High time resolution offline analysis of biogenic secondary organic aerosol in Guangzhou, China.

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PM₂.₅ is considered to be the most dangerous form of air pollution and is formed of a complex mixture of both primary and secondary species, from both biogenic and anthropogenic sources. Organic aerosol, comprised of modern carbon has been shown to dominate even in urban settings, but sources and formation mechanism of these biogenic aerosol in the ambient atmosphere remain uncertain. The collection and offline analysis of PM₂.₅ aerosol samples allows for highly detailed molecular level compositional information to be obtained, but at the cost of time resolution. Previous studies have collected 23-hour offline filters, which although allowing for seasonal changes to be studied, cannot resolve diurnal variations. However, due to recent advances in high-resolution mass spectrometers, the time resolution of offline filters can now be increased. This study utilises high time resolution offline filters collected in Guangzhou, China across two campaigns during summer and winter. Filters were collected every 2 hours during the day (06:00 – 21:00), with a longer collection overnight (21:00-06:00), alongside a suite of complementary gas phase measurements. Guangzhou represents an interesting case study for biogenic secondary organic aerosol (BSOA) especially biogenic-anthropogenic interactions due to its tropical location and high levels of flora, but also located in one of the most densely populated regions of the world within the Guangdong-Hong Kong-Macau Greater Bay area, with a combined population of 71.2 million people.

This study presents ultra-high-performance liquid chromatography, high-resolution mass spectrometry measurements of BSOA tracers identified in the ambient PM₂.₅ samples at the highest time resolution studied so far. A library of 180 potential BSOA tracers from isoprene, monoterpenes and sesquiterpenes was developed containing acid species (CHO), organosulfates (CHOS) and nitrooxy organosulfates (CHOSN). The BSOA tracers were quantified using a mixture of authentic standards, proxy standards and modelled RIE factors for accurate quantification. Matrix suppression factors were also determined for both CHO and CHOS/CHOSN species, splitting the compounds into groups based on their retention time (RT), with species eluting before 2 min showing the largest matrix suppression.

Strong diurnal variations were observed for some species while others showed little or no diurnal variation suggesting nonlocal sources, and as such provides insight into how long-range sources
can affect BSOA concentrations. Tracers were also correlated to anthropogenic pollutants such as NO\textsubscript{X} and SO\textsubscript{2} as well as sulfate and nitrate measured via ion chromatography, improving our understanding of biogenic-anthropogenic interactions. Comparisons between summer and winter allowed insight into seasonal processes and concentrations, with the potential for different long-range sources. Finally, this study presents comparisons to a growing field of offline BSOA measurements, providing a more comprehensive picture of the contributions BSOA makes to PM\textsubscript{2.5} concentrations.