



Supplement of

Evolution of nucleophilic high molecular-weight organic compounds in ambient aerosols: a case study

Chen He et al.

Correspondence to: Yang Chen (chenyang@cigit.ac.cn)

The copyright of individual parts of the supplement might differ from the article licence.

18 **1. Methods**

19 **1.1 FT-ICR MS analysis**

20 The mass spectrometer was initially calibrated using sodium formate and then
21 recalibrated with a known mass series in natural organic matter (Suwannee River fulvic
22 acids), which contains a relatively high abundance of CHO formulae, providing a mass
23 accuracy of 0.2 ppm or higher throughout the mass range of interest.

24 FT-ICR MS was calibrated using a reference list formed by the manually assigned
25 known formula in Data Analysis. Mass peaks with a signal-to-noise (S/N) ratio ≥ 4
26 were exported to a data sheet. Data analysis was performed using in-house software.

27 The assigned formulae were limited in the following elemental composition: $^{12}\text{C}_{0-100}$,
28 $^1\text{H}_{0-200}$, $^{14}\text{N}_{0-10}$, $^{16}\text{O}_{0-20}$, and $^{32}\text{S}_{0-2}$. The formula assignment section set the mass accuracy
29 window was set to 1.0 ppm in formula assignment section. All elemental formulae
30 should meet basic chemical criteria: (1) the number of H atoms should be at least 1/3
31 that of C atoms and cannot be greater than that of $2\text{C} + \text{N} + 2$; (2) the sum number of
32 N and H atoms should be even; and (3) the H/C and O/C value should be restricted to
33 be less than 3 and 1.5, respectively (He et al., 2020; Kujawinski and Behn, 2006).

34 These compound groups were: ; lipids (O/C = 0–0.2, H/C = 1.7–2.2); Aliphatics (O/C
35 = 0.2–0.6, H/C = 1.5–2.2); lignin (O/C = 0.1–0.6, H/C = 0.6–1.7, $\text{AI}_{\text{mod}} < 0.67$);
36 carbohydrates (O/C = 0.6–1.2, H/C = 1.5–2.2); tannins (O/C = 0.6–1.2, H/C = 0.5–1.5,
37 $\text{AI}_{\text{mod}} < 0.67$); unsaturated hydrocarbons (O/C = 0–0.1, H/C = 0.7–1.5); saturated
38 compounds (H/C > 2.0); polycyclic aromatics (PCAs, $\text{AI}_{\text{mod}} \geq 0.67$); polyphenols (0.67

39 $\geq AI_{\text{mod}} \geq 0.50$); and highly unsaturated compounds ($AI_{\text{mod}} < 0.50$, $H/C < 1.5$) (Seidel
40 et al., 2014; Antony et al., 2014).

41 The double bond equivalent (DBE) and modified aromaticity index (AI_{mod}) value are
42 calculated as Eqs. S1 and S2 (Koch and Dittmar, 2016; Koch and Dittmar, 2006):

$$43 \quad \text{DBE} = C - 0.5H + 0.5N + 1 \quad (\text{S1})$$

$$44 \quad AI_{\text{mod}} = (1 + C - 0.5O - S - 0.5H)/(C - 0.5O - S - N - P) \quad (\text{S2})$$

45 A Kendrick mass defect (KMD) analysis is used to provide an overview of the
46 composition of the identified formulae in NFC samples. The KMD calculations are
47 shown in Eqs. (S3 and S4) (Sleighter and Hatcher, 2007):

$$48 \quad \text{Kendrick mass (F)} = (\text{observed mass}) \times \frac{\text{nominal mass(F)}}{\text{exact mass(F)}} \quad (\text{Eq. S3})$$

$$49 \quad \text{KMD} = \text{nominal mass} - \text{Kendrick mass (F)} \quad (\text{Eq. S4})$$

50 where F stands for the functional groups or repeated groups, including COO, OO,
51 CH₂O, and H₂O.

