

Supplemental Information

Atmospheric organic matter in clouds: exact masses and molecular formula identification using ultrahigh-resolution FT-ICR mass spectrometry

Y. Zhao¹, A. G. Hallar² and L. R. Mazzoleni^{1,3*}

[1] Department of Chemistry, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931 USA

[2] Division of Atmospheric Science, Desert Research Institute, Storm Peak Laboratory, Steamboat Springs, CO 80488, USA

[3] Atmospheric Science Program, Michigan Technological University, 1400 Townsend Drive, Houghton, MI 49931 USA

*Correspondence to: L. R. Mazzoleni, Email address: lrmazzol@mtu.edu; Phone: +1-906-487-1853; and Fax: +1-906-487-2061.

Relative abundance weighted AOM properties

The average composition properties of atmospheric organic matter (AOM) isolated from supercooled clouds including oxygen-to-carbon ratio (O/C), hydrogen-to-carbon ratio (H/C), double bond equivalents (DBE) and organic mass to organic carbon ratio (OM/OC) are discussed in the main paper. Further evaluation of the overall properties for comparison with other studies is done with relative abundance weighting. The relative abundance weighted elemental ratios (O/C_w , H/C_w), double bond equivalents values (DBE_w) and organic mass to organic carbon ratios (OM/OC_w) are determined by the following equations (Sleighter and Hatcher, 2008; Bateman et al., 2009):

$$O/C_w = \frac{\sum(w_i o_i)}{\sum(w_i c_i)} \quad (S1)$$

$$H/C_w = \frac{\sum(w_i h_i)}{\sum(w_i c_i)} \quad (S2)$$

$$DBE_w = \frac{\sum(w_i DBE_i)}{\sum w_i} \quad (S3)$$

$$OM/OC_w = \frac{\sum(w_i OM/OC_i)}{\sum w_i} \quad (S4)$$

for elemental compositions of $C_c H_h N_n O_o S_s$, where w_i is the relative abundance for each individual molecular formula, i .

Supplemental Tables and Figures

Table S1: A complete list of the assigned molecular formulas is provided in Table S1, available as a separate Microsoft Excel 2010 workbook (“Zhao_etal_2013_Table S1.xlsx”). A description of the provided data is as follows:

Column ‘A’ provides the molecular formula assigned to either of the two cloud samples (CW1 and CW2);

Column ‘B’ lists the number of carbon atoms in the assigned formula;

Column ‘C’ lists the number of hydrogen atoms in the assigned formula;

Column ‘D’ lists the number of nitrogen atoms in the assigned formula;

Column ‘E’ lists the number of oxygen atoms in the assigned formula;

Column ‘F’ lists the number of sulfur atoms in the assigned formula;

Column 'G' provides the theoretical mass-to-charge ratio (m/z) for the negative ion;

Column 'H' indicates if the molecular formula was used in the internal recalibration procedure. The formulas used as recalibrant are homologous of $C_4H_4O_4(CH_2)_{1-18}$ and $C_9H_{10}O_8(CH_2)_{1-19}$, some of which are not shown in the table since they were blank subtracted;

Column 'I' lists the calculated double bond equivalents values for each molecular formula;

Column 'J' lists the group assignments (based on the elemental composition);

Column 'K' lists the subgroup assignments;

Column 'L' lists the CW1 measured negative ion m/z;

Column 'M' lists the CW1 relative abundance (%) for each identified m/z;

Column 'N' lists the CW1 absolute error (ppm) associated with each formula assignment;

Column 'O' lists the number of ^{13}C peaks detected for each monoisotopic negative ion in CW1;

Column 'P' lists the number of ^{34}S peaks detected for each monoisotopic negative ion in CW1;

Column 'Q' lists the CW2 measured negative ion m/z;

Column 'R' lists the CW2 relative abundance (%) for each identified m/z;

Column 'S' lists the CW2 absolute error (ppm) associated with each formula assignment;

Column 'T' lists the number of ^{13}C peaks detected for each monoisotopic negative ion in CW2;

Column 'U' lists the number of ^{34}S peaks detected for each monoisotopic negative ion in CW2;

Column 'V' indicates if the molecular formula was observed in any of the 19 biogenic SOA samples described in Dalbec et al. (2013): 3 α -pinene ozonolysis SOA, 4 β -pinene ozonolysis SOA, 6 d-limonene ozonolysis SOA, and 6 β -caryophyllene ozonolysis SOA generated under different relative humidity (0, 4% and 30%) with or with OH scavenger under dark conditions.

