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

Anonymous Referee #3

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This manuscript is concerned with the size (molecular weight) determination of high-molecular weight compounds (humic-like substances; HULIS) in urban aerosol, using size exclusion chromatography (SEC) and laser desorption ionization mass spectrometry (LDI-MS). The topic is of considerable interest, not only to the field of atmospheric chemistry, but also to environmental chemistry in general, considering the universal distribution of humic substances in the environment, and the important role humic substances play in a vast array of environmental processes. There is a very rich and venerable literature concerning characterization of humic substances. The manuscript authors (and others interested in characterizing HULIS), are strongly encouraged to consult that literature, and to include in their work a serious, rigorous comparison to previous studies. This would help avoid many pitfalls and problem areas, as well as possibly incorrect data interpretations. I identified several problem areas in this work:

1. The aerosol extracts were not purified from other water soluble materials, which include both inorganic salts and low molecular weight organic compounds such as organic acids, alcohols, etc. Such "impurities" may represent hundred of compounds, as can be seen in the literature (e.g., Graham et al., 2002, JGR, v. 107, no. D20, 8047; Kubatova et al., 2000, Atmos. Environ., 34:5037; Gao et al, 2003, JGR, v. 108, D13, 8491; and others). These impurities may affect both SEC and MS results, by complicating the mass spectra and by skewing the SEC chromatograms to lower average molecular weights. Formally, these results cannot be said to strictly relate to HULIS.

2. A recently published study of humic substances by LDI-MS and MALDI-MS (Mugo and Bottaro, 2004, Rapid Comm. In Mass Spectrometry, 18:2375) is very instructive in this regard. They studied standard, purified fulvic and humic acid obtained from the International Humics Substances Society (IHSS). The LDI-MS spectra they obtained, with the same laser wavelength as the current manuscript (important for determining formation of positive or negative ions), are vastly simpler and better resolved than the mass spectra presented in this work. Can this be a result of the lack of purification? In any event, it is suggested that the authors to review other similar studies for comparison purposes.

3. In the same Mugo and Bottaro study, only ions up to m/z 642 could be consistently observed using LDI-MS. This was attributed to the low stability of higher mass ions produced by the higher energy LDI (see also references in that study). Their MALDI comparison rendered peaks up to m/z 1848 for the same materials. Thus the low mass assignment in the present manuscript may incorrect due to excessive fragmentation in the analytical method. Although the authors mention this point, they do not emphasize it; rather they emphasize that their results point to HULIS having low molecular mass. However, LDI is well known to be a relatively energetic ionization method.

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4. Use of Aldrich humic acid (AHA) as standard material:

a. AHA and other commercial humic acids have been found to have high ash contents (e.g., Malcolm and McCarthy, 1986, 20:904; Chin et al., 1994, EST 26:1853; Hur and Schlautman, 2003, EST 37:880; and many others), and require extensive purification procedures to eliminate ash, and residual fulvic acids and humin. This was not done in this study, and may cause problems for calibration/quantification results.

b. 13C-NMR spectra of AHA exhibited markedly lower carboxyl content, high saturated aliphatic carbon content, and lower aromatic carbon content than stream, soil, and peat-derived humic acids, and higher C/N ratios (Malcolm and Thurman, 1986). As a result, AHA is generally not regarded as a good model substance for soil and aquatic humic acids. The origin of AHA is unknown.

c. AHA has been repeatedly found to have substantially higher MW than fulvic acids, which are frequently used as model compounds for HULIS. See for example, Beckett et al., 1987, EST 1987 21:289; Chin et al., 1994, EST, 28: 1853; Hur and Schlautman, EST 2003: 37:880; Hu and Schlautman, 2003, J Colloid Interface Sci. 264:313, and the many references sited in those papers. Average molecular weight for AHA has been reported to vary from about 4000 to more than 14000, substantially different from the $<$ 1000 Dalton proposed for HULIS. Seeing that the manuscript reports that the SEC results for AHA were similar to those of the HULIS, this points the suggestion that there was insufficient resolution in the employed SEC technique (see comment 6 below).

5. Considering the high average MW of AHA, it would be instructive to analyze it by LDI-MS using the same technique as for the aerosol samples. If similar m/z results are recorded, it will be a clear indication that larger m/z compounds/components/fragments are not detected with the method employed. As such, it would not be possible to conclude about the size of the aerosol-derived material. Obviously, the converse is also true, and the results may then take on more significance.

6. Size exclusion chromatography results -it has been often emphasized that SEC analysis of humic substances must be performed and interpreted with great care - researchers in the field of humic substances (HS) have been demonstrating this for many years. SEC is a very commonly used method for molecular weight determination of HS, although it is acknowledged to be problematic and even to render controversial results. Other separation mechanisms apart from size exclusion, i.e., molecular structure, steric effects, hydrophobicity, electrostatic effects, and molecular interactions with the gel, may significantly complicate the chromatography results, such that its interpretation must be done with care. An important aspect is the choice of standards. Several studies have determined that the most appropriate standard for humic substances is polystyrene sulfunate (PSS) (Chin et al., 1994; EST, 28:1853; Peuravuori and Pihlaja, 1997, Analytica Chimica Acta 337: 133; Perminova et al. 1998, Water Res 32:872). Indeed, in the very thorough study by Perminova et al (1998), they showed that PMA, as used in the present manuscript, gives much smaller molecular weights than PSS. As such, the low molecular weights reported in the manuscript may be an artifact of the standards employed and the chromatographic conditions. The authors are encouraged to consult the literature on this subject, including those already mentioned, and others (for example: Kudryavtsev et al, 2000; Analytica Chimica Acta 407:193; Shafer et al, 2002, EST 36: 2572; Christl et al, 2000, Eur J Soil Sci 51: 617).

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