



Supplement of

Long-term air concentrations, wet deposition, and scavenging ratios of inorganic ions, HNO₃, and SO₂ and assessment of aerosol and precipitation acidity at Canadian rural locations

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Section S1: Correlation analysis between particulate ions and meteorological variables

The influence of meteorological parameters including temperature, relative humidity and precipitation rates on the temporal trends of particulate ions and trace gases were also investigated by performing correlation analyses on the monthly averaged data. The descending trend in K^+ between 1993 and 2010 at the majority of the sites was not strongly influenced by precipitation as evident by the weak correlation coefficients (Table S1). Higher correlation between monthly average K^+ and temperature were found at Sprucedale, Freightsburg and Lac Edouard ($r = 0.52-0.69$, $p < 0.05$). At these sites, the monthly average K^+ peaked in March-April and was at the minimum concentration during December-January, which resembled the seasonal temperature cycle (Fig. S2a). The higher K^+ in the early spring could be attributed to increase soil emissions from agriculture operations and forest fires during springtime since the major sources of particulate K^+ are from biomass and soil. Decreasing NH_4^+ observed at most of the sites was only weakly correlated with monthly precipitation rates and relative humidity, implying these meteorological parameters had little influence on the long-term temporal trend. Higher correlation between monthly average NH_4^+ and temperature was found at Kejimkujik ($r = 0.63$, $p < 0.05$). The maximum NH_4^+ typically occurred during April-May and reached its lowest concentration during December-January (Fig. S2b). This seasonal trend is linked to the formation of SO_4^{2-} through SO_2 oxidation, which tends to occur at higher temperatures because of increase production of atmospheric oxidants. This theory is consistent with the very high correlation between monthly average NH_4^+ and SO_4^{2-} ($r = 0.91$, $p < 0.05$) at Kejimkujik. Overall, strong correlations between NH_4^+ and SO_4^{2-} were observed at all the sites ($r = 0.6-0.94$, $p < 0.05$). The high correlation between SO_4^{2-}/SO_2 ratio and temperature ($r = 0.61-0.84$, $p < 0.05$) suggests SO_4^{2-} formation from the gas-phase oxidation of SO_2 (Yao et al., 2002). Besides the relationship between NH_4^+ and SO_4^{2-} , three of the sites including Saturna, ELA and Egbert exhibited strong correlations between NH_4^+ and NO_3^- ($r = 0.52-0.7$, $p < 0.05$) indicating that NH_4^+ also followed the temporal trend of NO_3^- at some locations. In summary, precipitation and relative humidity had little impact on the long-term temporal patterns of particulate ions. Seasonal temperature trends are linked with the seasonal cycle of atmospheric oxidants which explains the short-term patterns in SO_4^{2-} and NH_4^+ . However, the correlation analysis using monthly data did not find a strong relationship between long-term temperature changes and long-term trends in SO_4^{2-} and NH_4^+ concentrations. The lack of trends is related to the combined effects of increasing temperature and decreasing sulfur dioxide emissions. Studies suggest an increase in temperature would increase ammonia emissions and the partitioning of ammonium nitrate to ammonia (Sutton et al., 2013; Yao and Zhang, 2016). However, the decreasing trend in sulfur dioxide emissions would likely reduce atmospheric sulfate and subsequently lead to lower ammonium sulfate production (Yao and Zhang, 2016).

