Supplementary materials

Surface snow bromide and nitrate at Eureka, Canada in early spring and implications for polar boundary layer chemistry

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Table S1. Overview of relative standard deviations of duplicate analyses for 2019 samples (n=36), and average limits of detection (LOD)[a] and limits of quantification (LOQ)[b]. The units are μM.

	MSA	Cl^-	Br^-	NO_3^-	$SO_4^{=}$	Na^+	K^+	Mg^{2+}
Relative Standard deviation	-	0.034	0.023	0.037	0.011	0.109	0.263	0.391
LOD[a] (μM)	0.070	0.367	0.200[c]	0.484[d]	0.531	0.696	1.228	0.741
LOQ[b] (μM)	0.260	1.185	0.238[c]	0.484[d]	1.780	2.305	4.092	2.510

[a] LOD = 3x standard deviation of filter blank average peak area. [b] LOQ = 10x standard deviation of filter blank average peak area. [c] and [d] Br^- and NO_3^- did not have filter blank background and therefore LOD and LOQ were defined as 3x and 10x the minimum measurable peak area, respectively.

Table S2. Statistical results for the ionic analysis of the 2018 snow samples at the Sea ice, Onshore, PEARL and Creek sites. The units are μM.

		2018							
		0-0.5cm				Column average			
		n	mean	std	median	n	mean	std	median
Sea ice	$[Br^-]$	36	0.23	0.10	0.24	80	10.74	8.52	7.63
	$[Cl^-]$	30	12.55	6.15	12.66	80	5822.27	5166.40	3131.57
	$[Ca^{2+}]$	33	2.42	2.62	1.20	80	63.43	51.40	28.23
	$[F^-]$	30	0.09	0.03	0.10	73	1.16	0.40	1.21
	$[K^+]$	30	1.64	0.04	1.62	80	55.35	41.15	28.47
	[MSA]	26	0.07	0.05	0.06	2	0.32	0.04	0.32
	[Acetate]	34	15.16	9.92	16.26	24	91.49	9.74	89.94
	[Formate]	26	6.02	0.08	5.98	28	4.90	2.36	4.04
	$[NH_4^+]$	34	0.43	0.24	0.38	53	5.11	3.88	3.96
	[Oxalate]	34	3.69	2.54	4.40	41	8.24	7.69	2.27
	$[Mg^{2+}]$	32	1.86	0.77	1.84	81	338.56	259.62	172.65
	$[Na^+]$	32	3.18	2.00	3.29	75	1437.78	722.12	1120.23
	$[NO_3^-]$	33	3.17	1.00	3.32	87	4.95	2.75	4.66
	$[SO_4^{2-}]$	34	0.73	0.38	0.57	69	163.62	97.14	176.53
	nss-$[Br^-]$	36	0.22	0.10	0.23	82	5.69	6.79	3.71
	nss-$[SO_4^{2-}]$	32	0.49	0.26	0.43	70	87.17	115.13	66.67
Onshore	$[Br^-]$	33	0.27	0.11	0.30	60	0.33	0.23	0.25
	$[Cl^-]$	27	11.46	6.69	11.41	66	122.82	70.75	106.86
	$[Ca^{2+}]$	32	6.28	5.23	3.31	66	16.11	7.74	18.14
