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Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers, even during conditions of high dissolved organic carbon and low flow

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Section S1. Tables

Table S1.1 Al_i terminology, speciation methodology, and trends from published studies. Several methods do not measure Al_i in situ, which can cause error due to changes in temperature, DOC and pH, which vary during transit to the lab. Increased pH and increased temperature in lab conditions can cause the underestimation of Al_i. Al_{nl}=non-labile Al, Al_{tm}=total monomeric Al, Al_{om}=organic monomeric Al, Al_{tr}=total reactive Al, Al_{nlm}=non-labile monomeric Al, Al_m=monomeric Al. CEC= Cation Exchange Column, ICP-AES= Inductively Coupled Plasma-Atomic Emission Spectroscopy. AWMN= Acid Waters Monitoring Network.

Al Species	**Definition**	**Analysis Method**	**Trend**	**Location**	**Reference**^{1}
Al_i	Inorganic Al	Colourimetry (Al_t-Al_{nl})	Decreasing Al_i from 1988-2008	AWMN in UK	Monteith et al. (2014)
Al_{im}	Inorganic monomeric Al	Colourimetry (Al_{tm}-Al_{om})	Decreasing Al_i from 2001-2011	New York, USA	Josephson et al. (2014)
Al_i	Ionic Al	CEC (Al_t-Al_o)	Mean NS Al_i=25.3 µg/L Mean NB Al_i=31.0 µg/L	Atlantic Canada	Dennis and Clair (2012)
Al_i	Ionic Al	Colourimetry	Decreasing Al_i in lakes	Norway	Hesthagen et al. (2011)
LA1	Inorganic Al (sum of inorganic and monomeric Al species)	ICP-AES, Flow injection, Pyrocatechol violet, and CEC (Al_{tr}-Al_{nl})	15% of LA1 samples were >10 µg/L	Norway	Kristensen et al. (2009)
Al-l	Labile/cationic/inorganic monomeric Al	Colourimetry (Al_{tm}-Al_{nlm})	Decreasing Al-l across the UK	AWMN in UK	Evans & Monteith (2001)
Al_{im}	Labile Al (free and inorganically complexed Al)	Van Benschoten method	Mean Al_{im} of 72 µg/L from 2009-2010	China	Wang et al. (2013)
Al_i	Inorganic monomeric	Colourimetry and CEC (Al_m-Al_o)	Al_i fraction decreased in catchments between 1991 & 2007	Czech Republic	Kram et al. (2009)
Al_i	Inorganic Al	AAS	Decreasing Al_i from 1990-2010	Adirondack Mountains, USA	Strock et al. (2014)

References for Table S1.1:

Dennis, I. F. and Clair, T. A.: The distribution of dissolved aluminum in Atlantic salmon (Salmo salar) rivers of Atlantic Canada and its potential effect on aquatic populations, Can. J. Fish. Aquat. Sci., 69, 1174-1183, 2012.

Evans, C. D. and Monteith, D. T.: Chemical trends at lakes and streams in the UK Acid Waters Monitoring Network, 1988-2000: Evidence for recent recovery at a national scale, Hydrology and Earth System Sciences Discussions, 5, 351-366, 2001.

Hesthagen, T., Larsen, B. M. & Fiske, P. (2011). Liming restores Atlantic salmon populations in acidified Norwegian rivers. Canadian Journal of Fisheries and Aquatic Sciences 68, 224–231.

Josephson, D. C., Robinson, J. M., Chiotti, J., Jirka, K. J. and Kraft, C. E.: Chemical and biological recovery from acid deposition within the Honnedaga Lake watershed, New York, USA, Environ. Monit. Assess., 186, 4391-4409, 2014.

Krám, P., Hruška, J., Driscoll, C. T., Johnson, C. E. and Oulehle, F.: Long-term changes in aluminum fractions of drainage waters in two forest catchments with contrasting lithology, J. Inorg. Biochem., 103, 1465-1472, 2009.

Kristensen, T., Åtland, Å, Rosten, T., Urke, H. A. and Rosseland, B. O.: Important influent-water quality parameters at freshwater production sites in two salmon producing countries, Aquacult. Eng., 41, 53-59, 2009.

Monteith, D. T., Evans, C. D., Henrys, P. A., Simpson, G. L. and Malcolm, I. A.: Trends in the hydrochemistry of acid-sensitive surface waters in the UK 1988–2008, Ecol. Ind., 37, 287-303, 2014.

Strock, K. E., Nelson, S. J., Kahl, J. S., Saros, J. E. and McDowell, W. H.: Decadal trends reveal recent acceleration in the rate of recovery from acidification in the northeastern US, Environ. Sci. Technol., 48, 4681-4689, 2014.

Wang, D., He, Y., Liang, J., Liu, P. and Zhuang, P.: Distribution and source analysis of aluminum in rivers near Xi’an City, China, Environ. Monit. Assess., 185, 1041-1053, 2013.

Table S1.2 Raw sample data. RL: rising limb of hydrograph, FL: falling limb of hydrograph, and BF: base flow. Air temperature (T_a) data were collected from the Kejimkujik 1 weather station (Climate ID: 8202592; 44.24’11.020 ºN, 65.12’11.070 ºW) for MR, MPB, PMB, and MB, and the Stanfield Airport weather station (Climate ID: 8202251; 44°52'52.000" N, 63°30'31.000" W) for CC, KB, ALD, BLB, UKR, and LR. Missing T_a data were replaced with data from another local meteorological tower located one kilometer to the northwest of the MPB site (44.469549, -65.061295).

Site	**Date**	**Al$_i$ (μg L^{-1})**	**Al$_o$/Al$_d$ (%)**	**Season**	**Al$_d$ (μg L^{-1})**	**Ca (μg L^{-1})**	**DOC (mg L^{-1})**	**SO$_4$ (μg L^{-1})**	**pH (unit)**	**T$_w$(°C)**	**T$_a$ (°C)**	**Discharge (m^3 s^{-1})**	**Runoff (mm day^{-1})**	**Hydrograph Stage**
ALD	2016-04-29	19	87.7	1	155	591	7	899	4.67	6.8	4			
ALD	2016-05-19	12	94.1		202	800	10.7	1414	5.89		12.0			
ALD	2016-06-03	25	90.7	2	268	722	12.5	639	5.02	16.6	13.2			
ALD	2016-06-16	32	88.3	2	274	674	12.9	578	4.99	13.2	13			
ALD	2016-06-28	28	89.4	2	265	720	12.2	959	5.26	22.1	24.2			
ALD	2016-07-15	37	87	2	285	792	15	761	5.11	20.7	19.6			
ALD	2016-08-05	48	79.9		239	700	19.4	1414	5.98		21.2			
ALD	2016-09-10	48	78.2		220	1000	14.8	2000	5.03		20.8			
ALD	2016-10-02	13	92.3		169	1000	14.4	3000	5.27		11.4			
ALD	2016-11-19	44	82		245	900	14.6	1414	5.03		7.6			
ALD	2017-04-19	27	81.1	1	143	600	10.4	1209	4.55	7.8	3.2			
ALD	2017-05-14	69	61	2	177	600	12.1	923	4.92	13.4	4			
ALD	2017-05-30	37	85.8	2	261	600	11.8	2536	4.77	14.3	12.2			
ALD	2017-06-22	100	59.8	2	249	700	15.2	1414	5.17	22.8	25			
ALD	2017-07-13	62	80.3	2	315	800	19.3	1414	5.24	20.6	18.5			

ALD	2017-08-01	26	89	2	236	800	15.1	1414	4.96	25.6	28.4
ALD	2017-08-23	35	84.4	2	224	700	13.2	1125	5.14	21.8	21
ALD	2017-09-16	77	82.5	2	439	1000	23.5		4.73	20.7	18.7
ALD	2018-05-10	46	75.7		189	700	8.8	1414	5.64		7.5
ALD	2018-06-07	43	83.8		266	700	16.1	1414	5.13		11.0
ALD	2018-07-05	119	62.5		317	800	13.6	1414	5.61		23.8
ALD	2018-11-23	50	76		208	800	10.1	1414	5.45		-9.1
BLB	2016-04-29	20	89.5	2	190	476	7.2	936	5.03	5.7	4
BLB	2016-06-03	60	82.1	4	336	770	11.9	669	4.78	10.1	13.5
BLB	2016-06-16	33	91.2	4	373	789	13.2	1158	4.77	9.8	13
BLB	2016-06-28	26	93.3	4	388	894	13.6	1251	4.67	13.1	23.9
BLB	2016-07-15	42	90.5	4	443	887	16.7	723	4.77	14.3	18.7
BLB	2016-08-05	6	98.6		429	1000	26.2	1414	5.29		21.2
BLB	2016-09-10	81	77.1		354	900	48.3	1414	4.87		20.8
BLB	2016-10-02	33	90.1		335	1000	18.5	2000	5.1		11.4
BLB	2016-11-19	28	92.6		379	1000	17.2	1414	4.76		7.6
BLB	2017-04-19	41	79.1	4	196	600	9.6	1927		4.2	4
BLB	2017-05-14	46	82.6	4	264	800	12.9	1550		7.7	6
BLB	2017-05-30	36	88.3	4	308	700	11.3	1795		8.4	14.9
BLB	2017-06-22	110	70.1	4	368	800	14.9	1414	4.8	17.3	24.6
BLB	2017-07-13	50	88.3	4	427	900	17.6	1414	4.87	15.8	17

BLB	2017-08-01	37	90.7	4	396	800	17.9	1414	4.7	20.6	29
BLB	2017-08-23	54	85.8	3	381	1000	17.1	1172	4.94	18.3	21
BLB	2017-09-16	34	91.9	4	420	1000	17.3		4.52	16.6	18.9
BLB	2018-05-10	37	85.5		256	700	8.5	1414	5.16		7.5
BLB	2018-06-07	86	75		344	800	15.7	1414	5.29		11.0
BLB	2018-07-05	83	80.3		421	900	13.8	1414	5.42		23.8
BLB	2018-10-02	104	67.4		319	1600	12.4	1414	5.04		7.7
BLB	2018-11-23	24	93.5		367	70.7	10.5	1414	4.8		-9.1
CC	2016-06-03	32	91.9	4	397	501	15.2	385	4.66	11.2	13.5
CC	2016-06-16	46	88.9	4	413	520	17.7	304	4.71	10.4	12.8
CC	2016-06-28	107	78.9	4	507	537	21	401	4.82	14.8	24.2
CC	2016-07-15	53	89.9	4	524	642	26	208	4.6	14.6	18.7
CC	2016-08-05	140	68.6		446	400	29.3	1414	5.73		21.2
CC	2016-09-10	32	86.9		244	400	22.2	1414	4.72		20.8
CC	2016-10-02	34	85.5		234	900	28.8	1414	4.95		11.4
CC	2016-11-19	27	94.9		527	2100	24.9	1414	6.11		7.6
KB	2016-04-29	14	90.6	2	149	1110	5.7	1061	5.69	8.2	4
KB	2016-06-03	20	92.5	2	267	459	9.9	611	4.89	14.1	13.5
KB	2016-06-16	38	87.7	2	310	515	11.3	852	4.9	12.3	10.8
KB	2016-06-28	28	91.3	2	323	486	11.7	887	5.06	17.8	24.5
KB	2016-07-15	41	88.5	2	356	535	15.6	621	5.03	18.7	18.7