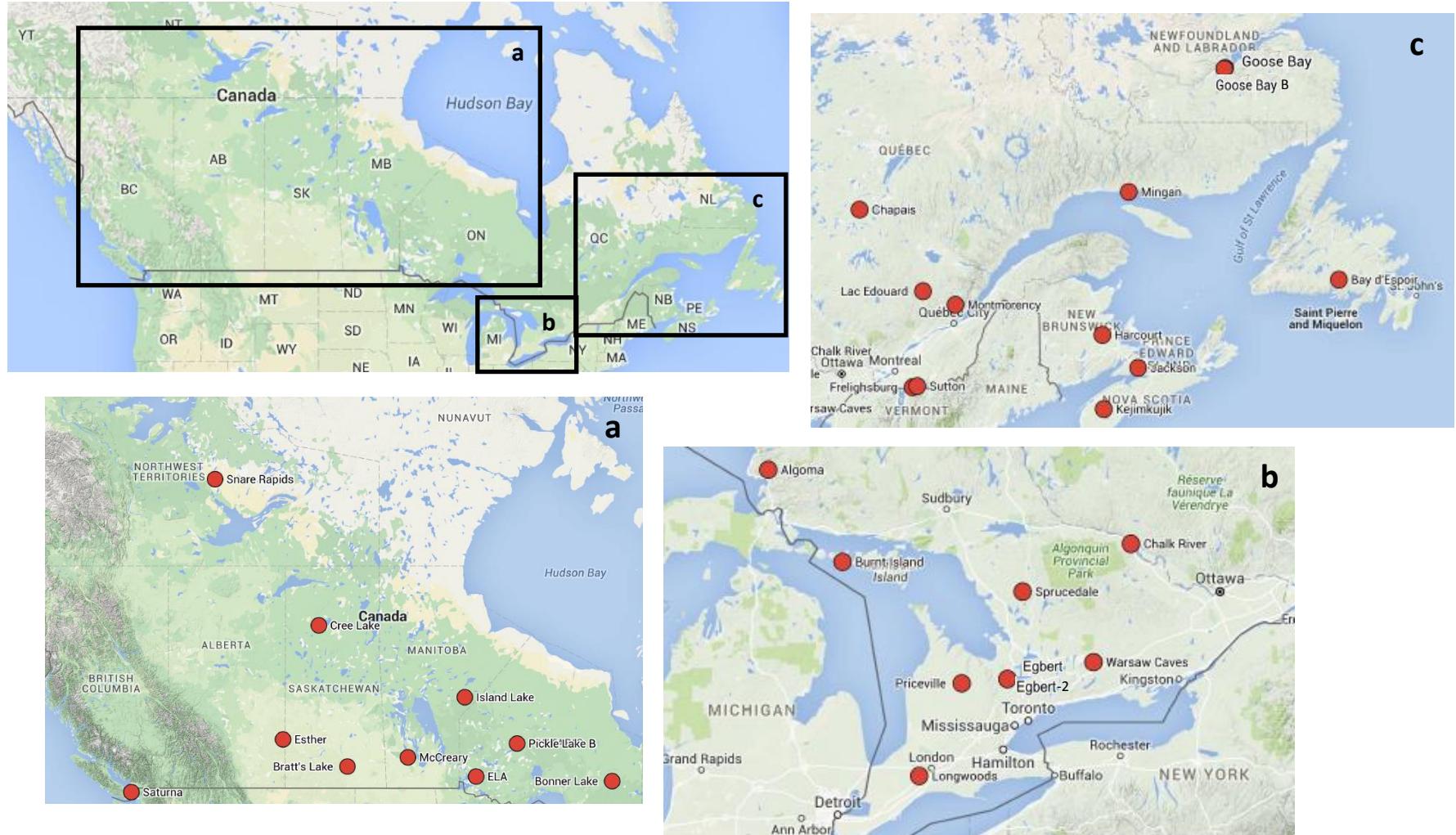


Figure S1: Map of 31 CAPMoN sites in western/central Canada (a), southern Ontario (b), and Quebec and eastern Canada (c).