52

53 The value of X_c is used to characterize aromatic and polyaromatic compounds in highly
54 complex compound mixtures. X_c normally ranges from 0 to 3.0 and is calculated as Eqs.
55 (S5) (Yassine et al., 2014):

$$56 \quad X_c = \frac{3(\text{DBE} - mN_O - nN_S) - 2}{\text{DBE} - mN_O - nN_S} \quad (\text{Eq. S5})$$

57 If $\text{DBE} \leq mN_O + nN_S$, then $X_c = 0$. For (-)ESI and (+)ESI mode, we used $m=n=0.5$ and
58 $m=n=1.0$ for the X_c in this study.

59

60 The EC-tracer method has been widely used to estimate SOC (Turpin and Lim, 2001),
61 which can be defined as

$$62 \quad \text{POC} = (\text{OC/EC})_{\text{prim}} \times \text{EC} \quad (\text{Eq. S6})$$

63

$$\text{SOC} = \text{OC} - \text{POC} \quad (\text{Eq. S7})$$

64

where POC, SOC, and OC stands for the estimated primary OC, secondary OC, and

65

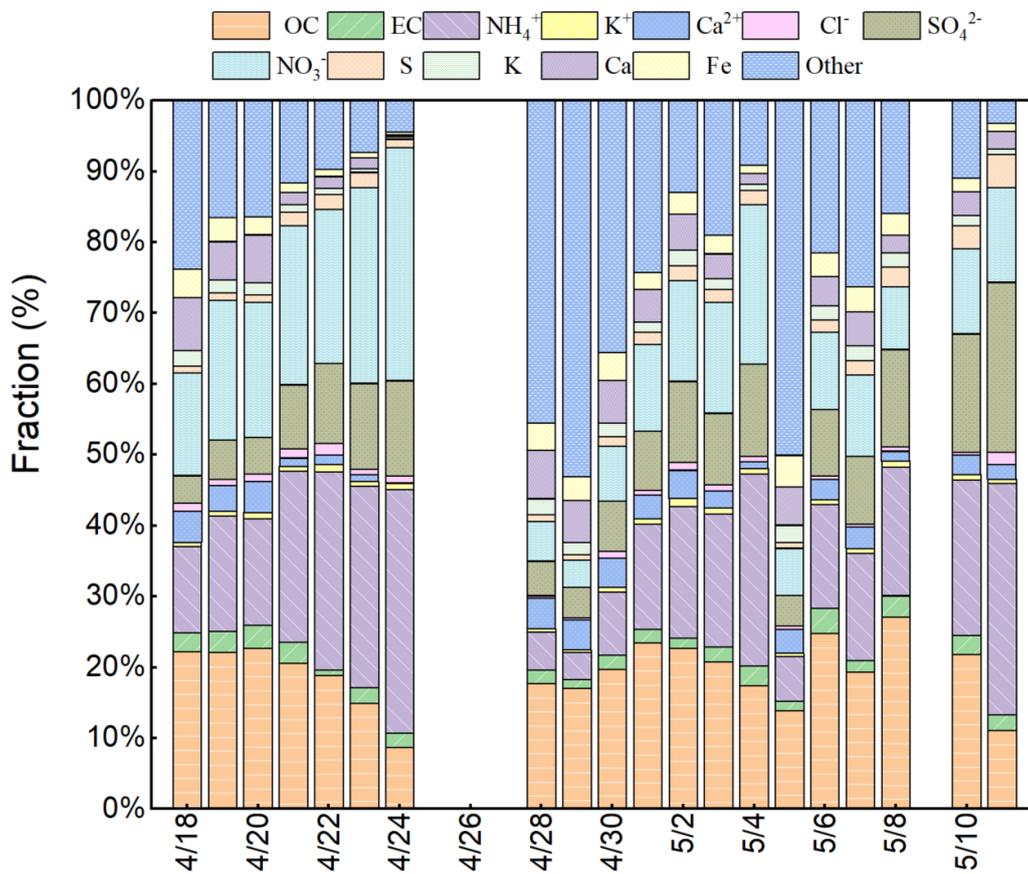
measured total OC, respectively.