LR	2016-08-05	27	50		54	1100	5.7	1414	6.03		21.2
LR	2016-09-10	3	92.1		38	800	4.4	1414	6.07		20.8
LR	2016-10-02	6	95.2		124	900	10.1	2000	5.76		11.4
LR	2017-04-19	4	96.6	1	116	600	7.1	1416	4.87	6	1.7
LR	2017-05-14	20	84.6	2	130	600	8.1	1213	4.95	12.3	6
LR	2017-05-30	17	89	2	154	600	8.6	1572	5.21	15	12.5
LR	2017-06-22	34	69.9	2	113	700	8.2	1414	5.51	19.6	19
LR	2017-07-13	12	88.7	2	106	600	6.4	1414	5.54	21.8	18
LR	2017-08-01	2	96.9	2	65	600	6.6	1414	5.1	19.6	24.8
LR	2017-08-23	5	88.4	2	43	600	4.1	1371	5.37	21.6	21.3
LR	2017-09-16	5	94.9	2	99	700	6.7	1414	5.01	19.4	15.8
LR	2018-05-10	35	74.1		135	800	6.7	1414	5.54		7.5
LR	2018-06-07	26	84.0		162	900	8.2	1414	5.55		11.0
MB	2016-05-27	30	88.9	2	270	1200	6.8	1278	5.14	9.8	12
MB	2016-06-15	15	94.2	2	260	1590	8.4	1497	5.61	11.2	14.6
MB	2016-06-27	27	90.5	2	284	1610	7.6	1851	5.28	16.3	16.7
MB	2016-07-14	40	86.9	2	305	1780	6.4	1747	5.4	15.5	28.5
MB	2017-04-20	25	89.8	1	246	848	7	1996	4.86	2.3	4
MB	2017-05-13	48	84.1	1	302	977	7.2	1385	4.76	9.1	17
MB	2017-05-29	40	87.9	2	330	1100	9	1977	4.99	9.1	14.5
MB	2017-06-21	96	81.2	2	510	1480	15.8	551	5.18	13.7	23.3

MB	2017-07-12	46	87.7	2	375	1320	11.5	28968	5.13	15.8	25.9			
MB	2017-07-31	43	87.7	2	351	1470	12.1	1629	5.08	15.6	27.4			
MB	2017-08-22	80	85.7	2	560	1500	21	828	4.91	15.5	27.6			
MB	2017-09-17	30	89.3	3	280	1600	11	1258	5.14	14.7	23			
MPB	2015-04-22	2	97.1	1	77	323	4.3	1009			7.3	6.41	34.992	RL
MPB	2015-04-30	4	95.9	1	88	379	5.4	1272	4.77	3.5	4.5	1.49	8.134	FL
MPB	2015-05-06	5	95.8	1	120	446	6.6	1304			14	0.76	4.149	BF
MPB	2015-05-13	5	96.8	2	158	498	8.2	958	5.18	13.6	7	0.36	1.965	RL
MPB	2015-05-20	1	99.4	2	170	621	9.3	815	5.25	10.4	12	0.23	1.256	RL
MPB	2015-05-27	5	97.2	2	177	567	10.4	699	5.39	14.1	21	0.15	0.819	RL
MPB	2015-06-03	13	95	2	260	710	17.3	639	5.03	9.2	8	1.27	6.933	RL
MPB	2015-06-10	17	92.8	2	236	651	13.6	443	5.24	14.6	10	0.32	1.747	RL
MPB	2015-06-17	28	88.3	2	239	751	15.6	560	5.15	14.6	16	0.2	1.092	RL
MPB	2015-06-24	18	93.4	2	271	751	19	357	5	13.2	18	1.38	7.533	RL
MPB	2015-07-02	42	83.8	2	259	705	17.6	322	5.05	16.9	20	0.29	1.583	BF
MPB	2015-07-08	19	92.3	2	247	724	16.4	400	5.24	19.4	23	0.07	0.382	BF
MPB	2015-07-15	19	92.3	2	248	710	17	464	5.18	20.1	18	0.05	0.273	BF
MPB	2015-07-22	21	91.5	2	247	756	16.3	552	5.36	18.4	17	0.05	0.273	RL
MPB	2015-07-29	18	92.5	2	240	912	18.2	1146	5.29	17.7	19	0.15	0.819	RL
MPB	2015-08-05	15	93.9	2	244	863	19	650	5.35	21.5	19	0.04	0.218	FL
MPB	2015-08-12	25	88.2	2	211	798	16.5	618	5.37	18.9	21	0.04	0.218	RL

MPB	2015-08-19	36	85.4	2	247	941	16.3	721	4.83	21.2	24	0.02	0.109	BF
MPB	2015-08-26	20	91.1	2	224	761	10	607	5.26	21.1	16	0.02	0.109	BF
MPB	2015-09-02	26	87.5	3	208	760	14.7	711	4.9	17.4	21	0.02	0.109	BF
MPB	2015-09-09	18	90.8	3	196	722	14.5	823	5.2	18.5	20		0	RL
MPB	2015-09-16	20	92	3	250	1330	13	4375	5.13	16.5	19	0.08	0.437	BF
MPB	2015-09-23	35	88.2	3	297	1320	20	2598	5	14.3	17	0.02	0.109	BF
MPB	2015-09-30	32	88.1	3	268	1170	18.1	1902	4.87	15.7	19		0	BF
MPB	2015-10-07	48	88.9	3	434	1900	28	2576	4.81	10.3	13	0.15	0.819	BF
MPB	2015-10-14	28	92.8	3	390	1560	24	1963	4.83	12.7	16	0.36	1.965	RL
MPB	2016-04-28	14	90.1	1	141	573	7.1	800	4.9	6.6	4	0.15	0.819	RL
MPB	2016-05-27	20	91.7	2	240	740	14	489	4.79	14.2	12	0.15	0.819	RL
MPB	2016-06-15	14	94.6	2	257	775	15.7	478	4.89	12.7	14.1	0.07	0.382	FL
MPB	2016-06-27	21	92.4	2	275	778	17.2	587	4.93	18	27	0.01	0.055	FL
MPB	2016-07-14	16	92.9	2	225	828	15	1447	4.86	15.5	20	0.03	0.164	FL
MPB	2017-04-20	9	94.5	1	163	595	9.4	1625	4.65	5	1		0	
MPB	2017-05-13	11	95.2	1	229	712	11.5	1430	4.54	10.4	17	0.79	4.313	FL
MPB	2017-05-29	10	96.2	1	260	790	13	1567	4.74	10.9	12	0.44	2.402	FL
MPB	2017-06-21	46	86.5	1	341	901	17.8	226	4.73	16.8	24.2	0.32	1.747	FL
MPB	2017-07-12	27	93	2	384	1060	22.3	229	4.96	19.5	25.9	0.05	0.273	FL
MPB	2017-07-31	23	92.4	2	303	972	22.8	724	4.65	17.8	27	0.02	0.109	FL
MPB	2017-08-22	40	91.3	2	460	1300	30	255	4.54	16.9	28.4	0.62	3.385	FL

MPB	2017-09-17	40	90.5	3	420	1300	30	301	4.6	17.3	20.1	0.1	0.546	FL
MR	2015-04-22	12	90.2	1	122	648	5.9	1321			7.3	58.61	1.837	RL
MR	2015-04-30	2	98	1	102	500	5.6	1189	5	4.2	4.5	33.03	1.454	FL
MR	2015-05-06	9	91.8	1	110	527	4.8	1112			14	22.33	1.269	BF
MR	2015-05-13	10	91.8	1	122	517	5.5	1117	5.23	13.3	7	12.05	1.048	FL
MR	2015-05-20	9	92.3	1	117	574	5.3	1101	5.19	14.2	12	6.95	0.912	FL
MR	2015-05-27	7	94.1	1	118	548	5.8	1161	5.28	15.7	21	4.53	0.835	FL
MR	2015-06-03	16	89.2	2	148	629	6.6	1069	5.35	12.7	8	8.42	0.946	RL
MR	2015-06-10	39	74.2	2	151	590	6.2	1220	5.33	17.4	10	7.8	0.934	RL
MR	2015-06-17	24	83.1		142	575	6.1	1175	5.39	19.2		4.98	0.858	
MR	2015-06-24	26	86.2		188	647	8.8	968	5.3	16.6		10.58	1.028	
MR	2015-07-02	35	82.1	2	196	602	8.1	897	5.25	19.9	20	10.94	1.018	BF
MR	2015-07-08	35	80.2	2	177	713	7.3	972	5.37	23.1	23	5.14	0.864	BF
MR	2015-07-15	23	87	2	177	593	7.9	959	5.46	24.5	18	2.9	0.76	BF
MR	2015-07-22	17	90.4	2	177	652	7	1011	5.49	21.9	17	1.9	0.701	BF
MR	2015-07-29	24	85.3	2	163	611	7.7	1146	5.54	21.2	19	2.45	0.735	RL
MR	2015-08-05	30	82	2	167	670	7.5	1077	5.65	25.2	19	1.46	0.671	FL
MR	2015-08-12	13	91	2	145	629	6.5	1094	5.43	22	21	1.53	0.686	RL
MR	2015-08-19	23	86.9	2	176	641	7.4	1097	5.48	25.3	24	0.96	0.632	BF
MR	2015-08-26	42	83.9	2	261	808	9	1179	5.33	24.1	16	4.47	0.731	BF
MR	2015-09-02	34	87.5	3	271	859	12.3	1168	5.3	21.5	21	1.59	0.681	BF

MR	2015-09-09	22	90.4	3	229	751	10.2	776	5.47	22.3	20	0.93	0.63	BF
MR	2015-09-16	34	87	3	261	828	12.5	1108	5.2	18.9	19	3.2	0.781	BF
MR	2015-09-23	13	94.7	3	246	675	11.3	900	5.34	18.3	17	3.44	0.789	BF
MR	2015-09-30	31	86.2	3	225	662	9.6	911	5.05	18.6	19	2.3	0.733	BF
MR	2015-10-07	21	91.3		241	794	10.7	989	4.87	13		5.16	0.869	
MR	2015-10-14	24	90.7	3	257	824	11.4	1166	4.87	14.1	16	6.26	0.905	RL
MR	2015-10-21	25	89.5	3	237	735	9	890	4.91	8.9	5	4.83	0.855	BF
MR	2015-10-28	22	91.3	3	253	837	10	1153	4.95	6.9	3	3.98	0.814	FL
MR	2015-11-04	25	91.3	3	286	945	14.4	967	4.7	7.9	7	8.1	0.947	RL
MR	2015-12-02	20	92.4	3	262	946	12	1139	4.73	3.2	6	17.96	1.183	FL
MR	2016-01-05	30	88.9	3	270	880	11	1245			-20	9.62	0.998	FL
MR	2016-02-02	18	91.7	3	217	875	10.1	1290	4.62	0.2	-3	7.75	0.926	RL
MR	2016-02-23	14	92	1	175	651	7.9	1316	4.59	0.8	-6	18.21	1.2	BF
MR	2016-03-29	13	91.1	1	146	606	6.1	1060	4.65	4.2	2	19.81	1.248	RL
MR	2016-04-28	13	91	1	145	572	6	937	4.75	10.2	4	5.85	0.892	FL
MR	2016-05-27	12	92.3	1	156	635	6.8	922	4.98	16.8	12	3.11	0.81	FL
MR	2016-06-15	12	92.3	1	155	595	6.7	1217	5.1	15.7	14.4	2.05	0.773	FL
MR	2016-06-27	16	89.5	2	153	624	6.8	1263	5.24	22.7	24	1.04	0.649	FL
MR	2016-07-14	8	94	2	134	654	6.4	1697	5.42	15	16	0.68	0.635	BF
MR	2017-04-20	22	87.3	3	173	692	5.3	1625	4.56	8.5	1	13		FL
MR	2017-05-13	27	86.3	3	197	683	10.5	1437	4.7	13.4	13	20.5	1.28	FL

MR	2017-05-29	20	91.3	3	230	810	9	1774	4.87	13.9	10.4	7.08	0.905	FL
MR	2017-06-21	63	74.2	2	244	752	10.1	458	5.17	19.4	20.2	5.42	0.881	FL
MR	2017-07-12	32	87.4	2	254	729	10	982	5.15	22.9	23.9	3.55	0.813	FL
MR	2017-07-31	50	76.7	2	215	766	9.88	1116	5.13	22.5	24.9	1.37	0.665	FL
MR	2017-08-22	20	93.5	3	310	910	15	861	4.92	20.4	25.5	5.26	0.878	FL
MR	2017-09-17	20	92	3	250	890	15	817	4.84	20.6	17.3	1.98	0.715	FL
PMB	2015-05-27	2	98.4	2	128	742	7.2	845	5.62	12.6	21			
PMB	2015-06-03	6	95.7	2	138	586	8.8	1042	5.28	12.2	8			
PMB	2016-04-28	6	93.6	2	93	675	3.6	1244	5.25	8.2	4			
PMB	2016-05-27	35	78.1	2	160	900	8	691	4.93	12.7	12			
PMB	2016-06-15	5	96.7	2	151	1150	8.1	1229	5.14	10.9	14.2			
PMB	2016-06-27	5	94.3	2	82	1570	5.4	3167	5.35	14	24			
PMB	2016-07-14	10	89.3	2	96	1770	6.9	5652	5.4	15	12			
PMB	2017-04-20	4	96.5	1	114	71	5.3	2234	4.78	8.5	2			
PMB	2017-05-13	11	92.1	1	139	71	6.2	1328	4.69	9.8	16			
PMB	2017-05-29	10	93.8	2	160	730	7	2405	5.03	13.9	10.8			
PMB	2017-06-21	32	85.6	2	222	955	11.1	289	4.98	15.5	21.4			
PMB	2017-07-12	35	80.3	2	178	1580	10.7	1428	5.21	16	24.6			
PMB	2017-07-31	1	99.3	2	148	1780	13	2746	4.99	13.8	25.6			
PMB	2017-08-22	20	90.9	3	220	960	13	571	4.85	16.4	26.9			
PMB	2017-09-17	20	90	3	200	990	15	640	4.7	16	17.8			
UKR	2016-05-19	21	89.7		203	700	10.4	1414.2	5.83		12.0			