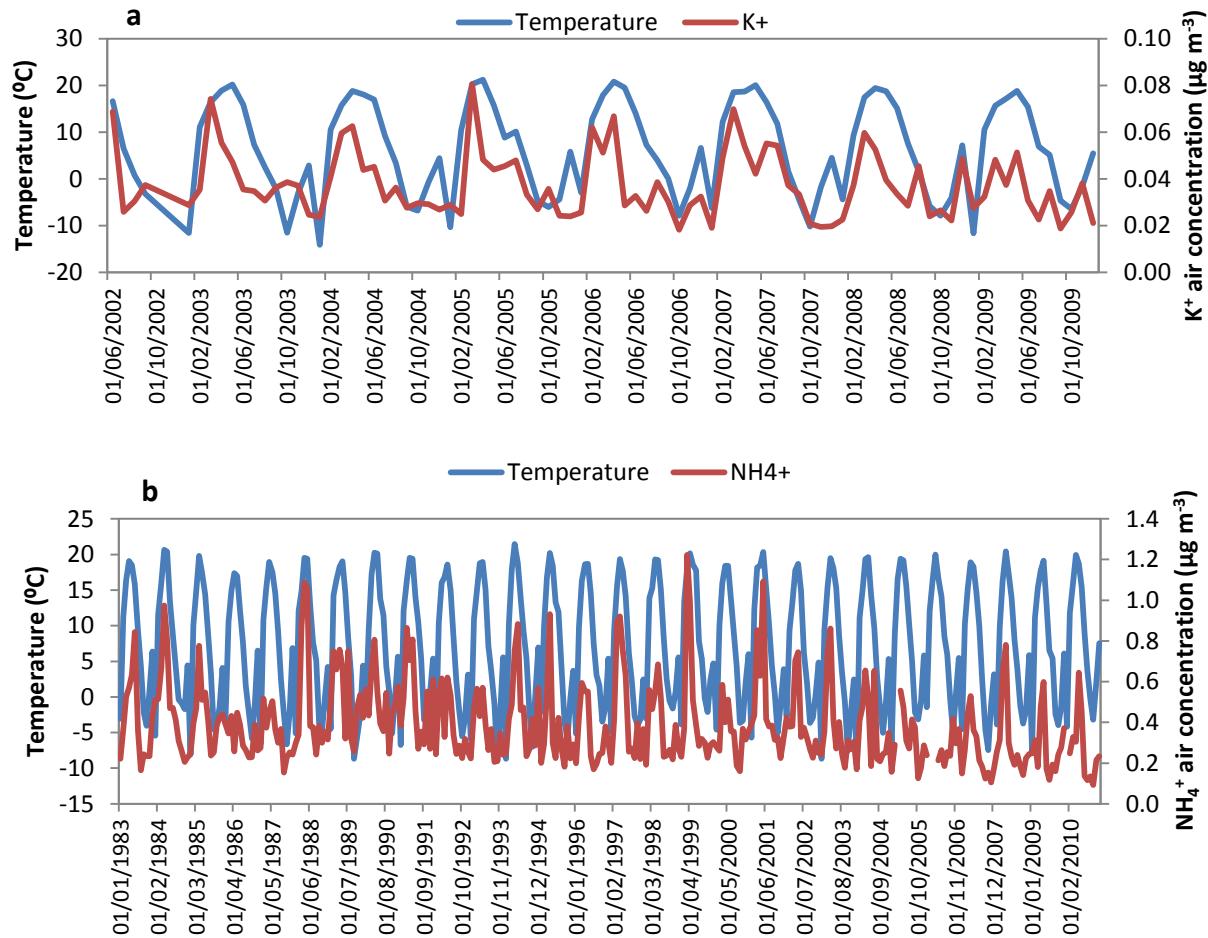


Figure S2: Time-series plots of monthly average air temperature and atmospheric K^+ from Sprucedale, Freleighsburg and Lac Edouard (combined) (a) and monthly average air temperature and atmospheric NH_4^+ at Kejimkujik (b).

