Supporting Information

Farmer et al. 10.1073/pnas.0912340107

SI Text

Error Analysis for ON Estimation Methods. If we take the observed NO_x^+ ratio to be the combination of NO_x^+ ions from NH_4NO_3 and organonitrate (ON), and the fractional contribution of ON ions to NO_x^+ to be proportional to the fractional contribution of ON to total NO_{3^-},

$$x = \frac{NO_{ON} + NO_{2,ON}}{NO_{obs} + NO_{2,obs}}, \quad \textbf{[S1]}$$

$$R_{obs} = \frac{NO_{obs}}{NO_{2,obs}} = \frac{NO_{NH_4NO_3} + NO_{ON}}{NO_{2,NH_4NO_3} + NO_{2,ON}}, \quad \textbf{[S2a]}$$

$$R_{NH_4NO_3} = \frac{NO_{NH_4NO_3}}{NO_{2,NH_4NO_3}}, \quad \textbf{[S2b]}$$

$$R_{ON} = \frac{NO_{ON}}{NO_{2,ON}}, \quad \textbf{[S2c]}$$

Combining Eq. S2a–S2c,

$$R_{obs} = \frac{R_{NH_4NO_3}NO_{2,NH_4NO_3} + R_{ON}NO_{2,ON}}{NO_{2,NH_4NO_3} + NO_{2,ON}}. \quad \textbf{[S3]}$$

Taking $NO_{2,NH4NO3} = NO_{2,obs} - NO_{2,ON}$, Eq **S3** can be rewritten,

$$R_{obs}(NO_{2,obs}) = R_{NH_4NO_3}(NO_{2,obs} - NO_{2,ON}) + R_{ON}NO_{2,ON}, \quad \textbf{[S4]}$$

$$NO_{2,obs}(R_{obs} - R_{NH_4NO_3}) = NO_{2,ON}(R_{ON} - R_{NH_4NO_3}). \quad \textbf{[S5]}$$

Thus, the NO_2^+ derived from ON in the high-resolution version of the aerosol mass spectrometer (HR-AMS) is

$$NO_{2,ON} = \frac{NO_{2,obs}(R_{obs} - R_{NH_4NO_3})}{(R_{ON} - R_{NH_4NO_3})}. \quad \textbf{[S6]}$$

From our definition of R_{ON},

$$NO_{ON} = \frac{R_{ON}NO_{2,obs}(R_{obs} - R_{NH_4NO_3})}{(R_{ON} - R_{NH_4NO_3})}. \quad \textbf{[S7]}$$

Eq. **S1** can then be rewritten,

$$x = \frac{(R_{ON} + 1)NO_{2,obs}(R_{obs} - R_{NH_4NO_3})/(R_{ON} - R_{NH_4NO_3})}{(NO_{obs} + NO_{2,obs})}, \quad \textbf{[S8]}$$

$$x = \frac{(R_{ON} + 1)NO_{2,obs}(R_{obs} - R_{NH_4NO_3})}{(R_{ON} - R_{NH_4NO_3})(R_{obs}NO_{2,obs} + NO_{2,obs})}, \quad \textbf{[S9]}$$

$$x = \frac{(R_{obs} - R_{NH_4NO_3})(1 + R_{ON})}{(R_{ON} - R_{NH_4NO_3})(1 + R_{obs})}. \quad \textbf{[S10]}$$

By error propagation from Eq. **S10** (Eq. **1** in manuscript) and Eq. **2**, the uncertainty associated with ON_{NOx} (Δ_x) and ON_{CHON} (Δ_{ON}) are

$$\Delta_x = x * \sqrt{\frac{S^2_{R_{obs}} + S^2_{R_{NH_4NO_3}}}{(R_{obs} - R_{NH_4NO_3})^2} + \frac{S^2_{R_{ON}} + S^2_{R_{NH_4NO_3}}}{(R_{ON} - R_{NH_4NO_3})^2} + \left(\frac{S_{R_{ON}}}{R_{ON}}\right)^2 + \left(\frac{S_{R_{obs}}}{R_{obs}}\right)^2}, \quad \textbf{[S11]}$$

$$\Delta_{ON} = \frac{\sum CHON_{major,obs}}{R_{CHON_{major}}} * \sqrt{\left(\frac{\Delta(\Sigma CHON_{major,obs})}{\Sigma CHON_{major,obs}}\right)^2 + \left(\frac{\Delta R_{CHON_{major}}}{R_{CHON_{major}}}\right)^2}. \quad \textbf{[S12]}$$