	$[F^-]$	8	0.05	0.05	0.05	63	0.13	0.06	0.11
	$[K^+]$	33	0.57	0.65	0.23	65	3.40	2.04	3.65
	[MSA]	4	0.13	0.06	0.12	34	0.01	0.01	0.01
	[Acetate]	32	7.26	0.75	7.27	56	1.21	0.31	1.18
	[Formate]	31	1.39	0.27	1.39	58	0.75	0.27	0.71
	$[NH_4^+]$	30	1.33	0.35	1.25	57	1.12	0.32	1.08
	[Oxalate]	33	0.19	0.05	0.20	73	0.50	0.34	0.41
	$[Mg^{2+}]$	26	1.40	1.19	0.96	66	19.22	12.31	18.77
	$[Na^+]$	27	7.17	4.75	7.26	65	79.70	56.94	71.62
	$[NO_3^-]$	34	3.22	1.45	2.83	66	3.91	0.73	3.97
	$[SO_4^{2-}]$	33	1.55	1.12	0.97	64	6.20	1.78	6.35
	nss-$[Br^-]$	33	0.23	0.09	0.24	61	0.18	0.14	0.16
	nss-$[SO_4^{2-}]$	23	0.51	0.36	0.34	65	1.11	3.12	0.97
PEARL	$[Br^-]$	8	0.08	0.06	0.05	37	0.03	0.02	0.02
	$[Cl^-]$	8	25.22	20.67	14.22	38	7.70	5.46	7.01
	$[Ca^{2+}]$	8	1.41	1.48	1.09	42	1.91	0.95	1.65
	$[F^-]$	6	0.06	0.03	0.06	24	0.03	0.02	0.02
	$[K^+]$	7	0.36	0.29	0.25	37	0.19	0.08	0.20
	[MSA]	6	0.01	0.00	0.01	37	0.18	0.07	0.16
	[Acetate]	7	5.90	0.16	5.84	36	1.53	1.39	1.06
	[Formate]	8	6.34	3.15	8.03	39	0.51	0.10	0.56
	$[NH_4^+]$	2	1.50	0.54	1.50	43	0.72	0.60	0.47
	[Oxalate]	8	0.91	0.46	1.16	37	0.08	0.03	0.09
	$[Mg^{2+}]$	7	1.13	1.77	0.36	38	0.99	0.62	0.79
	$[Na^+]$	7	5.92	13.78	0.65	37	6.69	4.93	5.68
	$[NO_3^-]$	8	2.07	0.66	1.86	37	0.71	0.26	0.66
	$[SO_4^{2-}]$	8	0.94	0.40	0.87	41	1.75	0.89	1.64
	nss-$[Br^-]$	8	0.06	0.03	0.05	36	0.01	0.01	0.01
	nss-$[SO_4^{2-}]$	7	0.50	0.54	0.70	44	1.06	0.78	1.01
Creek	$[Br^-]$	12	0.06	0.01	0.06	27	0.63	0.58	0.41
	$[Cl^-]$	12	7.53	3.22	6.82	27	0.93	104.62	162.47
	$[Ca^{2+}]$	13	6.26	4.26	5.43	22	9.16	6.93	8.31
	$[F^-]$	12	0.03	0.02	0.03	27	0.25	0.16	0.21
	$[K^+]$	11	0.13	0.05	0.11	22	0.56	0.40	0.47
	[MSA]	10	0.24	0.14	0.28	18	0.01	0.01	0.01
	[Acetate]	12	6.59	0.71	6.45	23	5.87	0.05	5.86
	[Formate]	13	1.34	0.54	1.22	27	5.75	3.31	8.03
	$[NH_4^+]$	13	1.67	0.57	1.55	20	1.10	1.30	0.14
	[Oxalate]	13	0.17	0.02	0.16	27	0.97	0.41	1.17
	$[Mg^{2+}]$	13	1.44	1.12	1.23	23	5.14	5.06	3.96
	$[Na^+]$	12	5.22	2.32	4.55	23	15.76	13.32	14.08
	$[NO_3^-]$	13	1.45	0.52	1.46	25	4.15	0.75	4.03
	$[SO_4^{2-}]$	13	1.28	0.27	1.37	26	60.48	36.41	60.95
	nss-$[Br^-]$	11	0.05	0.01	0.05	27	0.56	0.54	0.39
	nss-$[SO_4^{2-}]$	12	0.97	0.19	0.96	26	58.02	35.58	54.43

