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Interfacial Ozone Oxidation Chemistry at the Riverine Surface Microlayer as a source of light-absorbing and toxic compounds in the ambient air

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Water surface microlayer (SML) is ubiquitous in the environment and provides a unique medium for interfacial processing. To investigate the formation of organic compounds including the N-containing organics released in the gas phase, under more realistic conditions, in this study, we used authentic surface microlayers collected at three different places located at upper, middle and lower reaches of East Pearl River within urban area of Guangzhou, China. We present real-time measurements of volatile organic compounds (VOCs) produced by interfacial oxidation chemistry of gaseous O_3 (100 ppb) with an authentic SML by using a novel secondary electrospray ionization ultra-high-resolution quadrupole Orbitrap mass spectrometer (SESI-UHR-MS).

We show that ozone oxidation chemistry at the surface microlayer of the river can lead to a large suite of unsaturated and saturated CHO organic compounds in the ambient air of the urban environment. In addition, a large fraction of N-containing organic compounds is produced during this chemistry which can have an impact on human health and the environment. In particular the compounds containing C=N bond are known by their toxicity.

We also used Fourier transform ion cyclotron resonance mass spectrometry (FTI-CR MS) for molecular characterization of the organic compounds produced by interfacial oxidation chemistry of gaseous O_3 with an authentic SML.

We show that ozone oxidation chemistry at the SML of the river can lead to a large suite of unsaturated and saturated CHO organic compounds including nitrogen (N) containing organic compounds and sulfur(S)-containing organics. The results indicate that the ozone oxidation chemistry at the SML collected near the Estuarine zone of South China Sea leads to the formation of N-containing compounds ten times more than the N-containing compounds formed by this chemistry on the SML sampled at the upper part of the river at the periphery of the city.

We also show that an important number of aromatic compounds with light-absorbing- and toxic- properties are formed which could be discharged into the ocean or atmosphere *via* gas-water interchange, imposing a great concern on the urban area, in term of human health impact and environmental issues.