1. Hogrefe O, Drewnick F, Lala GG, Schwab JJ, Demerjian KL (2004) Development, operation and applications of an aerosol generation, calibration and research facility. *Aerosol Sci Technol* 38:196–214.

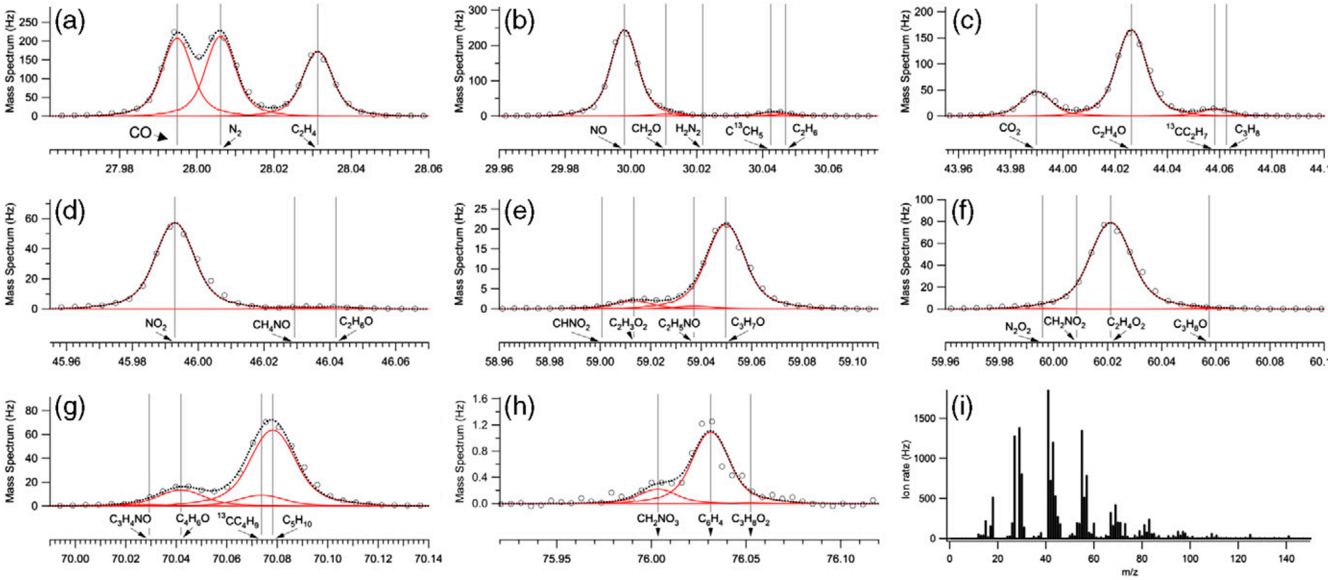

Fig. S1. High-resolution mass spectra (*a*–*h*) at dominant N-containing *m*/*z* ratios, along with *m*/*z* 28 and 44, for the oleic acid-derived hydroxynitrate (OlA-HN), taken at $T_v = 600\,°C$. The complete mass spectrum (*i*) is presented at unit mass resolution.

