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*Supplement of*

## **Quantitation of 11 alkylamines in atmospheric samples: separating structural isomers by ion chromatography**

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{Initial Time} Instrument Setup
Pump_ECD.Pressure.UpperLimit      3000 [psi]
Sampler.DelayVolume                 125 [µl]
Pump_ECD.%A.Equate                  "MSA"
Pump_ECD.Pressure.LowerLimit        200 [psi]
Pump_ECD.ColumnTemperature.Nominal  55.0 [°C]
Pump_ECD.CellTemperature.Nominal    30.0 [°C]
Pump_ECD.Data_Collection_Rate      5.0 [Hz]
Pump_ECD.Suppressor_Type            CERS_4mm
Pump_ECD.Suppressor_MSA             10.0 [mM]
Pump_ECD.Suppressor_RecommendedCurrent 37 [mA]
Pump_ECD.Suppressor_Current         37 [mA]
Pump_ECD.CR_TC                       On
Sampler.FlushFactor                  1
Sampler.DeliverSpeed                 1.0 [ml/min]
Sampler.InjectPosition
Sampler.DeliverRinse                 500,Position=Rinse
Sampler.DeliverSample                Volume=Bleed
Sampler.LoadPosition
Sampler.DeliverSample
Sampler.EndSamplePrep
Pump_ECD.Flow                         1.25
Pump_ECD.EluentGenerator_2.Concentration 1.00 [mM]
-5.000 Equilibration                 Duration = 5.000 [min]
Pump_ECD.EluentGenerator_2.Concentration 1.00 [mM]
0.000 Inject
Wait Sampler.CycleTimeState,
      Run=Hold,
      Timeout=Infinite
Sampler.Inject
Start Run
Pump_ECD.Channel_Pressure.AcqOn
Pump_ECD.Autozero
Pump_ECD.ECD_1.AcqOn
Pump_ECD.ECD_Total.AcqOn
Run                                    Duration = 45.000 [min]
Pump_ECD.EluentGenerator_2.Concentration 1.00 [mM]
Pump_ECD.EluentGenerator_2.Curve       5
20.000
Pump_ECD.EluentGenerator_2.Concentration 1.00 [mM]
Pump_ECD.EluentGenerator_2.Curve       7
Pump_ECD.EluentGenerator_2.Concentration 4.00 [mM]
Pump_ECD.EluentGenerator_2.Curve       7
