

1 Water-Soluble Atmospheric Organic Matter in Fog
2 Water: Exact Masses and Chemical Formula
3 Identification by Ultrahigh-Resolution Fourier
4 Transform Ion Cyclotron Resonance Mass Spectrometry

5 *Lynn R. Mazzoleni^{1*}, Brandie M. Ehrmann², Xinhua Shen³, Alan G. Marshall^{2,4},*

6 *and Jeffrey L. Collett, Jr.³*

7 ¹Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI
8 49931 USA

9 ²Department of Chemistry & Biochemistry, Florida State University, 95 Chieftain Way, Tallahassee, FL
10 32306 USA

11 ³Department of Atmospheric Science, Colorado State University, 200 Lake Street, Fort Collins, CO,
12 80523 USA

13 ⁴Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University,
14 1800 East Paul Dirac Drive, Tallahassee, FL 32310-4005 USA.

15 Email address: lrmazzol@mtu.edu

16 *Corresponding author: Dr. Lynn Mazzoleni, Phone 906-487-1853, Fax 906-487-2061, and Email
17 address lrmazzol@mtu.edu.

19 **Experimental: Data Filtering Strategies (Adapted from Koch *et al.*, 2005)**

20 The sum of rings and double bonds in each molecule (aka double bond equivalents, DBE) must result
21 with a positive integer value for uncharged molecules. DBE was calculated from Equation (1):

22
$$\text{DBE} = c - h/2 + n/2 + 1$$
 (1)

23 for elemental composition $\text{C}_c\text{H}_h\text{N}_n\text{O}_o\text{S}_s$ (McLafferty, 1993). Note that sulfur is divalent in Eq. (1).

24 Therefore, any additional double bonds from tetravalent and hexavalent S are not included.

25 The maximum permitted number of hydrogen atoms (h) was further limited by Equation (2) (i.e., a fully
26 saturated aliphatic hydrocarbon):

27
$$h < 2c + 2$$
 (2)

28 The “rule of 13” was used as a data quality check to determine the maximum number of non-hydrogen
29 atoms. It was calculated by dividing the nominal mass of the unknown molecule by 13, representing
30 CH. This number is compared to the number of assigned non-hydrogen atoms (C, O, N and S) by
31 equation (3):

32
$$\text{Maximum number of heavy atoms} < (\text{nominal mass})/13$$
 (3)

33 Finally, the O:C ratio was limited to values ≤ 2.0 and H:C ratios were limited to values ≥ 0.3 .

34

35 **Table S-1:** A complete list of the assigned molecular formulas is provided via a Microsoft Excel 2003
36 workbook named “Mazzoleni_etal_2010_SI.xls”. A description of the provided data is as follows:
37 column “A” lists the negative ion mass-to-charge ratio (m/z) measured and internally recalibrated;
38 column “B” lists the neutral mass after addition of the mass of one proton to each negative ion of
39 column “A;” column “C” lists the relative abundance for each m/z; column “D” listed the common ions
40 between the field blank and the fog sample, “E” lists the group assignments (based on the elemental
41 composition); column “F” lists the subgroup assignments; column “G” lists the calculated double bond
42 equivalents (DBE) of the neutral molecule as described in the Experimental Methods; column “H” lists
43 the number of carbon atoms in the assigned formula; column “I” lists the number of hydrogen atoms in
44 the assigned formula; column “J” lists the number of nitrogen atoms in the assigned formula; column

45 “K” lists the number of oxygen atoms in the assigned formula; column “L” lists the number of sulfur
46 atoms in the assigned formula; column “M” lists the number of carbon-13 atoms in the assigned
47 formula; column “N” lists the number of sulfur-34 atoms in the assigned formula; column “O” lists the
48 oligomer series number (assigned for sorting purposes); column “P” lists the first mass in the oligomer
49 series (when applicable); and column “Q” lists the number of C₃H₄O₂ units added. Please refer to the
50 “Experimental Methods” section for further details regarding the formula assignments and data quality
51 control. Please see the Results and Discussion for further information regarding the selection of the
52 oligomer series and assignments. Note the assigned formulas are reported for the neutral molecule, after
53 addition of one proton.