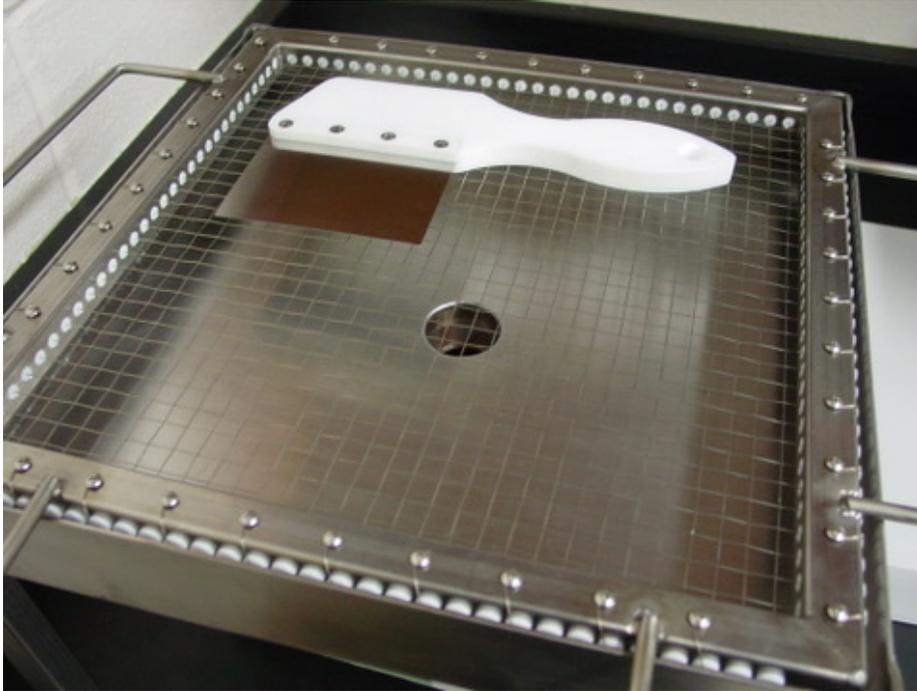


Figure S1: Photo of the custom stainless steel and teflon cloud sieve and rime collection tray.

NOAA HYSPLIT MODEL
 Backward trajectories ending at 0800 UTC 25 Feb 10
 GDAS Meteorological Data