30.000
Pump_ECD.EluentGenerator_2.Concentration 10.00 [mM]
Pump_ECD.EluentGenerator_2.Curve       7
40.000
Pump_ECD.EluentGenerator_2.Concentration 10.00 [mM]
Pump_ECD.EluentGenerator_2.Curve       5
Pump_ECD.EluentGenerator_2.Concentration 1.00 [mM]
Pump_ECD.EluentGenerator_2.Curve       5
45.000 Stop Run
Pump_ECD.Channel_Pressure.AcqOff
Pump_ECD.ECD_1.AcqOff
Pump_ECD.ECD_Total.AcqOff
End

```

Fig S1. Chromeleon method data file for final gradient method at 55 °C

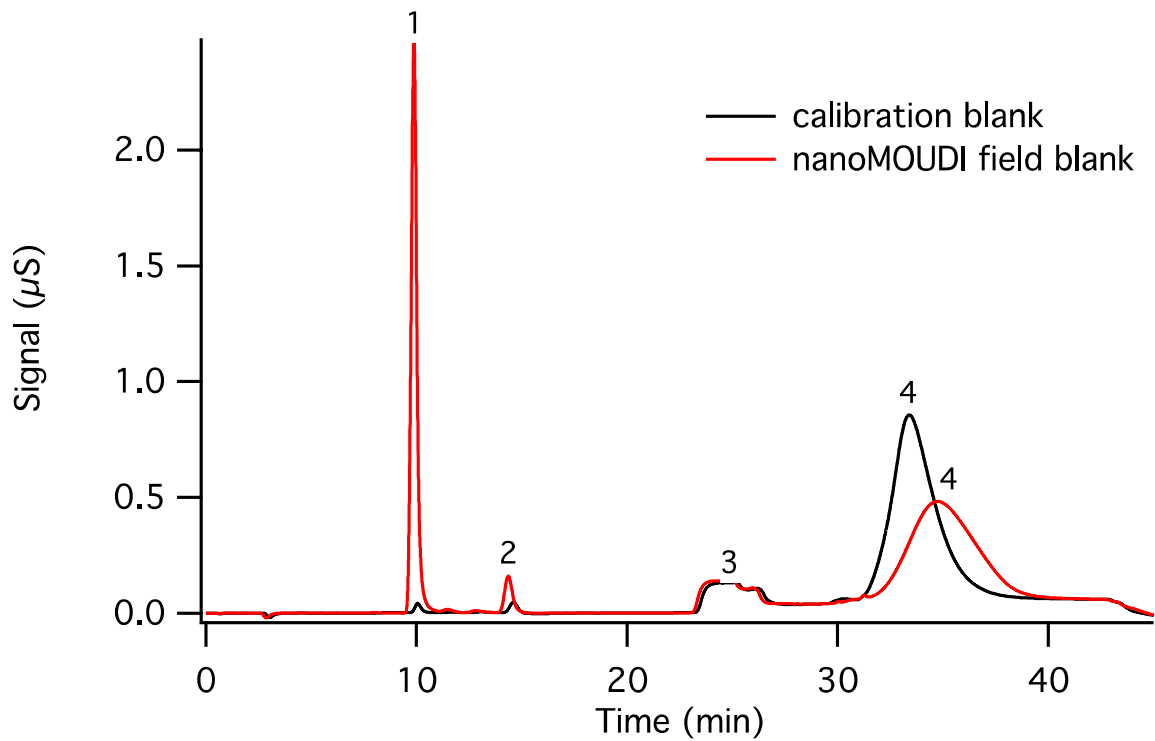
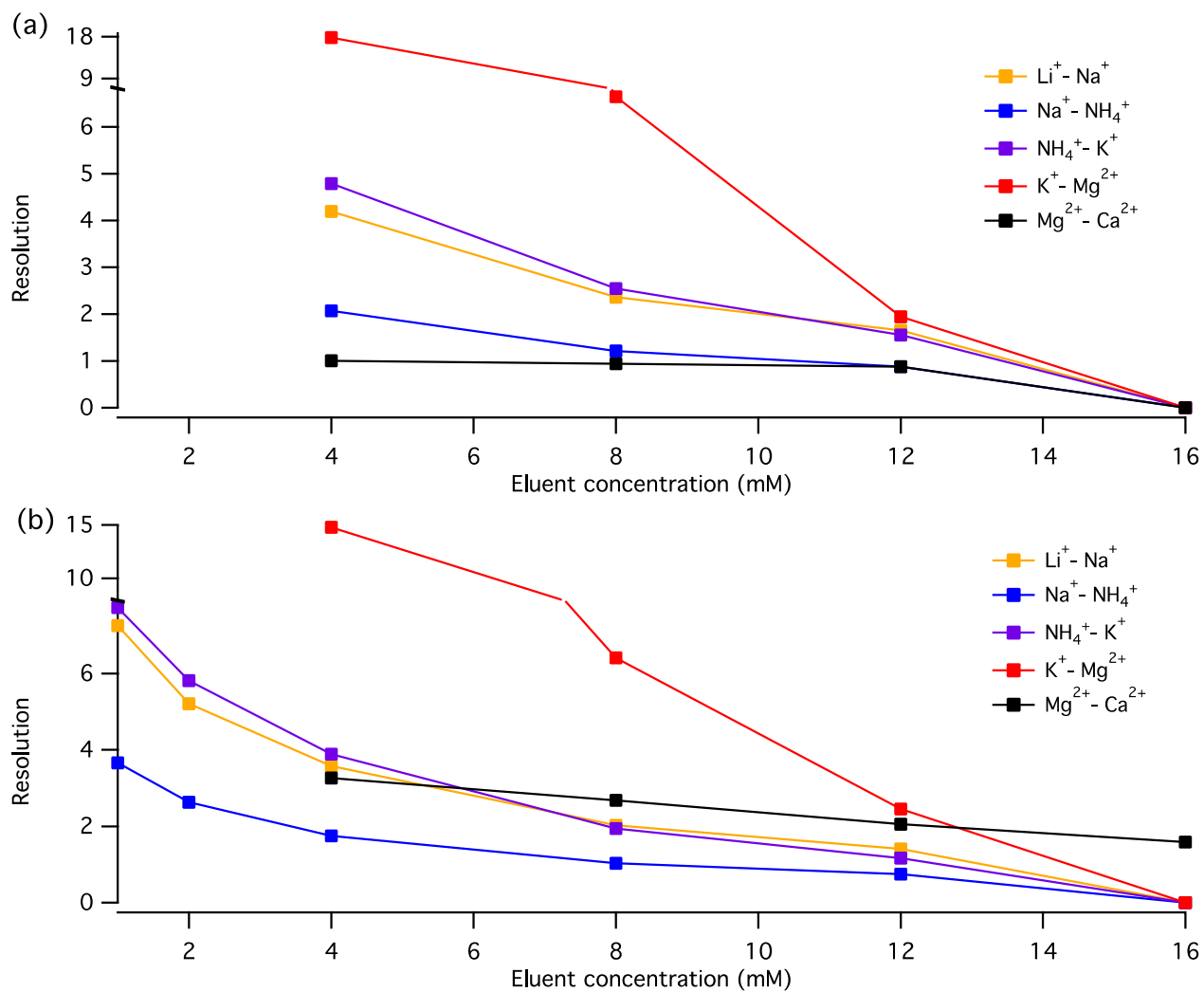


Fig S2. Sample chromatograms of a calibration blank and a size-resolved BB MOUDI foil substrate field blank. The peaks labelled above are as follows:  $\text{Na}^+$  (1),  $\text{K}^+$  (2), System peak (3), and  $\text{Ca}^{2+}$  (4).

