summer. However, no seasonal cycle has been shown to occur for cities other than Grenoble. Therefore, a common phenomenology of HULIS over France is only hypothetical. It is difficult to assess the actual causes of the observed changes in HULIS absorbance in Grenoble without supporting information from meteorological data, back-trajectories and transport patterns, proxies for the various sources, etc.. In the absence of supporting data, the discussion about the sources of HULIS is too speculative and the quality of the paper may not meet the standards of Atmos Chem Phys.

2. Wintertime and summertime HULIS are discriminated based on the UV absorbance at 254 nm, and the Authors must acknowledge that their analysis exploits only a very simple spectroscopic parameter, and that taking into account measurements performed at different wavelengths or using high-resolution spectroscopic techniques may lead to a more complex classification of the samples. Some studies have shown that the UV absorbance at 254 nm is not specific for aromatic compounds and can be associated to aliphatic polymeric materials (Guzman et al., J. Phys. Chem. A, 2006, 110, 3619 – 3626). Clearly, without recording the absorbance over the whole spectral range, any interpretation about the underlying chemical mechanisms, like changes in aromaticity or in the substituents of the aromatic rings, must be considered with caution.

3. The title of the paper suggests that specific features of HULIS for the urban environment will be presented. On the contrary, the Authors conclude that the chemistry

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of HULIS can be explained by regional scale processes, even in very big cities (Paris). Is there any rural site (except Chamonix, whose location cannot be considered representative for the whole France) to compare with? If there is no evidence for specific characteristics of HULIS related to their occurrence in the urban atmosphere, I suggest to refocus the title to the actual results presented in the paper.

Minor comments:

- Paragraph 3.3.2. The Authors quote the literature on SOA polymers, but I suggest to focus on the studies really presenting data about aromatic or UV-absorbing compounds.

- Table 1. The classification of the samples collected in Grenoble in "March, April, October" and in "Mid-April and September" into cold season and mid-season is not clear.

- I contest that the slope of the line of wintertime HULIS in Figure 1 can be simply explained by mixing biomass burning and fossil fuel combustion aerosols in the same proportions at all locations (end of section 3.3.1). The same emission inventory cannot be assumed for all sites.

- I suggest to group the samples shown in Figure 2 according to location not to season.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 21561, 2009.