Table S3. Statistical results for the ionic analysis of the 2019 snow samples at the Sea ice, Onshore, PEARL and 0PAL sites. Note that the airborne samples were collected by the mounted tray above the ground (~1 m at 0PAL and 11 m at PEARL). The units are μM.

		2019																			
		Airborne				0-0.2cm				0.2-0.5cm				0.5-1-5cm				Column average			
		n	mean	std	median	n	mean	std	median	n	mean	std	median	n	mean	std	median	n	mean	std	median
Sea ice	$[Br^-]$					40	0.40	0.20	0.37	51	3.03	4.14	0.84	36	9.31	5.14	10.72	66	6.47	5.36	5.79
	$[Cl^-]$					41	61.25	68.76	25.06	33	180.72	244.14	64.42	16	2887.67	2472.62	2718.74	33	1660.12	2080.86	510.54
	$[Mg^{2+}]$					36	9.68	12.49	4.46	43	168.88	213.56	57.26	17	264.31	221.14	392.24	46	202.59	196.83	78.13
	$[Na^+]$					38	29.52	32.25	14.98	34	149.80	197.82	43.99	12	1189.99	1470.62	320.53	19	390.39	304.56	382.34
	$[NO_3^-]$					37	3.46	1.55	3.50	61	4.83	2.32	5.15	61	2.90	1.18	2.88	75	2.67	1.18	2.56
	$[SO_4^{2-}]$					41	4.54	2.96	4.74	42	29.51	43.19	9.23	21	122.89	96.44	99.36	40	58.89	62.52	25.56
	nss-$[Br^-]$					39	0.35	0.20	0.34	32	0.24	0.19	0.19	8	0.58	0.77	0.20	17	0.22	0.18	0.14
	nss-$[SO_4^{2-}]$					39	2.52	1.53	2.89	28	1.85	2.73	1.24	8	3.12	3.01	2.42	19	1.54	2.67	0.69
Onshore	$[Br^-]$					38	0.40	0.17	0.37	58	0.38	0.22	0.31	64	0.97	0.86	0.53	104	0.99	0.93	0.49
	$[Cl^-]$					39	28.60	24.93	14.82	46	54.09	44.48	41.13	38	86.52	93.13	62.15	62	101.74	84.59	68.54
	$[Mg^{2+}]$					31	1.79	1.95	0.70	56	31.53	43.17	8.80	62	51.75	52.64	9.76	102	52.30	51.99	21.94
	$[Na^+]$					39	17.06	15.32	10.20	46	37.60	32.62	27.57	56	278.79	343.11	52.32	93	297.66	336.14	70.87
	$[NO_3^-]$					36	3.76	1.99	3.58	61	3.84	2.18	3.67	63	3.41	1.52	4.16	101	3.06	1.53	3.19
	$[SO_4^{2-}]$					42	4.11	2.41	4.38	51	6.06	4.86	5.01	64	14.67	11.49	8.61	104	14.98	11.47	11.49
	nss-$[Br^-]$					38	0.36	0.19	0.34	50	0.21	0.17	0.20	56	0.35	0.32	0.21	89	0.30	0.31	0.17
	nss-$[SO_4^{2-}]$					42	2.56	2.21	2.84	46	2.40	1.90	1.90	50	-1.36	10.17	1.47	91	-4.65	13.11	1.22
PEARL	$[Br^-]$	21	0.35	0.18	0.39	31	0.30	0.12	0.31	32	0.22	0.10	0.17	28	0.19	0.05	0.18	32	0.19	0.05	0.18
	$[Cl^-]$	19	26.82	12.14	22.87	33	17.71	6.54	18.59	57	120.88	115.60	47.27	58	127.37	88.05	52.73	66	117.73	85.33	51.17
	$[Mg^{2+}]$	19	2.06	1.92	1.11	32	1.04	0.67	0.84	56	13.23	14.65	3.84	58	13.39	11.26	5.37	66	12.29	10.82	4.37
	$[Na^+]$	19	19.86	9.75	17.65	34	11.80	5.20	10.84	56	85.49	79.83	36.53	58	93.06	63.96	43.03	66	87.62	61.60	40.15
	$[NO_3^-]$	18	2.23	1.37	2.29	23	1.24	0.50	1.13	51	1.29	0.63	1.00	58	1.42	0.63	1.15	57	1.42	0.64	1.12
	$[SO_4^{2-}]$	20	5.51	3.55	5.92	35	3.82	2.16	4.04	58	7.74	4.44	7.65	57	5.74	3.17	4.41	63	6.13	3.60	5.69
	nss-$[Br^-]$	21	0.28	0.20	0.23	31	0.28	0.12	0.29	33	0.00	0.13	-0.03	31	-0.05	0.08	-0.07	34	-0.05	0.08	-0.07
	nss-$[SO_4^{2-}]$	22	4.63	4.24	4.55	36	3.19	2.20	3.46	56	2.32	2.24	2.05	56	0.01	1.53	-0.10	58	0.18	1.74	-0.10
OPAL	$[Br^-]$	42	0.38	0.24	0.34	5	0.15	0.01	0.15	9	0.30	0.15	0.28	5	0.35	0.07	0.39	5	0.35	0.07	0.39
	$[Cl^-]$	42	57.33	55.82	35.20	6	44.90	47.59	27.38	9	86.66	53.97	108.75	5	99.09	49.44	69.82	5	99.09	49.44	69.82
	$[Mg^{2+}]$	38	6.13	6.48	4.00	3	9.11	5.68	7.80	9	9.77	7.56	13.16	5	11.80	7.26	7.71	5	11.80	7.26	7.71
	$[Na^+]$	41	36.99	38.42	23.25	6	31.33	34.37	19.07	9	62.31	39.36	80.94	5	70.64	34.89	50.67	5	70.64	34.89	50.67
	$[NO_3^-]$	40	3.41	2.05	2.81	3	0.96	0.21	0.91	8	2.16	1.07	1.82	5	2.02	0.23	2.07	5	2.02	0.23	2.07
	$[SO_4^{2-}]$	45	5.47	3.61	4.31	6	2.45	1.95	2.00	9	5.06	3.69	5.58	5	6.14	0.52	5.98	5	6.14	0.52	5.98
	nss-$[Br^-]$	40	0.24	0.19	0.18	6	0.10	0.07	0.14	9	0.18	0.11	0.12	5	0.22	0.12	0.31	5	0.22	0.12	0.31
	nss-$[SO_4^{2-}]$	44	2.17	2.37	2.46	4	0.56	0.10	0.59	9	1.32	1.90	0.28	5	1.90	1.75	3.08	5	1.90	1.75	3.08

