Fulvic Acids and their sulfated and nitrated analogues in atmospheric aerosol – Determination by Ultrahigh Resolution Electrospray Mass Spectrometry

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Keywords: LC-MS, ultrahigh resolution mass spectrometry, organic matter, PM2.5, SOA.

The occurrence of humic acid like substances (HULIS) in the atmospheric aerosol is well documented. As long as individual humic acid molecules were not analytically amenable it was impossible to clarify whether the HULIS fraction was only similar to humic acids or whether compounds were identical to those found in terrestrial or aquatic humic or fulvic acid isolates.

Fourier Transform Ion Cyclotron Resonance mass spectrometry (FTICR-MS) with its ultrahigh mass resolution \((m/\Delta m > 100,000)\) can fully resolve the molecules in natural organic matter isolates such as humic and fulvic acids in a mass range up to approx. 500 Da.

We have used FTICR-MS to investigate the water soluble organic matter fraction of PM\(_{2.5}\) aerosol samples collected in Riverside, CA, USA (Reemtsma et al., 2006). Mass spectra in the mass range \(m/z\) 200 to \(m/z\) 600 were dominated by a few strong signals. This work focused on the vast majority of „background“ signals occupying each nominal mass. Molecular formulas for about 1000 signals in the mass range 200 – 420 were calculated (Fig.1) and could be ascribed to four classes of organic matter.

(I) About 460 molecular formulas consisted solely of C, H and O and were identical to molecular series found in aquatic fulvic acids. Product ion spectra confirmed that these molecules are dominated by carboxylate groups with other functional groups being almost absent. This is the first identification of fulvic acids outside of the soil/water environment.

(II) The 210 sulfur-containing molecules showed the same intensity pattern as the fulvic acids. Product ion spectra confirmed the presence of sulfate groups. We, therefore, propose that these are sulfated fulvic acid analogues. However, the presence of sulfonate groups cannot be ruled out.

(III and IV) Furthermore a series of nitrogen-containing analogues were found and, finally a series where S and N were present in the same molecules. For the nitrogenous molecules the presence of nitrate groups was proven by their product ion spectra.

The identification of fulvic acids together with three series of sulfated, nitrated and mixed sulfated and nitrated molecules in the atmospheric aerosol raises the question as to their origin. From the particle size of the aerosol (< 2.5 µm) investigated here and owing to the fact that sulfated and nitrated analogues of fulvic acids have never been reported to occur in soils we conclude that this was secondary organic aerosol (SOA).

We do not yet know whether oxidative transformation of primary biological material or free radical oligomerization of the oxidation products of primary volatile organic compounds led to the formation of fulvic acids. Further investigations will also have to elucidate whether sulfate and nitrate were introduced after SOA was formed or whether they were incorporated as part of the (acid catalyzed) SOA formation.

FTICR-MS will be an inevitable tool to study processes of SOA formation and their products.