

Investigation of Molecular Characteristics, Formation and Impacts of Oxygenated Organic Vapors at a coastal background site in Hong Kong

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The atmospheric oxidation of anthropogenic VOCs plays an important role in the formation of O₃ and secondary organic aerosols (SOA) in the urban and regional atmosphere. Despite extensive studies, our understanding of the oxidation pathways, the intermediate and oxygenated products from various anthropogenic precursors remains unclear. By using a high-resolution chemical ionization time-of-flight mass spectrometry (HR-ToF-CIMS), ambient measurement of oxygenated organic molecules (OOMs) was conducted at a coastal background site in Hong Kong in South China. Abundant semi- and low-volatile OOMs were measured at the site, and elevated organo-nitrate compounds were observed in continental outflows. More than a thousand OOMs were identified and characterized at the molecular level. Most of the identified OOMs contained more than 3 oxygen with a high oxidation state, and more than 2/3 of them were nitrogen-containing organic compounds due to the high NO_x levels in the environment. The variation and relationship of those oxygenated products with precursors and environmental factors were examined to understand their formation mechanisms. Based on the Positive matrix factorization and mechanism analysis, a novel classification framework was developed and applied to attribute the complex OOMs to potential precursors and to identify key functional groups formed in RO₂ termination reactions. The results show that the oxidation of aromatic and aliphatic VOCs dominates OOMs formation in the coastal region, and the multifunctional groups formed in the OOMs included carbonyls, hydroperoxides, nitrates, and peroxy nitrates, etc. Further modeling and data analysis were also performed to quantify the impacts of these oxygenated products on photochemistry and air quality. The irreversible condensation of low-volatile vapors promotes the growth of SOA and nanoparticles. Our results provide quantitative insights into the formation and impacts of oxygenated organic vapors and point to the need for further research to understand their reaction mechanisms and environmental impacts.