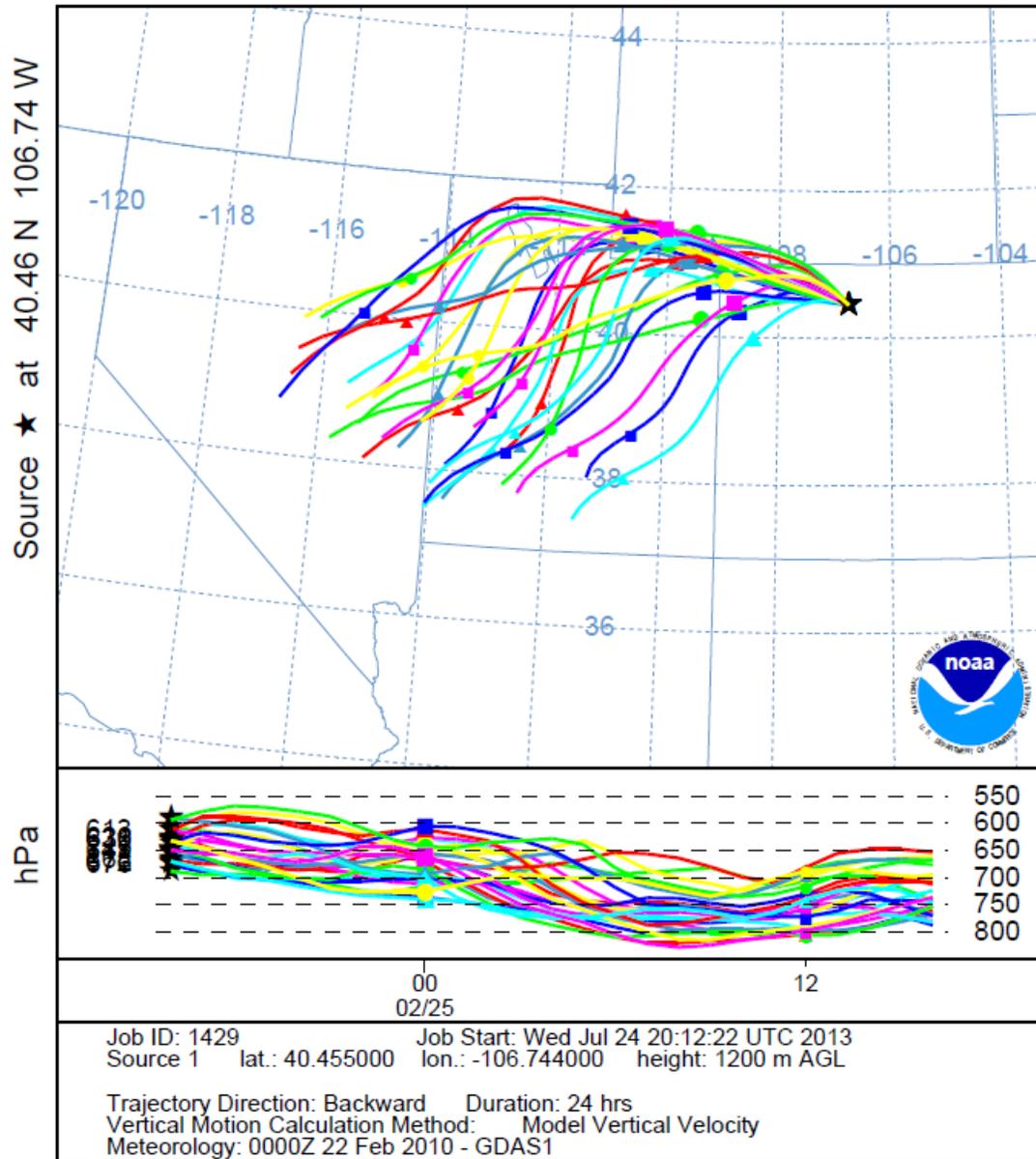


Figure S2: 24-hour air back trajectory analysis for CW1.

NOAA HYSPLIT MODEL
 Backward trajectories ending at 1100 UTC 26 Feb 10
 GDAS Meteorological Data