UKR	2016-08-05	18	88.5		157	700	15.1	1414.2	5.56		21.2
UKR	2016-09-10	16	89.9		158	100	12.1	1414.2	5.58		20.8
UKR	2016-10-02	15	91.8		182	900	13.8	1414.2	5.77		11.4
UKR	2016-11-19	41	84.4		262	1100	15.1	2000	4.89		7.6
UKR	2017-04-19	38	72.3	3	137	500	9.5	1292		7.3	3.4
UKR	2017-05-14	24	87.2	2	187	600	12.6	1049		12.9	6
UKR	2017-05-30	37	83.3	2	221	600	9.8	1115		15.2	12.5
UKR	2017-06-22	66	67.5	2	203	800	12.1	1414	5.22	23.4	24.2
UKR	2017-07-13	47	85.4	2	322	800	17.6	1414	5.21	22.3	19
UKR	2017-08-01	26	89.1	2	239	800	15	1414	5.29	25.6	29.1
UKR	2017-08-23	74	65.6	2	215	700	12.8	889	5.31	21.8	21.1
UKR	2017-09-16	76	82	2	422	1000	20.6		4.77	20.8	19.2
UKR	2018-05-10	37	78.1		169	600	8.2	1414.2	5.31		7.5
UKR	2018-06-07	59	73.3		221	700	12.9	1414.2	5.34		11.0
UKR	2018-07-05	99	66.3		294	800	12.2	1414.2	5.46		23.8
UKR	2018-10-02	47	77.3		207	1100	10.5	1414.2	5.78		7.7
UKR	2018-11-23	43	81.1		227	800	10.8	1414.2	4.81		-9.1

Table S1.3 Generalized linear mixed model (GLMM) results for complete field data.

Fixed Effect	Parameter Estimate	Wald t Test Statistic	P-Value	AIC
Ca	0.281	1.551	0.121	1316.9
DOC	0.536	3.285	**0.001**	
F	-0.04	-0.79	0.429	
NO3	0.068	3.269	**0.001**	
pH	-1.123	-0.952	0.341	
SO4	-0.295	-3.038	**0.002**	
Tw	0.34	1.551	**0.046**	
DOC	0.321	5.647	**0**	1946.3
DOC	0.149	4.954	**0**	1816.7
NO3	0.417	2.721	**0.007**	
SO4	-0.417	-2.667	**0.008**	
DOC	0.256	6.908	**0**	1837.2
NO3	0.12	3.335	**0**	
DOC*NO3	1.1	4.545	**0**	
Tw	0.548	4.574	**0**	1467.8
DOC	1.135	3.445	**0**	1438.2
Tw	0.678	2.215	**0.027**	
DOC*Tw	-0.470	0.109	0.109	
DOC	0.623	6.391	**0**	1438.6
Tw	0.24	1.943	*0.052*	

-significant parameters at the 5% significance level are bolded

-significant parameters at the 10% significance level are italicized

-Effect connected by "*" represent an interaction term.

Table S1.4 Linear correlation r^2 values and significance ($\alpha = 0.05$) between Al_i/Al_d and other water chemistry parameters across all sites.

Variable	**Unit**	**Correlation with Al_i/Al_d (R^2)**	**Significance (p-value)**
Al_d	µg L⁻¹	0.007	0.247
Ca	µg L⁻¹	0.001	0.676
DOC	mg L⁻¹	0.007	0.247
pH	unit	0.077	0.000
Water Temp.	°C	0.114	0.000
F^+	µg L⁻¹	0.003	0.537
NO_3^-	µg L⁻¹	0.002	0.624
SO_4^{2-}	µg L⁻¹	0.000	0.952

Table S1.5 Kendal-tau correlation and significance ($\alpha = 0.05$) between Al_i and other water chemistry parameters for each study site. One Al_i outlier removed for MR calculations (value: 2 µg L^{-1}, date: 30 April 2015).

Site	Variable	Unit	Correlation Slope	Significance (p-value)
ALD	Ald	µg L^{-1}	0.29	0.044
	Ca	µg L^{-1}	0.22	0.143
	DOC	mg L^{-1}	0.36	0.013
	pH	unit	0.19	0.190
	Water Temp.	°C	0.32	0.093
	F^+	µg L^{-1}	0.182	0.533
	NO_3^-	µg L^{-1}	0.600	0.142
	SO_4^{2-}	µg L^{-1}	-0.037	0.876
BLB	Ald	µg L^{-1}	0.03	0.852
	Ca	µg L^{-1}	0.17	0.238
	DOC	mg L^{-1}	0.08	0.575
	pH	unit	0.07	0.622
	Water Temp.	°C	0.35	0.099
	F^+	µg L^{-1}	-0.036	0.901
	NO_3^-	µg L^{-1}	-0.109	0.708
	SO_4^{2-}	µg L^{-1}	-0.184	0.468
CC	Ald	µg L^{-1}	0.11	0.708
	Ca	µg L^{-1}	-0.22	0.451
	DOC	mg L^{-1}	0.25	0.383
	pH	unit	-0.04	0.901
	Water Temp.	°C	0.67	0.174
	F+	µg L^{-1}		
	NO_3^-	µg L^{-1}		
	SO_4^{2-}	µg L^{-1}		
KB	Ald	µg L^{-1}	0.800	0.050
	Ca	µg L^{-1}	0.200	0.624
	DOC	mg L^{-1}	0.800	0.050
	pH	unit	-0.200	0.624
	Water Temp.	°C	0.600	0.142
	F+	µg L^{-1}	0.800	0.050
	NO_3^-	µg L^{-1}		

	SO_4^{2-}	µg L^{-1}	-0.400	0.327
LR	Ald	µg L^{-1}	0.37	0.047
	Ca	µg L^{-1}	0.24	0.226
	DOC	mg L^{-1}	0.25	0.189
	pH	unit	0.19	0.319
	Water Temp.	°C	0.02	0.937
	F+	µg L^{-1}		
	NO_3^-	µg L^{-1}	-0.333	0.348
	SO_4^{2-}	µg L^{-1}	0.105	0.801
MB	Ald	µg L^{-1}	0.739	0.001
	Ca	µg L^{-1}	-0.062	0.783
	DOC	mg L^{-1}	0.400	0.073
	pH	unit	-0.279	0.214
	Water Temp.	°C	0.125	0.580
	F+	µg L^{-1}	-0.028	0.917
	NO_3^-	µg L^{-1}	-0.182	0.533
	SO_4^{2-}	µg L^{-1}	-0.463	0.050
MPB	Ald	µg L^{-1}	0.550	0.000
	Ca	µg L^{-1}	0.580	0.000
	DOC	mg L^{-1}	0.574	0.000
	pH	unit	-0.169	0.146
	Water Temp.	°C	0.280	0.016
	Runoff	mm day^{-1}	-0.232	0.042
	F+	µg L^{-1}	0.239	0.042
	NO_3^-	µg L^{-1}	0.190	0.160
	SO_4^{2-}	µg L^{-1}	-0.206	0.067
MR	Ald	µg L^{-1}	0.459	0.000
	Ca	µg L^{-1}	0.317	0.002
	DOC	mg L^{-1}	0.382	0.000
	pH	unit	0.097	0.362
	Water Temp.	°C	0.285	0.007
	RunOff	mm day^{-1}	-0.108	0.291
	F+	µg L^{-1}	0.139	0.188
	NO_3^-	µg L^{-1}	0.086	0.450
	SO_4^{2-}	µg L^{-1}	-0.127	0.215
PMB	Ald	µg L^{-1}	0.46	0.019

	Ca	µg L^{-1}	0.01	0.960
	DOC	mg L^{-1}	0.21	0.295
	pH	unit	-0.23	0.232
	Water Temp.	°C	0.36	0.065
	F+	µg L^{-1}	-0.063	0.782
	NO_3^-	µg L^{-1}	0.276	0.444
	SO_4^{2-}	µg L^{-1}	-0.293	0.135
UKR	Ald	µg L^{-1}	0.34	0.071
	Ca	µg L^{-1}	0.38	0.053
	DOC	mg L^{-1}	0.32	0.086
	pH	unit	0.35	0.063
	Water Temp.	°C	0.14	0.621
	F+	µg L^{-1}		
	NO_3^-	µg L^{-1}		
	SO_4^{2-}	µg L^{-1}	-0.600	0.142

Table S1.6 Generalized linear mixed model (GLMM) results for seasonal field data.

Fixed Effect	Parameter Estimate	Wald t Test Statistic	P-Value	AIC
Ald	0.264	6.17	**0**	1736.5
Ca	-0.007	-0.183	0.855	
DOC	0.143	3.727	**0**	
F	-0.020	-0.207	0.836	
NO3	0.146	0.991	0.322	
SO4	-0.133	-1.129	0.259	
ALd	0.281	6.921	**0**	1867.3
DOC	0.078	1.877	*0.061*	
ALd	0.313	7.393	**0**	1862.8
DOC	0.158	3.152	**0.002**	
ALd*DOC	-0.076	-2.490	**0.013**	
ALd	0.332	11.49	**0**	1868.3
DOC	0.229	9.445	**0**	1909.9
DOC	0.247	9.744	**0**	1768.4
NO3	0.329	-2.399	**0.016**	
SO4	-0.316	2.515	**0.012**	
DOC	0.287	9.453	**0**	1797.3
NO3	0.063	1.733	*0.083*	
DOC*NO3	0.41	1.709	*0.088*	

-significant parameters at the 5% significance level are bolded

-significant parameters at the 10% significance level are italicized

-Effect connected by "*" represent an interaction term.

Table S1.7 R^2 values for scatterplots of water chemistry relationships shown in Figure 4

Site	Season	Season Dates	Relationship	R^2
MR	S1	April-May	Al_i-pH	0.78131
MR	S2	June-Aug	Al_i-pH	0.27845
MR	S3	Sept-Feb	Al_i-pH	0.04551
MR	S1	April-May	Al_i-DOC	0.48879
MR	S2	June-Aug	Al_i-DOC	0.51343
MR	S3	Sept-Feb	Al_i-DOC	0.0014
MR	S1	April-May	Al_i-T_w	0.42004
MR	S2	June-Aug	Al_i-T_w	0.03442
MR	S3	Sept-Feb	Al_i-T_w	0.08795
MR	S1	April-May	Al_i-Al_d	0.66782
MR	S2	June-Aug	Al_i-Al_d	0.52313
MR	S3	Sept-Feb	Al_i-Al_d	0.0141
MR	S1	April-May	Al_i-Ca	0.50399
MR	S2	June-Aug	Al_i-Ca	0.37339
MR	S3	Sept-Feb	Al_i-Ca	0.00009
MR	S1	April-May	Al_i-Ca/Al_d	0.41377
MR	S2	June-Aug	Al_i-Ca/Al_d	0.32486
MR	S3	Sept-Feb	Al_i-Ca/Al_d	0.0382
MR	S1	April-May	Al_i-Q	0.0374
MR	S2	June-Aug	Al_i-Q	0.0703
MR	S3	Sept-Feb	Al_i-Q	0.0063
MR	S1	April-May	Al_d-Ca	0.55308
MR	S2	June-Aug	Al_d-Ca	0.63892
MR	S3	Sept-Feb	Al_d-Ca	0.5074

MPB	S1	April-June	Al_i-pH	0.00447
MPB	S2	July-Aug	Al_i-pH	0.21629
MPB	S3	Sept-Oct	Al_i-pH	0.56
MPB	S1	April-June	Al_i-DOC	0.70785
MPB	S2	July-Aug	Al_i-DOC	0.43036
MPB	S3	Sept-Oct	Al_i-DOC	0.72722
MPB	S1	April-June	Al_i-T_w	0.72067
MPB	S2	July-Aug	Al_i-T_w	0.2356
MPB	S3	Sept-Oct	Al_i-T_w	0.4353
MPB	S1	April-June	Al_i-Al_d	0.67571
MPB	S2	July-Aug	Al_i-Al_d	0.4225
MPB	S3	Sept-Oct	Al_i-Al_d	0.65683
MPB	S1	April-June	Al_i-Ca	0.59175
MPB	S2	July-Aug	Al_i-Ca	0.4214
MPB	S3	Sept-Oct	Al_i-Ca	0.49111
MPB	S1	April-June	Al_i-Ca/Al_d	0.51142
MPB	S2	July-Aug	Al_i-Ca/Al_d	0.03067
MPB	S3	Sept-Oct	Al_i-Ca/Al_d	0.02961
MPB	S1	April-June	Al_i-Q	0.1734
MPB	S2	July-Aug	Al_i-Q	0.0039
MPB	S3	Sept-Oct	Al_i-Q	0.0004
MPB	S1	April-June	Al_d-Ca	0.96289
MPB	S2	July-Aug	Al_d-Ca	0.7685
MPB	S3	Sept-Oct	Al_d-Ca	0.72173

Table S1.8 Laboratory detection limit comparison.