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5 Fig S3. (a) Resolution of the six inorganic cation peak pairs using isocratic eluent methods at a flow rate of 0.75 ml min<sup>-1</sup>. (b) Resolution of the six inorganic cation peak pairs using isocratic eluent methods at a flow rate of 1.25 ml min<sup>-1</sup>. The resolution axis is split to indicate eluent concentrations where dramatic increases in separation occurred.

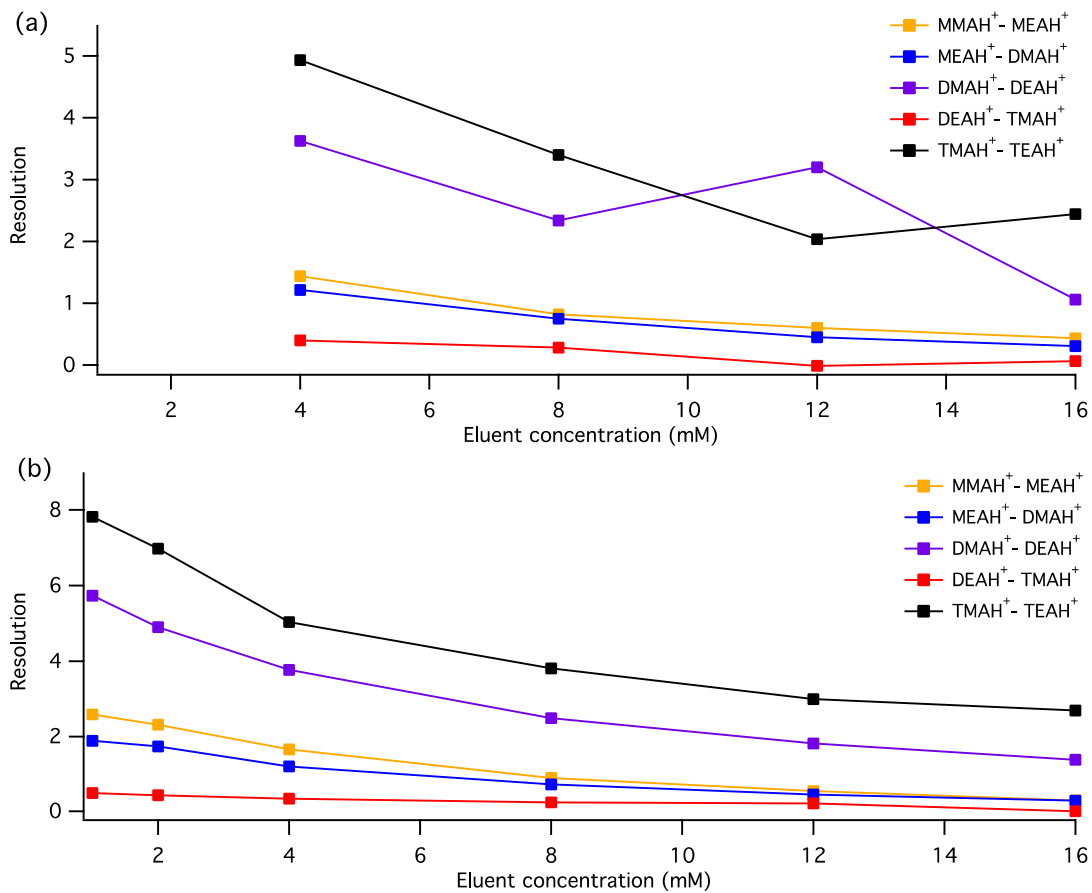


Fig S4. (a) Resolution of the six alkyl amine cation peak pairs using isocratic eluent methods at a flow rate of 0.75 ml min<sup>-1</sup>.

5 (b) Resolution of the six alkyl amine cation peak pairs using isocratic eluent methods at a flow rate of 1.25 ml min<sup>-1</sup>.

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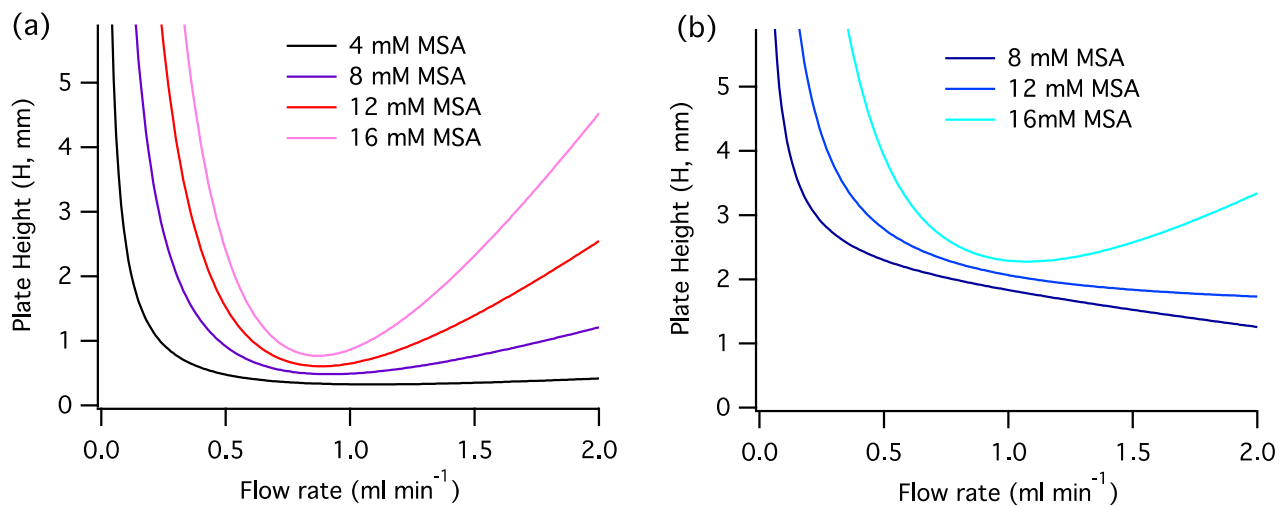


Fig S5. Calculated Van Deemter plots for the isocratic elutions of (a) MMAH<sup>+</sup> and (b) TEAH<sup>+</sup> at various MSA eluent concentrations and flow rates.

