

LC/MS analysis of molecular markers present in biogenic secondary organic aerosols collected during year-round observations at a cool-temperature forest

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To understand formation processes for organic nitrogen and dimeric compounds present in forest aerosols, we analyzed molecular markers present in forest aerosols collected during year-round observations using negative/mode electrospray ionization-liquid chromatography-mass spectrometry (ESI-LC/MS). Thirty-seven aerosol filter samples were collected at Tomakomai Experimental Forest between January and December in 2013, and 33 of the collected samples were analyzed in this study. Molecular markers analyzed in this study were cis-pinonic acid, 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA), α -pinene-derived dimer detected by ESI at m/z 357 (α -pinene dimer), isoprene-derived organosulfate detected at m/z 215 (isoprene OS), and isoprene-derived nitroxyorganosulfate detected at m/z 260 (isoprene NOS). Each aerosol filter sample was extracted in methanol; the extract was concentrated under gentle stream of nitrogen; the concentrated extract was dissolved in an analytical solvent to obtain an analytical sample; and the analytical sample was analyzed by an LC/MS instrument (Sato et al., 2007). The seasonal change in the concentration of cis-pinonic acid, formed from α -pinene oxidation, was peaked in spring and fall, whereas the seasonal change in the concentration of 3-MBTCA, formed from oxidation of pinonic acid, was peaked in summer. Very similar results were reported in a previous paper on the GC/MS analysis of the same samples (Müller et al., 2017). The seasonal change in the concentration of α -pinene dimer was similar to that of cis-pinonic acid, suggesting that a major formation process of the detected dimers was the atmospheric oxidation of α -pinene. The seasonal changes in the concentrations of isoprene OS and isoprene NOS, which are derived from isoprene epoxydiol (IEPOX), were peaked at fall and summer, respectively. The seasonal change in the concentration of isoprene NOS agreed well with that of 2-methyltetrols, molecular markers of isoprene secondary organic aerosol. These results suggest that a major formation process of isoprene NOS is secondary organic aerosol formation from isoprene in the presence of air pollutants.

References

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Keywords: Biogenic volatile organic compound, Secondary organic aerosol, Organosulfate, Nitroxy organosulfate, Organic nitrogen