

Review of “Argon offline-AMS source apportionment of organic aerosol over yearly cycles for an urban, rural and marine site in Northern Europe” by Bozzetti et al.

This manuscript reported an analysis of PM<sub>1</sub> compositions and sources at three different sites in Lithuania based on filter samples. The authors applied AMS and other instruments to analyze the filter samples, and then performed PMF analysis to study the sources of OA and PM<sub>1</sub>. This study presented a method/case to study the sources of total ambient OA based on the measurements of water soluble OA only. That is, apply PMF analysis on the water soluble organic mass spectra, identify multiple factors, and rescale the water soluble concentration to total concentration by applying recovery ratios. This is an interesting method but has large uncertainties, which arise from the recovery ratio. I think this manuscript is suitable for publication in ACP once the following comments have been addressed.

### **Major comments**

1. Ambient total OA source apportionment based on the measurement of water soluble OA.

The major uncertainty of this method arises from the recovery ratio ( $R_z$ ), which is a reflection of the bulk extraction efficiency and water solubility of OA factors. It is not clear how the  $R_z$  values are obtained in this study. As I understand, the authors randomly selected  $R_z$  from Daellenbach et al. (2016) as initial conditions and fit Eq. (6) to get  $R_{LOA}$ . If so, how are  $R_{BBOA}$  and  $R_{OOA}$  obtained? Why are they different from the values in Daellenbach et al. (2016). Also, it is not clear which  $R_z$  values are eventually applied, from Daellenbach et al. (2016) or the values calculated in this study?

The authors mentioned that the bulk extraction efficiency in this study is lower than that in Daellenbach et al. (2016). This result is not surprising since one OA factor likely has contribution from multiple sources and the water solubility of OA factors may vary with site and season. For example, the water solubility of BBOA ranges from 64% to 80% (Sciare et al., 2011; Timonen et al., 2008). In addition, this method is not sensitive to primary OA factors (e.g., HOA and Cooking OA), which is largely water insoluble. This is another reason why HOA cannot be resolved from the PMF analysis. The limitations should be better discussed in the manuscript.

What suggestions do the authors have for researchers who want to use the method as proposed in this manuscript? For example, should they follow the same filter extraction procedures as in this study? How to calculate the R<sub>Z</sub>?

2. Discussions on instruments comparison are required.

(1) Inorganic ions such as NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> are measured by both AMS and IC. The authors should present the instruments comparison.

(2) Page 9 Line 29-30. The AMS measured concentration is scaled to match the WSOC measurement. What's the scale ratio? Is the scale ratio the same for all filter samples?

3. The difference in separation and classification of OA factors between online and offline-AMS (Page 20 Line 14-27).

I disagree with the statement that “online-AMS OOA factors are commonly classified based on their volatility”, because chemistry and sources also affect the factor separation. For example, the separation of IEPOX-OA factor (Budisulistiorini et al., 2013; Hu et al., 2015) or called isoprene-OA factor (Xu et al., 2015) is driven by IEPOX chemistry, but not volatility. Also, Xu et al. (2015) showed that nighttime monoterpene oxidation by nitrate radical contributes to less-oxidized OOA (as termed SV-OOA in this study).

The authors stated that “the offline-AMS sources apportionment separates factors by seasonal trends rather than volatility”. However, sometimes, seasonal trend affects the source apportionment through volatility. For example, Page 23 Line 26-27 discussed that higher NO<sub>3</sub><sup>-</sup>-related SA exhibits higher concentration in winter than summer, which is due to the semi-volatile nature of NO<sub>3</sub><sup>-</sup> (Page 19 Line 20).

4. OM/OC ratio.

In this study, the OM/OC is calculated by Aiken method (Page 12 Line 20). However, a recent study by Canagaratna et al. (2015) improved the estimation from Aiken method by including composition-dependent correction factors. The Canagaratna method is recommended to use. Since many calculations in this study depend on the OM/OC ratio, how would it affect the results/conclusions if the authors use Canagaratna method to calculate the OM/OC ratio?

5. Background-OOA (B-OOA) factor.

When the authors selected solutions, one criterion is the correlation between B-OOA and NH<sub>4</sub><sup>+</sup> (Page 12 Line 8). The authors should explain the use of NH<sub>4</sub><sup>+</sup>. SO<sub>4</sub><sup>2-</sup> is regional and usually used as background OA. What's the correlation between B-OOA and SO<sub>4</sub><sup>2-</sup>? In Page 20 Line 30,

it is stated that B-OOA correlates well with  $\text{NH}_4^+$ . However, the correlation between B-OOA and  $\text{NH}_4^+$  varies with site as shown in Fig. S11. For example, the correlation is really weak for the Rugsteliskis site.

If B-OOA represents background OA, why is B-OOA lower in urban site than the other sites? I disagree with the authors' argument that this difference is caused by PMF residual uncertainties or biases (Page 29 Line 10). The authors' argument is flawed because it is based on circular assumptions. When the authors calculate  $\text{B-OOA}_{\text{marker}}$ , the LOA and S-OOA are based on PMF analysis without considering "some residual uncertainties or biases". If the authors considered "some residual uncertainties or biases" and re-performed PMF analysis, the concentrations of LOA and S-OOA would change, which would influence and concentration of  $\text{B-OOA}_{\text{marker}}$ . In that circumstance,  $\text{B-OOA}_{\text{offline-AMS}}$  may agree among all three sites, but  $\text{B-OOA}_{\text{marker}}$  may be different among all three sites.

