

## ***Interactive comment on “A new comprehensive approach to characterizing carbonaceous aerosol with an application to wintertime Fresno, California PM<sub>2.5</sub>” by P. Herckes et al.***

### **Anonymous Referee #1**

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This paper dealing with the chemical composition of organic aerosol is the follow-up of a previous study (Herckes et al., ES&T 2007) focused on fog water. PM<sub>2.5</sub> samples collected in the period December 2003 - January 2004 in Fresno (CA) were combined to provide a single highly loaded sample containing ca. 100 mg of aerosol organic matter. In this way, the Authors could apply separation techniques such as centrifugation, and low-sensitivity spectroscopic methods such as <sup>13</sup>CNMR, which are unsuitable for the analysis of daily samples. Due to the huge amount of material needed for the analysis, this approach prevents the acquisition of time trends as well as any application to remote environments. On the other hand, thanks to the innovative techniques employed, this study provides an interesting point of view to test some paradigms of the current

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knowledge about the composition of organic aerosols, especially with respect to the chemical nature of elemental carbon (EC) and humic-like substances (HULIS). It came out that 1) the EC determined by thermal-optical methods exhibits a less polyaromatic character than expected, 2) HULIS occur in comparable amounts with previous studies and are related to lignin derivatives, thus probably forming by processed biomass burning emissions, 3) the amount of nitrogen-containing hydrophilic compounds is larger than indicated by previous studies. These are interesting findings and should be clearly stated in the abstract of the paper, otherwise the reader might get the impression that this work has a purely analytical content. Except the abstract, the paper is well-written and well-documented by tables and figures. My specific comments are reported below:

1) Although the fractionation of the complex mixture of aerosol organic compounds depends on the specific methodology used, the Authors can try to compare their data with the results of previous attempts to separate the organics on the basis of their molecular size, polarity and neutral/acidic/basic character, as in the characterization study provided by Sullivan and Weber (JGR, V. 111, D05315, doi:10.1029/2005JD006486, 2006).

2) Section 2.1. A brief survey of the prevalent weather conditions during the sampling period would be useful here.

3) Page 8429. The isolation of the hydrophilic acids plus neutrals fraction demands an extensive use of solvents and concentrated acids and bases. I would like to see here an acknowledgment of the possible degradation reactions (e.g., hydrolysis of esters) which may affect the samples at this stage.

4) Section 2.2. The very complex and time-consuming procedure for fractionating the sample and purifying the fractions is provided as a “black box”: it is not clear whether the single operations are essential for the overall procedure or, alternatively, they are aimed to remove interferences for specific analyses ( $^{13}\text{C}$ NMR, FTIR, or elemental) to which the isolated fractions will be subjected. This kind of information is very useful for

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simplifying the fractionation and isolation procedure in case the user intends to reduce the suite of analyses on the isolated fractions (or choose alternative ones).

5) The use of the term “particulate organic matter” throughout the paper is misleading. For two reasons: a) in atmospheric chemistry, particulate organic matter (POM) usually refers to the overall organic aerosol, b) the isolated fraction contains BC as well as OC. Based on the this ambiguous terminology (used also in the legends of the figures), the reader might understand that this paper deals only with the OC composition, not with BC. Instead, it is important to stress that CPMAS  $^{13}\text{C}$ NMR spectroscopy was able to provide a (non-trivial) characterization of the BC fraction. Instead of “particulate organic matter”, the Authors can use “non-extractable carbonaceous matter” or “non-extractable organic matter + BC”.

6) Last lines of page 8436 and first lines of page 8437. What is the carbohydrates/anhydrosugars fraction of OC based on the CPMAS  $^{13}\text{C}$ NMR spectra?

7) Page 8437, second paragraph. Isoprene SOA are very unlikely to form in wintertime.

8) Figures 1 to 4. Please, find alternatives for the term “particulate organic matter” (see previous comments).

9) Figure 4. Indicating the frequency of the bands directly on the figure would greatly improve its readability.

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