Table S4 Geographic heterogeneity of snow ions (Na^+, NO_3^-, Br^- and nss[Br^-]) at each sampling site with snow samples randomly collected from a small area (2m × 2m) during two periods in 2019.

Period	Sites	Depth (cm)	Na^+		NO_3^-		Br^-		nss-Br^-	
			mean	std	mean	std	mean	std	mean	std
Feb 26-Mar 3, 2019	Sea ice	0.0-0.5	129.33	148.65	4.27	1.74	0.67	0.74	0.43	0.48
		0.5-1.5	336.12	316.92	2.96	0.94	7.67	5.51	0.98	0.97
	Onshore	0.0-0.5	26.13	21.04	2.27	0.71	0.30	0.13	0.25	0.13
		0.5-1.5	581.53	315.89	3.62	1.01	3.87	3.76	0.67	0.29
	PEARL	0.0-0.5	185.09	65.44	2.06	0.47	0.28	0.14	-0.05	0.07
		0.5-1.5	150.87	30.09	2.00	0.38	0.25	0.10	-0.02	0.08
Mar 4 & 5, 2019	Sea ice	0-0.2	-	-	1.98	0.34	0.38	0.04	-	-
		0.2-0.5	520.98	27.56	3.22	1.50	5.73	5.57	0.01	0.04
		0.5-1.5	-	-	1.77	0.19	12.91	-	-	-
	Onshore	0-0.2	32.39	0.64	-	-	0.12	0.00	0.06	0.00
		0.2-0.5	75.56	14.85	1.59	0.17	0.22	0.04	0.09	0.03
		0.5-1.5	49.31	9.41	1.92	0.58	0.23	0.02	0.14	0.03
	0PAL	0-0.2	71.22	25.51	1.19	0.00	0.14	0.02	0.01	0.03
		0.2-0.5	104.82	2.44	2.73	1.23	2.42	2.54	0.10	0.00
		0.5-1.5	-	-	-	-	-	-	-	-

Table S5 Regression analyses (i.e., number of observations, standard error of slope (μM), and *p*-values) for key linear models used in this study and associated with Figures 5, 6 and 7.

Figures	linear regressions	Sites	Number of observations	Standard error of slope (μM)	p-value
Figure 5	(d) $[Na^+]$ vs time	sea ice	11	0.65117	0.17666
		Onshore	11	1.3248	0.018913
		PEARL	2	-	-
	(e) $[NO_3^-]$ vs time	sea ice	11	0.031625	3.37E-05
		Onshore	11	0.07233	0.047092
		PEARL	2	-	-
	(f) $[Br^-]$ vs time	sea ice	11	0.0059219	0.31536
		Onshore	11	0.0058544	0.21431
		PEARL	2	0	-
	(g) nss-$[Br^-]$	sea ice	11	0.0054474	0.42219
		Onshore	11	0.0050932	0.8453
		PEARL	2	-	-
Figure 6	(d) Tray $[Na^+]$ vs time	PEARL	14	1.6482	0.19785
		OPAL	24	1.1562	0.47351
	(e) Tray $[NO_3^-]$ vs time	PEARL	12	0.06437	0.35704
		OPAL	24	0.07293	0.024153
	(f) Tray $[Br^-]$ vs time	PEARL	14	0.0038572	0.00091149
		OPAL	24	0.0057058	0.0010769
	(g) Tray nss-$[Br^-]$ vs time	PEARL	14	0.0056266	0.04216
		OPAL	24	0.0058292	0.00069418
Figure 7	(a) 0-0.2cm $[NO_3^-]$ vs time	Sea ice	21	0.10137	0.022069
		Onshore	20	0.12408	0.033649
		PEARL	13	0.033592	0.63919
	(b) 0.2-0.5cm $[NO_3^-]$ vs time	Sea ice	22	0.053913	0.00030065
		Onshore	21	0.062582	0.016509
		PEARL	18	0.013772	0.24503
	(c) 0.5-1.5cm $[NO_3^-]$ vs time	Sea ice	29	0.024566	0.027422
		Onshore	27	0.027371	0.0071189
		PEARL	26	0.0081262	7.64E-07
	(d) 0-0.2cm nss-$[Br^-]$ vs time	Sea ice	21	0.0096136	0.019895