66

67

68 Figures

69



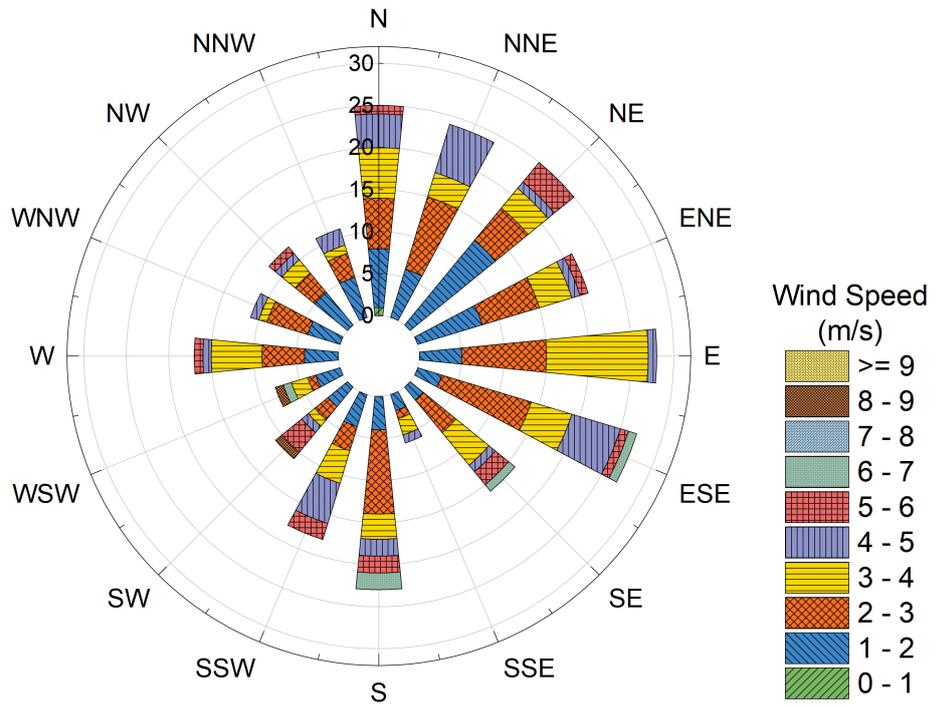
70

71 Figure S1. Fraction of OC, EC, water-soluble ions, and crustal elements during the

72

sampling period.