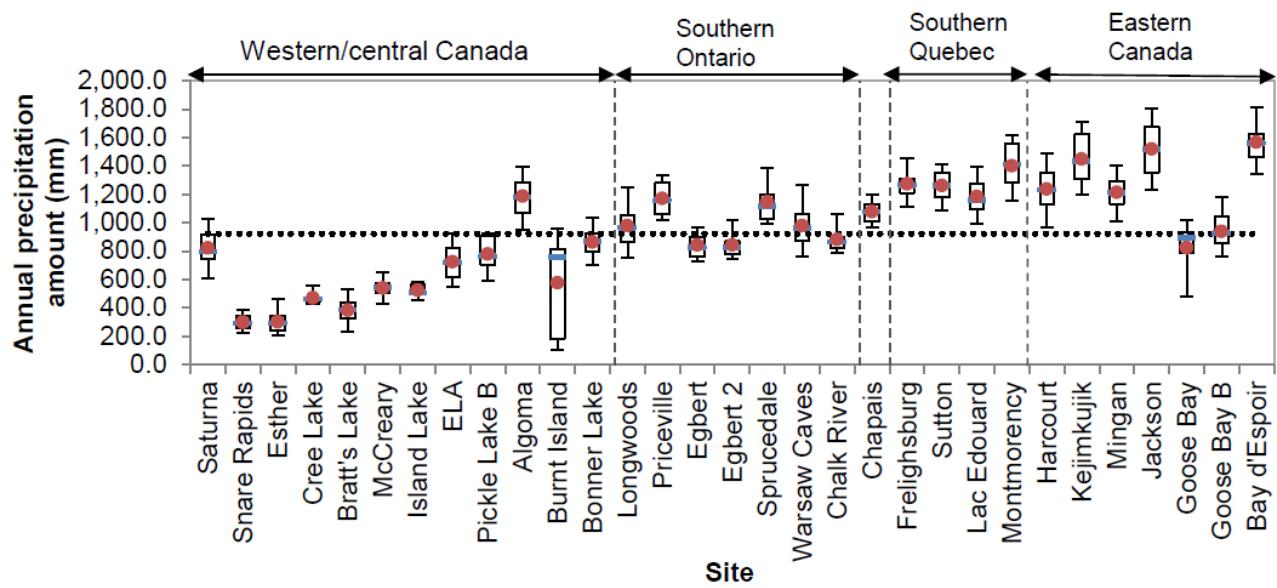


Figure S3: Geographical pattern of the annual precipitation amount. The blue line indicates the median; the red dot indicates the mean; the box and whiskers include the interquartile range and the 5th to 95th percentile range, respectively; the dotted line is the overall median among the sites.

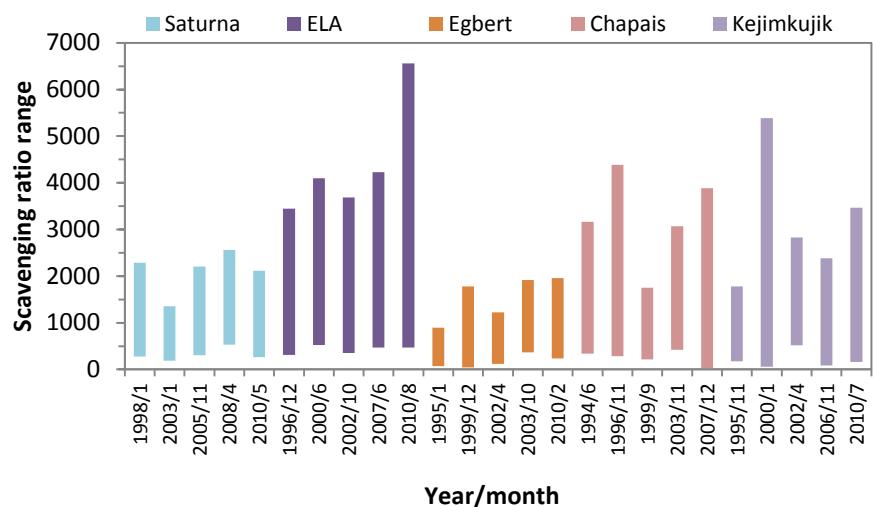


Figure S4: Variability in scavenging ratios among different inorganic ions and trace gases within the same month for five different years at five of the sites.