Chemistry		Value		
Parameter	Units	HERC	Maxxam	AGAT
pH	μg L^{-1}	n/a	n/a	n/a
DOC	mg L^{-1}	n/a	0.50	n/a
TOC	mg L^{-1}	n/a	n/a	0.5
SO_4	μg L^{-1}	10.00	n/a	2000
Al_d	μg L^{-1}	n/a	5.00	5
Al_t	μg L^{-1}	n/a	5.00	5
Al_o	μg L^{-1}	n/a	5.00	5
Ca_t	μg L^{-1}	n/a	100 μg L^{-1}	0.1 mg L^{-1}
Ca_d	μg L^{-1}	n/a	100	100

Section S2. Figures

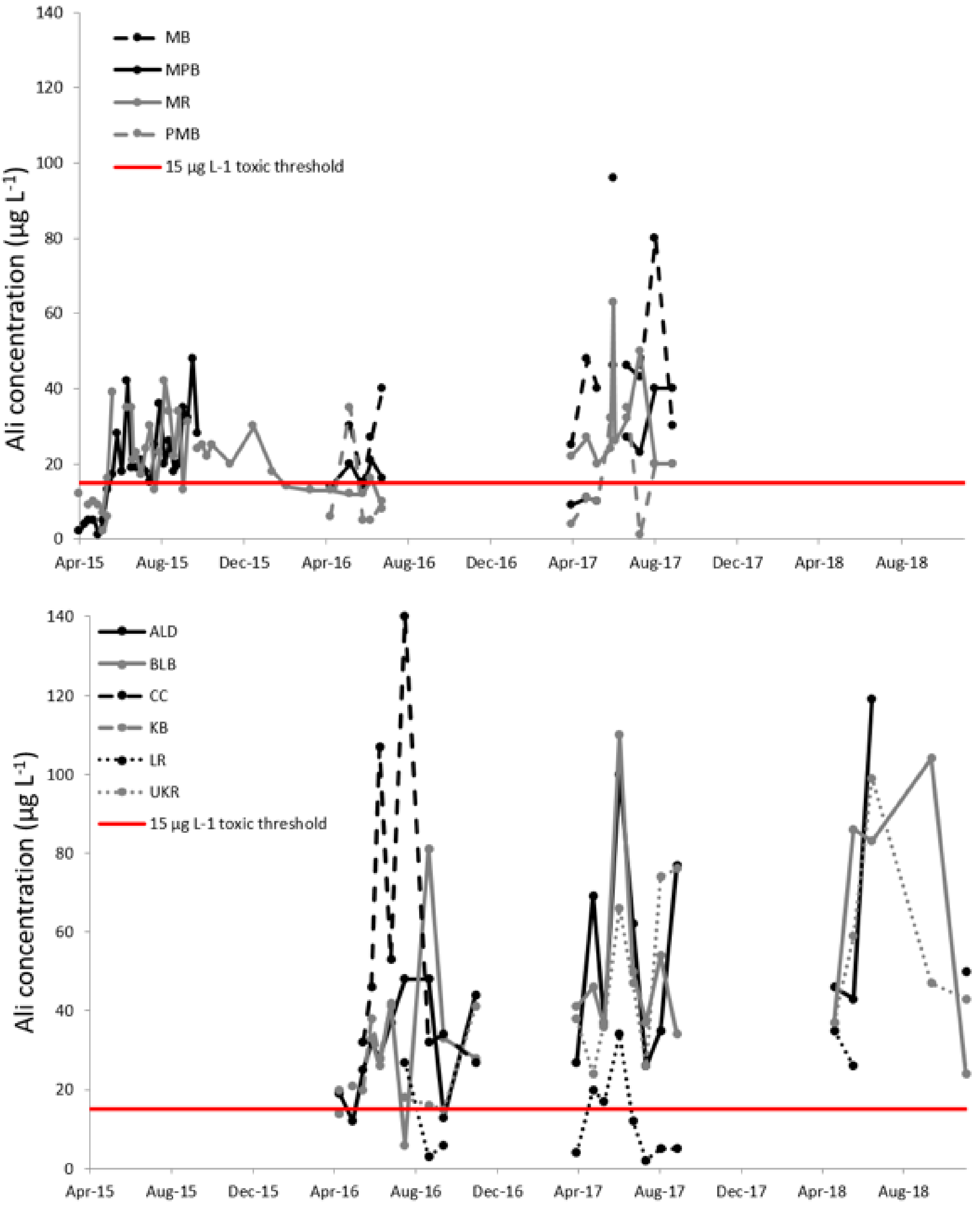


Figure S2.1 Timeseries of Al_i concentration between 22 April 2015 and 23 November 2018.

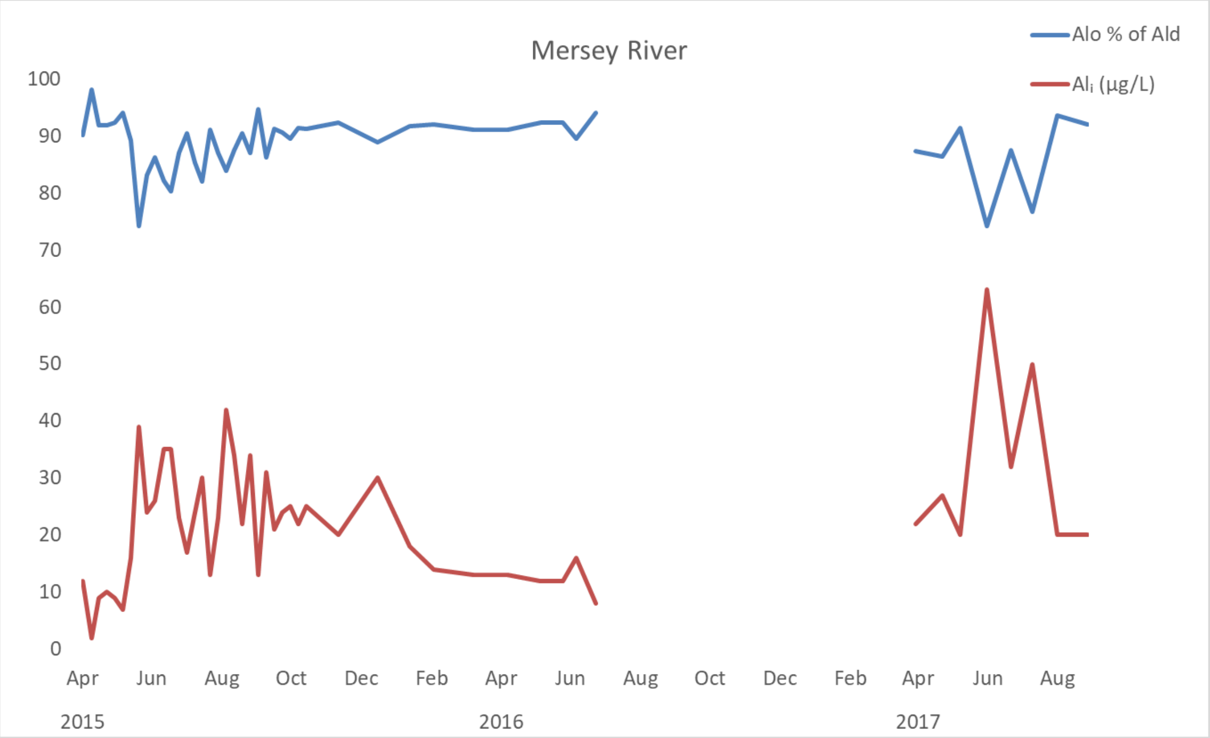


Figure S2.2 Time series of percentage Al_d comprised of Al_o for MR, compared to absolute value of Al_i in ug L^{-1}.

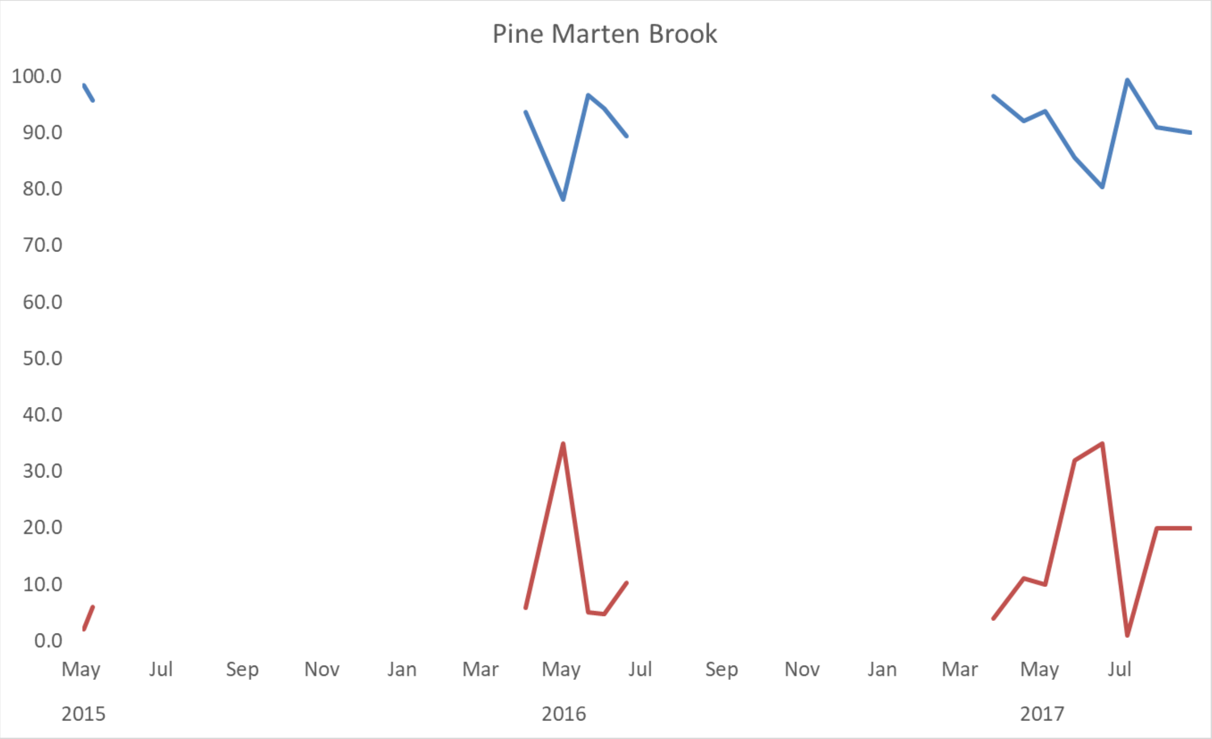


Figure S2.3 Time series of percentage Al_d comprised of Al_o for PMB, compared to absolute value of Al_i in ug L^{-1}.