54 **Table S-2:** A complete list of the assigned molecular formulas is provided via a Microsoft Excel 2003
55 workbook named “Mazzoleni_etal_2010_SI.xls”. A description of the provided data is as follows:
56 column “A” lists the negative ion mass-to-charge ratio (m/z) measured and internally recalibrated;
57 column “B” lists the neutral mass after addition of the mass of one proton to each negative ion of
58 column “A;” column “C” lists the relative abundance for each m/z; column “D” lists the group
59 assignments (based on the elemental composition); column “E” lists the subgroup assignments; column
60 “F” lists the calculated double bond equivalents (DBE) of the neutral molecule as described in the
61 Experimental Methods; column “G” lists the number of carbon atoms in the assigned formula; column
62 “H” lists the number of hydrogen atoms in the assigned formula; column “I” lists the number of
63 nitrogen atoms in the assigned formula; column “J” lists the number of oxygen atoms in the assigned
64 formula; column “K” lists the number of sulfur atoms in the assigned formula; column “L” lists the
65 number of carbon-13 atoms in the assigned formula; and column “M” lists the number of sulfur-34
66 atoms in the assigned formula. Please refer to the “Experimental Methods” section for further details
67 regarding the formula assignments and data quality control. Please see the Results and Discussion for
68 further information regarding the selection of the oligomer series and assignments. Note the assigned
69 formulas are reported for the neutral molecule, after addition of one proton.

Table S-3: Contains a list of the total and dissolved organic carbon values for the fog water sample collected on January 06, 2006, the fog collector blank and the field blank. A description of the provided data is as follows: column “A” lists the sample description; column “B” lists the total organic carbon concentration in parts per million; column “C” lists the dissolved organic carbon concentration in parts per million. Please refer to the experimental methods sections for method details.

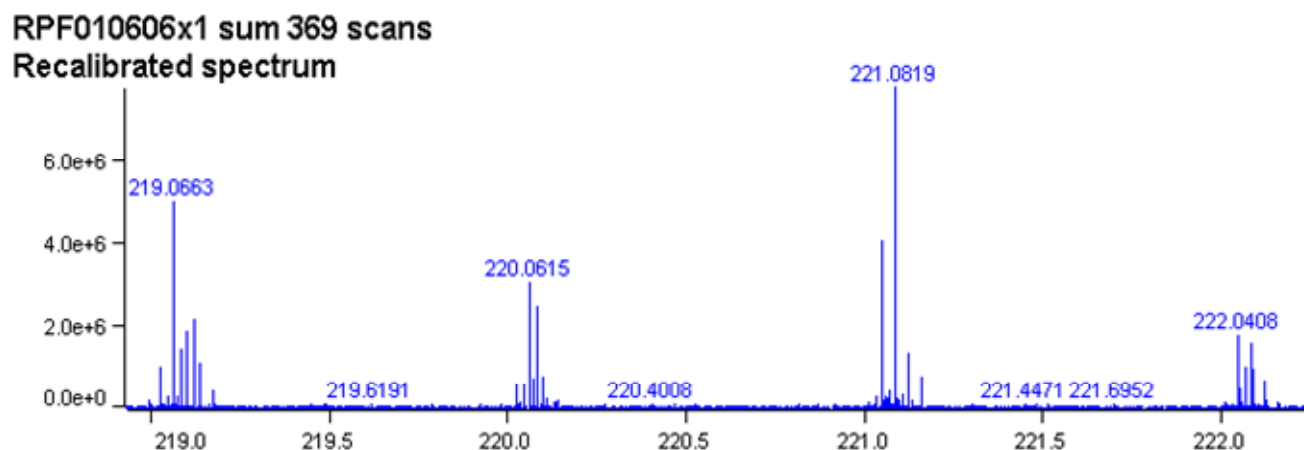
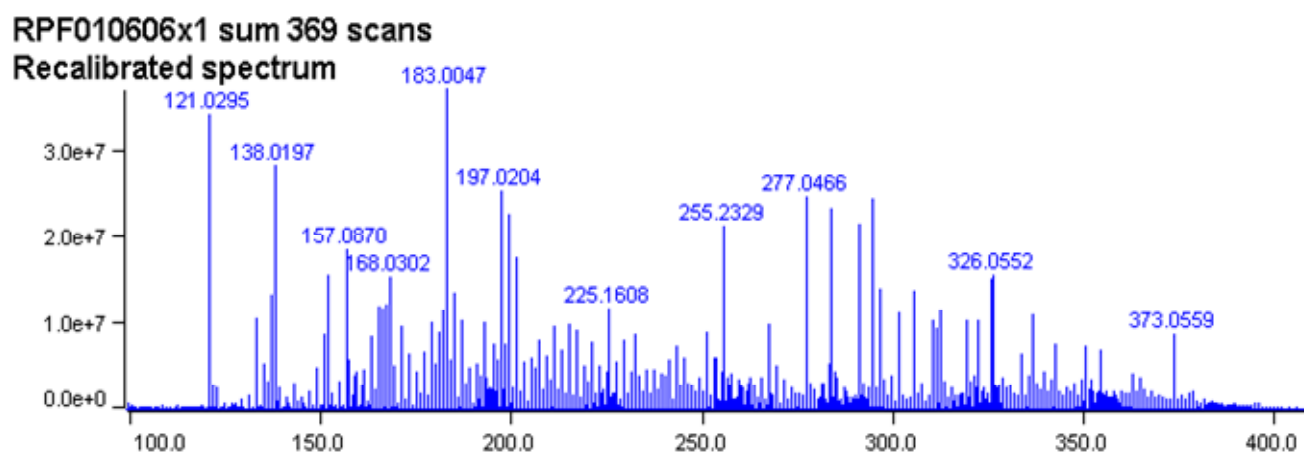
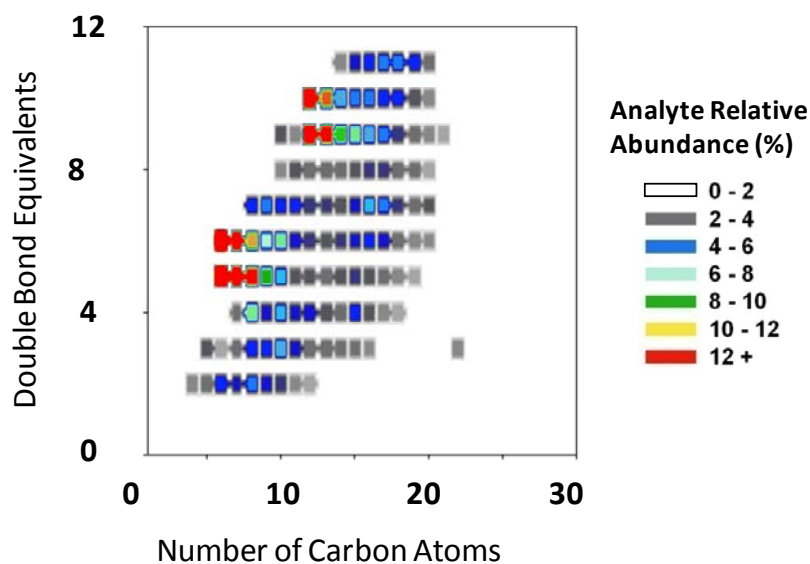


