Atmos. Chem. Phys. Discuss., 13, C5463–C5471, 2013
www.atmos-chem-phys-discuss.net/13/C5463/2013/

Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #1

Received and published: 2 August 2013

This paper presents Aerosol Mass Spectrometer (AMS) measurements and off-line filter analysis of water-soluble organic carbon (WSOC) by proton-Nuclear Magnetic Resonance (1H-NMR) and ion-exchange chromatography for humic-like substances (HULIS) from a sampling campaign conducted in Cabauw, Netherlands in May 2008. Positive Matrix Factorization (PMF) was applied to the AMS data. Factor analysis was applied to the NMR spectra. The classes of compounds (or factors) obtained from these two analyses were compared to discuss how they overlap, differ, and can provide information on oxygenated organic aerosols.

Organic aerosols are a hot topic in aerosol science. In addition, the more oxygenated fraction is of great interest since it is believed one of its main sources is secondary organic aerosol formation, a process that is still not well understood. This paper is examining the data analysis techniques for a number of measurements that can help to better understand this fraction. Many in the atmospheric chemistry and aerosol science communities would be interested in this paper.

Overall, this is a very good paper. Currently, PMF and factor analysis are used very often on aerosol data. This work is showing what the various factors obtained from these data analysis methods can tell us about organic aerosols and how the factors can and cannot be linked. The only part of the paper I don't see as clearly as the authors is that there is no NMR factor that matches with the AMS SV-OOA factor. I am not sure I see how this falls out of the data considering there is a high R value between NMR factor 2 and AMS SV-OOA. Otherwise, I have a number of minor comments outlined below to help with the flow of the discussion that need to be addressed before the paper can be considered for publication.

Specific Comments: Abstract Page 17199, Line 5 – Suggest adding an an before approach

Page 17199, Line 12 – Suggest removing the the after correspond to

Page 17199, Line 19 – The abbreviation H-NMR is not defined

1.Introduction Page 17200, Line 3 – The chemical name for the formula used is not provided

Page 17200, Line 17 - The abbreviation NMR is not defined

Page 17201, Line 23 – Suggest adding an a before standard

Page 17201, Line 28 – Suggest removing the hyphen between biomass and burning

Page 17202, Line 28 – The references are not listed in alphabetical order as previously

done throughout the text

Page 17203, Line 3 – Suggest adding (2012) before also present

Page 17203, Line 11 – There should be a hyphen between water and soluble

Page 17203, Line 19 – Suggest changing with aim of comparison to with the aim of comparing it

2.Experimental methods 2.1.Measurement site Page 17203, Line 23 – Suggest adding a the before Cabauw

Page 17203, Line 24 – Suggest changing frame of EUCAARI to framework of the EUCAARI

2.2.3.IC Analyses Page 17205, Line 17 – Suggest putting 2 x 250 mm in parentheses

Page 17205, Line 18 – I am not sure what the term gradient 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.

Page 17205, Line 19 – Suggest putting 3 x 250 mm in parentheses

Page 17205, Line 20 – The chemical name for the formula used is not provided

2.2.4.EC/OC analyses Page 17205, Line 26 – Suggest changing on filter to of filter

Page 17206, Lines 1-2 - The references are not listed in alphabetical order as previously done throughout the text

2.2.5.1H-NMR analyses Page 17206, Line10 – Suggest adding an a before reference

2.3.High-resolution time-of-flight Aerosol Mass Spectrometry Page 17207, Line 16 – Suggest adding a the before inlet

Page 17207, Line 18 – Suggest changing lens to len

Page 17207, Line 27 – Suggest adding a the before same

2.4.1.Factor analysis of NMR spectra Page 17210, Line 1 - The references are not listed in alphabetical order as previously done throughout the text

2.4.2.PMF of AMS-spectra Page 17210, Line 10 – Suggest adding a the before organic

Page 17210, Line 23 – The charges are missing on the ions listed

Page 17210, Line 24 - The chemical names for the formula used are not provided

3.Results and discussion 3.1.Meteorological regimes and air mass origin Page 17211, Line 8 – Suggest adding a the before campaign

Page 17211, Line 19 – Suggest adding the word May after 12, changing general to generally, and easterly is misspelled

Page 17211, Line 20 - easterly is misspelled

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

Page 17212, Line 28 - The references are not listed in alphabetical order as previously done throughout the text

Page 17213, Line 7 – Suggest changing worth to mention to worth mentioning

Page 17213, Line 16 – Suggest changing with aim of comparison to with the aim of comparing

3.3.NMR-factors for WSOC Page 17214, Line 24 – Suggest adding a the before major

Page 17214, Line 25 – Suggest adding a the before concentration

Page 17215, Line 1 – The abbreviation CTMs is not defined

Page 17215, Line 11 – Suggest changing Such to The

Page 17215, Line 21 – Suggest changing Differently to Different

3.4.Organic aerosol factors from AMS-PMF analysis Page 17216, Line 16 – Suggest adding a (Fig. S4) after supplement

Page 17216, Line 21 – Suggest changing (Lanz et al., 2007) to Lanz et al. (2007) (Fig. S4)

Page 17217, Line 1 - Suggest adding a (Fig. S4) after (2005)

Page 17217, Line 2 – Suggest adding the word being before dominated

Page 17217, Line 6 - Suggest adding a (Fig. S4) after (2004)

Page 17217, Line 19 – Suggest adding an a before Multi

Page 17217, Line 20 – The abbreviation TNO is not defined

Page 17217, Line 29 to Page 17218, Line 2 – Suggest removing the sentence starting Correlation between. . . as it was already stated earlier in this section

3.5.Comparison between NMR and AMS-factors for OA Page 17218, Line 10 – Suggest adding a the before OM/OC

Page 17218, Lines 14-15 – There is a difference in the number of significant figures used in the text compared to Table 4.