### **Minor comments**

1. TEOA is resolved from CMB, not PMF. This needs to be clarified in multiple places in the manuscript, such as Page 2 Line 9 and Page 23 Line 30. Considering that the TEOA concentration is small and only one filter has statistical significant TEOA concentration (Page 22 Line 27), I suggest the authors to remove the comparison about TEOA concentration between sites (for example, Page 32 Line 15-17).
2. Page 2 Line 10. Please rephrase to "two oxygenated OA factors, summer OOA (S-OOA) and background OOA (B-OOA)".
3. Page 2 Line 16 vs. Line 18. Use OA or OM. Be consistent.
4. Page 4 Line 3. Please rephrase to "source apportionment on the submicron water soluble OA" in order to be precise about the method.
5. Page 5 Line 24. The nebulizer temperature is  $60^\circ\text{C}$ , which is different from Daellenbach et al. (2016). Also, the nebulizer system in this study is different from that in Daellenbach et al. (2016). Would these differences cause the difference in Rz between studies?
6. Page 5 Line 27-28. The correction of blank is not appropriate. This is because the particles generated from nebulizing DI water only are too small to be detected by AMS. However, the organics associated with DI water will be detected by AMS when nebulizing real filter extracts because the particles are big. I suggest the authors to nebulize ammonium sulfate solution (i.e.,

dissolve ammonium sulfate in DI water with similar concentration as ambient filters) and use the detected organic concentration as blank.

7. Page 9 Line 7-9. Although the detailed procedures have been discussed in Daellenbach et al. (2016), it is still helpful to briefly discuss the method in the manuscript, especially how the recovery ratios are calculated.
8. Page 10 Line 28. Please rephrase to “this factor has too small contribution in the water extracts to be resolved”.
9. Page 12 Line 6. This sentence has been repeated twice. Delete.
10. Page 12 Line 13-16. AMS measures OM, instead OC. Please be clear that the conversion from OM to OC is for the carbon mass closure in Eq. (6).
11. Page 12 Eq. (6). WSW-OOA should be WSB-OOA. Is  $R_z$  the same for S-OOA and B-OOA since the same  $R_{OOA}$  is applied for both factors?
12. Page 14 Line 20. What’s the  $OM_{res}/OM$  ratio?
13. Page 15 Line 21. List the non-source specific variables.
14. What’s the  $Hopanes_{sum}/OC$  ratio in the traffic exhaust factor? Is it consistent with the CMB method (i.e., 0.0012 in Page 11 Line 15)?
15. Page 16 Line 25. Should be “ $EC/OM_{res}$ ” ratio.
16. Page 17 Line 10-16. The discussion is not clear. Suggest re-wording.
17. Page 20 Line 1-3. List the levoglucosan/BBOC range in the literature. Similar suggestions for other places. For example, list the non-fossil primary organic carbon in Page 25 Line 13 and average fossil primary OC in Page 25 Line 29.
18. Page 21 Line 2. I disagree with that S-OOA increases exponentially with average daily temperature from the data points in this study (Fig. S12). For example, many data points with  $T > 25^\circ C$  do not have high S-OOA concentration and do not follow the exponential fit.
19. Page 22 Line 13-15. This has been mentioned previously in Page 20 Line 1-3. It is not proper to discuss BBOC here because this section focuses on the marker-PMF, instead of offline AMS. Similar problem for Page 22 Line 23-24.
20. Page 23 Line 14-15. The observation that nitrate concentration is higher in urban site than rural site has been shown in many previous studies (Xu et al., 2016; McMeeking et al., 2012), which should be cited here.

21. Page 23 Line 30-31. This sentence is confusing. The remaining OM fraction is termed as  $OM_{res}$  in Page 10 Line 20, but termed as Other-OA here. It should be clearly stated that Other-OA refers to OA after excluding BB and TE.
22. Page 24 Line 18. Should be “higher”
23. Page 24 Line 21-23. (1) Which method did the authors use to get the BBOA concentration and correlation in this sentence? (2) It would be helpful to include a scatter plot between Preila and Vilnius. (3) I disagree with “the importance of regional meteorological conditions” as stated in this sentence and Page 32 Line 31-32. Firstly, the BBOA concentrations are different between two sites. Secondly, the BBOA in the Rugsteliskis site does not correlate with the other two sites.
24. Page 24 line 29. Both methods have the same time resolution (one filter per day).
25. Page 25 line 15. In the statistical significance test, why is sometimes  $1\sigma$  is used but sometimes  $3\sigma$  is used (for example, Page 26 Line 28).
26. Page 26 Line 30. Should be “factor” instead of “fraction”.
27. Table 2. The correlation coefficient R between  $NO_3$ -related SOA and B-OOA is only 0.21. Thus, it is not meaningful to discuss the relationship between  $NO_3$ -related SA and B-OOA (Page 28 Line 17). Similar problem for the relationship between MSA-related SOA and S-OOA (Page 28 Line 21).
28. Page 29 Line 18. Please rephrase to “ $f_{CO_2}$  value is higher than  $f_{CO}$ ”.
29. Page 29 Line 24-25. The logic is not clear. Why does higher  $CO_2^+/CO^+$  ratio of gas  $CO_2$  suggest a minor contribution from WSOM decarboxylation to  $CO^+$ .
30. Page 30 Line 7. Many data points from the Rugsteliskis site are outside the triangle range in Fig. 7a.
31. Page 31 Line 4. The correlation between  $CO^+$  and  $C_2H_3O^+$  is not shown in Fig. 7b. It would be helpful to show a scatter plot.
32. Page 31 Line 16. Canagaratna et al. (2015) carefully discussed the  $CO_2^+/CO^+$  ratio of a number of standards, which should be discussed and mentioned more in the manuscript.
33. Figure 5. The grey caps of traffic exhaust are not clear in this figure.

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