{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

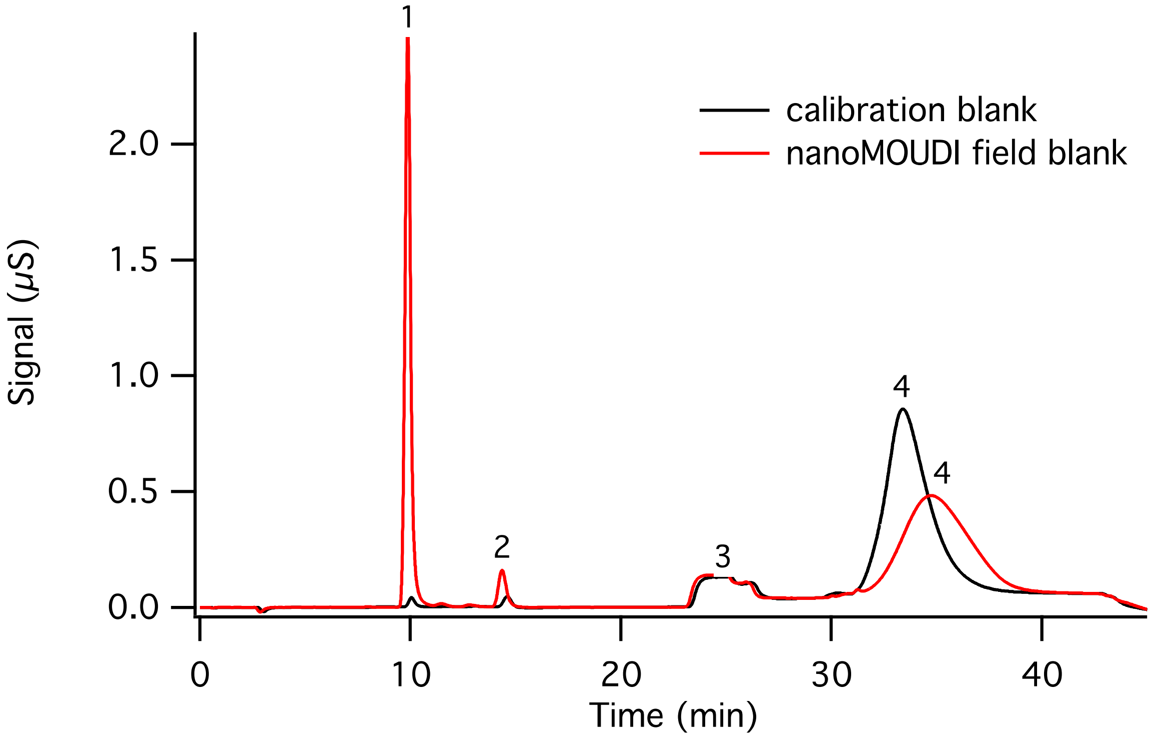

Fig S2. Sample chromatograms of a calibration blank and a size-resolved BB MOUDI foil substrate field blank. The peaks labelled above are as follows: Na^+ (1), K^+ (2), System peak (3), and Ca^{2+} (4).