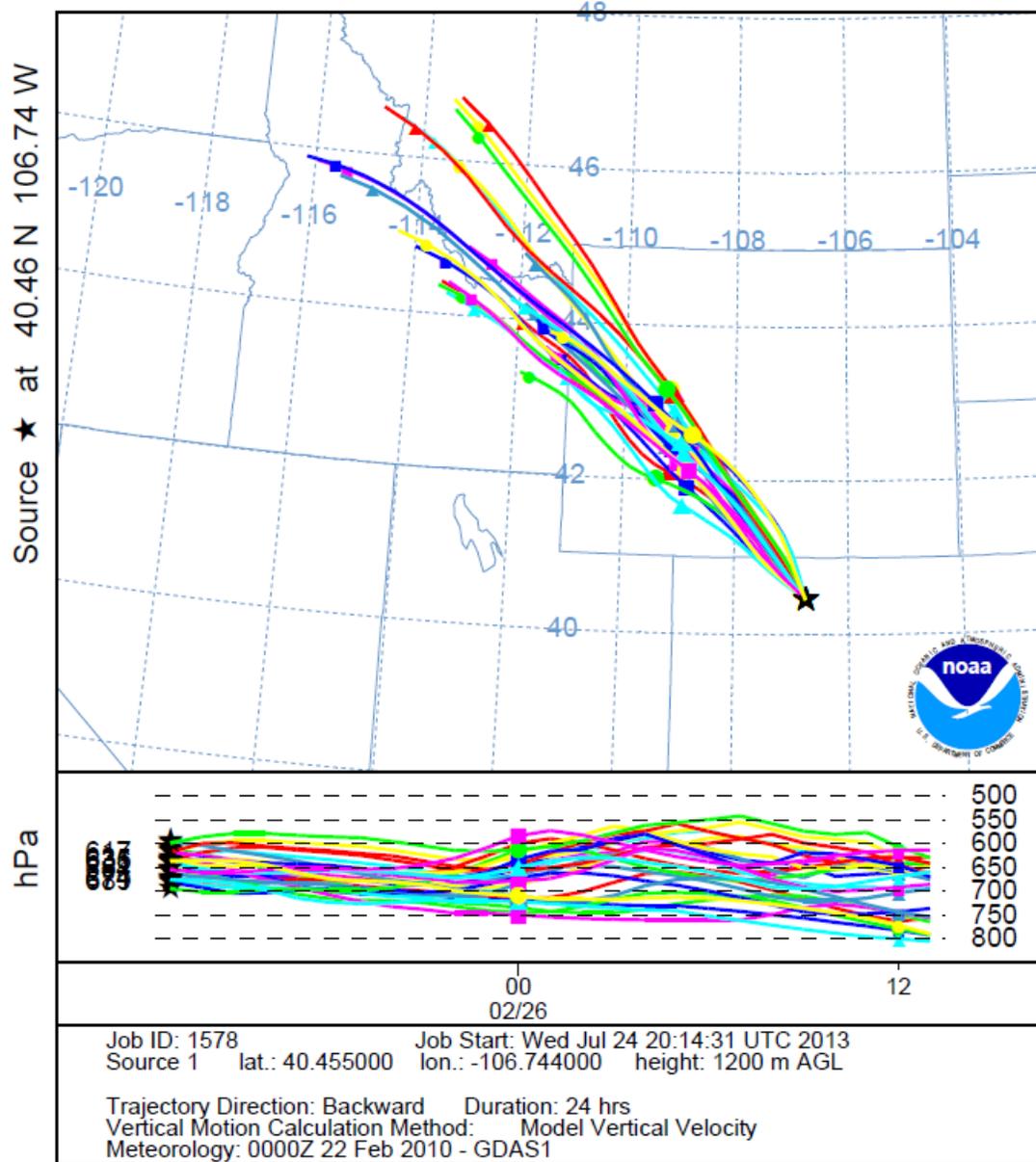


Figure S3: 24-hour air back trajectory analysis for CW2.

