Atmos. Chem. Phys. Discuss., 13, C8368–C8372, 2013 www.atmos-chem-phys-discuss.net/13/C8368/2013/

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Interactive Comment

Interactive comment on "Identification of humic-like substances (HULIS) in oxygenated organic aerosols using NMR and AMS factor analyses and liquid chromatographic techniques" by M. Paglione et al.

M. Paglione et al.

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Received and published: 23 October 2013

The authors would like to thank Anonymous Referee #1 for his/her comments.

The Referee's comments followed by our replies are listed below.

The text has been revised according for all specific grammatical and stylistic correction suggested.

Comment 2.2.3.IC Analyses Page 17205, Line 18 – I am not sure what the term gradi-

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ent 20 KOH elution means? If it is a gradient, I think time steps and concentrations are missing. Also, the chemical name for the formula used is not provided.

Reply. The phrase is incorrect. Actually, the elution method consists of a gradient from 0.1 mM to 38 mM, in a 35 minutes long run (0.1 mM for 10 min, 5 mM reached at 15 min, 10 mM at 20 min and 38 mM at 35 min). We will complete section 2.2.3 in the revised version of the manuscript.

Comment 3.2.PM1 chemical composition from filter measurements Page 17212, Line 12 – The authors mention that period III had an increase in sodium, chloride, and MSA concentrations, but sodium data is not provided in Table 2

Reply. In the table below (Extra Tab.1) we show that in fact sodium accounts for a large fraction of PM1 during marine period. We will add Na concentrations in the Table 2 of the manuscript.

Comment Page 17221, Lines 6-10 – The authors mention that the NMR factor analysis did not identify a factor matching F2-AMS (SV-OOA). But in Table 5a there is a high R value between NMR-F2 and F2-AMS. Having a high R value was part of the argument between the relationship of NMR F2 and F4AMS (FA-OOA). I guess I don't clearly see what is different here.

Reply. The moderate positive correlation between SV-OOA and F2-NMR reported in Table 5a is due to the fact that SV-OOA, similarly to FA-OOA, experiences a concentration minimum during the Marine period while the concentrations remain sustained during the other three ("continental") periods. However, the AMS measurements show that SV-OOA concentrations have a clear diurnal pattern with maxima in nocturnal hours (Fig. 5), and such pattern should be visible also at the degraded time resolution of the PM1 filters (roughly 12 h), as shown by the following table (Extra Tab.2). Clearly, F2-NMR does not show the 35% enrichment in the evening/night samples with respect to diurnal samples expected for a component tracing the AMS SV-OOA. None of the NMR factors did actually. In conclusion, no assignment of NMR factors to the

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SV-OOA seemed satisfactory for the lack of evidence of the characteristic diurnal pattern in concentrations of the SV-OOA. For this reason, our best match for F2-NMR is with AMS FA-OOA, which do not show any clear diurnal trend. In addition, Pearson's correlation coefficient is higher between F2-NMR and FA-OOA than between F2-NMR and SV-OOA.

Comment Page 17225, Lines 8-9 – The authors mention that no suitable NMR factor was found to match the time series of AMS SV-OOA. Was this shown in the text or figures? This might be part of the reason that I did not feel that I clearly followed the discussion in section 3.5 about the NMR factor analysis not identifying a factor matching F2AMS (SV-OOA). Perhaps this could be more clearly illustrated in the paper.

Reply. See previous reply.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17197, 2013.

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Extra Tab.1: Sodium (Na⁺) and chloride (Cl⁻) conc. (ug/m3) and their relative concentration respect to the PM1 total concentrations in the different campaign periods.

| Period | Na | СГ | Na ^T /TOT | CI/TOT |
|------------|------|------|----------------------|--------|
| Cont-Dry | 0.23 | 0.02 | 4.3% | 0.4% |
| Cont-Humid | 0.19 | 0.05 | 2.8% | 0.7% |
| Marine | 0.16 | 0.03 | 5.3% | 1.0% |
| Cont-Var. | 0.08 | 0.03 | 1.4% | 0.5% |

Fig. 1.

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Extra Tab.2: Average concentrations (μ gC/m³) of the NMR factors in nocturnal and diurnal PM1 samples. Concentrations of the AMS factors (μ g/m³) averaged in the same sampling intervals are shown for comparison.

| | AMS factors | | | | NMR factors | | |
|---------------|-------------|--------|------|--------|-------------|------|------|
| | LV-OOA | SV-OOA | HOA | FA-OOA | F1 | F2 | F3 |
| Evening/Night | 0.95 | 0.78 | 0.37 | 0.48 | 0.17 | 0.42 | 0.22 |
| Day | 1.01 | 0.58 | 0.45 | 0.45 | 0.16 | 0.43 | 0.44 |

Fig. 2.

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