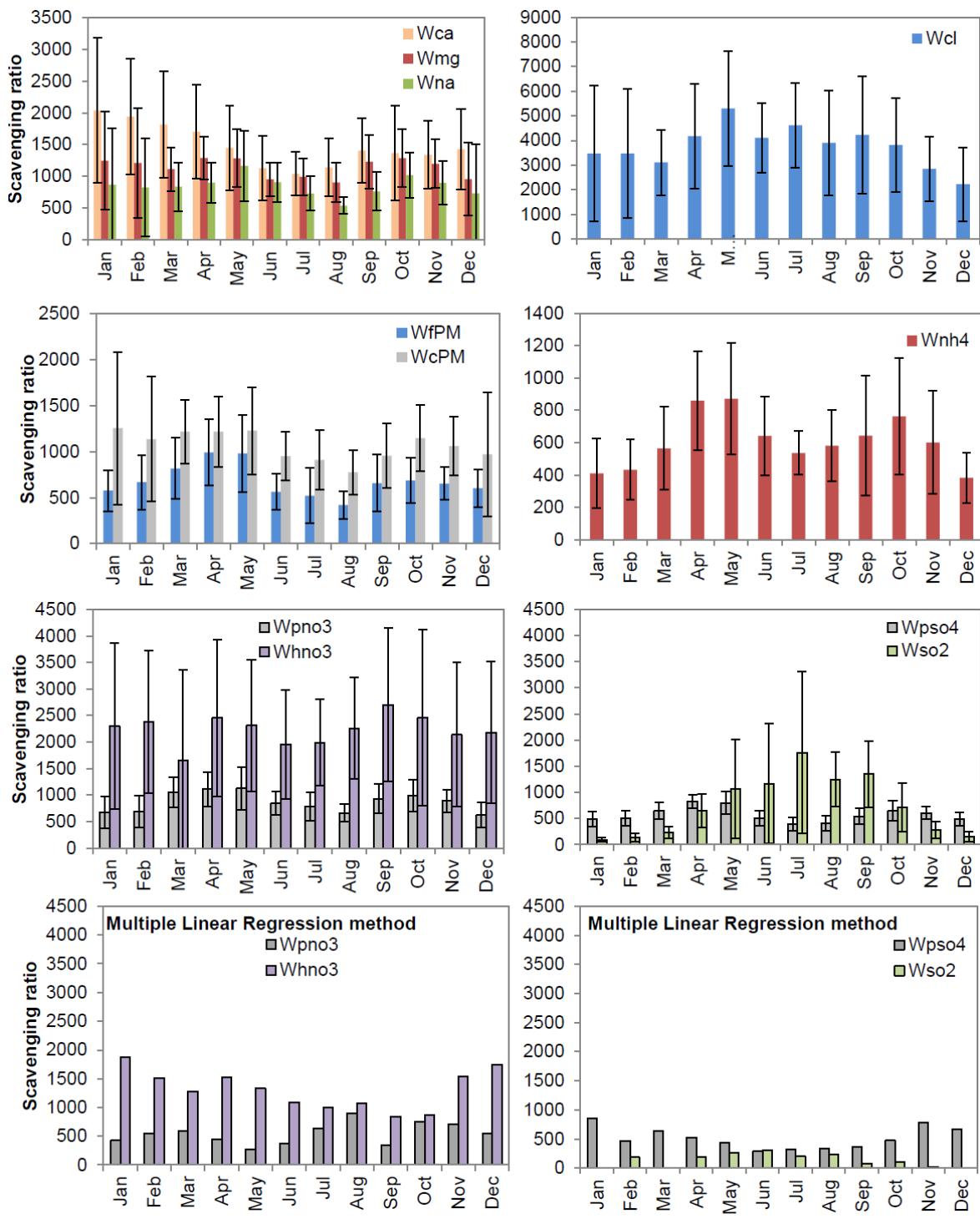


Figure S5: Monthly variation in scavenging ratios among 13 sites. Error bars represent the standard deviation of scavenging ratios between sites. W_{fPM} and W_{cPM} are the fine and coarse particle scavenging ratios, respectively.

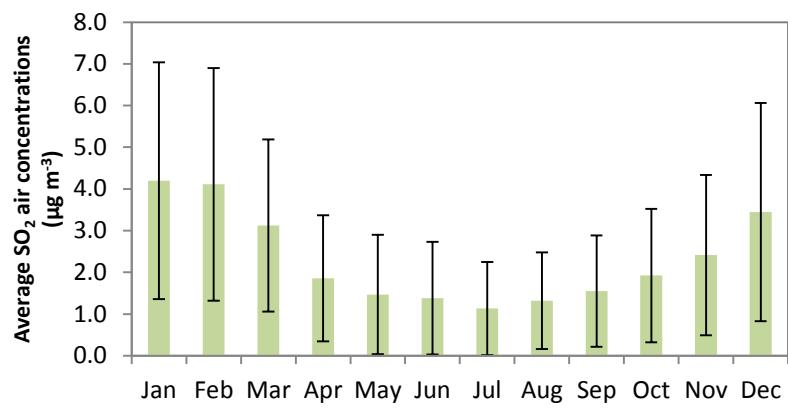


Figure S6. Monthly variation in SO_2 air concentrations. Error bars represent the standard deviation between sites.

Table S1: Pearson correlation coefficients between selected ions and meteorological parameters (significant at p<0.05; otherwise non-significant (ns)). Note that the ion concentrations and meteorological parameters are monthly averages.

