EGU21-2819
https://doi.org/10.5194/egusphere-egu21-2819
EGU General Assembly 2021

Molecular composition and volatility of gaseous organic compounds in a boreal forest: from volatile organic compounds to highly oxygenated organic molecules

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The molecular composition and volatility of gaseous organic compounds were investigated during April–July 2019 at the Station for Measuring Ecosystem – Atmosphere Relations (SMEAR) II situated in a boreal forest in Hyytiälä, southern Finland. A Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-ToF; hereafter Vocus) was deployed to measure volatile organic compounds (VOC) and less oxygenated VOC (i.e., OVOC). In addition, a multi-scheme chemical ionization inlet coupled to an atmospheric pressure interface time-of-flight mass spectrometer (MION APi-ToF) was used to detect less oxygenated VOC (using Br^- as the reagent ion; hereafter MION-Br) and more oxygenated VOC (including highly oxygenated organic molecules, HOM; using NO_3^- as the reagent ion; hereafter MION-NO_3). The comparison among different measurement techniques revealed that the highest elemental oxygen-to-carbon ratios (O:C) of organic compounds were observed by the MION-NO_3 (0.9 ± 0.1, average ± 1 standard deviation), followed by the MION-Br (0.8 ± 0.1); and lowest by Vocus (0.2 ± 0.1). Diurnal patterns of the measured organic compounds were found to vary among different measurement techniques, even for compounds with the same molecular formula, suggesting contributions of different isomers detected by the different techniques and/or fragmentation from different parent compounds inside the instruments. Based on the complementary molecular information obtained from Vocus, MION-Br, and MION-NO_3, a more complete picture of the bulk volatility of all measured organic compounds in this boreal forest was obtained. As expected, the VOC class was the most abundant (about 49.4 %), followed by intermediate-volatility organic compounds (IVOC, about 48.9 %). Although condensable organic compounds (low-volatility organic compounds, LVOC; extremely low-volatility organic compounds, ELVOC; and ultralow-volatility organic compounds, ULVOC) only comprised about 0.3 % of the total gaseous organic compounds, they play an important role in new particle formation as shown in previous studies in this boreal forest. Our study shows the full characterization of the gaseous organic compounds in the boreal forest and the advantages of combining Vocus and MION APi-ToF for measuring ambient organic compounds with different oxidation extent (from VOC to HOM). The results therefore provide a more comprehensive

understanding of the molecular composition and volatility of atmospheric organic compounds as well as new insights in interpreting ambient measurements or testing/improving parameterizations in transport and climate models.

Wei Huang and Haiyan Li contributed equally to this work.

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