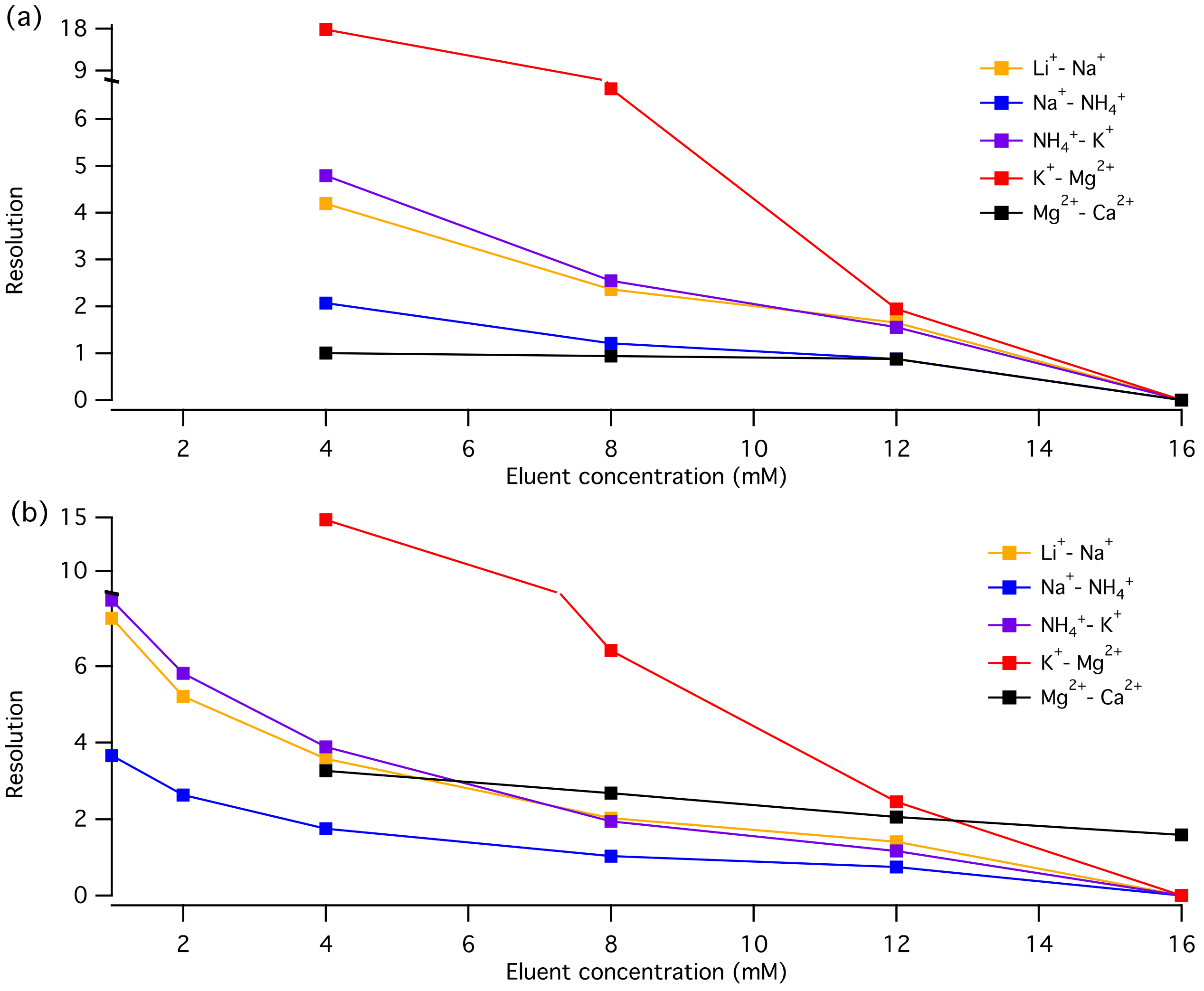

Fig S3. (a) Resolution of the six inorganic cation peak pairs using isocratic eluent methods at a flow rate of 0.75 ml min^{-1}. (b) Resolution of the six inorganic cation peak pairs using isocratic eluent methods at a flow rate of 1.25 ml min^{-1}. The resolution axis is split to indicate eluent concentrations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