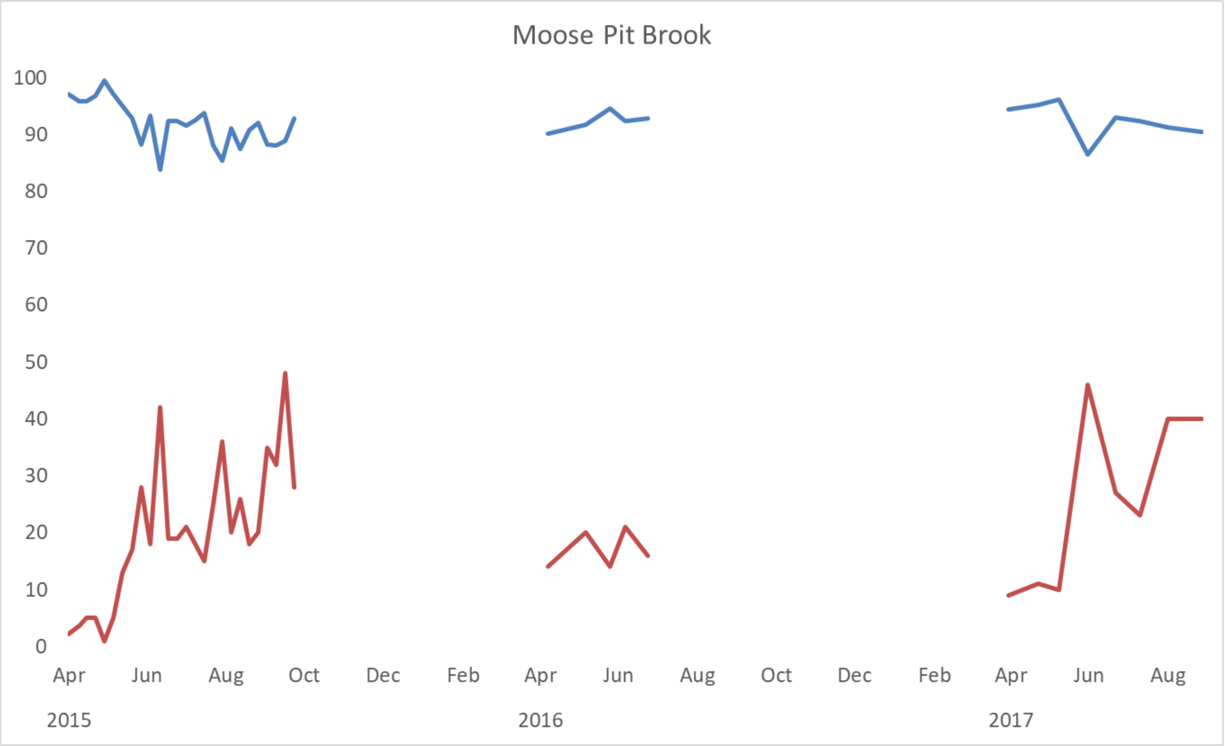


Figure S2.4 Time series of percentage Al_d comprised of Al_o for MPB, compared to absolute value of Al_i in ug L^{-1}.

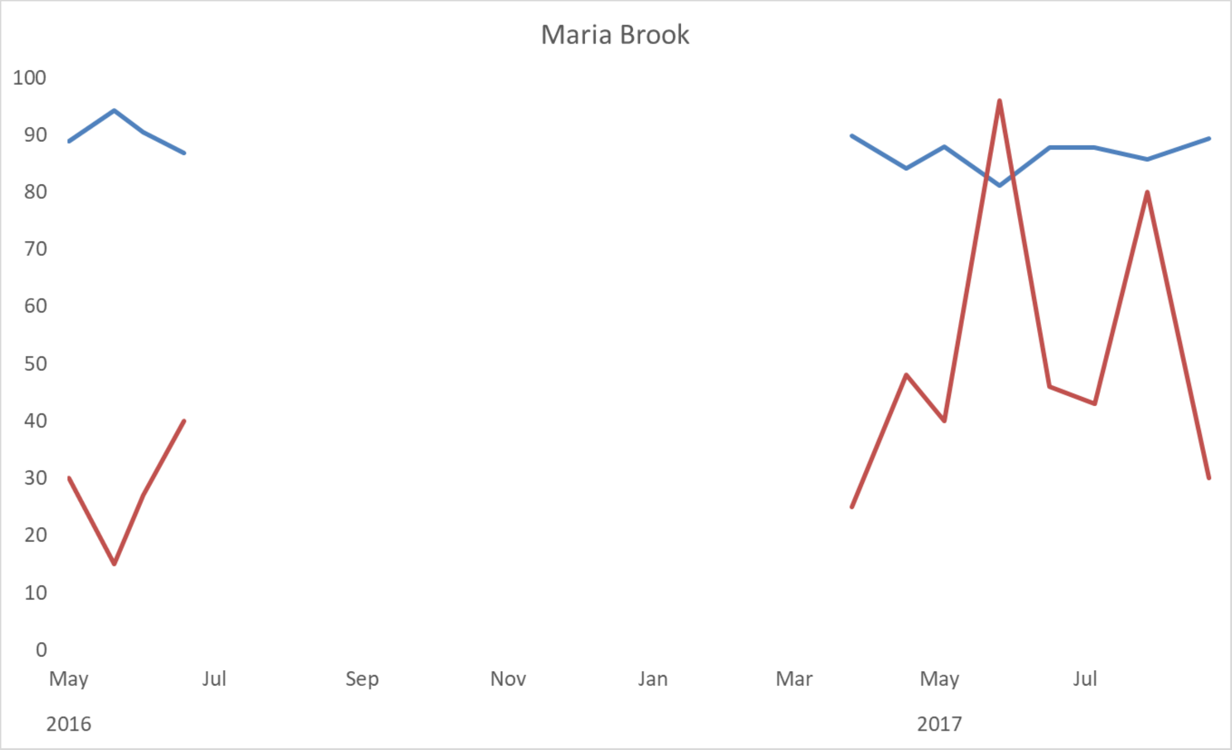


Figure S2.5 Time series of percentage Al_d comprised of Al_o for MB, compared to absolute value of Al_i in ug L^{-1}.

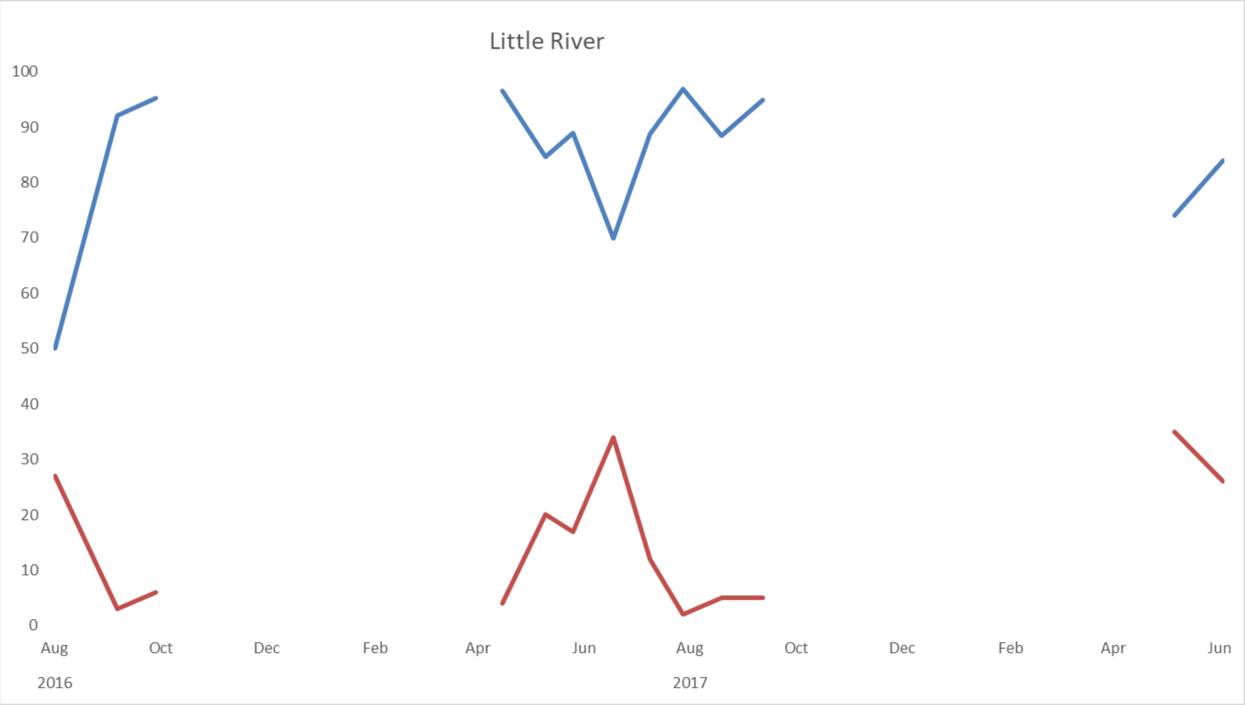


Figure S2.6 Time series of percentage Al_d comprised of Al_o for LR, compared to absolute value of Al_i in ug L^{-1}.

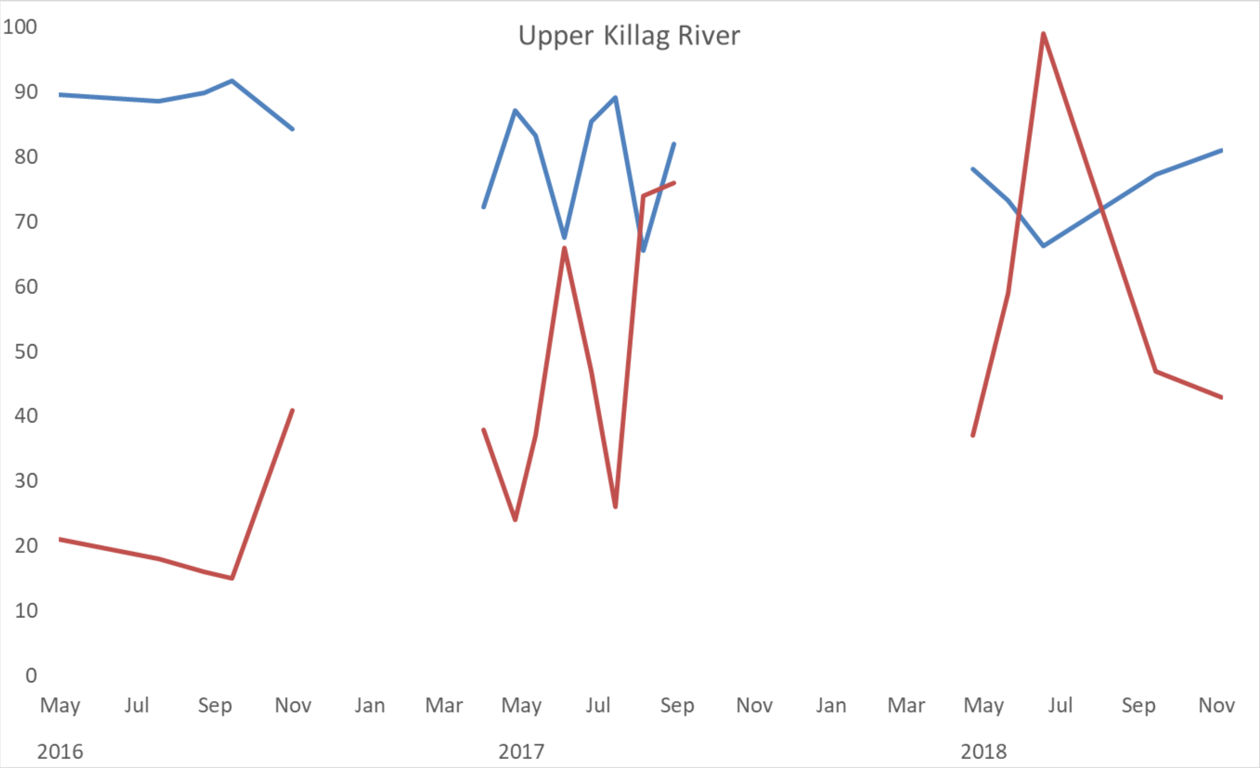


Figure S2.7 Time series of percentage Al_d comprised of Al_o for UKR, compared to absolute value of Al_i in ug L^{-1}.

