

Interactive comment on “Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe – implications for origin” by Zoran Kitanovski et al.

Anonymous Referee #1

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This study quantified some important nitro-aromatic species and nitrated/oxygenated-PAHs at two urban sites in Europe. The mass size distributions and sources of targeted species are analyzed. The topic is valuable, while the manuscript is not so well organized and sometimes is hard to follow. Some important conclusions drawn in this study are not very validated and sometimes inconsistent, especially for the source analysis (pls see following major comments), which is important part of the paper. The following major comments need to be carefully addressed before re-considered by ACP.

1. The discussion on the sources or origins of NMAHs and O/NPAHs is important

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part of the manuscript, while related discussions in the main text cannot support the conclusions and sometimes inconsistent. The authors concluded that fresh biomass burning emissions dominated at the TK site, while aged air masses were predominant at the MZ site in the abstract (lines 18-20), however:

Lines 263-293: The authors hypothesize the TK site was greatly influenced by BB emissions based on the high concentrations of NC, MNC and NSA. This is also an important conclusion drawn in the abstract (lines 18-19: fresh biomass burning emissions dominated at the TK site). However, the authors found NC and MNC showed low correlations with K⁺ (biomass burning tracer) in line 274. And then draw the conclusion that gas-phase nitration of anthropogenic precursors, rather than BB, was the main source of NC and MNC in lines 283-286. NC and MNCs are the most abundant species among the quantified NMAHs in this study, so the bad correlations with K⁺ indicated the less importance of BB emissions at TK site.

If the conclusion in line 266 (The air masses over TK during sampling were greatly influenced by BB emissions) is true, why not use the fire maps and back trajectories during the sampling to validate this?

Again, the authors concluded that aged air masses were predominant at MZ site in lines 19-20. However, good correlations between K⁺ and NC, MNCs were reported in lines 296-297. NC and MNC are the most abundant NMAHs at MZ site (lines 246-247). Thus, BB emission seems the more important source of NMAHs at the MZ site.

Lines 297-303: The formation of NSA, NP, MNP and DNP via aqueous-phase nitration may be arbitrary. For example, 4-NP can form via gas-phase oxidation and then partition into the particle phase. There is another possibility that the nitrate (very hygroscopic) facilitates the aerosol absorbing more water, resulting in higher aerosol liquid water content, which promote the gas-phase NPs or other NMAHs partitioning into the particles. In this case, nitrate and the NMAHs can also show good correlations.

Lines 418-421: How could the correlations between the analyzed species and WSOC

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or HULIS, and bad correlations between analyzed species and K^+ suggest the sources from both primary and secondary sources? Bad correlations with K^+ indicate the less contribution of BB emissions. Both WSOC and HULIS have primary BB emission and secondary formation sources.

What's more, there were only four or five points to do the correlations, which I think it's not quite convincing to analyze the sources.

2. Section 3.5 lines 461-470 and lines 11-13: This study calculated the contributions of NMAHs to HULIS and WSOC. HULIS and WSOC are just the water soluble organics, while NMAHs were extracted by methanol in this study. I agree that NMAHs could be the constituents among HULIS and WSOC, while using methanol-extracted NMAHs to calculate their contributions to HULIS or WSOC may not reasonable. I am not sure if the methanol extracted fractions are equal to the water soluble fractions in WSOC or HULIS (I think the NMAHs among HULIS or WSOC may be lower than the methanol-extracted NMAHs). Furthermore, some of the water-extracted NMAHs could be excluded from the HULIS fraction during the SPE processes. Can you show data (e.g. the ratios of water-extracted/methanol-extracted NMAHs) or any evidence to suggest the calculation is reasonable? Also, N/O-PAHs are extracted by dichloromethane. Are the water-extracted N/O-PAHs in HULIS or WSOC are equal to the dichloromethane-extracted fractions?

Lines 331-333: I think similar mass size distributions of NMAHs and HULIS only indicate they may have similar atmospheric processes, and cannot indicate NC and NSAs are important constituents of HULIS.

3. Lines 260-261 and related analysis throughout the paper: How do the authors know the different concentration levels of the two sites are not due to different cut-off of the aerosol samples? I notice that both sites have the same cut-off of 0.49-0.95, 0.95-1.5, 1.5-3, 3-7.2 μm , it would be meaningful to compare the concentrations of the same particle size ranges and then analyze the different sources at the two sites.

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4. Some important information should be added in the Experimental section:

1) Section 2.2: Why sampling is conducted at the two sites? They are both urban sites. Please specify the differences of the two sites in section 2.2, such as referring previous studies in the two sites to address the differences. It is not quite clear for me what's the differences between the two sites even after finish reading the paper.

2) Section 2.2 and Table 2: Only four sets of sample were collected at MZ site, and five sets at TK site. How can the authors confirm that only four or five samples can represent the conditions at the sites?

3) Section 2.3: Please show the recoveries of the quantified species in Table 1. And pls show the compound peaks and resolution of NMAHs in the LC-MS chromatograms.

4) The extraction and quantification of K⁺, WSOC and HULIS are omitted in the experimental section.

5. Besides, I suggest the authors to carefully check the data and analysis throughout the paper, and to draw scientific and validated conclusions. A better proofing reading is also needed.

Specific comments:

Lines 71-73: This sentence is confusing. Which source is more dominated in urban areas? Primary sources or secondary formation? Pls revise to be clear.

Lines 103-105: I think these three references are more focused on the light absorption of nitro-aromatics. Could the authors add more references suggesting the light absorption capacity of PAHs and N/O-PAHs?

Lines 309-401: Please clarify what are "these OPAHs" and what are "other N/OPAHs".

Lines 465-466: Could the authors further explain why larger particle size suggests aqueous-phase processes and slower formation?

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