Page 17218, Line 20 – Suggest adding a the before filter and changing measurement to measurements

Page 17218, Line 26 – Suggest adding an and before somewhat

Page 17219, Line 2 – Suggest changing et al., 2012, to et al. (2012)

Page 17219, Line 3 – Suggest changing in case to for this case

Page 17219, Line 4 – Suggest changing by AMS (Mensah et al., 2012). to by the AMS.

Page 17219, Line 8 – dichotomous is misspelled

Page 17219, Line 10 – Suggest changing of PM1 to for the PM1 and adding a the before AMS

Page 17219, Line 11 – Suggest adding a the before AMS

Page 17219, Line 12 – Suggest changing magnitude of the deviation on OC to magnitude as the deviation for the OC

Page 17219, Line 13 – The units should be ug C/m3

Page 17219, Line 16 – Suggest adding the word concentrations after AMS

Page 17221, Lines 6-10 – The authors mention that the NMR factor analysis did not identify a factor matching F2AMS (SV-OOA). But in Table 5a there is a high R value between NMR F2 and F2AMS. 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.

Page 17221, Line 9 – Suggest adding an a before characteristic

Page 17221, Line 14 – Suggest adding a the before AMS

Page 17221, Line 17 – Suggest adding a the before AMS

Page 17221, Line 28 – Suggest adding a the before AMS

3.6.Comparison of HULIS from chromatographic and spectroscopic techniques Page 17222, Line 20 and 22 – Believe an accent mark is missing on Krivacsy

Page 17222, Line 22 – Havers is misspelled

3.7.Link between AMS factors and water-insoluble organic Page 17222, Line 4 – Suggest adding the word carbon after organic

Page 17223, Line 22 – Suggest adding a the before AMS

Page 17223, Line 25 – Suggest changing of AMS to from the AMS

4.Conclusions Page 17224, Line 19 – Suggest changing insights to to insights into

Page 17224, Line 21 – Suggest changing chain with the to chains and the

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.

Page 17225, Line 21 – Suggest changing despite of to despite the

Acknowledgements Page 17226, Line 10 – Suggest adding a the before European

References Page 17226, Line 23 – Believe it should be time-of-flight

Page 17231, Line 8 – Accent marks are missing on Prevot

Page 17232, Line 1 – Accent marks are missing on Krivacsy, Gelencser, and Molnar

Page 17233, Line 4 - Accent marks are missing on Prevot

Page 17235, Line 31 – A comma is missing after Dattler. The Limbeck can be removed.

Page 17236, Line 19 – A comma is missing after Prevot and Wahlin

Page 17237, Line 7 – A space is missing between anthropogenically and influenced

Tables Table 2 -In caption, suggest adding a the before campaign -The units for TC, OC, WSOC, and EC should be ug C/m3

Table 3 -Charges are missing on nitrate and sulfate

Table 4 -In caption, suggest changing founded to determined and adding a the after thereby to

Table 5a -Charges are missing on nitrate and sulfate for the PM1 filter and AMS values

Table 5b -Charge is missing on sulfate

Figures Figure 1 -In caption, suggest adding a the before relationship

Figure 2 -In caption, suggest changing classes to class -The abbreviations used to represent the four campaign periods are different than in Figure 1

Figure 3 -In caption, suggest changing groups to group -The caption mentions a pie chart and histogram. Only the histogram is shown. -The abbreviations used to represent the four campaign periods are different than in Figure 1

Figure 4 -The abbreviations used to represent the four campaign periods are different than in Figure 1

Figure 5 -Units for HULIS and BC should be ug C/m3 -Charges are missing on nitrate and sulfate

Figure 6 -In caption, for CH3SO2+ the 2 should be subscripted -On left hand y-axis, the charge is missing for CH3SO2+ -The abbreviations used to represent the four campaign periods are different than in Figure 1

Figure 7 -On right hand y-axis of top plot, PA is missing from axis label -The abbreviations used to represent the four campaign periods are different than in Figure 1

Supplementary Material Criteria for choosing factor number in NMR factor analysis Q-value Analysis Line 12 – Suggest changing factor to factors

Principal Components Analysis (PCA) Line 17 – Suggest adding an a before function

Line 18 – Suggest adding a the before Cabauw

Uniqueness of NMR spectral profiles and contribution Line 24 – Suggest adding a the after decompose

Line 26 – Suggest changing two factors result to two of the factors were

Line 27 – Suggest adding a from before each

Line 29 – Suggest removing the comma after forced

Line 30 – Suggest changing distinct to defined

Line 32 – Suggest changing could take to provided

Line 34 – Suggest adding a the before p=4 and removing the one after p=3

NMR-factors correlations with aerosol components (from filters and AMS measurements) Line 39 – Suggest removing the the before best

Line 43 – Suggest changing exhibit diurnal maxima at to exhibited diurnal maxima in

Supplementary Figures Figure S2 -Plots are not labeled a and b to match the caption

Figure S3 -Line 76 – main should be capitalized -Lines 77-78 – Suggest changing originated by to originating from -Line 78 – agriculture is misspelled -The units for y-axes on plots a and c should be ug C/m3

Figure S4 -The abbreviation MS is not defined

Figure S5 Line 94 – comparison should be capitalized

Figure S6 Line 98 - comparison should be capitalized

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