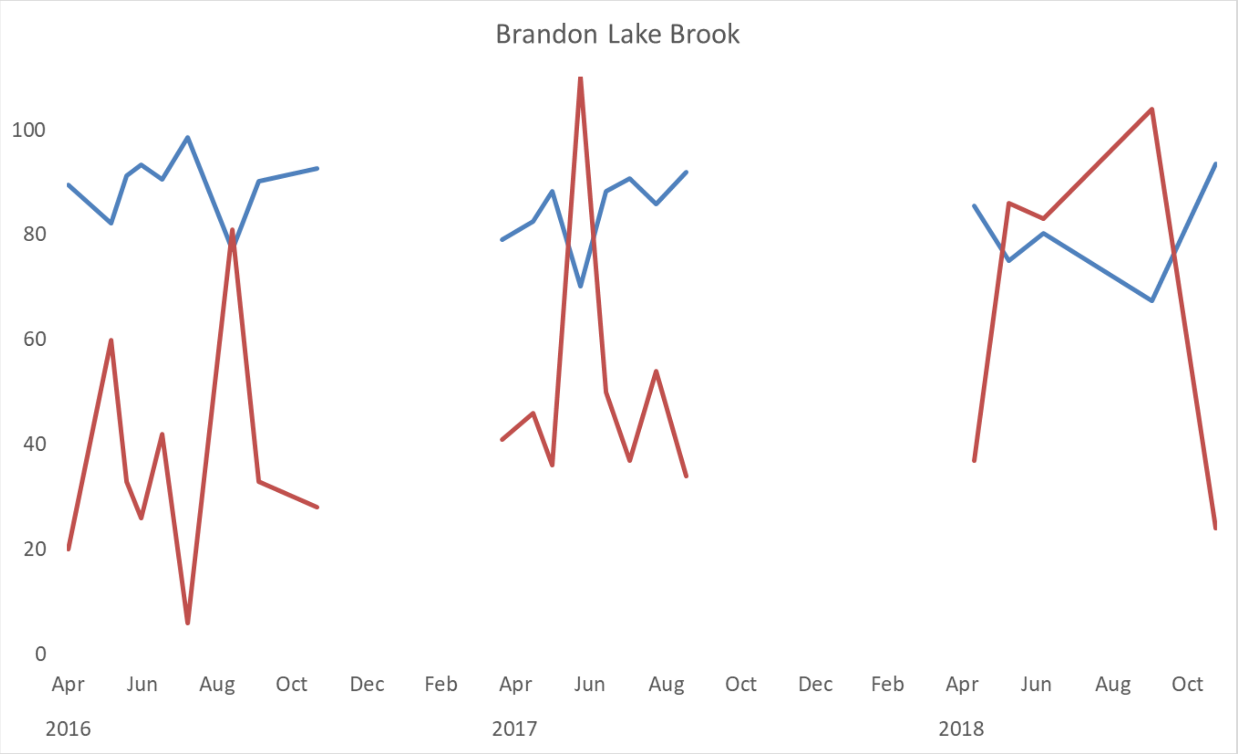


Figure S2.8 Time series of percentage Al_d comprised of Al_o for BLB, compared to absolute value of Al_i in ug L^{-1}.

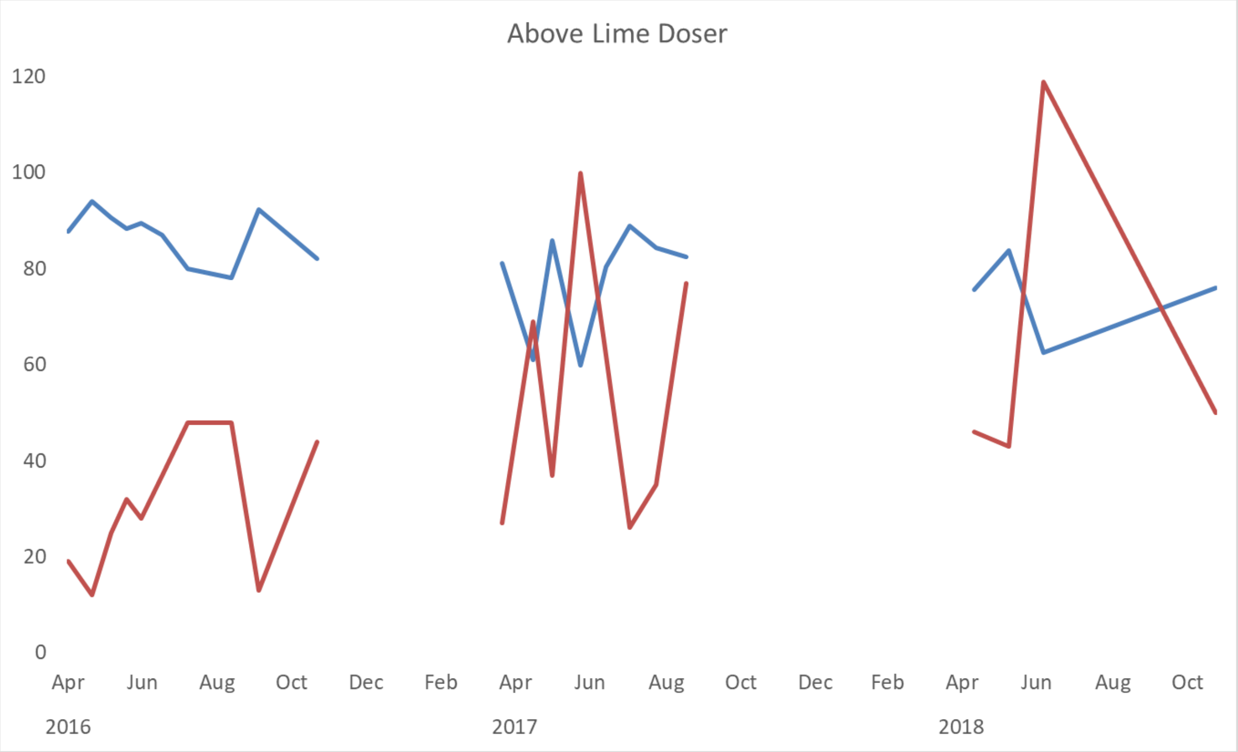


Figure S2.9 Time series of percentage Al_d comprised of Al_o for ALD, compared to absolute value of Al_i in ug L^{-1}.

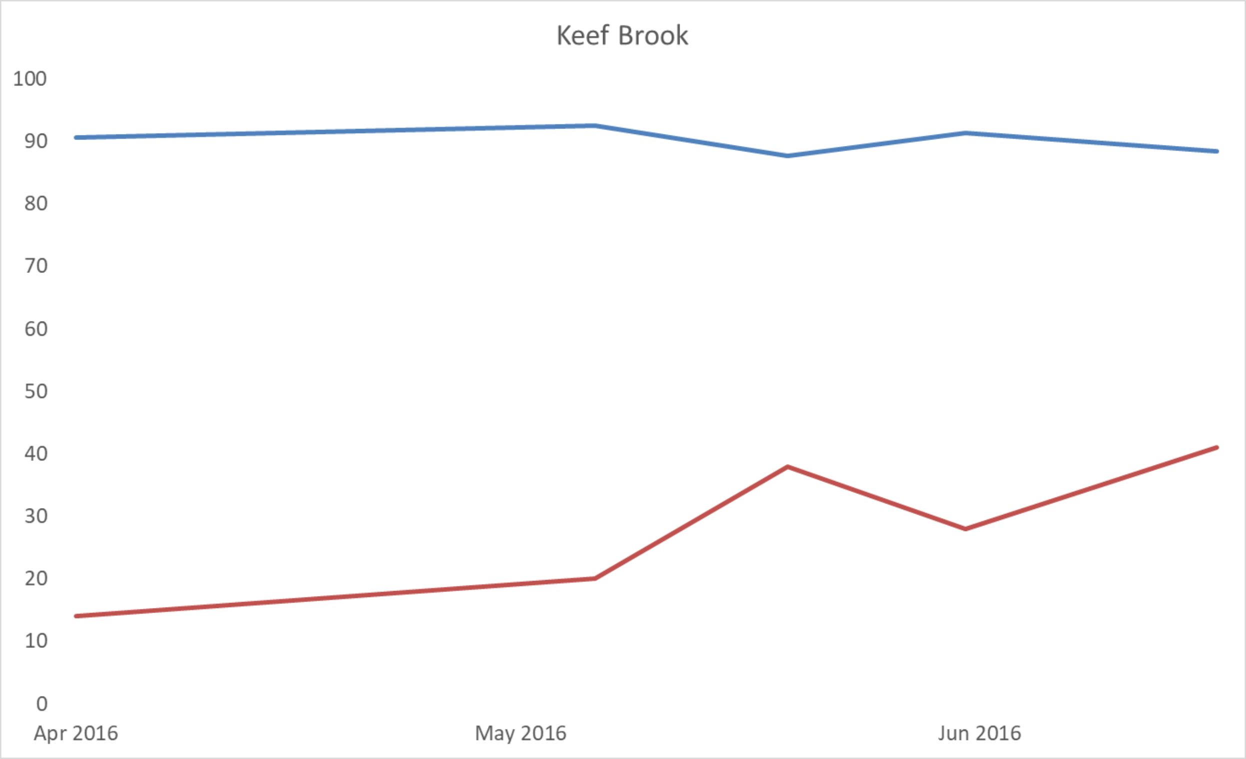


Figure S2.10 Time series of percentage Al_d comprised of Al_o for KB, compared to absolute value of Al_i in ug L^{-1}.

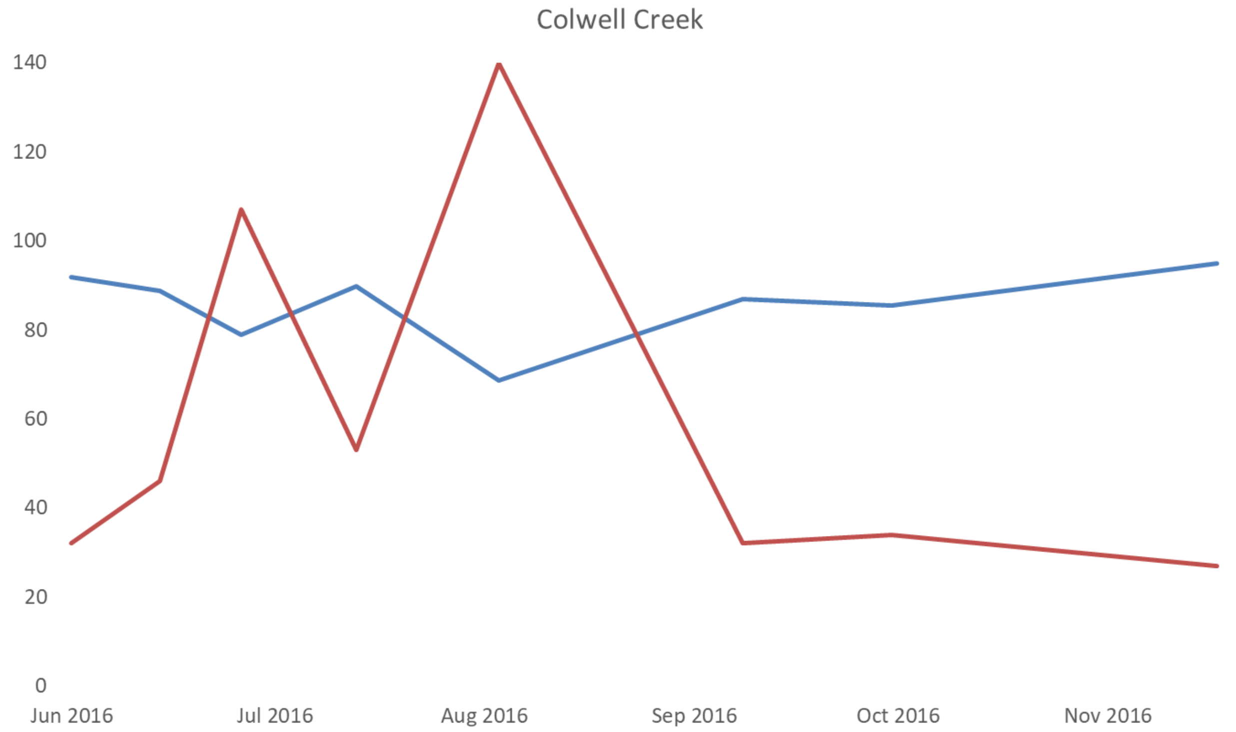


Figure S2.11 Time series of percentage Al_d comprised of Al_o for CC, compared to absolute value of Al_i in ug L^{-1}