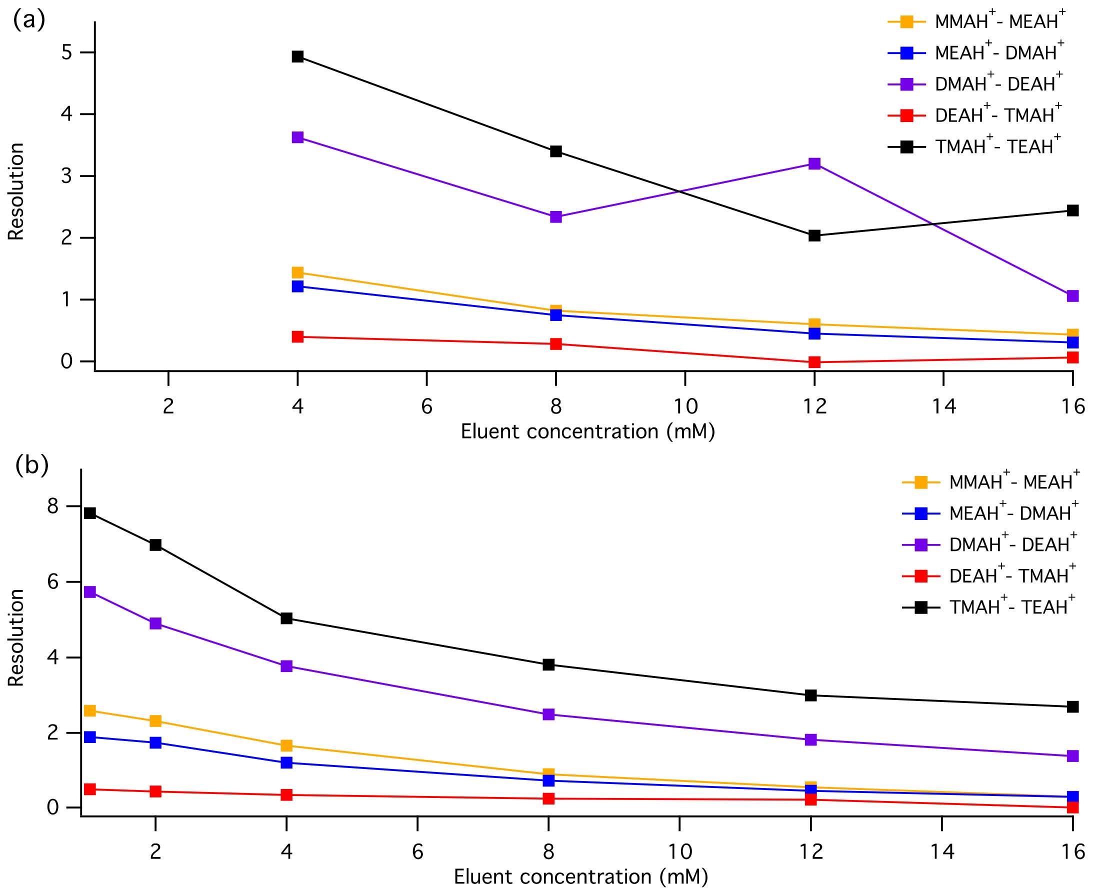

Fig S4. (a) Resolution of the six alkyl amine cation peak pairs using isocratic eluent methods at a flow rate of 0.75 ml min^{-1}. (b) Resolution of the six alkyl amine cation peak pairs using isocratic eluent methods at a flow rate of 1.25 ml min^{-1}.

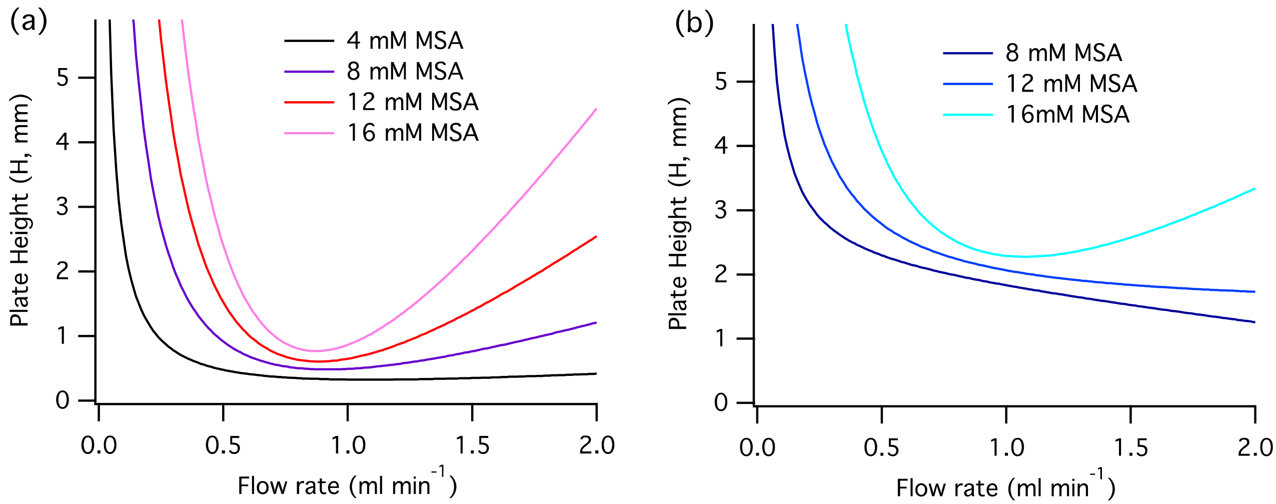

Fig S5. Calculated Van Deemter plots for the isocratic elutions of (a) $MMAH^+$ and (b) $TEAH^+$ at various MSA eluent concentrations and flow rates.