		Onshore	20	0.0080688	0.010627
		PEARL	17	0.0035759	0.0048613
	(e) 0.2-0.5cm nss-[Br-] vs time	Sea ice	12	0.012075	0.17789
		Onshore	17	0.0088479	0.13183
		PEARL	10	0.0069285	0.035824
	(f) 0.5-1.5cm nss-[Br-] vs time	Sea ice	4	0.05373	0.1602
		Onshore	23	0.0070587	0.63092
		PEARL	13	0.0048105	0.9346

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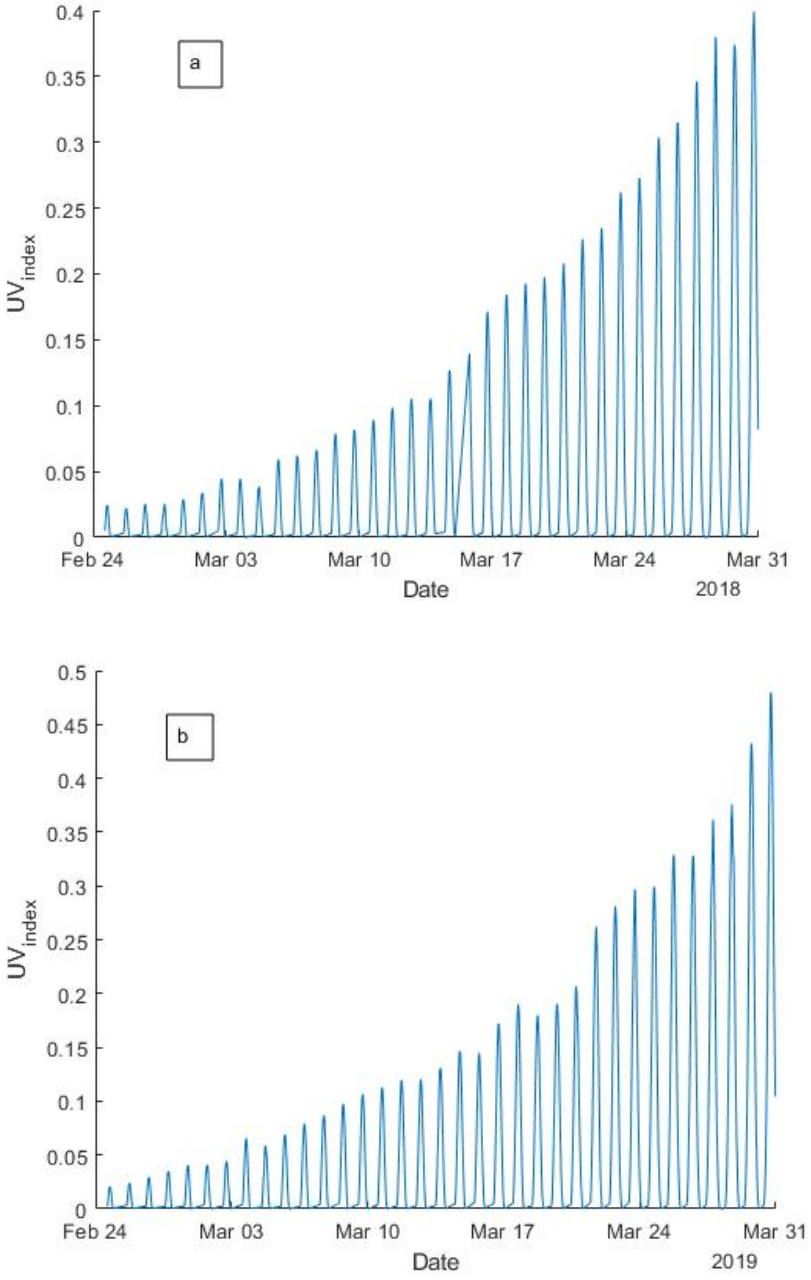

Figure S1. UV index at Eureka, Canada (79.989N, 85.934W, 8.7 m) during (a) March 24-31, 2018 and (b) March 24-31, 2019.

