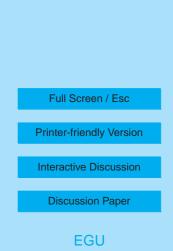**Atmospheric
Chemistry
and Physics
Discussions**

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.

P. Herckes et al.

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A first concern of the reviewer is the bias introduced by a specific site as the analyzed sample is a pooled sample over many sites and could conceivably be strongly skewed towards one high concentration site. We agree with the reviewer that this is a theoretical possibility. Separate analyses of samples from these sites (Gorin et al., 2006), however, serve to alleviate this concern. While there are differences between sites in terms of PM2.5, OC concentrations and source apportionment, these differences are surprisingly small. We have measurements of OC and TC for each individual sample and so we can detail the contributions of each individual site to the composite sample OC/TC(in %)
First Street (downtown) 31/32

Drummond (industrial) 14/15
Pacific (residential) 19/16
Clovis (residential) 12/13
Fresno State University (residential) 24/24
While the downtown site (First Street) has the highest contribution to the sample carbon (32%) and one suburban site has the lowest (13%), the study includes 3 suburban settings for one downtown setting and one industrial suburban site. Overall, we think the sample provides a reasonably representative picture of wintertime aerosol in the Fresno metropolitan area.

Another concern of the reviewer was the use of solvents and potential impurities. The only solvent used was methylene chloride; all other elutions were performed with aqueous solutions or dilute acids/bases. For the organic solvent, a total of 800mL of methylene chloride solvent was used. The methylene chloride used has a dry residue following evaporation of less than 1 ppm. Assuming a 1ppm residue as an upper limit, we would have in our isolated CH_2Cl_2 soluble fraction a total of 1mg for an isolated weight of 38.3mg or in other words a maximum contamination of 2.6%, unlikely to substantially impact ^{13}C-NMR or FT-IR spectra or our estimated OC recovery.

A further concern was the oscillation between dry and liquid state. There is however, no oscillation between these states. Most fractions stay liquid until the final freeze-drying step. Resolubilization is not happening, hence there is no "oscillation". Volatile species could potentially be lost but this is discussed as part of the missing carbon in the final balance.

We agree with the reviewer that our use of "recovery" could be confusing as it is often used relative to individual organic species for which a recovery could be investigated. However, in the absence of model compounds, it is not possible to do any kind of recovery study on defined species. The only recovery that can be calculated is based on total carbon present at the beginning of the experiment. This is a common approach for comprehensive studies and hence our use of the term "recovery" seems appropri-

ate. Given the small maximum possible solvent impurity contribution to recovered OC we believe our estimate stands as an accurate measure of actual sample OC recovery. In addition, recoveries as well as cleaning procedures and procedural blanks are described extensively in Leenheer and Huffman (1976) and Leenheer (1981).

We don't agree with the reviewer's statement regarding the usage of very aggressive solvents. Again only methylene chloride (DCM) is used as an organic solvent for the DCM soluble fraction. Hydrofluoric acid (HF) is used to digest the quartz fiber filters; however, HF is only a weak acid and the resulting pH >2 is in the range of what is seen in many atmospheric processes. While a degradation in these conditions (e.g. hydrolysis of esters) can not be excluded, these processes also occur naturally in the atmosphere.

We agree with this reviewer and other reviewers that the use of the term "particulate organic carbon" was a bad choice and we have changed it to "non-extractable carbonaceous matter". The reviewer pointed out a confusing use of the terms total organic matter and organic matter as well as total organic carbon and total carbon. We have made changes accordingly and now always refer to it as TC/OC/EC as derived from the Sunset laboratories measurements (Birch and Cary, 1996) as is common practice.

The discussion on woodsmoke, which was largely derived from levoglucosan has been removed as following the re-examination of the data, we can not unambiguously assess the levoglucosan peaks. That issue is better addressed in the Gorin et al. (2006) manuscript where levoglucosan measurements are reported for individual samples from this study.

References

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