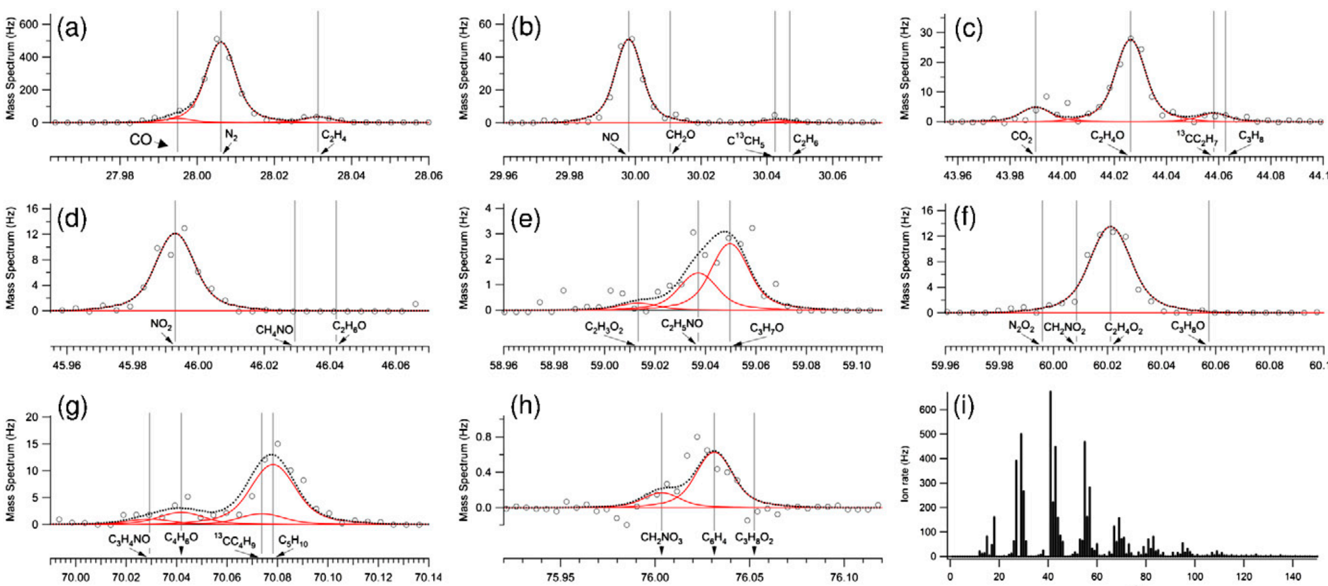

Fig. S2. High-resolution mass spectra (*a*–*h*) at dominant N-containing *m*/*z* ratios, along with *m*/*z* 28 and 44, for the oleic acid-derived carbonylnitrate (OlA-CN), taken at $T_v = 600\,°C$. The complete mass spectrum (*i*) is presented at unit mass resolution.