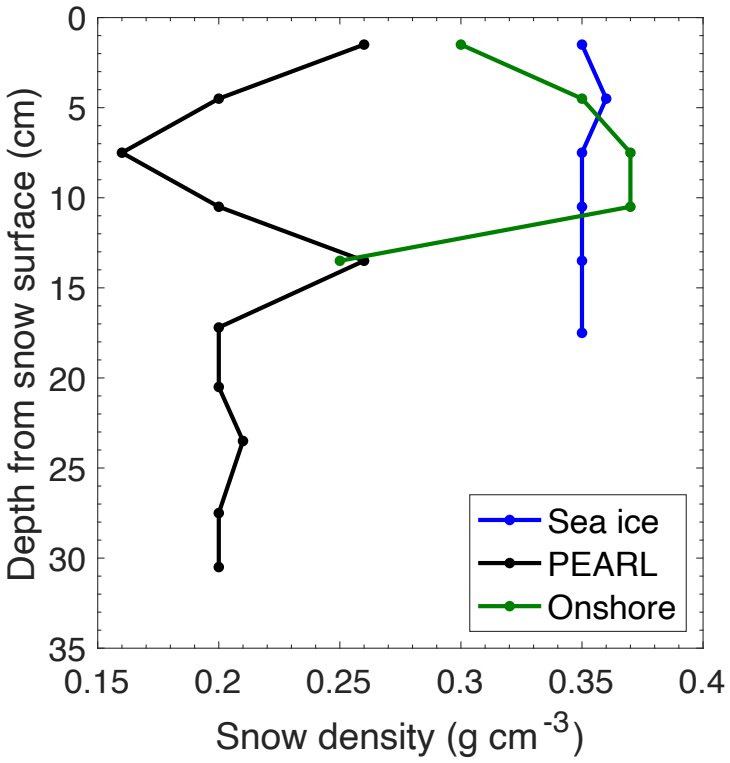

Figure S2. Snow density profiles measured in 2018 at the Sea ice, Onshore, and PEARL sampling sites (see Figure 1).