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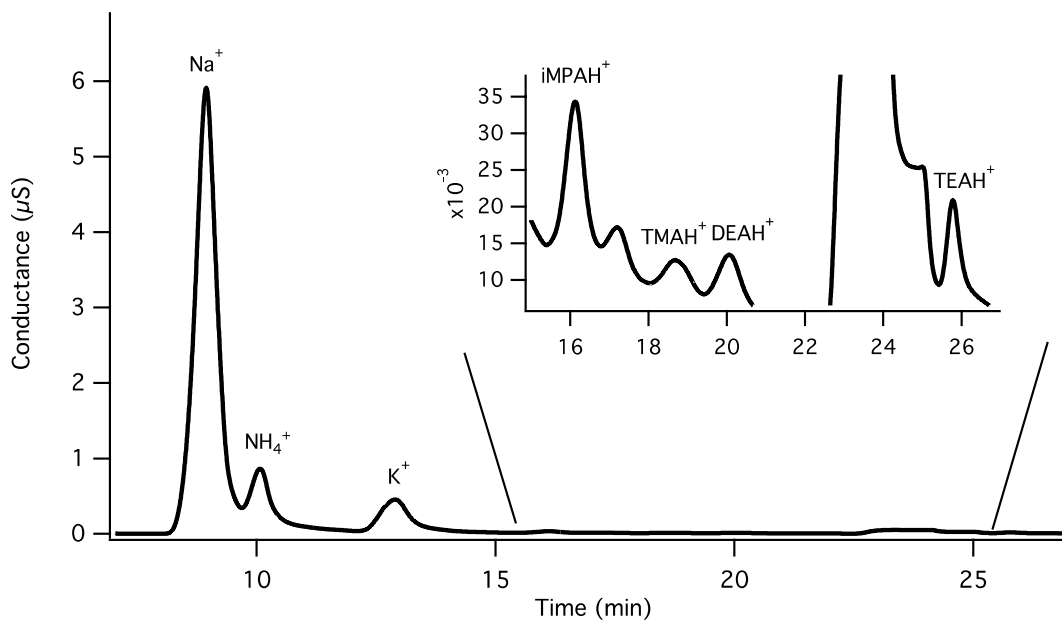


Fig S6. A chromatogram from an extracted PM<sub>2.5</sub> sample collected during a biomass-burning event in British Columbia at the Burnaby Kensington Park site.

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Table S1. Comparison of methyl and ethyl amine external and standard addition calibration slopes and retention times ( $t_r$ )

Analyte	External ( $\mu\text{S} \cdot \text{min mol}^{-1}$ )	Standard addition ( $\mu\text{S} \cdot \text{min mol}^{-1}$ )	Difference (%)	External $t_r$ range (min)	Standard addition $t_r$ range (min)
MMAH <sup>+</sup>	0.41E08	0.42E08	2	9.0 – 9.4	9.3 – 9.6
DMAH <sup>+</sup>	0.98E08	1.01E08	3	10.4 – 10.8	10.6 – 11.0
TMAH <sup>+</sup>	0.13E08	0.13E08	0	13.2 – 13.5	13.4 – 13.8
MEAH <sup>+</sup>	0.47E08	0.51E08	8	10.1 – 10.5	10.3 – 10.8
DEAH <sup>+</sup>	1.06E08	1.08E08	2	13.9 – 14.2	14.1 – 14.5
TEAH <sup>+</sup>	0.57E08	0.57E08	0	23.6 – 24.0	23.9 -24.2

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Table S2. Analytical performance of other IC methods used for the determination of atmospheric methyl and ethyl amines.

