Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC1
https://doi.org/10.5194/amt-2022-221-RC1, 2022

Comment on amt-2022-221

Anonymous Referee #2

Referee comment on "Mass spectrometry-based *Aerosolomics*: a new approach to resolve sources, composition, and partitioning of secondary organic aerosol" by Markus Thoma et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-221-RC1, 2022

General comments:

This study deals with a relatively new analytical approach, namely, non-targeted aerosolomics combined with hierarchical cluster analysis to gain detailed information on sources, composition and partitioning of secondary organic aerosol (SOA). Non-targeted aerosolomics has its roots in non-targeted metabolomics, which is a well-established biomedical tool, and definitely holds promise for gaining deeper insights into various aspects of SOA. It would be useful to say a few words about the historical origin of this approach in the introduction, as the atmospheric community may not be aware about this development. The aerosolomics data base is fed with information gained on 5 biogenic volatile organic compounds (VOCs) (alfa- and beta-pinene, delta-3-carene, d-limonene and beta-caryophyllene) and 4 anthropogenic VOCs (toluene, o-xylene, 1,2,4-trimethylbenzene and naphthalene), and additional work is planned for the biogenic VOC, isoprene. The use of non-targeted aerosolomics allows to connect the various detected SOA products to their VOC precursor, while the combined use with hierarchical cluster analysis is shown to reduce the complexity of the ambient dataset and to assign compounds to certain formation processes or emission sources.

The data have been partly interpreted, but could have been more thoroughly interpreted taking into account the available literature, for example, the molecular assignments for SOA products related to alfa- and beta-pinene (see specific comments). Literature citations to original papers, in which the SOA products were first reported, are missing in many instances.

Specific comments:

Line 162: Here, a reference to the paper in which MBTCA was first reported would be appropriate: Szmigielski R., et al., 2007.

Line 179: The authors mention here that they were not able to determine the individual chemical structure of the different SOA compounds, but, in my opinion, it is feasible to assign most of them taking into account available knowledge, certainly for SOA related to alfa- and beta-pinene, on the basis of MS/MS and reversed-phase LC retention data. See below.

Lines 188 - 207: In this section, the oxidation products of alfa-pinene are discussed, which have been well documented in the literature. References to the early literature, in which these SOA products were first characterized on the molecular level, are appropriate. Many of the products mentioned have even been unambiguously assigned, not only tentatively. For example, the following molecular markers related to alfa- and beta-pinene:

$C_9H_{14}O_4$ (MW 186): characterized as pinic acid (e.g., Yu et al., 1999; Glasius et al., 2000)

$C_{10}H_{16}O_4$ (MW 184): characterized as hydroxypinonic acid (e.g., Glasius et al., 1999)

$C_8H_{12}O_6$ (MW 204): characterized as MBTCA (Szmigielski et al., 2007)

$C_8H_{12}O_4$ (MW 172): characterized as terpenylic acid (Claeys et al., 2009; Yasmeen et al., 2011)

$C_8H_{12}O_5$ (MW 188): characterized as hydroxyterpenylic acid isomers (Kahnt et al., 2014)

$C_{17}H_{26}O_8$ (MW 358): characterized as cis-pinyl-diaterpenyl ester (Yasmeen et al., 2010; Kahnt et al., 2018)

The same comment applies to molecular markers related to delta-3-carene and d-limonene, and to other molecular markers discussed in the text.

Legend Figure 4: Molecular weight has no dimensions; delete "Da" in the x-axis.

Lines 279-283: Here, mention is made of CHNO biomass burning markers, such as nitrosalicylic acid and methylnitrophenol. It would be appropriate to cite the early papers in which products like methylnitrophenol were first reported in ambient fine aerosol by the group of Grgic, e.g., Kitanovski, Z., et al., J. Chrom. A 2012.

Line 344: The abundant $C_8H_{12}O_5$ product can be assigned to the alfa-pinene-related SOA markers, characterized as hydroxyterpenylic acid isomers. See Kahnt et al., 2014.

Line 360 and many places elsewhere: Molecular weight has no dimensions but molecular mass has; thus: ‵'The molecular mass reaches up to 440 Da and ….'' or "The molecular weight reaches up to 400 and …..''.

Lines 371-374: Here, alfa-pinene-related dimers $C_{17}H_{26}O_8$ and $C_{19}H_{28}O_7$ are discussed; see the detailed chemical characterization study by Kahnt et al., 2018. It is also relevant to mention that the $C_{17}H_{26}O_8$ dimer, characterized as cis-pinyl-diaterpenyl ester, was first reported in nighttime ambient fine aerosol (Yasmeen et al., 2010).

Line 395: Here, mention is made of a CHNOS compound with a mass of 295 Da. New intriguing insights about abundant MW 295 nitrooxy organosulfates related to alfa-pinene have more recently been gained by the group of Yu; see Wang, Y.-C., et al., Environ. Sci. Technol., 2021.

References cited:

Claeys, M., et al., Terpenylic acid and related compounds from the oxidation of alfa-pinene: Implications for new particle formation and growth above forests. Environ. Sci. Technol. 43, 6976–6982, 2009.

Glasius, M., et al., Determination of polar terpene oxidation products in aerosols by liquid chromatography – ion trap mass spectrometry. J. Chrom. A 833, 121–135, 1999.

Kahnt, A., et al., High-molecular-weight esters in alfa-pinene ozonolysis secondary organic aerosol: structural characterization and mechanistic proposal for their formation from highly oxygenated molecules. Atmos. Chem. Phys. 18, 8453–8467, 2018 https://doi.org/10.5194/acp-18-8453-2018.

Kahnt A., et al., 2-Hydroxyterpenylic acid: An oxygenated marker compound for alpha-pinene secondary organic aerosol in ambient fine aerosol. Environ. Sci. Technol. 48, 4901-4908, 2014.

Kitanovski, Z., et al., Liquid chromatography tandem mass spectrometry method for characterization of monoaromatic nitro-compounds in atmospheric particulate matter. J. Chrom. A 1268, 35-43, 2012.

Szmigielski, R., et al., 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol. Geophys. Res. Lett. L24811, 2007.

Wang, Y.-C., et al., Chemical synthesis of multifunctional air pollutants: Terpene-derived nitrooxy organosulfates. Environ. Sci. Technol. 55, 8573-8552, 2021.

Yasmeen, F., et al., Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of alfa- and beta-pinene. Atmos. Chem. Phys. 10, 9383–9392, doi:10.5194/acp-10-9383-2010, 2010.

Yasmeen, F., et al., Mass spectrometric characterization of isomeric terpenoic acids from the oxidation of alfa-pinene, beta-pinene, d-limonene, and delta-3-carene in fine forest aerosol. J. Mass Spectrom. 46, 425–442, 2011.

Yu, J., et al., Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products, J. Atmos. Chem. 34, 207–258, 1999.

Technical comments:

Line 47: $PM_{2.5}$ (2.5 in subscript).

Line 59 and many places elsewhere in the text: …. (98%, Alfa ….; remove the space before "%"

Line 156: …. of this mode …..??

Line 221: …. ß-norcaryophyllonic acid ??

Legend Fig. 3: …. The most abundant compounds …..

Line 350: However, it needs …..