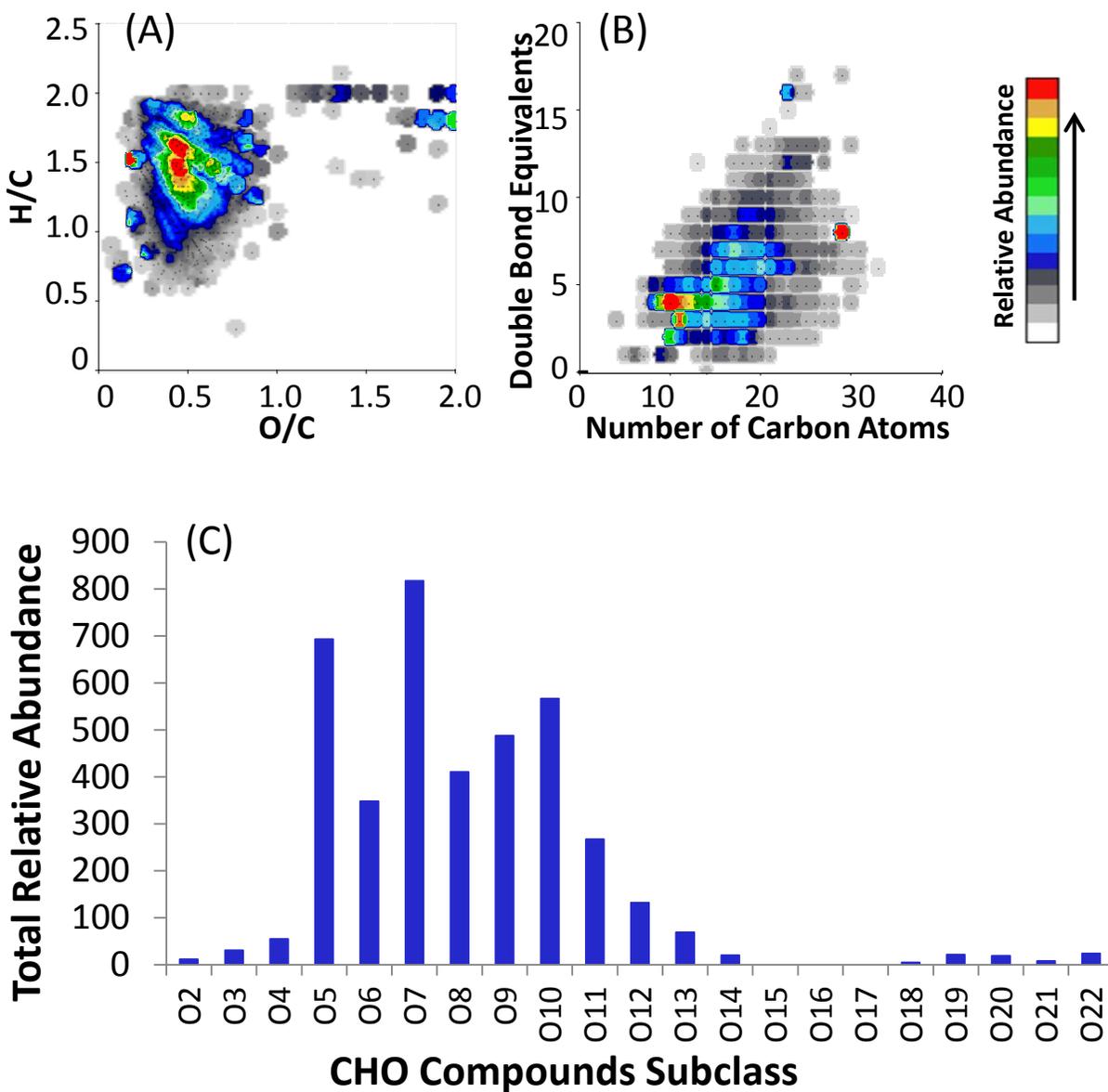


Figure S4: Isoabundance van Krevelen diagram for CW2 CHO compounds (A). Isoabundance plot of double bond equivalents (DBE) vs. number of carbon atoms in molecular formulas for CW2 CHO compounds (B). Total relative abundance (RA) of each subclass for CW2 CHO compounds (C).

