Direct Observation of Increased Aloft Organic Dinitrates and Oxidized Organosulfates from the Southern Great Plains and TRACER Campaign

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Significant knowledge gaps remain regarding the vertically resolved organic molecular-level composition of atmospheric particles due to aloft sampling challenges. To address this, we use a tethered balloon system to collect ground level and aloft (up to 950 m) samples followed by direct sampling high-resolution mass spectrometry to characterize organic molecular formulas (MF). At the Southern Great Plains (agricultural region; April 2022), we show that organic MF uniquely detected aloft were dominated by organonitrates (139 MF; 54% of all uniquely detected aloft MF). Organonitrates that were uniquely detected aloft featured elevated O/C ratios (0.73±0.23) compared to aloft organonitrates that were commonly observed at the ground level (0.63±0.22). Unique aloft organic molecular composition was positively associated with increased cloud coverage, increased aloft relative humidity (~40% increase compared to ground level), and decreased vertical wind variance. Furthermore, 29% of extremely low volatility organic compounds in the aloft sample were truly unique to the aloft sample compared to the ground level, emphasizing potential aloft oligomer formation at higher altitudes. At this location, we hypothesize that aqueous phase transformations and vertical wind variance may be key variables affecting the molecular composition of aloft organic aerosol. We furthermore characterized aloft organic MF from the TRACER campaign (urban atmosphere; June 2022). For select days, we directly observe increased aloft organic dinitrates compared to ground level, whereas oxidized organosulfates dominated aloft samples for other events. This effort is ongoing, but via leveraging aerosol chemical speciation measurements and remote sensing data, we currently hypothesize that the increase in aloft organic dinitrates results from nighttime biogenic SOA formation, consistent with previous aircraft campaigns in polluted airmasses. Overall, these efforts highlight the inherent value in assessing organic molecular composition of atmospheric particles from a vertically resolved perspective and offer predictive metrics for the occurrence when atmospheric heterogeneity may occur.