**Characterization of CHOS Compounds In Rainwater from Continental and Coastal Storms by Ultrahigh Resolution Mass Spectrometry**

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**Introduction**

Elucidating the composition of rainwater dissolved organic matter (DOM) has remained at the forefront of atmospheric research principally because of its central role in a host of fundamentally important atmospheric processes. Rainwater DOM is a complex heterogeneous mixture of organic compounds, the composition of which remains to a large extent unknown. This is particularly true when describing organic entities that contain one or more sulfur atoms. Organo-sulfur containing compounds play a pivotal role in the formation of secondary organic aerosols (SOA) leading to high molecular weight oligomers. These compounds are of particular interest in the chemistry of the troposphere because they can enhance hydroscopicity of droplets acting as cloud condensation nuclei.

The present study represents the first detailed analysis of organo-sulfur containing compounds in rainwater by FT-ICR MS collected on an event basis from a series of continental and coastal storms at one geographical location. The data generated therefore provide the most comprehensive examination to date of the chemical formulas of the organo-sulfur containing components of rainwater DOM from various air-mass back trajectories.

**Results and Discussion**

There were 899 and 695 total molecular formula assignments in the continental and coastal storms respectively. Of these, 33% and 15% were unique to continental and coastal storms. The average unique molar ratios of O:C and H:C of all CHOS assignments for continental derived storms were 0.4 ± 0.4 and 1.2 ± 0.4 respectively. Similarly the coastal derived storm average O:C and H:C unique molar ratios were 0.5 ± 0.2 and 1.5 ± 0.4 respectively. The average unique molecular weight of continental and coastal storms were 345 ± 89 and 427 ± 67 respectively. Kendrick mass analysis of methylene units highlighted oligomers present in both storm types illustrating their ubiquitous occurrence in atmospheric waters. There was also evidence of organo-sulfate containing molecular formulas as well as highly condensed aromatic structures containing one sulfur and one oxygen. These condensed aromatic sulfur containing structures likely originate from fossil fuel sources and were only detected in continental derived rainwater.

**Conclusions**

This study represents the first comprehensive examination of CHOS containing molecular formulas from different air mass back trajectories. Continental rain contained a number of organo-sulfate CHOS compounds based upon the observed O:S ratio. Of particular interest was the occurrence of highly condensed aromatic structures containing only one S and one O in continental derived rainwater. To the best of our knowledge, this is the first study to definitively demonstrate the occurrence of these compounds. These molecules may arise from anthropogenic or natural sources but their highly condensed nature suggests that they are derived from combustion processes.[1]

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**Reference**

[1] Mead, R.N., et al., Atmos. Environ., **105**, 162-168 (2015).