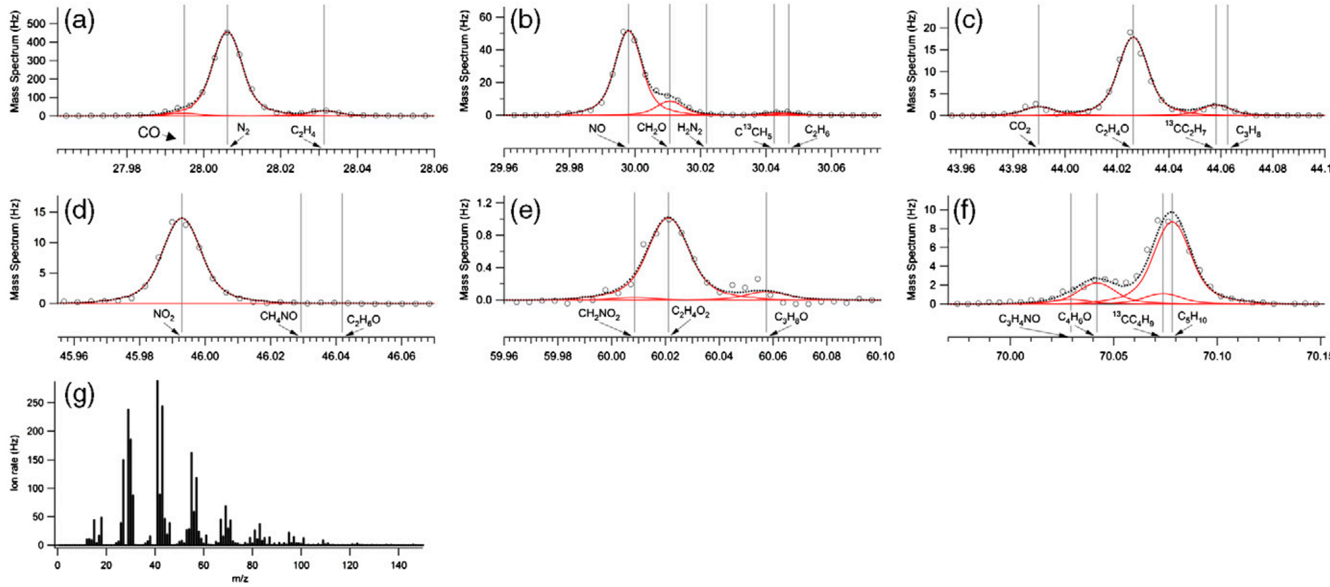

Fig. S3. High-resolution mass spectra (*a–f*) at dominant N-containing m/z ratios, along with m/z 28 and 44, for the tetradecene-derived dihydroxynitrate (TD-DHN), taken at $T_v = 600\,^{\circ}C$. The complete mass spectrum (*g*) is presented at unit mass resolution.

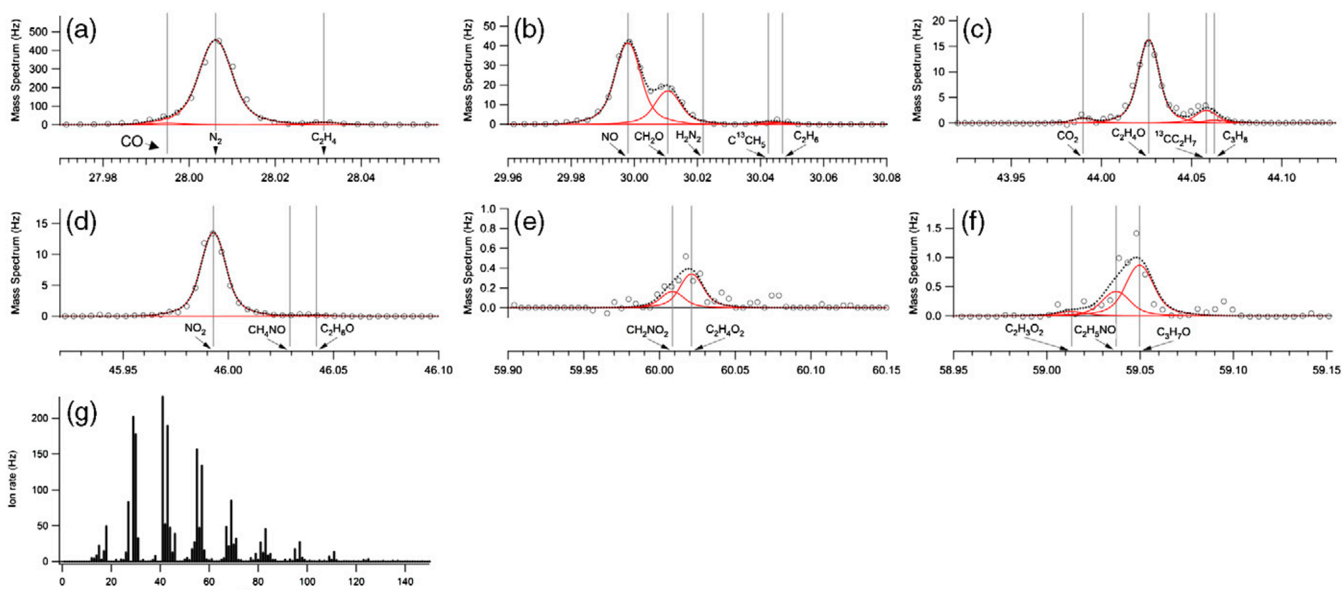

Fig. S4. High-resolution mass spectra (*a–f*) at dominant N-containing m/z ratios, along with m/z 28 and 44, for the tetradecene-derived 2-hydroxynitrate (TD-2OH-HN), taken at $T_v = 600\,^{\circ}C$. The complete mass spectrum (*g*) is presented at unit mass resolution.