73

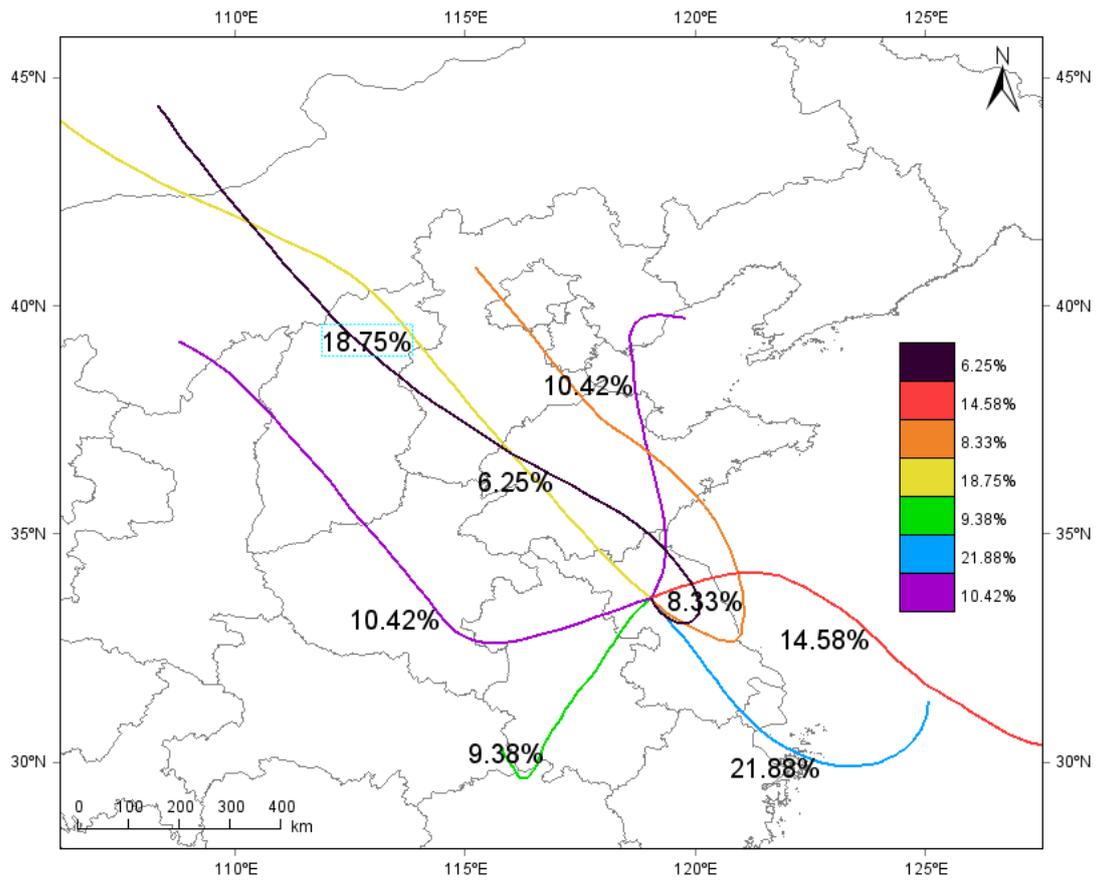


74

75

76 Figure S2. Windrose plot during the sampling period.

77

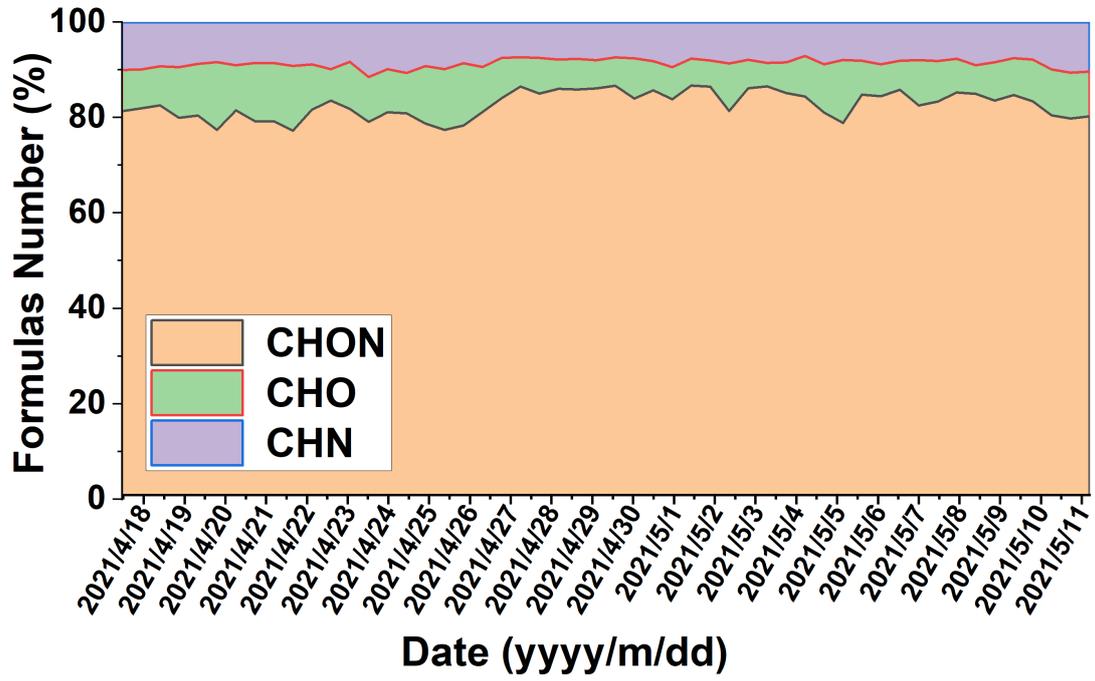


78

79 Figure S3. Backward trajectory of air mass passing through the sampling site during
 80 the sampling period.

81

82

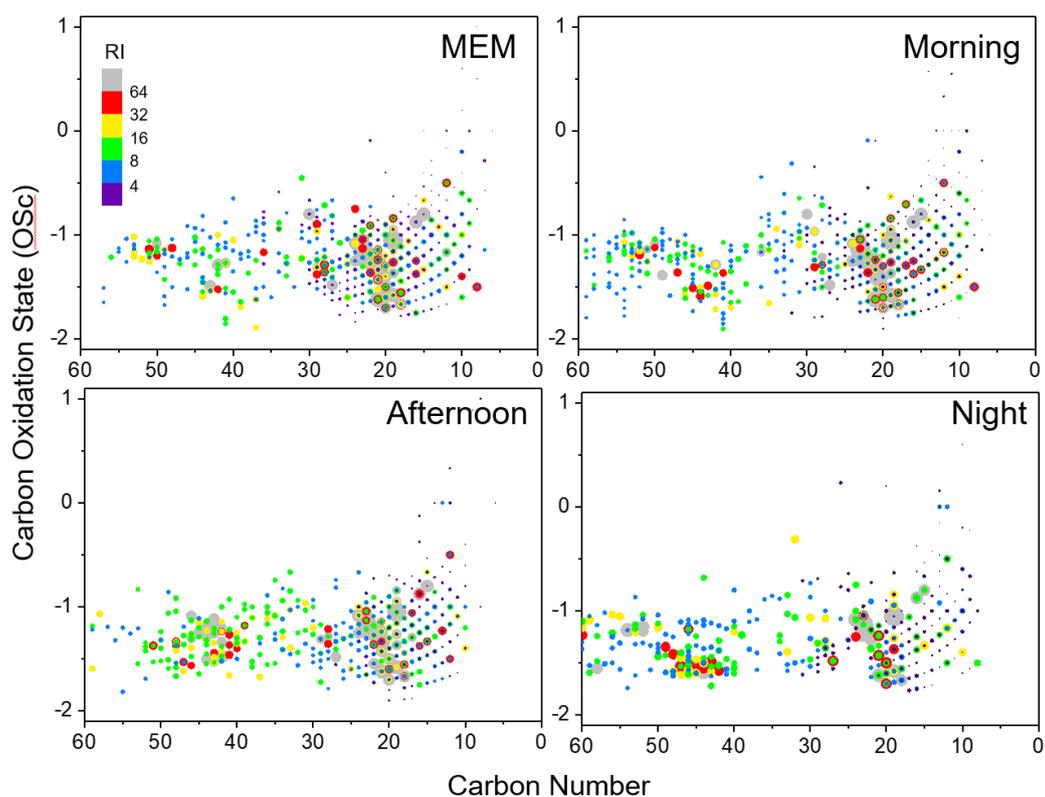


83

84 Figure S4. Ratios of formula numbers among the sampling period.

85

86



88

89

90 Figure S5. Overlaid carbon oxidation state (OSc) symbols for CHO species. The size
91 and color bar of the markers reflect the relative peak intensities of molecular formulae
92 on a logarithmic scale. RI: relative intensity.