Site	K ⁺			NH ₄ ⁺					SO ₄ ²⁻ /SO ₂
	Temp	RH	Precip	Temp	RH	Precip	NO ₃ ⁻	SO ₄ ²⁻	
Saturna	-0.20	0.18	0.18	-0.04 ^{ns}	-0.23	-0.17	0.67	0.60	0.61
Bratt's Lake	0.09 ^{ns}	-0.20	-0.25						
ELA	0.20	-0.03 ^{ns}	0.12	-0.26	0.13	-0.22	0.70	0.78	0.75
Algoma	0.42	-0.07 ^{ns}	-0.04 ^{ns}	0.36	0.10	-0.17	0.23	0.87	0.73
Longwoods				-0.05 ^{ns}	0.20	-0.06 ^{ns}	0.44	0.68	0.81
Egbert				-0.07 ^{ns}	0.03 ^{ns}	-0.21	0.52	0.75	0.77
Sprucedale	0.69	0.05 ^{ns}	-0.14 ^{ns}	0.30	0.06 ^{ns}	-0.23	0.20 ^{ns}	0.92	0.73
Chalk River	0.31	-0.005 ^{ns}	0.05 ^{ns}	0.37	0.09	0.02 ^{ns}	0.10 ^{ns}	0.85	0.64
Chapais	0.41	-0.17	0.18	0.38	-0.21	0.04 ^{ns}	0.23	0.85	0.77
Freelighsburg	0.53	0.08 ^{ns}	0.13 ^{ns}	0.11 ^{ns}	0.13 ^{ns}	-0.13 ^{ns}	0.36	0.86	0.84
Lac Edouard	0.52	-0.15 ^{ns}	0.21	0.34	0.01 ^{ns}	0.11 ^{ns}	0.23	0.94	0.76
Kejimkujik	0.31	-0.17	-0.15	0.63	-0.30	-0.32	-0.16	0.91	0.83

Table S2: Average cation and anion concentrations (neq m⁻³) in particulate matter by site and year

Site	Cation	Anion		Year	Cation	Anion
Saturna	0.047	0.045		1994	0.074	0.066
Esther	0.052	0.033		1995	0.071	0.063
Bratt's Lake	0.060	0.031		1996	0.073	0.063
ELA	0.024	0.024		1997	0.073	0.063
Algoma	0.024	0.028		1998	0.076	0.064
Longwoods	0.133	0.108		1999	0.075	0.066
Egbert	0.096	0.072		2000	0.067	0.062
Sprucedale	0.024	0.024		2001	0.078	0.068
Chalk River	0.028	0.034		2002	0.073	0.061
Chapais	0.016	0.019		2003	0.065	0.055
Frelighsburg	0.060	0.043		2004	0.063	0.054
Sutton	0.062	0.054		2005	0.069	0.059
Lac Edouard	0.016	0.018		2006	0.058	0.046
Montmorency	0.023	0.026		2007	0.058	0.048
Kejimkujik	0.035	0.041		2008	0.060	0.048
				2009	0.052	0.041
				2010	0.048	0.037

Table S3: Scavenging ratio (W) statistics from this study (mass basis). na indicates no available data. “C” indicates coastal locations.

Site	$W_{Ca^{2+}}$	$W_{Mg^{2+}}$	W_{Na^+}	$W_{coarsePM}$	$W_{finePM} = W_k$	W_{Cl}	W_{NH4}	W_{pNO3}	W_{HNO3}	W_{pSO4}	W_{SO2}
Mean											
Saturna ^C	1671	1493	1390	1505	567	2103	445	897	776	602	233
ELA	1893	1347	1208	1496	885	3519	848	1224	3079	696	1247
Algoma	2413	1510	1002	1426	911	5779	762	1204	2064	734	330
Longwoods	911	901	865	881	996	2011	303	657	749	601	125
Egbert	625	748	713	697	554	1914	283	583	982	473	181
Sprucedale	1822	1299	905	1342	611	4278	577	998	2012	611	445
Chalk River	na	na	666	666	580	5065	466	632	3005	547	560
Chapais	2077	899	475	1043	758	1855	625	932	5527	661	1291
Freelighsburg	852	838	647	781	553	2554	411	642	1375	471	414
Sutton	1010	936	594	753	497	4377	350	631	1616	473	396
Lac Edouard	1702	1105	577	1128	512	3192	465	842	2398	496	771
Montmorency	1200	1148	599	742	607	4969	406	697	2201	471	1222
Kejimkujik ^C	1729	1980	2120	2077	702	4959	303	1120	1842	571	1339
Max avg/min avg ratio	3.9	2.6	4.5	3.1	2.0	3.1	3.0	2.1	7.4	1.6	10.7
Median											
Saturna ^C	1552	1404	1245	1430	502	1934	416	796	650	533	208
ELA	1395	1141	993	1358	765	3235	726	1151	2711	628	1141
Algoma	1946	1266	816	1272	769	4532	655	1046	1880	698	203
Longwoods	840	832	775	802	682	1684	252	601	857	531	60
Egbert	535	693	585	635	440	1355	245	521	829	428	127
Sprucedale	1504	1238	765	1218	556	3872	582	945	1906	582	204

