



## **Ultrahigh resolution mass spectrometry and hyphenation mass spectrometry for molecular level identification of fulvic acids and their sulfated and nitrated analogues in PM<sub>2.5</sub> atmospheric aerosol**

T. Reemtsma(1), A. These(1), M. Linscheid(2) and P.K. Hopke(3)

1Department of Water Quality Control, Technical University of Berlin, Sekr KF 4, Str des 17 Juni 135, 10623 Berlin, Germany

2 Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin, Germany

3 Center for Air Resources Engineering and Science, Clarkson University, Box 5708, Potsdam, NY 13699-5708, USA

We have used Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) to investigate the water soluble organic matter fraction of PM<sub>2.5</sub> aerosol samples collected in Riverside, CA, USA. Molecular formulas for about 1000 signals in the mass range 200 – 420 could be calculated and belonged to four series of molecules.

1. Molecular formulas consisted solely of C, H and O that were identical to molecular series found in aquatic fulvic acids.
2. Series of nitrogen-containing analogues showed the same intensity pattern as the fulvic acids. Further investigation by hyphenation mass spectrometry provided clear evidence that these were series of nitrated molecules.
3. Sulfur-containing molecules. Here, product ion spectra confirmed the presence of sulfate groups in these molecules.
4. Furthermore a series of molecules containing nitrogen and sulfur was detected.

In these molecules nitrate and sulfate groups were present.

It was the first time that molecular groups (II) to (IV) were unambiguously identified. The identification of fulvic acids together with three series of nitrated, sulfated, and mixed nitrated and sulfated molecules in the atmospheric aerosol raises the question as to their origin. Such nitrated and sulfated analogues of fulvic acids have never been reported to occur in soils or surface waters. Owing to this and from the particle size of the aerosol ( $< 2.5 \mu\text{m}$ ) investigated here we conclude that these molecules were formed as secondary organic aerosol (SOA). Either sulfate and nitrate groups were coupled to the fulvic acids after their formation or whether they were included already during an acid catalyzed fulvic acid formation process. FTICR-MS proved to be an adequate technique to resolve such complex mixtures of water soluble organic aerosol at the molecular level and to study its fate.