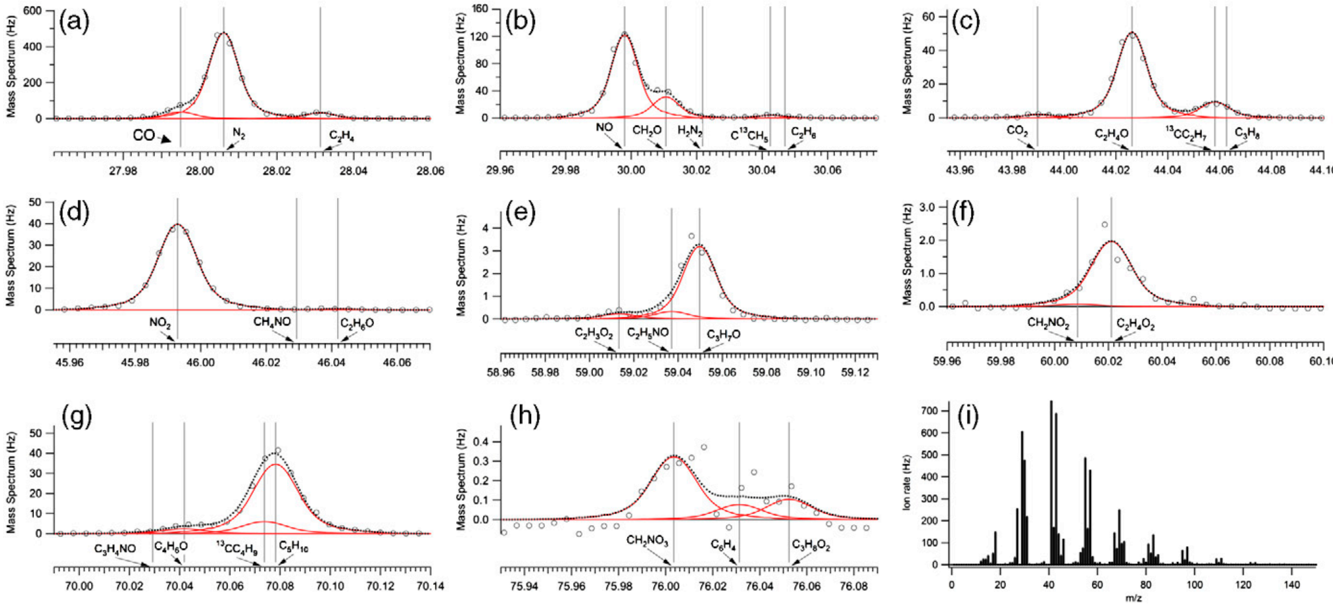

Fig. S5. High-resolution mass spectra (*a–h*) at dominant N-containing *m*/*z* ratios, along with *m*/*z* 28 and 44, for the tetradecene-derived 1-hydroxynitrate (TD-1OH-HN), taken at $T_v = 600\,°C$. The complete mass spectrum (*i*) is presented at unit mass resolution.