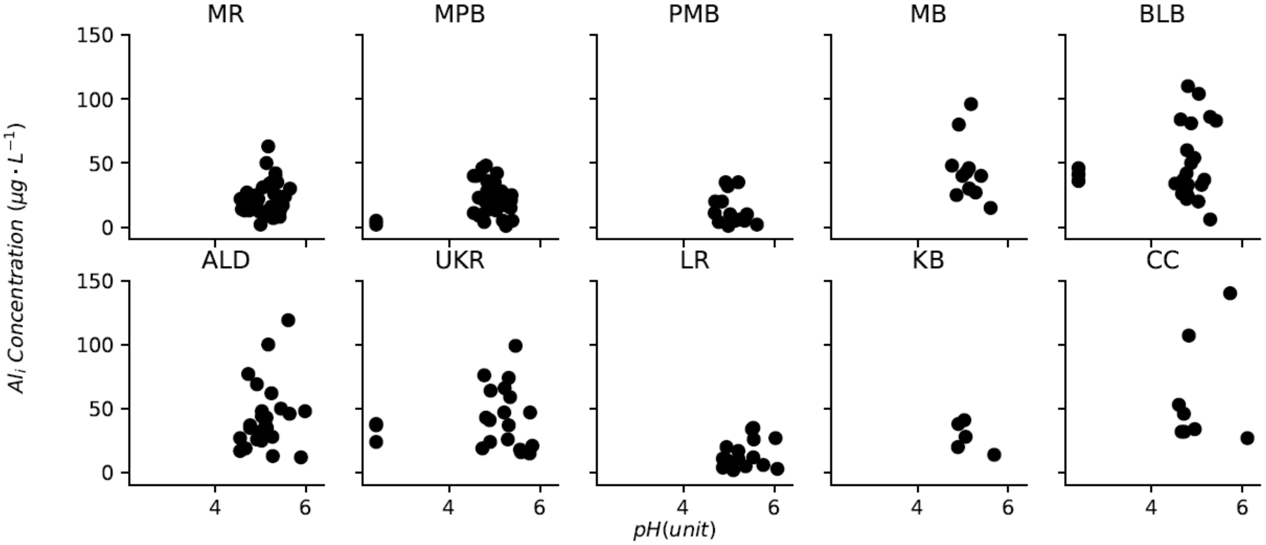


Figure S2.12 Least-squares linear regression of Al_i versus pH for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

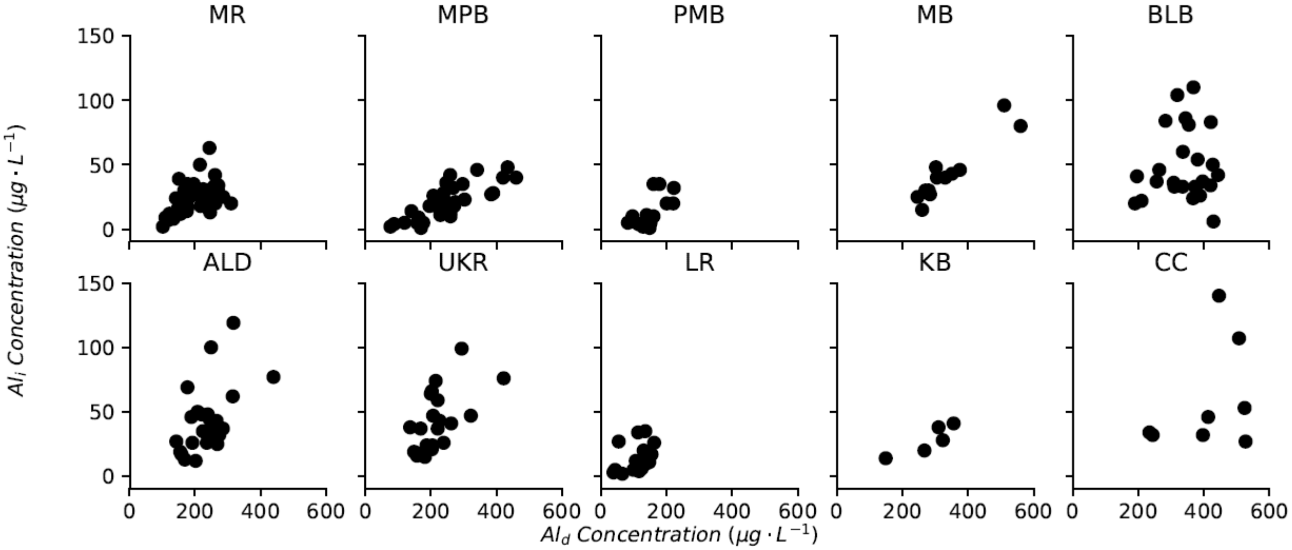


Figure S2.13 Least-squares linear regression of Al_i versus Al_d for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

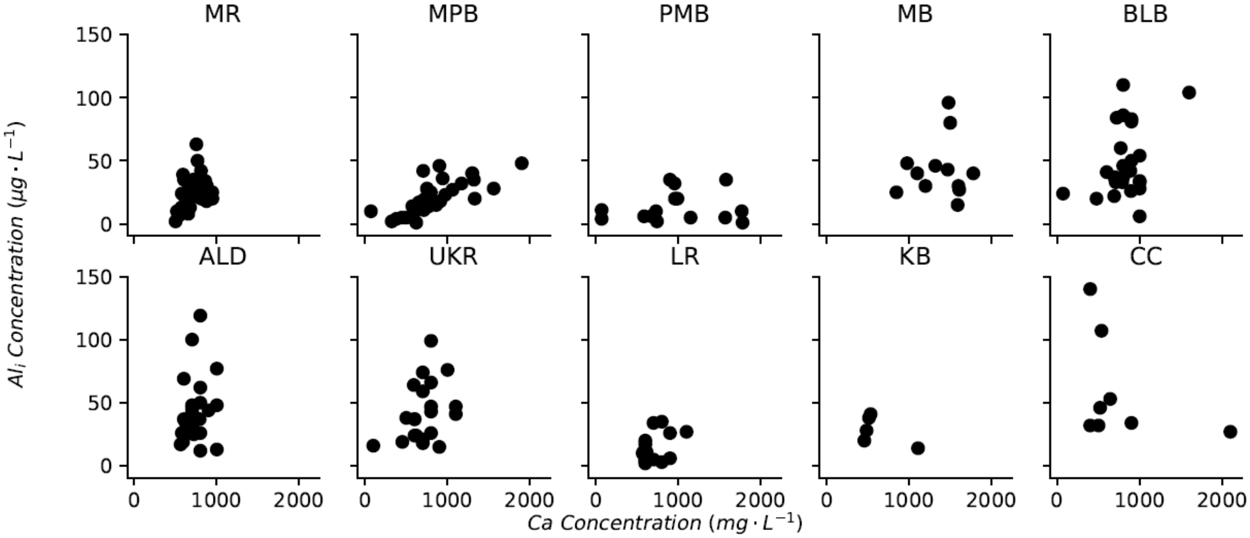


Figure S2.14 Least-squares linear regression of Al_i versus Ca for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015). One Ca outlier for KB removed (value: 1110 µg L-1, date: 29 April 2016).

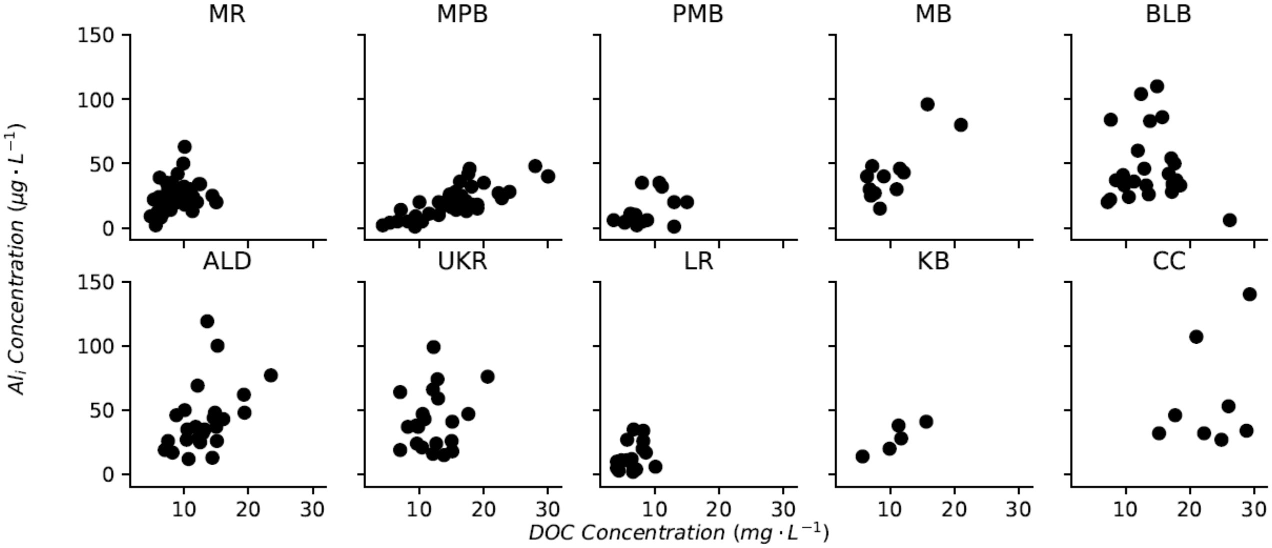


Figure S2.15 Least-squares linear regression of Al_i versus DOC for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

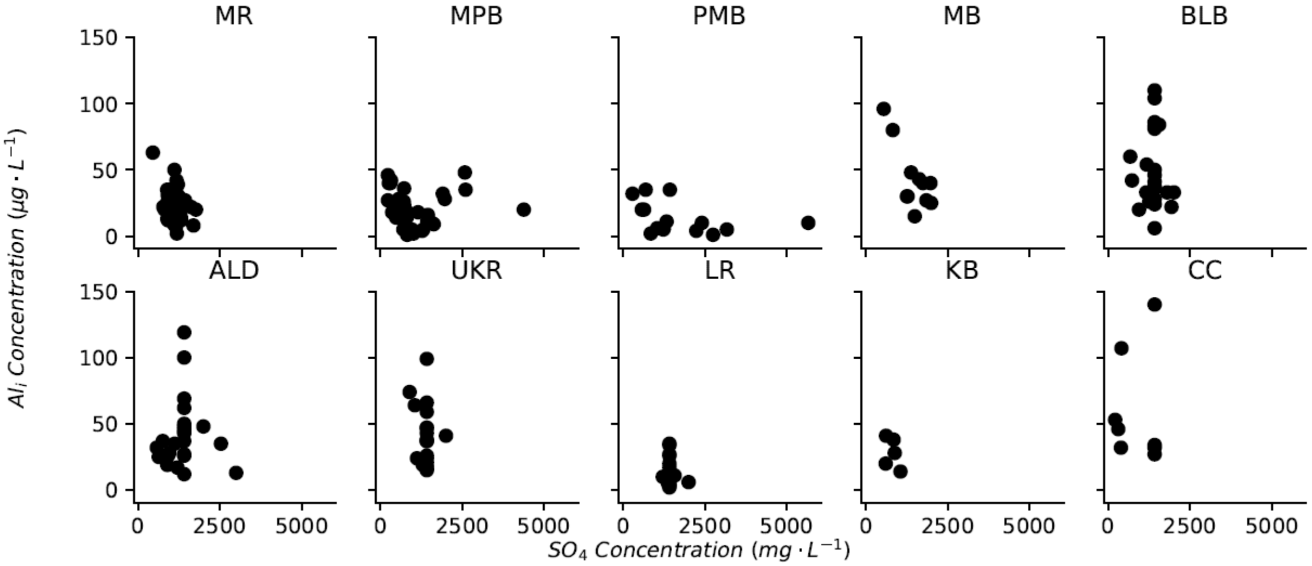


Figure S2.16 Least-squares linear regression of Al_i versus SO_4^{2-} for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