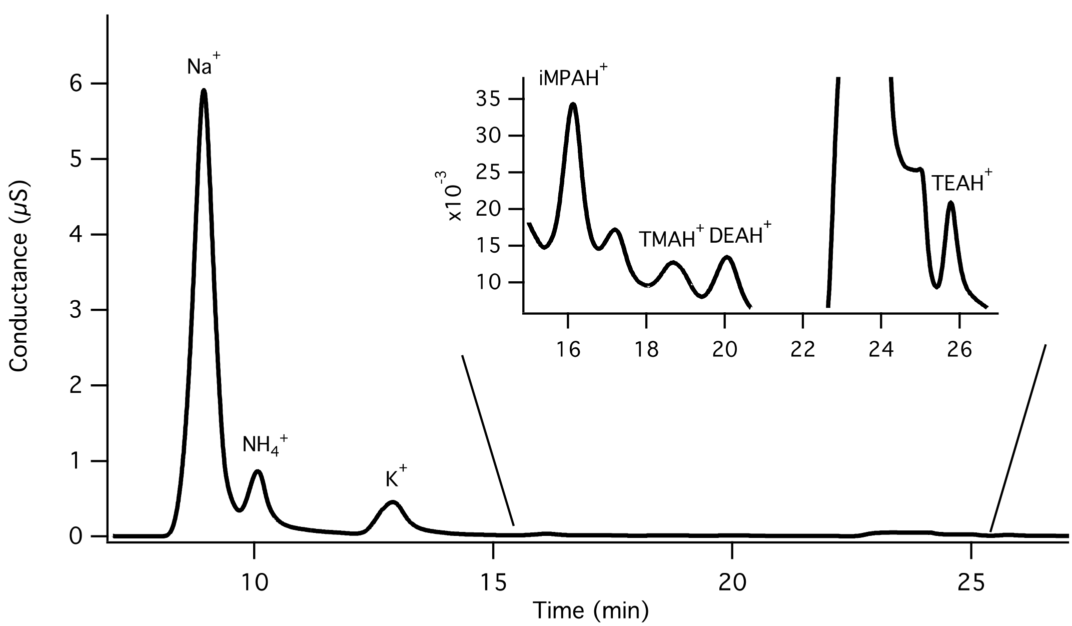

Fig S6. A chromatogram from an extracted $PM_{2.5}$ sample collected during a biomass-burning event in British Columbia at the Burnaby Kensington Park site.

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

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

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$^+$	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	Verriele et al., 2012
	MS	No	CS14	500	5.8	Verriele 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
	CD	No	Metrosep C4	160	7.3	Dawson et al., 2014
DMAH$^+$	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	Verriele et al., 2012
	MS	No	CS14	150	11.4	Verriele 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
	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
TMAH$^+$	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	Verriele et al., 2012
	MS	No	CS14	500	12.2	Verriele 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

	CD	No	Metrosep C2	38000	1.1	Erupe et al., 2010
	CD	No	Metrosep C4	970	6.1	Dawson et al., 2014
$MEAH^+$	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	Verriele et al., 2012
	MS	No	CS14	500	7.9	Verriele et al., 2012
	CD	Yes	CS17	790	10	VandenBoer et al., 2012
	CD	Yes	CS19	200 - 700	7	This work
	CD	Yes	Metrosep C4	2200	4.3	Huang et al., 2014
$DEAH^+$	CD	Yes	CS12A	195	14	VandenBoer et al., 2012
	CD	No	CS14	N/A	N/A	Verriele et al., 2012
	MS	No	CS14	35	9	Verriele et al., 2012
	CD	Yes	CS17	1140	3.5	VandenBoer et al., 2012
	CD	Yes	CS19	100 - 800	8	This work
	CD	Yes	Metrosep C4	4100	4.6	Huang et al., 2014
$TEAH^+$	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.

D_p (μm)	**Mass loading (ng m^{-3})**						
	NH_4^+	**$MMAH^+$**	**$DMAH^+$**	**$TMAH^+$**	**$MEAH^+$**	**$DEAH^+$**	**$TEAH^+$**
10 - 18	BDL	2.0 ± 0.2	0.6 ± 0.2	BDL	BDL	3 ± 1	2 ± 1
5.6 - 10	BDL	BDL	0.7 ± 0.3	2 ± 2	BDL	2.2 ± 0.9	2 ± 1
3.2 – 5.6	BDL	0.11 ± 0.03	0.4 ± 0.1	BDL	BDL	BDL	BDL
1.8 – 3.2	BDL	0.10 ± 0.03	0.25 ± 0.09	2 ± 1	BDL	1.4 ± 0.6	1.3 ± 0.7
1 – 1.8	BDL	2.9 ± 0.8	3 ± 1	3 ± 2	BDL	27 ± 4	4 ± 2
0.56 – 1	719 ± 7	1.4 ± 0.4	190 ± 4	5 ± 3	0.4 ± 0.2	1300 ± 200	2 ± 1
0.32 – 0.56	443 ± 4	11 ± 3	208 ± 4	4 ± 3	0.21 ± 0.08	1300 ± 200	4 ± 2
0.18 – 0.32	236 ± 2	6 ± 2	80 ± 2	BDL	BDL	560 ± 90	2 ± 1
0.10 – 0.18	30 ± 50	0.4 ± 0.1	30 ± 10	BDL	0.6 ± 0.2	200 ± 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

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 $PM_{2.5}$ intrusion.

Sampling site	**Relative Time (h)**	**Mass loading (ng m^{-3})**				
		NH_4^+	**$iMPAH^+$**	**$TMAH^+$**	**$DEAH^+$**	**$TEAH^+$**
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