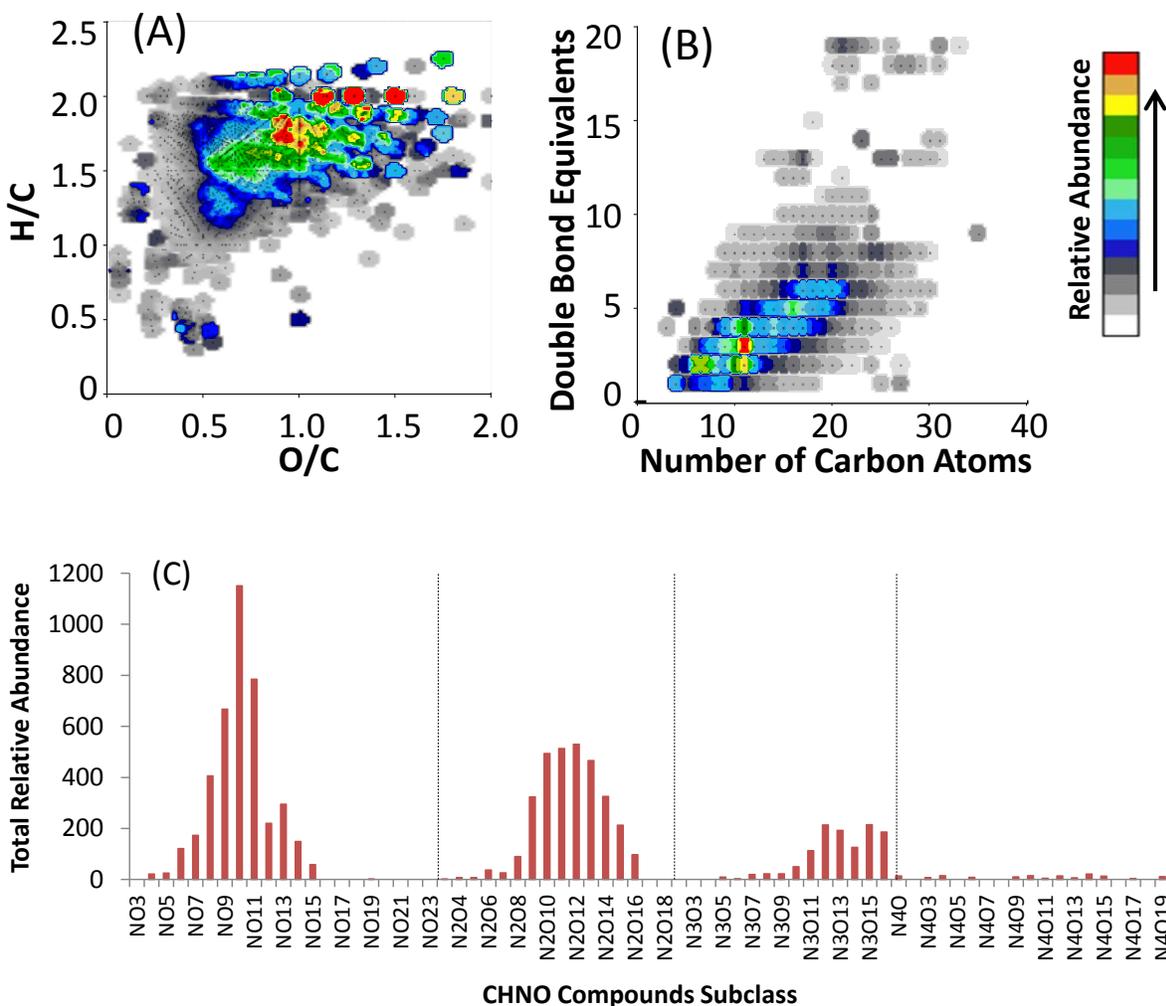


Figure S5: Isoabundance van Krevelen diagram for CW2 CHNO compounds (A). Isoabundance plot of double bond equivalents (DBE) vs. number of carbon atoms in molecular formulas for CW2 CHNO compounds (B). Total relative abundance (RA) of each subclass for CW2 CHNO compounds, the dashed lines separate the subclasses by number of nitrogen atoms contained in the molecular formulas (C).