Chalk River	na	na	531	531	437	4321	401	526	2568	449	284
Chapais	1743	712	363	883	640	1216	544	787	4914	578	828
Freighsburg	774	754	540	742	438	1788	405	599	1322	442	251
Sutton	968	888	549	706	445	2972	314	562	1452	435	241
Lac Edouard	1483	1015	497	1023	450	2480	380	780	2077	404	453
Montmorency	1130	833	474	623	432	3633	347	559	2173	386	809
Kejimkujik ^C	1482	1416	1447	1452	541	3511	279	926	1571	488	461
Max median/min median ratio	3.6	2.0	4.0	2.7	1.8	3.7	3.0	2.2	7.6	1.8	19.0
Standard deviation											
Saturna ^C	798	727	734	655	271	1001	217	381	547	276	123
ELA	1684	810	1016	990	483	2159	476	680	1636	336	880
Algoma	1869	1061	661	973	653	5161	517	753	1017	284	372
Longwoods	439	398	362	312	869	1331	159	233	453	273	142
Egbert	373	317	427	322	501	1547	170	307	647	214	180
Sprucedale	1039	634	637	597	286	2940	253	504	840	259	523
Chalk River	na	na	450	450	417	3763	313	392	1629	352	681
Chapais	1273	668	349	641	407	1969	328	529	2654	339	1373
Freighsburg	415	367	382	331	514	2288	157	311	523	170	438
Sutton	374	371	254	302	321	3320	155	284	618	234	445
Lac Edouard	1003	597	361	517	281	2188	257	412	1195	260	843
Montmorency	628	783	354	441	478	4489	231	425	960	324	1151
Kejimkujik ^C	1134	1643	1942	1823	671	4723	154	687	1172	391	2245

Table S4: Scavenging ratios from literature (mass basis). * Most literature values excluded gas scavenging except where indicated; ¹Derived from multiple linear regression; ²W_{pNO₃} based on sum of pNO₃⁻ and HNO₃ in air; ³W_{pSO₄} based on sum of pSO₄²⁻ and SO₂ in air; ⁴Snow events only.

Location	W _{Ca²⁺}	W _{Mg²⁺}	W _{Na⁺}	W _{K⁺}	W _{Cl}	*W _{NH₄}	*W _{pNO₃}	*W _{pSO₄}	W _{HNO₃}	W _{SO₂}	Reference
CAPMoN sites, Canada	625-2413	748-1980	475-2120	497-996	1855-5779	283-848	583-1224	471-734	749-5527	125-1339	This study
							523-1776	391-903	722-2848	31-409	This study ¹
Eastern Canada							832-2950	831-1550			Barrie et al. (1985) ²
NADP/CASTNET sites, U.S.	860-2526	656-2011	798-7409	265-885	1430- 22950						Cheng et al. (2015)
NADP/AIRMoN sites, U.S.						96-3050		216-2710	300-1700		Hicks (2005) ³
Northern Michigan				80-4600		40-2200	500	60-2280	3500- 4550	219-355	Cadle et al. (1990) ⁴
Barbados			578-869				336-409	264-315			Galloway et al. (1993)
Bermuda			560-749				273-447	182-242			Galloway et al. (1993)
Ireland			1692-5800				535-1258	321-734			Galloway et al. (1993)
Vitoria, Spain	3983		3625	1151	3030	1739	2303	2830			Encinas et al. (2004)
Central France				20000- 250000		500-8500	4500- 16500	750-5250			Bourcier et al. (2012)
Sardinia, Italy	3459-4605	1013-1524	1708-1815	1630- 1845	2085-2419		754-1062	1728-2173			Guerzoni et al. (1995)
Turkey	1649±466		789±176	619±138		624±147	612±228	1177±301			Tuncel and Ungör (1996)
Mt. Sonnblick, Austria						2160	3120	1680			Kasper-Giebl et al. (1999) ²
							1104	1056	3480	96	Kasper-Giebl et al. (1999) ¹
Hyderabad, India	2265	877	517	723	109	389	317	160			Kulshrestha et al. (2009)
Bay of Bengal	582	5039	5282	58	16085	336	3591	426			Kulshrestha et al. (2009)
Nepal	1805±1873	2580±2277	1393±1593	2436±20 92	2582±1870	1811±23 51	2502±2007	487±326			Shrestha et al. (2002)
Singapore	697±376	318±201	500±180	744±590	2624±1129	1660±12 84	2134±1671	2596±2076			He and Balasubramanian (2008)
Maldives	470-1200	500	1000-1100	140-220	1100-1200	530-600	930-2000	490-580			Granat et al. (2010)