Figure S-1: Negative-ion ultrahigh-resolution FT-ICR mass spectra of atmospheric organic matter extracted from radiation fog water collected in Fresno, CA. Top: mass spectra after internal recalibration of measured masses for the mass range 100-400 Da; Bottom: mass scaled-expanded segment, showing the large number of individual compounds within each nominal mass.

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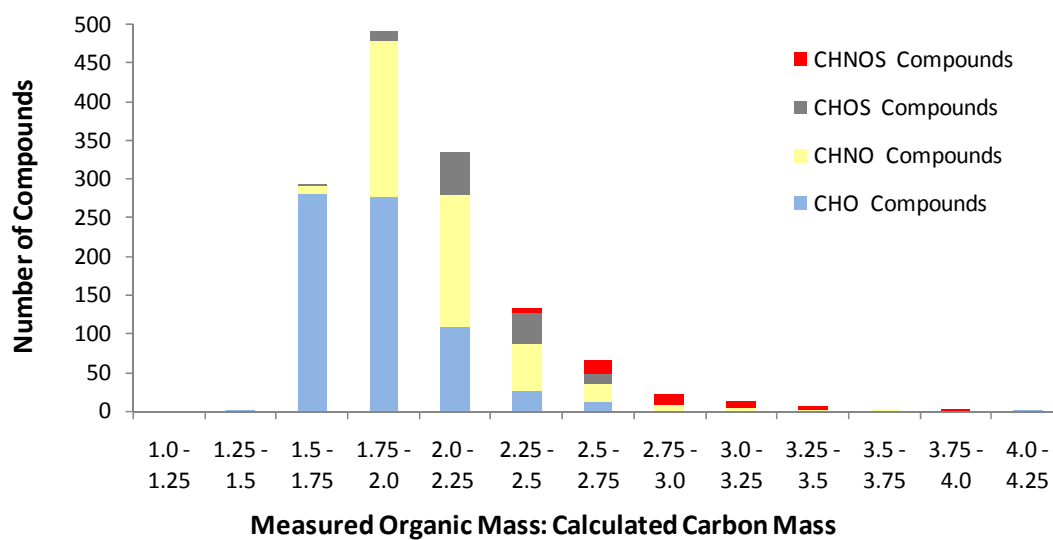


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84 **Figure S-2:** Isoabundance contoured plot of double bond equivalents versus carbon number for the 487
 85 compounds containing only C, H, N, and O atoms.

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87



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89

90 **Figure S-3:** Compound distribution sorted according to the ratio of the measured organic compound
 91 mass to the carbon mass; determined from all 1,368 assigned elemental compositions, $C_cH_hO_oN_nS_s$.

92

93 **Literature Cited**

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