93

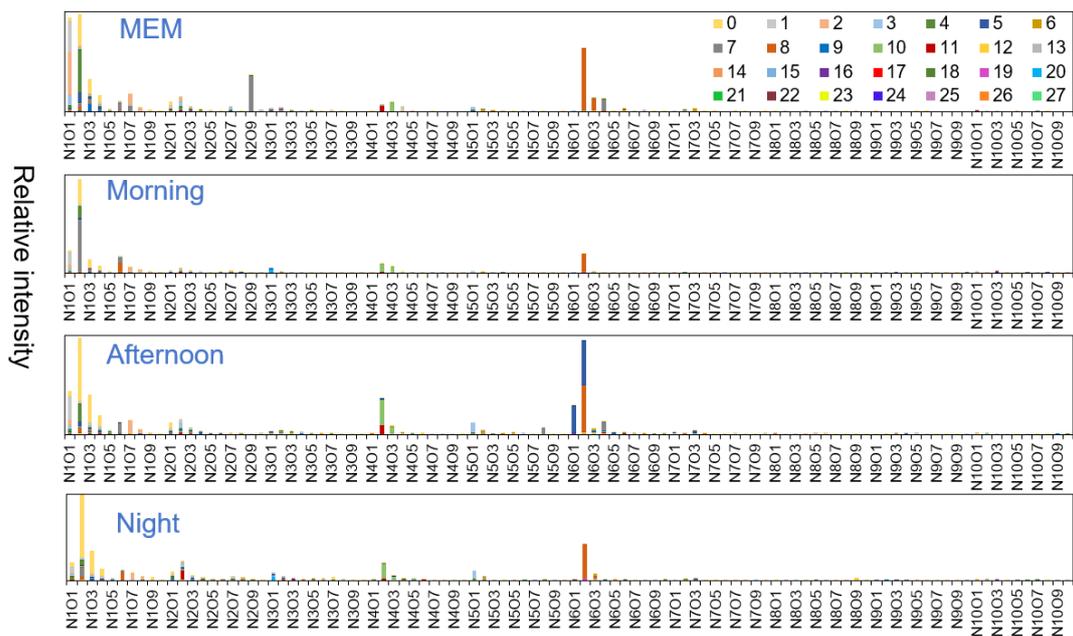
94

95

96

97

98



99

100 Figure S6. Relative abundance of CHON species in aerosol samples obtained by +ESI
 101 FT-ICR MS as well as the double bond equivalent (DBE) distribution. The color bar
 102 denotes the DBE value. The height of the symbols reflects the relative peak intensity of
 103 molecular formulae.

104

105

106 References

- 107 Antony, R., Grannas, A. M., Willoughby, A. S., Sleighter, R. L., Thamban, M., and
108 Hatcher, P. G.: Origin and sources of dissolved organic matter in snow on the East
109 Antarctic ice sheet, *Environ. Sci. Technol.*, 48, 6151-6159, 10.1021/es405246a, 2014.
- 110 He, C., Zhang, Y., Li, Y., Zhuo, X., Li, Y., Zhang, C., and Shi, Q.: In-House Standard
111 Method for Molecular Characterization of Dissolved Organic Matter by FT-ICR Mass
112 Spectrometry, *ACS omega*, 5, 11730-11736, 10.1021/acsomega.0c01055, 2020.
- 113 Koch, B. P. and Dittmar, T.: From mass to structure: an aromaticity index for high-
114 resolution mass data of natural organic matter, *Rapid Commun. Mass Spectrom.*, 20,
115 926-932, 10.1002/rcm.2386, 2006.
- 116 Koch, B. P. and Dittmar, T.: From mass to structure: an aromaticity index for high-
117 resolution mass data of natural organic matter, *Rapid Commun Mass Sp*, 30, 250-250,
118 10.1002/rcm.7433, 2016.
- 119 Kujawinski, E. B. and Behn, M. D.: Automated analysis of electrospray ionization
120 fourier transform ion cyclotron resonance mass spectra of natural organic matter, *Anal*
121 *Chem*, 78, 4363-4373, 10.1021/ac0600306, 2006.
- 122 Seidel, M., Beck, M., Riedel, T., Waska, H., Suryaputra, I. G. N. A., Schnetger, B.,
123 Niggemann, J., Simon, M., and Dittmar, T.: Biogeochemistry of dissolved organic
124 matter in an anoxic intertidal creek bank, *Geochim.Cosmochim. Acta*, 140, 418-434,
125 10.1016/j.gca.2014.05.038, 2014.
- 126 Sleighter, R. L. and Hatcher, P. G.: The application of electrospray ionization coupled
127 to ultrahigh resolution mass spectrometry for the molecular characterization of natural
128 organic matter, *Journal of Mass Spectrometry*, 42, 559-574, 2007.
- 129 Yassine, M. M., Harir, M., Dabek-Zlotorzynska, E., and Schmitt-Kopplin, P.: Structural
130 characterization of organic aerosol using Fourier transform ion cyclotron resonance
131 mass spectrometry: aromaticity equivalent approach, *Rapid communications in mass*
132 *spectrometry : RCM*, 28, 2445-2454, 10.1002/rcm.7038, 2014.

133