Table S5: Gas and particle scavenging ratios for nitrate and sulfate derived from multiple linear regression [$C_{\text{prec}} = \text{constant} + W_{\text{gas}}C_{\text{gas,air}} + W_{\text{part}}C_{\text{part,air}}$]. C_{prec} is the total precipitation concentration of nitrate or sulfate; W_{gas} and W_{part} are the gas and particle scavenging ratios, respectively; $C_{\text{gas,air}}$ and $C_{\text{part,air}}$ are the air concentrations of HNO_3 or SO_2 and pNO_3^- or pSO_4^{2-} , respectively. R^2 is the coefficient of determination and r-part is the partial correlation. ns indicates not significant coefficients ($p>0.05$).

Site	W_{pNO_3}	W_{HNO_3}	R^2	r-part pNO_3^-	r-part HNO_3		W_{pSO_4}	W_{SO_2}	R^2	r-part pSO_4^{2-}	r-part SO_2
Saturna	910	1175	0.20	0.22	0.33		903	45	0.14	0.31	0.06
Bratt's Lake	694	1359	0.16	0.29	0.25				<0.1		
Algoma	1121	1253	0.24	0.25	0.28		434	85	0.17	0.33	0.08
Longwoods	544	776	0.14	0.28	0.21		393	ns	0.12	0.33	-0.01
Egbert	523	722	0.18	0.30	0.20		391	ns	0.16	0.37	0.01
Sprucedale	882	1308	0.21	0.21	0.26		505	ns	0.13	0.35	-0.02
Chalk River	786	1510	0.17	0.15	0.28		487	ns	0.14	0.36	-0.01
Chapais	1776	2848	0.25	0.16	0.39		623	409	0.20	0.41	-0.04
Sutton	944	1241	0.15	0.19	0.25		535	31	0.17	0.39	0.03
Lac Edouard	1532	1289	0.33	0.25	0.22		482	80	0.19	0.37	0.06
Freelighsburg	958	1470	0.26	0.28	0.29		526	104	0.13	0.32	0.08
Montmorency	1470	1493	0.34	0.16	0.45		481	ns	0.22	0.46	-0.03
Kejimkujik	1561	2382	0.19	0.22	0.33				<0.1		
<i>Overall</i>	570	1253	0.21	0.22	0.29		489	32	0.20	0.38	0.04

Table S6: Monthly gas and particle scavenging ratios for nitrate and sulfate derived from multiple linear regression (similar to Table S5)

Month	$W_{p\text{NO}_3}$	W_{HNO_3}	R^2	r-part pNO_3^-	r-part HNO_3		W_{pSO_4}	W_{SO_2}	R^2	r-part pSO_4^{2-}	r-part SO_2
Jan	425	1871	0.23	0.16	0.37		851	ns	0.25	0.40	-0.06
Feb	548	1511	0.27	0.24	0.35		467	184	0.20	0.34	0.00
Mar	583	1283	0.26	0.26	0.31		633	ns	0.18	0.32	0.02
Apr	442	1518	0.21	0.18	0.30		525	195	0.22	0.28	0.09
May	270	1332	0.18	0.10	0.31		434	257	0.19	0.22	0.13
Jun	373	1093	0.22	0.11	0.31		284	307	0.22	0.22	0.17
Jul	636	1005	0.19	0.13	0.29		317	204	0.21	0.26	0.09
Aug	894	1065	0.24	0.17	0.30		333	230	0.20	0.26	0.09
Sep	345	842	0.11	0.08	0.20		362	77	0.17	0.29	0.05
Oct	749	862	0.17	0.24	0.19		472	107	0.24	0.28	0.11
Nov	712	1543	0.20	0.28	0.24		780	21	0.21	0.35	0.03
Dec	554	1741	0.24	0.25	0.33		670	ns	0.19	0.32	0.00

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