Analyte	Detection method	Pre- conc	Column	LOD (pg)	Precision (%)	Reference
MMAH <sup>+</sup>	CD	Yes	CS10	31	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	18	4.5	VandenBoer et al., 2012
	CD	No	CS14	2500	3.8	Verrielle et al., 2012
	MS	No	CS14	500	5.8	Verrielle et al., 2012
	CD	Yes	CS17	540	4.8	VandenBoer et al., 2012
	CD	Yes	CS19	30 - 650	5	This work
	CD	No	Metrosep C2	21500	0.4	Erupe et al., 2010
	CD	Yes	Metrosep C4	2100	12.2	Huang et al., 2014
DMAH <sup>+</sup>	CD	No	Metrosep C4	160	7.3	Dawson et al., 2014
	CD	Yes	CS10	40	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	25	1	VandenBoer et al., 2012
	CD	No	CS14	4000	10.5	Verrielle et al., 2012
	MS	No	CS14	150	11.4	Verrielle et al., 2012
	CD	Yes	CS17	870	14	VandenBoer et al., 2012
	CD	No	CS17	1500	1.2	Li et al., 2009
	CD	Yes	CS19	40 - 650	5	This work
TMAH <sup>+</sup>	CD	No	Metrosep C2	23000	1.4	Erupe et al., 2010
	CD	Yes	Metrosep C4	3800	15.7	Huang et al., 2014
	CD	No	Metrosep C4	320	1.1	Dawson et al., 2014
	CD	Yes	CS10	26	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	220	1	VandenBoer et al., 2012
	CD	No	CS14	2500	N/A	Verrielle et al., 2012
	MS	No	CS14	500	12.2	Verrielle et al., 2012
	CD	Yes	CS17	1580	3.3	VandenBoer et al., 2012
CD	No	CS17	2000	3.5	Li et al., 2009	
CD	Yes	CS19	300 - 1200	16	This work	

MEAH <sup>+</sup>	CD	No	Metrosep C2	38000	1.1	Erupe et al., 2010
	CD	No	Metrosep C4	970	6.1	Dawson et al., 2014
	CD	Yes	CS10	37	2 – 2.7	Chang et al., 2003
	CD	Yes	CS12A	33	12	VandenBoer et al., 2012
	CD	No	CS14	1000	5.1	Verrielle et al., 2012
	MS	No	CS14	500	7.9	Verrielle et al., 2012
	CD	Yes	CS17	790	10	VandenBoer et al., 2012
DEAH <sup>+</sup>	CD	Yes	CS19	200 - 700	7	This work
	CD	Yes	Metrosep C4	2200	4.3	Huang et al., 2014
	CD	Yes	CS12A	195	14	VandenBoer et al., 2012
	CD	No	CS14	N/A	N/A	Verrielle et al., 2012
	MS	No	CS14	35	9	Verrielle et al., 2012
	CD	Yes	CS17	1140	3.5	VandenBoer et al., 2012
	CD	Yes	CS19	100 - 800	8	This work
TEAH <sup>+</sup>	CD	Yes	Metrosep C4	4100	4.6	Huang et al., 2014
	CD	Yes	CS12A	32000	2	VandenBoer et al., 2012
	CD	Yes	CS17	1870	5.9	VandenBoer et al., 2012
	CD	Yes	CS19	500 - 1400	12	This work
	CD	Yes	Metrosep C4	15900	5.1	Huang et al., 2014

Table S3. Mass loadings of amines and ammonium in size-resolved particle diameter ( $D_p$ ) samples from an aged biomass burning plume sampled in St. John's, Newfoundland on July 6, 2013.

