

Interactive comment on “A new comprehensive approach to characterizing carbonaceous aerosol with an application to wintertime Fresno, California PM_{2.5}” by P. Herckes et al.

Anonymous Referee #3

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Review for “A new comprehensive approach to characterizing carbonaceous aerosol with an application to wintertime Fresno, California PM_{2.5}” by Herckes et al.

The authors present a very detailed, elaborative extraction scheme to obtain 8 different organic aerosol fractions, which are characterized with IR- and partially with NMR-spectroscopy. Such a detailed separation is a approach worthwhile to be tested, however, spectral interpretation of the different fractions often seems to be too detailed as discussed in detail below.

General remarks Why was solid state NMR used? Usually liquid state NMR is more sensitive. Most samples in this study are originally liquid extracts. Please justify this

method.

A very elaborate extraction scheme is presented. Were there any experiments performed with test compounds supporting the suggested separation of the described compound classes? How selective are the separation steps? On p.6/7 it is, e.g., described that water/acid-soluble compounds that were distilled with a vacuum rotary are “volatile organic acids”. It is likely that also many other compounds end up in this fraction.

IR spectra in Figure 4 are not very well reproduced. It is often hard to identify the peaks discussed in the text. Please indicate the peaks described in the text also in Figure 4. I suggest subdividing Figure 4.

Specific remarks 1. p.7 describes the cellulose dialysis method. This method should be described in more detail as it is rather unusual in the field of atmospheric science.

2. p.8. The separation of 4 salts is mentioned. Most of these salts are not very abundant in atmospheric particles. Why were these salts tested and how do more abundant salts behave?

3. p.8. Sulfate was partially removed as barium sulfate. Such precipitation steps are always prone to co-precipitation of organic material. Was this aspect investigated?

4. p.13. Quantification of the carbon content with C-NMR. In liquid NMR quantification is usually not straightforward, especially in C-NMR. Is this different in solid state NMR? Please add a respective remark or more experimental details.

5. p.13. The NMR signal of aromatic carbon is assigned as “elemental” carbon. How much of this signal is due to “organic aromatic” compounds?

6. p.13. From the observation that in a sample fraction peaks occur at 1700cm⁻¹ and 174ppm in the IR- and NMR-spectrum, respectively, it cannot be concluded that acids are present in the sample. The peak at 174ppm could also be due to esters and the peak at 1700cm⁻¹ due to other carbonyl groups. This is one of several examples,

where I think the data is over-interpreted. Another example is: p.14, band at 1620cm⁻¹ assigned to quinones.

7. p.14. Bands at 1710, 1735, 1620cm⁻¹: not visible in Figure 4.

8. p.16. Substructures of the aliphatic peak in the NMR spectrum of the “volatile acid” fraction are described. How certain are these assignments? The spectrum seems quite noisy. How reliable and reproducible are these fine structures in the aliphatic region?

9. p. 18. “Spectral features” of polyols are mentioned. Please describe these features specifically.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8423, 2007.

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