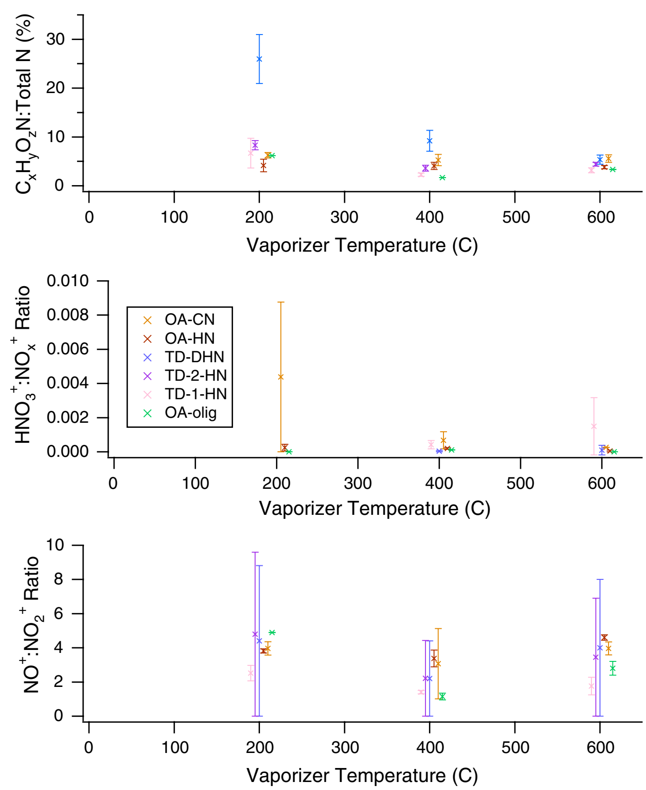

Fig. S6. The relative contribution of organonitrogen fragments to total N detected, HNO_3^+/NO_x^+ ratio, and NO^+/NO_2^+ ratio as a function of vaporizer temperature (T_v) in each of five standards, including the mix of oleic acid-derived oligomers, carbonyl nitrates, and hydroxy nitrates (uncertainty is standard error the mean). Vaporizer temperatures were 200, 400, and 600 °C for all standards, but are presented offset by ±5–15° for comparison purposes.

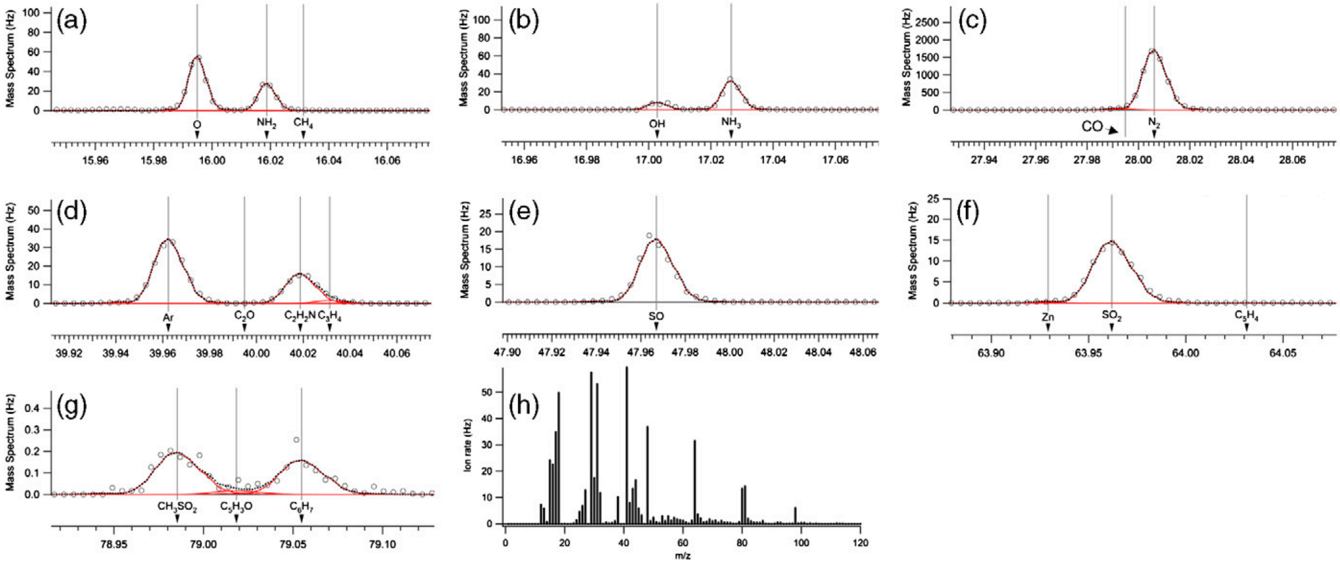

Fig. S7. High-resolution mass spectra (*a*–*g*) at select S-containing *m*/*z* ratios, along with *m*/*z* 28 and 40, for the organosulfate (OS) standard taken taken at $T_v = 600\,°C$. The complete mass spectrum (*h*) is presented at unit mass resolution.