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$D_p$ ( $\mu\text{m}$ )	Mass loading ( $\text{ng m}^{-3}$ )						
	$\text{NH}_4^+$	$\text{MMAH}^+$	$\text{DMAH}^+$	$\text{TMAH}^+$	$\text{MEAH}^+$	$\text{DEAH}^+$	$\text{TEAH}^+$
10 - 18	BDL	$2.0 \pm 0.2$	$0.6 \pm 0.2$	BDL	BDL	$3 \pm 1$	$2 \pm 1$
5.6 - 10	BDL	BDL	$0.7 \pm 0.3$	$2 \pm 2$	BDL	$2.2 \pm 0.9$	$2 \pm 1$
3.2 – 5.6	BDL	$0.11 \pm 0.03$	$0.4 \pm 0.1$	BDL	BDL	BDL	BDL
1.8 – 3.2	BDL	$0.10 \pm 0.03$	$0.25 \pm 0.09$	$2 \pm 1$	BDL	$1.4 \pm 0.6$	$1.3 \pm 0.7$
1 – 1.8	BDL	$2.9 \pm 0.8$	$3 \pm 1$	$3 \pm 2$	BDL	$27 \pm 4$	$4 \pm 2$
0.56 – 1	$719 \pm 7$	$1.4 \pm 0.4$	$190 \pm 4$	$5 \pm 3$	$0.4 \pm 0.2$	$1300 \pm 200$	$2 \pm 1$
0.32 – 0.56	$443 \pm 4$	$11 \pm 3$	$208 \pm 4$	$4 \pm 3$	$0.21 \pm 0.08$	$1300 \pm 200$	$4 \pm 2$
0.18 – 0.32	$236 \pm 2$	$6 \pm 2$	$80 \pm 2$	BDL	BDL	$560 \pm 90$	$2 \pm 1$
0.10 – 0.18	$30 \pm 50$	$0.4 \pm 0.1$	$30 \pm 10$	BDL	$0.6 \pm 0.2$	$200 \pm 30$	BDL



0.056 – 0.10	20 ± 30	3 ± 1	6 ± 2	4 ± 3	BDL	58 ± 9	3 ± 2
0.032 – 0.056	40 ± 70	0.11 ± 0.03	7 ± 3	BDL	BDL	49 ± 8	BDL
0.018 – 0.032	BDL	0.10 ± 0.03	BDL	BDL	BDL	4 ± 2	BDL
0.010 – 0.018	BDL	0.30 ± 0.08	BDL	BDL	BDL	BDL	BDL

BDL = below detection limits

- 5 Table S4. Mass loadings of amines and ammonium in a fresh biomass burning plume at Burnaby Kensington Park and North Vancouver/Second Narrows sites in British Columbia in July 2015. Relative time is calculated with respect to the local maximum PM<sub>2.5</sub> intrusion.

Sampling site	Relative Time (h)	Mass loading (ng m <sup>-3</sup> )				
		NH <sub>4</sub> <sup>+</sup>	iMPAH <sup>+</sup>	TMAH <sup>+</sup>	DEAH <sup>+</sup>	TEAH <sup>+</sup>
BKP	- 24	70 ± 20	1.4 ± 0.9	0.6 ± 0.5	0.9 ± 0.5	0.2 ± 0.1
BKP	- 16	90 ± 30	6 ± 4	3 ± 2	1.6 ± 0.8	0.08 ± 0.06
BKP	- 8	130 ± 40	BDL	5 ± 4	BDL	BDL
BKP	0	90 ± 30	20 ± 10	9 ± 7	8 ± 4	BDL
BKP	8	90 ± 30	2 ± 1	2 ± 1	1.2 ± 0.7	BDL
BKP	16	80 ± 20	BDL	BDL	BDL	BDL
BKP	24	31 ± 9	BDL	BDL	BDL	BDL
NVSN	- 24	130 ± 40	5 ± 3	BDL	BDL	BDL
NVSN	- 16	400 ± 100	14 ± 9	BDL	BDL	BDL
NVSN	0	300 ± 100	40 ± 30	BDL	BDL	BDL
NVSN	8	300 ± 100	60 ± 40	BDL	BDL	BDL
NVSN	16	70 ± 20	BDL	BDL	BDL	BDL
NVSN	24	100 ± 30	BDL	BDL	BDL	BDL

BDL = below detection limits