

## ***Interactive comment on* “Characterization of high molecular weight compounds in urban atmospheric particles” by V. Samburova et al.**

**Anonymous Referee #1**

Received and published: 21 March 2005

The present study deals with the quantification of organic polymers occurring in atmospheric aerosols and with their characterisation in terms of spectroscopic properties and average molecular weight. The subject has recently gained wide attention in the community because of the widespread occurrence of polymeric material in the aerosol and of its potential impact on the physical and chemical properties of the particles. Knowing chemical structure and molecular size of the polymers would elucidate their properties and possible mechanism of formation. The Authors exploited mass spectrometry and size-exclusion chromatography to characterise atmospheric polymers, providing confirmation of their “humic-like” character. However, there is little advancement in this work compared to the previous ones exploiting analogous analytical meth-

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

ods, and especially compared to Kiss et al. (2003). Indeed, both spectrometric and chromatographic techniques used by the Authors suffer from the same limitations already pointed out in the literature: A) possible fragmentation of molecular ions and multiple-charged ions in producing the MS spectra; B) large uncertainties in the estimated average molecular weight when calibrating SEC with different standards. Taking into account these uncertainties, the results presented in this study about the molecular weight of polymers and their concentrations in aerosol particles must be considered with extreme caution.

Specific comments:

- Introduction. The literature is not updated. The reviews by Janos (J. Chromatogr. 983, 1-18, 2003) and Perminova et al (Environ. Sci. Technol. 37, 2477-2485, 2003) about SEC analysis and MW determination of humic substances must be quoted. Also the detailed work by These et al. (Rapid Commun. Mass Spectrom., 18, 1777-1786, 2004) on SEC-ESI-MS of fulvic acids can be included in the references. The cited work by Likens et al. (1983) deals with rainwater samples not aerosol samples, and they did not postulate the high-molecular weight fraction of OC, while they determined it by ultrafiltration. For more recent studies on HULIS in atmospheric water samples, refer to Cappiello et al (Environ. Sci. Technol. 37, 1229-1240, 2003) and Feng and Moller (J. Atmos. Chem. 48, 217-233, 2004), both presenting the results of ESI-MS analyses.

- Section 2.3. A discussion of the set-up of the LDI-MS parameters should be included, since the experimental conditions are expected to affect the stability of the molecular ions.

- Section 3.2. On the basis of the spectrum in Fig. 3, the presumed “similarity” between the MS spectra of the aerosol extracts and those presented by Tolocka et al. (2004) or Kalberer et al. (2004) cannot be deduced. On the contrary, the three sets of spectra differ for many aspects, and clearly the maximum in the molecular weight distribution

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

of synthetic polymers is shifted towards higher masses compared to that in the spectra of the ambient samples. On the basis of the data presented in this section, it cannot be concluded that ambient HULIS are structurally similar to those produced in laboratory. On the other hand, if the Authors believe that ambient HULIS are similar to the synthetic polymers, which are essentially poly-acetals and poly-glycols (and not polycarboxylic acids), why do they prefer PMA to PEG for size calibration in SEC? There is definitely something unclear in this section.

- Section 3.3. The UV spectra of the aerosol extracts cannot be directly compared to that of AHA, because aerosol extracts presumably contain inorganic materials, such as nitrate and sulphate ions whose UV absorption cannot be neglected below 240 nm.

- Section 3.4. (A) There is no way to verify that the standards of humic substances have the same extinction coefficient of HULIS, therefore the readers must be warned that the concentrations presented in Table 1 can be affected by large errors. The Authors state that they have no alternatives to the use of HA standards for quantitative analyses. On the other hand, the choice of the humic reference material can be critical and, in principle, very different results can be obtained by using another humic or fulvic acid instead of Aldrich HA. The very qualitative similarities between the UV spectra in Fig. 4 may indicate that AHA and HULIS have similar chromophores but do not provide any information on the amount of chromophores per unit of mass (or carbon) and, in turns, on the extinction coefficients.

- Section 3.4. (B) The two sentences “Carbon-14 analyses... believed to be formed in secondary processes” report conclusions which cannot be held on the basis of the data presented in this study.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 437, 2005.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)