

Interactive comment on “Characteristics, primary sources and secondary formation of water soluble organic aerosols in downtown Beijing” by Qing Yu et al.

Anonymous Referee #2

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This work reported 4-season filter-based WSOC measurements including tracer measurements and group separation of the aqueous extracts into so-called hydrophobic and hydrophilic fractions by the SPE method. The sources of WSOC were speculated based on some correlations with O₃, RH, ALWC etc. The authors also conducted the PMF analysis to evaluate the source contributions. The problem is the quality of data analysis and discussion. Many of the discussions were not logically presented. Loss terms (e.g., photolysis, chemical reactions, gas-particle partitioning) were generally ignored. Conclusions about the relative contributions of photochemical vs aqueous pathways were made mainly on the basis of simple correlations with O₃ or ALWC etc., which can be largely uncertain especially for the winter-haze episodes when all com-

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ponents of PM2.5 including primary species were correlated with ALWC or RH. There is also a lack of sufficient information to validate the PMF analysis in this study. The presented PMF results seem quite arbitrary.

Specific comments are listed below.

Page 1, Line 14; Page 2, Line 53-57; Page 4, Line 106-112: Different SPE columns and extraction procedures (e.g., pH) result in various fractions of the WSOC (Sullivan et al., 2006). The authors used SPE (Oasis HLB) to separate the “hydrophilic and hydrophobic” fractions of WSOC. However, as described by Kiss et al. (2002), the one-step SPE on Oasis HLB column is to separate the WSOC into moderately hydrophilic (retained on the column) and strongly hydrophilic (passed through the column) fractions. I think it is wrong to simply assign the retained fraction herein as “hydrophobic” or “mainly HULIS” and the passed-through fraction as typical “hydrophilic (short-chain dicarboxylic acids and saccharides)”.

Introduction: Previous understanding of the characteristics of WSOC and its separated fractions as well as their primary and secondary sources were poorly summarized in the current Introduction section.

Page 4, Line 97 and Page 5, Line 124-125: How were the field blanks collected before and after sampling? What exactly were corrected?

Page 5, Line 129-131: Detailed information about the PMF analysis should be provided. The authors said that “the uncertainties were calculated referring to the measured RSD data of chemical analysis and previous studies”. It is unclear to me whether this is a right approach. What do “the measured RSD data of chemical analysis and previous studies” mean specifically? Also, the authors said “The PMF model was run repeatedly to obtain a clear and reasonable source profile”. How? The reasons of the selection of the numbers of PMF factors as well as the PMF uncertainty estimates and diagnostics are necessary.

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Page 5, Line 140-141: The equation calculates ion balance not “aerosol acidity”.

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Page 6, Line 166: Why would the reduction of open biomass burning lead to decreased WSOC/OC ratios? Please clarify and cite references to support the reduction of open biomass burning.

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Page 6, Line 173-176: The correlations ($r = 0.44-0.58$) are not strong. I think it is difficult to conclude that OA became more hygroscopic as pollution aggravated. Indeed, if primary sources make a large contribution, e.g., in winter when coal combustion was enhanced, OA might not be more hygroscopic although its concentration became greater.

Page 6, Line 180: Perhaps remove “ideal”. Levoglucosan is not chemically inert. It is also not a unique tracer for biomass burning. As the authors mentioned in Page 7, Line 199, biofuel and coal burning are also sources of levoglucosan.

Page 7, Line 183: MethylNitrocatechol is not necessarily secondary. Wang X et al. (2017) showed primary emissions of methylNitrocatechol from biomass burning. Coal burning is also a source. The statement that “4-methyl-5-nitrocatechol is a good indicator for biomass burning SOA” is perhaps inappropriate.