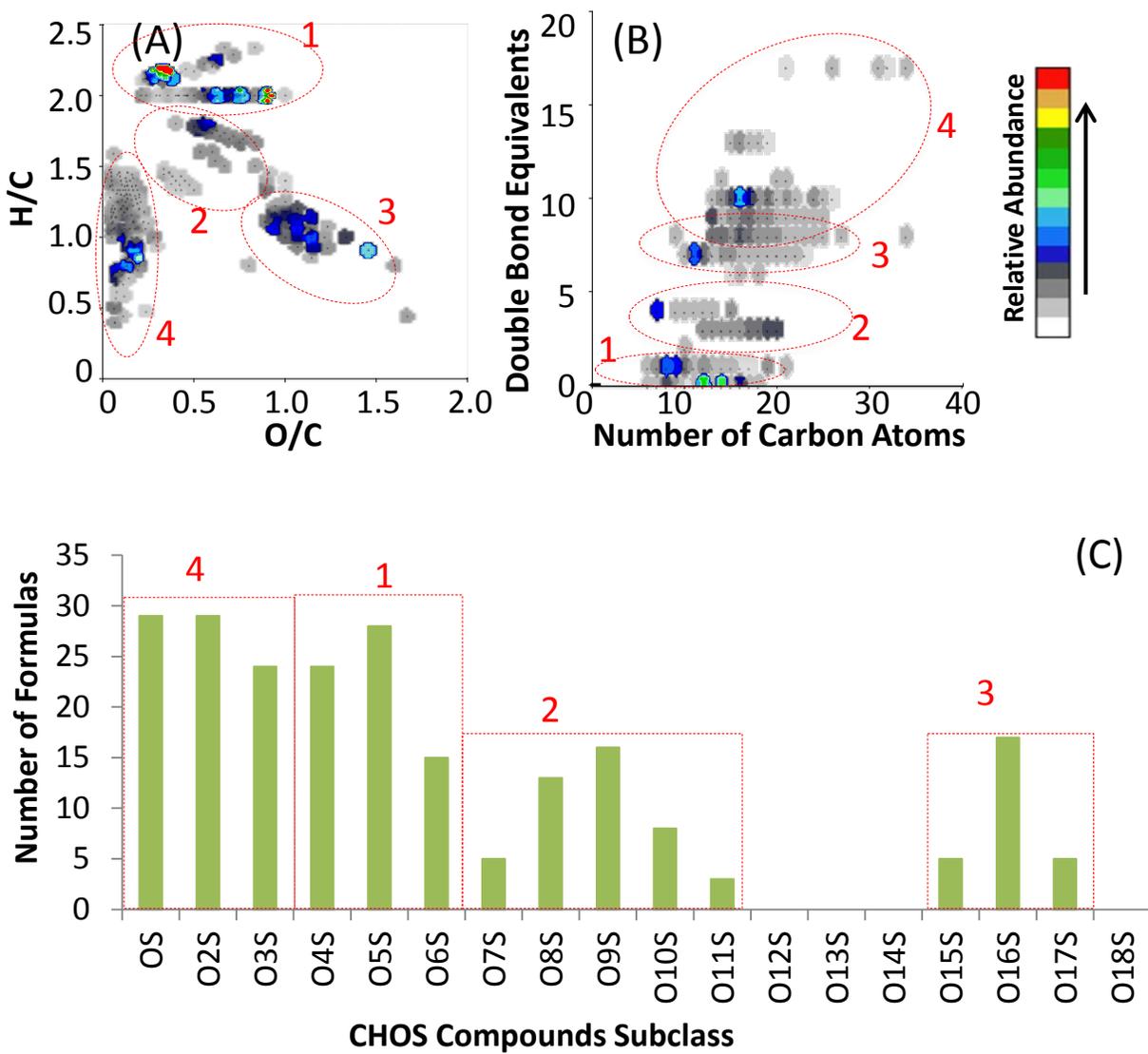


Figure S6: Isoabundance van Krevelen diagram for CW2 CHOS compounds (A). Isoabundance plot of double bond equivalents (DBE) vs. number of carbon atoms in molecular formulas for CW2 CHOS compounds (B). Number of molecular formulas identified in each of CW2 CHOS subclasses (C). The red circles and boxes indicate the approximate groupings (1 to 4) of the CW2 CHOS formulas.