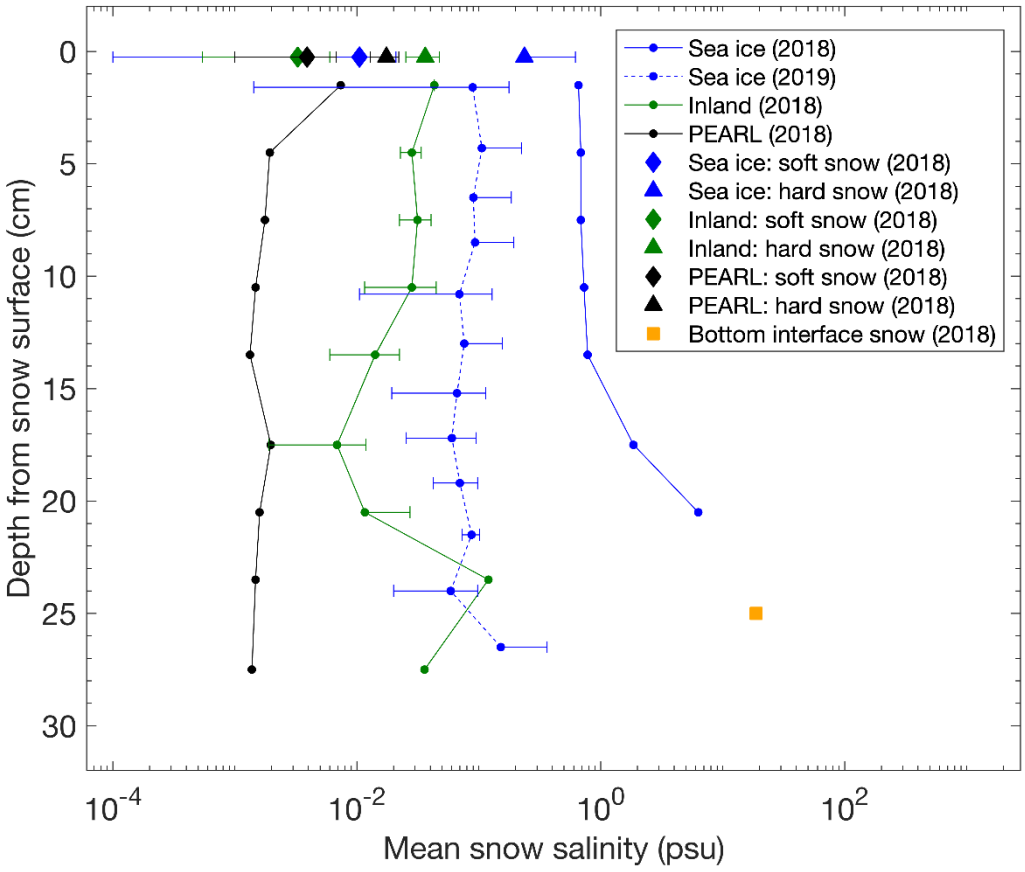

Figure S3. Snow salinity profiles in 2018 and 2019 samples. Top 0.5 cm snow sample mean salinities (collected in 2018) are plotted at a depth of 0.25 cm. At each site, two types of surface snow are collected: one is soft fluffy white colour snow and one is hard, light brown colour snow. The horizontal error bar represents one standard deviation value. 2019 sea ice profile includes only one column collected on Feb 27 at Sea ice site. 2018 inland profile includes two columns – one from Onshore and one from Creek site. The bottom interface snow-ice sample was collected on March 1 2018 at Sea ice site.

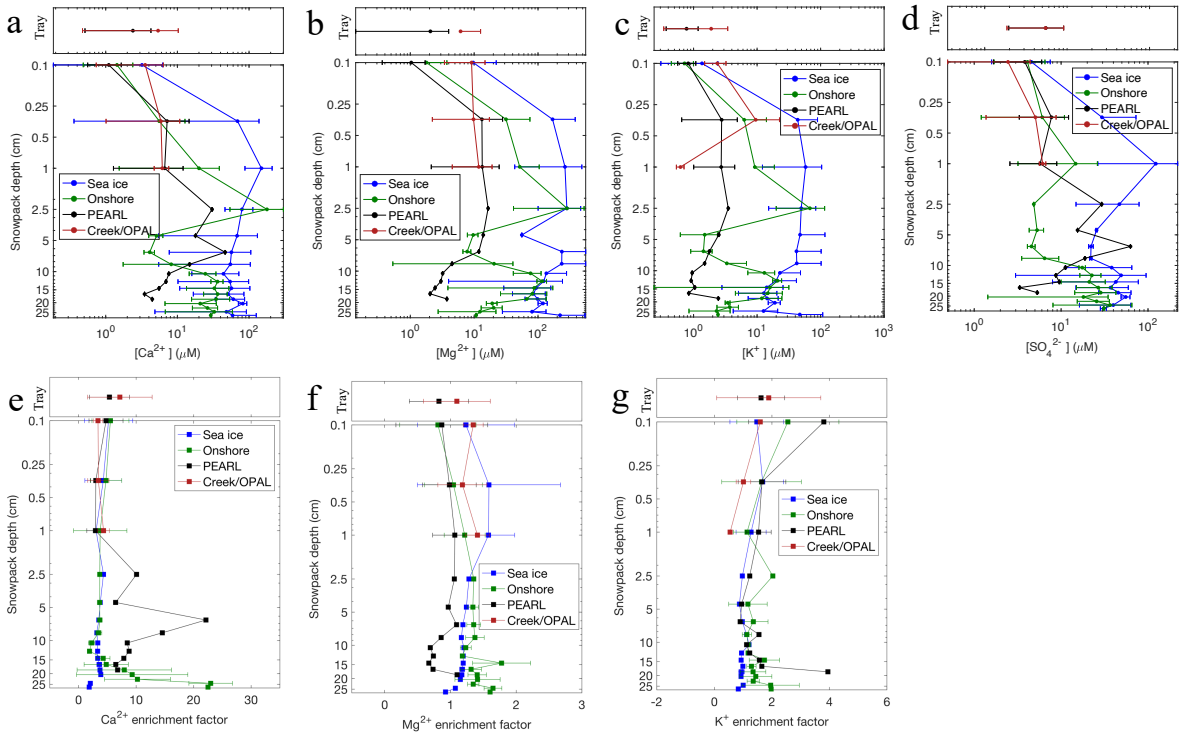

Figure S4. Vertical profiles of 2019 ions (a) [Ca^{2+}], (b) [Mg^{2+}], (c) [K^{+}], (d) [SO_4^{2-}], and enrichments of (e) [Ca^{2+}], (f) [Mg^{+}], and (g) [K^{+}] (see Section 3.2 for details).

