Supplementary Material

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

Irene Cheng and Leiming Zhang

Air Quality Research Division, Science and Technology Branch, Environment and Climate Change Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Canada

Correspondence to: Irene Cheng (irene.cheng@canada.ca)

Figure S1: Map of 30 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, Frelighsburg and Lac Edouard (combined) (a) and monthly average air temperature and atmospheric NH₄⁺ at Kejimikujik (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 months at five of the sites.

Figure S5: Monthly trend 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 trend in SO₂ 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)).

	K^+				NH_4^+						SO_4^{2-}/SO_2
Site	Temp	RH	Precip		Temp	RH	Precip	NO_3^-	SO_4^{2-}		Temp
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
Frelighsburg	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: Scavenging ratio (W) statistics from this study (mass basis). na indicates no available data. “C” indicates coastal locations.

Site	W _{Ca2+}	W _{Mg2+}	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
Frelighsburg	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
Kejimikujik ^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
Frelighsburg	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
Kejimikujik ^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
Frelighsburg	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
Kejimikujik ^C	1134	1643	1942	1823	671	4723	154	687	1172	391	2245

Table S3: 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. (1998) ²
							1104	1056	3480	96	Kasper-Giebl et al. (1998) 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±2092	2582±1870	1811±2351	2502±2007	487±326			Shrestha et al. (2002)
Singapore	697±376	318±201	500±180	744±590	2624±1129	1660±1284	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 S4: 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
Frelighsburg	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
Kejimikujik	1561	2382	0.19	0.22	0.33				<0.1		
Overall	570	1253	0.21	0.22	0.29		489	32	0.20	0.38	0.04

Table S5: Monthly gas and particle scavenging ratios for nitrate and sulfate derived from multiple linear regression (similar to Table S4)

Month	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
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