Table S1. Fragmentation pattern of NH_4NO_3 and ON standards in the HR-AMS at $T_v = 600\,°C$ and fragmentation of $(NH_4)_2SO_4$ (1) and organic sulfate (this study) standards in the HR-AMS at $T_v = 600\,°C$, presented as relative signal intensity

	NH_4NO_3	ON standards					
		OlA-HN	OlA-CN	OlA-olig	TD-DHN	TD-2OH HN	TD-1OH HN
NO^+	100	100	100	100	100	100	100
NO_2^+	65	22	25	36	25	29	57
HNO_3^+	0.4	0.04	0.4	0.3	—	—	—
O/C raw		0.15	0.18	0.18	0.18	0.22	0.22
O/C calibrated		0.2	0.24	0.24	0.24	0.29	0.29
O/C cal. w/o NO_x^+		0.11	0.11	0.09	0.11	0.11	0.08
O/C molecular		0.33	0.33	—	0.36	0.29	0.29
H/C raw		1.66	1.66	1.69	1.72	1.76	1.75
H/C calibrated		1.82	1.82	1.86	1.89	1.93	1.92
H/C molecular		1.94	1.83	—	2.07	2.07	2.07
N/C raw		0.03	0.04	0.04	0.04	0.05	0.04
N/C calibrated		0.03	0.04	0.04	0.04	0.05	0.04
N/C cal. w/o NO_x^+		0.0009	0.0009	0.0007	0.0009	0.0007	0.0004
N/C molecular		0.06	0.06	—	0.07	0.07	0.07

		OS standards	
Fragment	Mass	$(NH_4)_2SO_4$	$C_5H_{11}O_7S$ (OS)
S	31.9721	14	19
SO	47.9670	67	100
SO_2	63.9619	100	75
HSO_2	64.9697	6	8
CH_3SO_2	78.9854	—	1
SO_3	79.9568	57	37
HSO_3	80.9646	26	34
H_2SO_4	97.9674	17	14

Atomic ratios (the number of oxygen, hydrogen, or nitrogen atoms relative to carbon atoms: O/C, H/C, N/C) determined by elemental analysis of HR-AMS data, including $H_xN_yO_z^+$, are shown for each ON standard as raw (experimental, no corrections applied), calibrated (corrected by Aiken et al. (2008) typically used for AMS elemental analyses) and molecular atomic ratios. Atomic ratios determined without NO_x^+ fragments (cal. w/o NO_x^+) are also presented for each standard. $(NH_4)_2SO_4$ standards were taken at unit mass resolution, and include the $^{33}SO_2$ isotope and $^{33}SO_3$ isotope for HSO_2 and HSO_3, respectively (1).

OlA-HN: $CH_3(CH_2)_7CH(OH)CH(ONO_2)(CH_2)_7C(O)OH + CH_3(CH_2)_7CH(ONO_2)CH(OH)(CH_2)_7C(O)OH$

OlA-CN: $CH_3(CH_2)_7C(O)CH(ONO_2)(CH_2)_7C(O)OH + CH_3(CH_2)_7CH(ONO_2)C(O)(CH_2)_7C(O)OH$

TD-DHN: $CH_3(CH_2)_8CH(ONO_2)(CH_2)_2CH(OH)CH_2OH + CH_3(CH_2)_9CH(ONO_2)CH_2CH(OH)CH_2OH$

TD-2OH HN: $CH_3(CH_2)_{11}CH(OH)CH_2ONO_2$

TD-1OH HN: $CH_3(CH_2)_{11}CH(ONO_2)CH_2OH$