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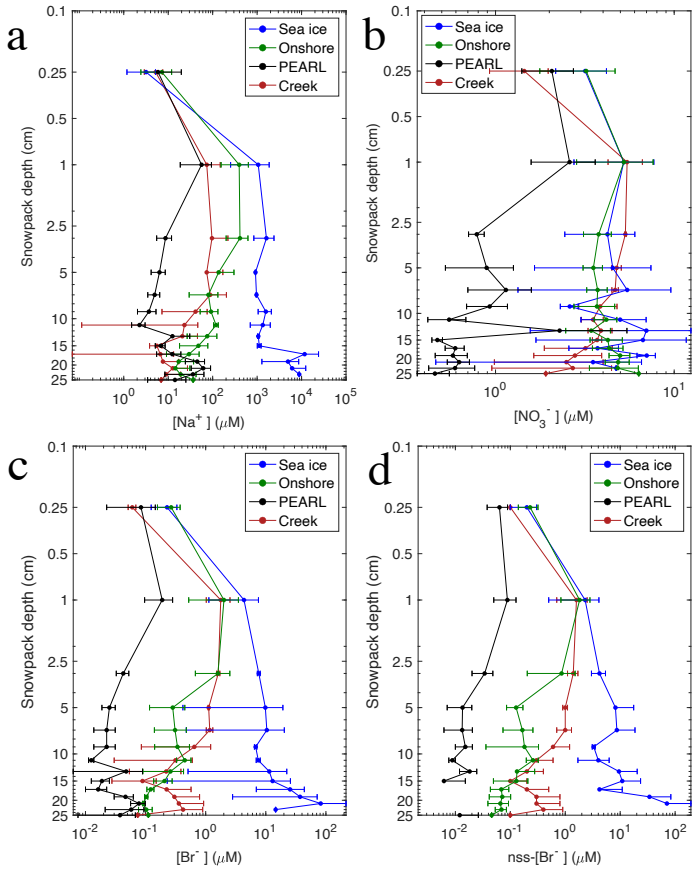

Figure S5. Vertical profiles of 2018 ions (a) [Na^+], (b) [NO_3^-], (c) [Br^-], and (d) nss[Br^-].

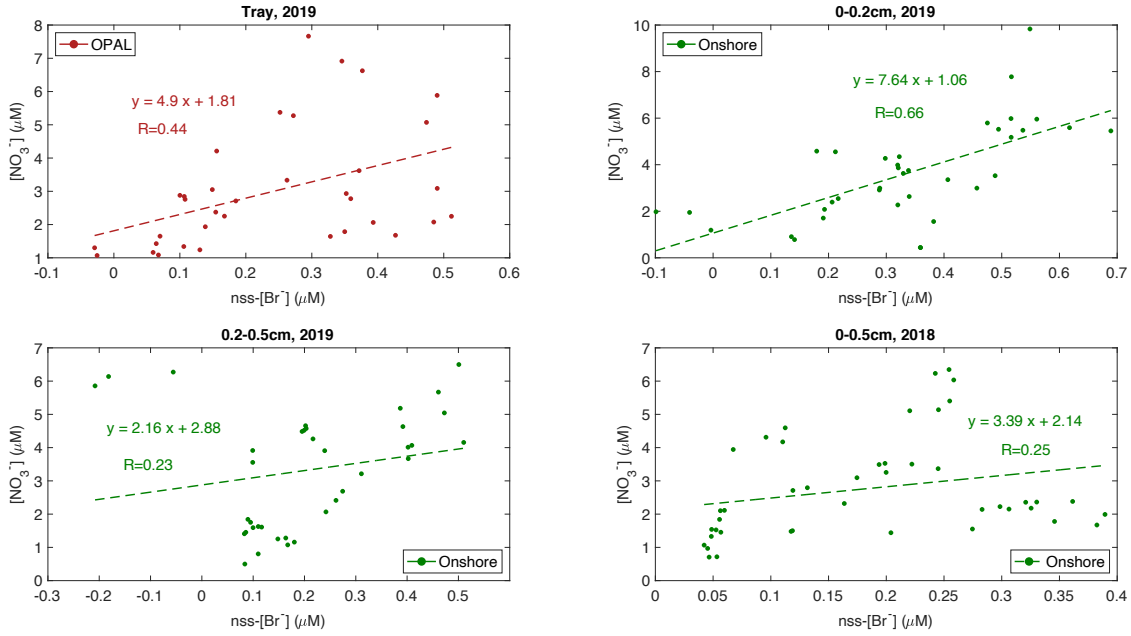

Figure S6. Same as Figure 7, except here nss[Br-] is used in the scatter plot and relationship analysis.