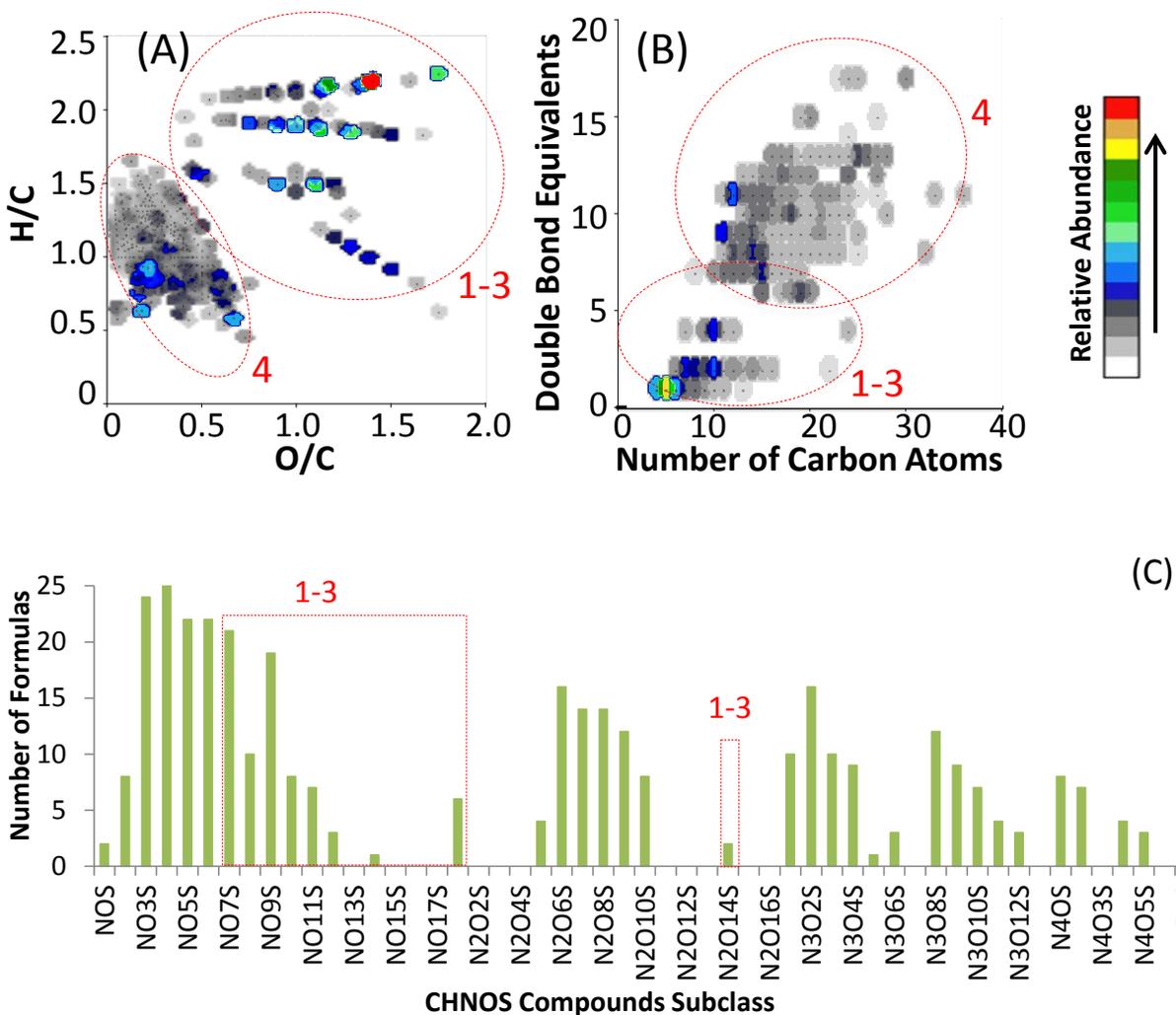


Figure S7: Isoabundance van Krevelen diagram for CW2 CHNOS compounds (A). Isoabundance plot of double bond equivalents (DBE) vs. number of carbon atoms in molecular formulas for CW2 CHNOS compounds (B). Number of molecular formulas identified in each of CW2 CHNOS subclasses (C). The red circles and boxes indicate the approximate groupings (1 to 4) of the CW2 CHNOS formulas. The bars not boxed in (C) belong to group 4.

References:

Bateman, A. P., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Time-resolved molecular characterization of limonene/ozone aerosol using high-resolution electrospray ionization mass spectrometry, *Physical Chemistry Chemical Physics*, 11, 7931-7942, 2009.

Dalbec, M. M., Zhao, Y., Fisseha, R., Putman, A. L., Rahn, T. A., and Mazzoleni, L. R.: Comprehensive biogenic secondary organic aerosol characterization and identification of specific indicator molecular formulas, 2013 In Preparation.

Sleighter, R. L., and Hatcher, P. G.: Molecular characterization of dissolved organic matter (DOM) along a river to ocean transect of the lower Chesapeake Bay by ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, *Marine Chemistry*, 110, 140-152, 2008.