Page 7, Line 200-203; Line 210-218; Page 8, Line 237-243: Errors can be propagated to the ratios in Figure 2b so that the day/night CO-scaled ratios can be discussed statistically (not just seasonal mean values). The authors said the CO-scaled concentration of cholesterol was close for the whole sampling period. However, panel a is in log scale. I think it is hard to conclude that 4 vs. 7 (i.e., 75% difference) is “close”.

Besides the statistical issue, other problems exist for the conclusions made on the basis of day/night ratios. First, biomass burning is not the only source of CO. The <1 day/night CO-scaled ratios of levoglucosan can be simply caused by enhanced CO emissions at night from other sources when the biomass burning contributions were constant. Similarly for cooking. Second, from emissions to concentrations, many fac-

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tors are involved. Biomass burning is not a local source in Beijing. Similar strength of emissions may lead to different concentrations in Beijing because of the atmospheric aging and dilution during the regional transport process. Also, scaling secondary tracers by CO has complicated meaning, especially for biogenic-related tracers. I can't understand the logic behind Line 236-243. Not to mention that the phthalic acid concentrations may be affected by the OA concentrations due to gas-particle partitioning and the photolysis of 4-methyl-5-nitrocatechol might be significant to affect its daytime concentrations.

Page 7, Line 205-207: The cited reference is only for PAH. How about other aromatic precursors (e.g., single-ring aromatics)? Do those typical SOA precursors show higher concentrations in winter? Please note that oxidation conditions are also important when discussing about the secondary formation potential of SOA. In winter, the oxidant concentrations (e.g., OH) might be lower.

Section 3.2.2 in Page 8-10: Conclusions in this section are generally arbitrary. Although correlations sometimes help diagnostics, connections between O₃, ALWC, RH, T and the tracer species as well as WSOC/OC are not simple/obvious. For example, in Line 248-251, it was said that "WSOC/OC did not correlate with O₃, suggesting that gas-phase photooxidation was not the dominant formation mechanism of SOC". Why? Do the authors assume that WSOC are SOC and gas-phase photooxidation is equivalent to O₃? What about terms other than chemical production in the mass balance (e.g., photolysis, primary contributions, and so on? Besides, the correlation isn't strong ($r = 0.5$) when the authors sometimes said "significantly correlated". Such kind of correlations might be used as non-conflict evidence for explaining the formation pathways but definitely insufficient to make any conclusions. A common argument is that in winter Beijing all components of PM_{2.5} often correlate with RH and ALWC, even for primary OA. It is not surprise that 4-methyl-5-nitrocatechol correlate with RH and ALWC. The study done by Wang L et al. (2018) suggest coal and traffic contributions to 4-methyl-5-nitrocatechol were the dominant sources in northern China.

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Page 11, Line 314-327: The interpretation of the PMF factors is over simple here. It looks like the authors intentionally choose a PMF solution that has separate factors for individual tracers. However, how do the tracers correlate each other? (1) Previous studies found that methyl-nitrocatechol correlates with AMS BBOA and levoglucosan (Linuma et al. 2010; Mohr et al. 2013). If the two temporally correlates, the split of the biomass burning factor into two (primary and secondary) may be highly uncertain given the small sample size of this study. (2) Factor 7, 8, and 9 are all associated with biogenic SOA tracers. It was said in Page 10, Line 297-298 that 3-hydroxyglutaric acid correlated strongly with 2-methylerythritol. Then how and why to separate Factor 8 and 9. Is 3-hydroxyglutaric acid a unique tracer for monoterpene SOA? For day and night samples which did not maintain much oxidation process information (meaning first-generation vs multi-generation), I am surprised that there were two monoterpene SOA factors (one is marked by cis-pinonic acid and the other is marked by 3-hydroxyglutaric acid). (3) For Factor 3, the profile has significant contributions of secondary species, is it really primary?

Technical remarks:

Page 7, Line 211: "secondary formation of aromatic SOA" - SOA is secondary.

Page 8, Line 239: "the diurnal patterns were close to 1" – What does this mean?

Page 9, Line 252: LWC has already defined.

References:

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