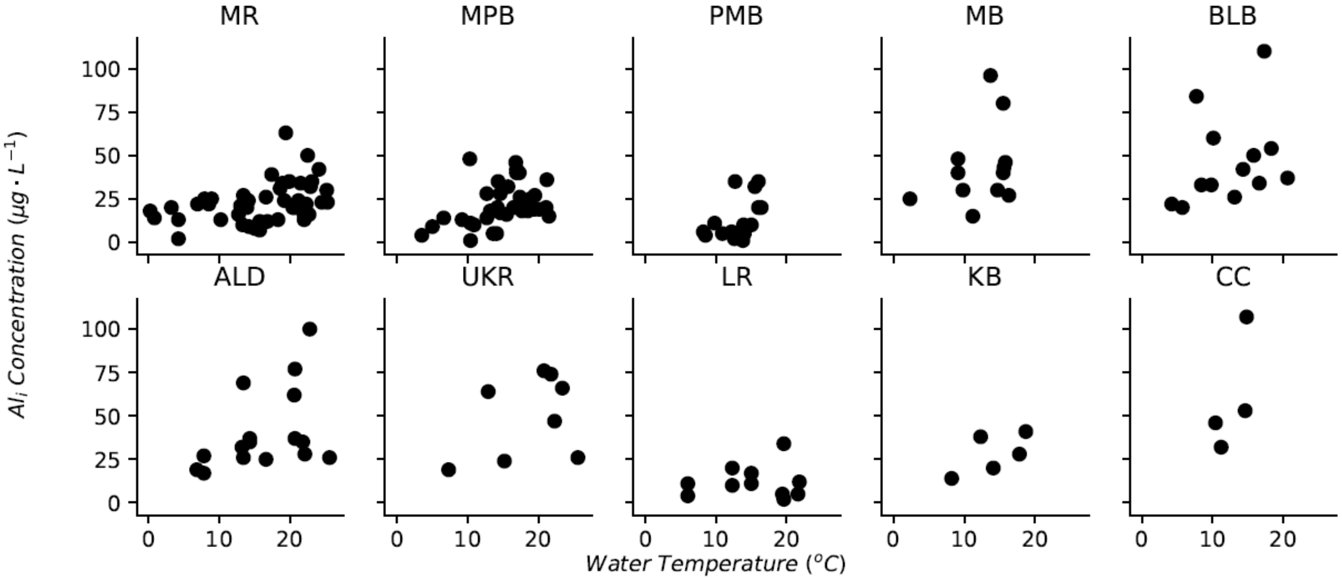


Figure S2.17 Least-squares linear regression of Al_i versus T_w for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

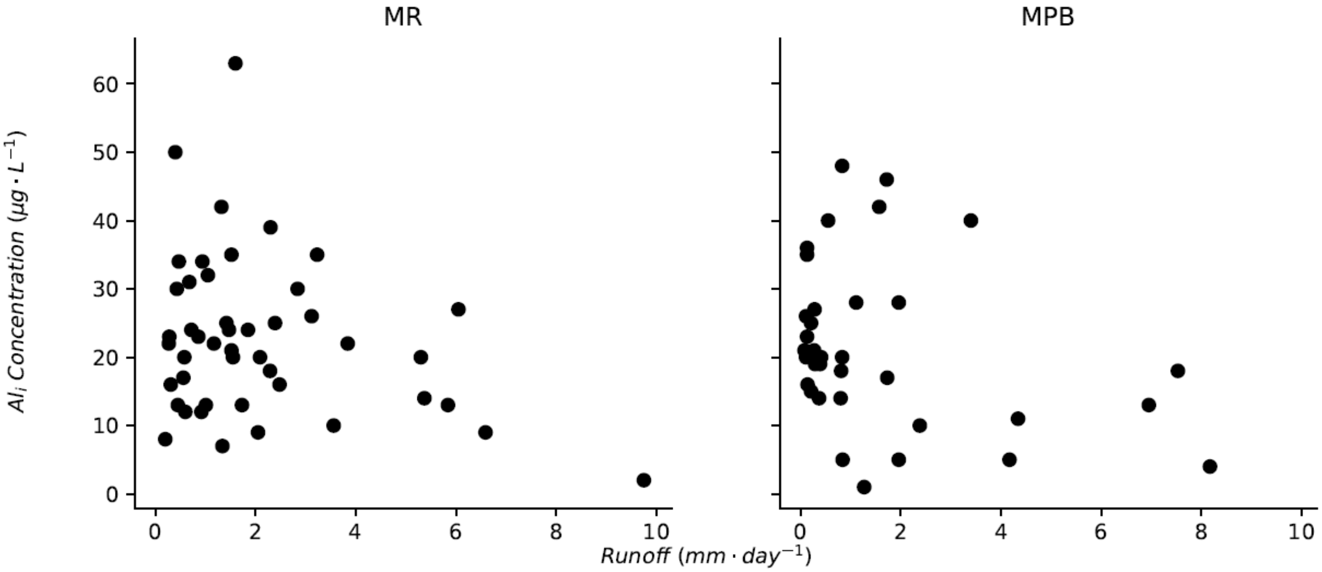


Figure S2.18 Least-squares linear regression of Al_i versus runoff for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015). One runoff outlier for MR removed (value: 17.294 mm day-1, date: 22 April 2015), and one runoff outlier for MPB removed (value: 34.994 mm day-1, date: 22 April 2015).

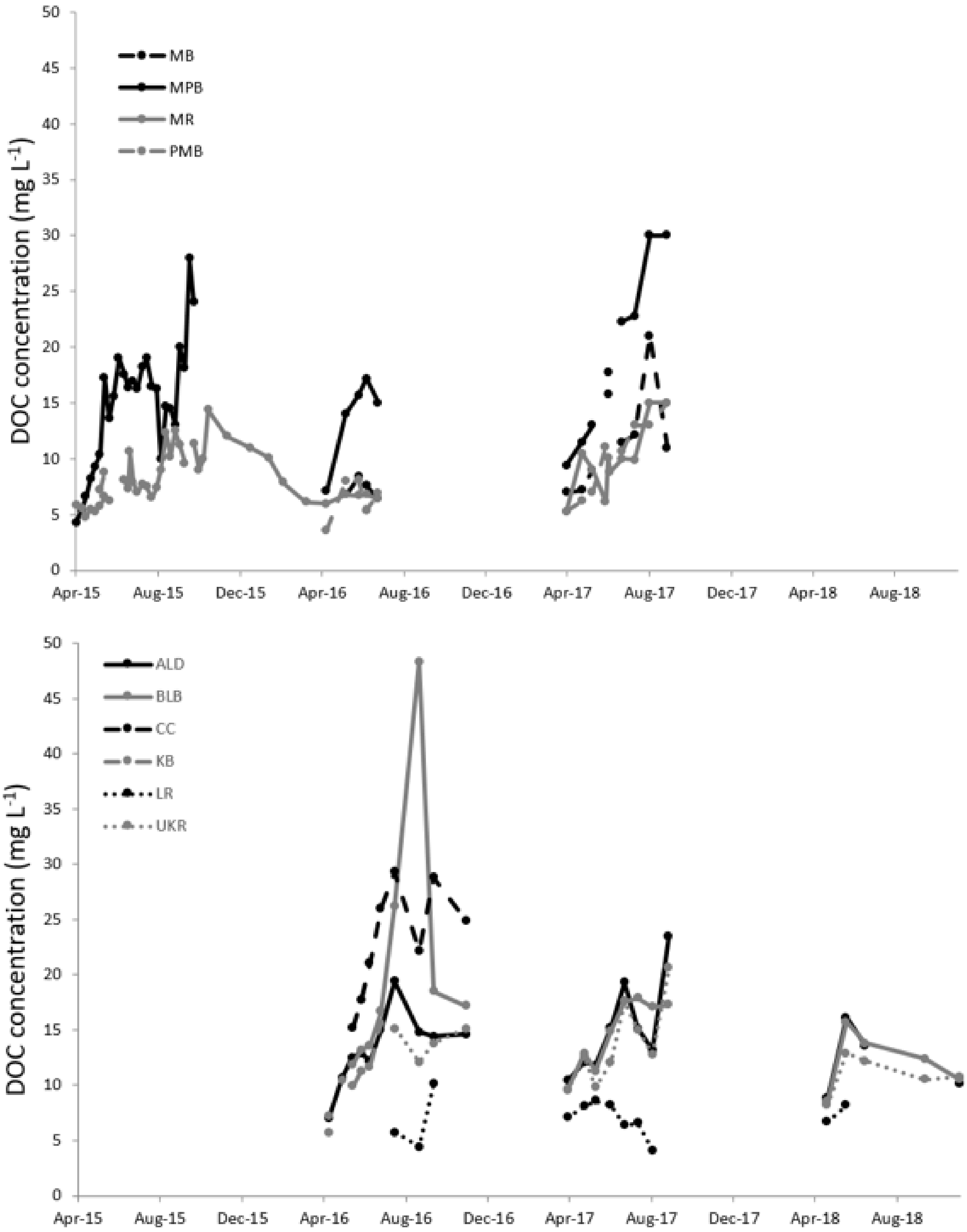
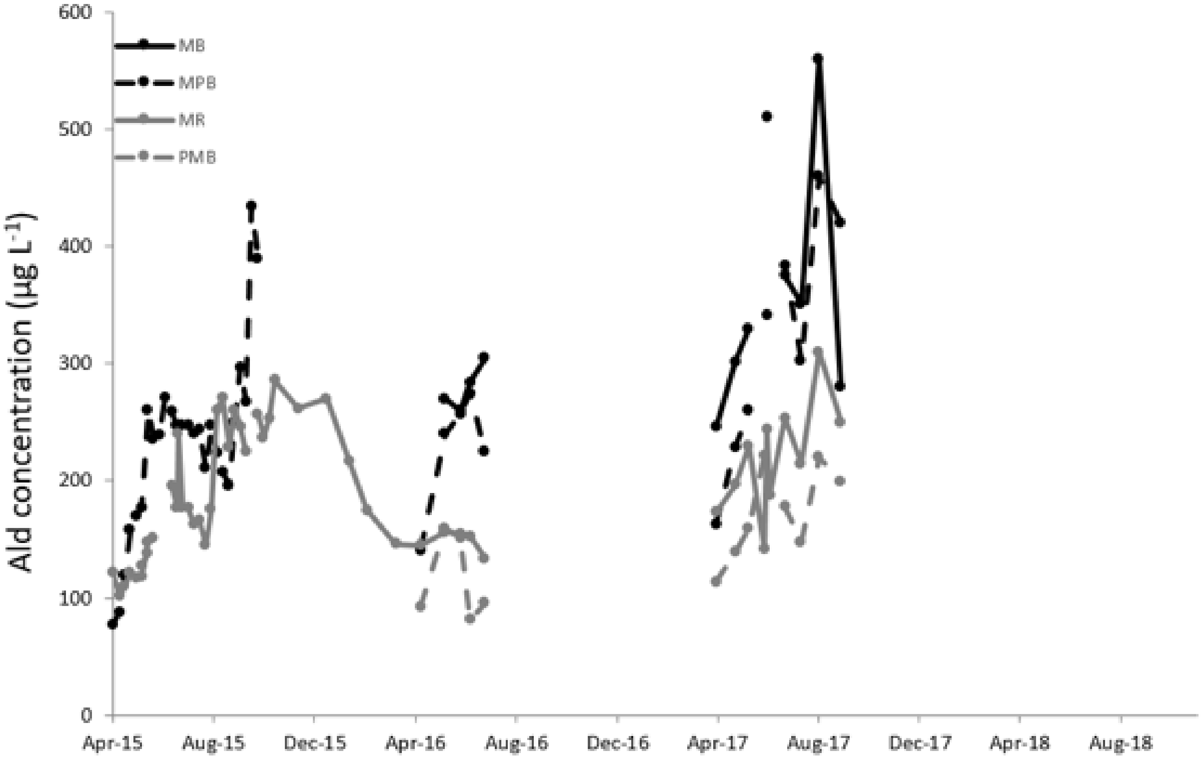


Figure S2.19 Time series of DOC concentration between 22 April 2015 and 23 November 2018



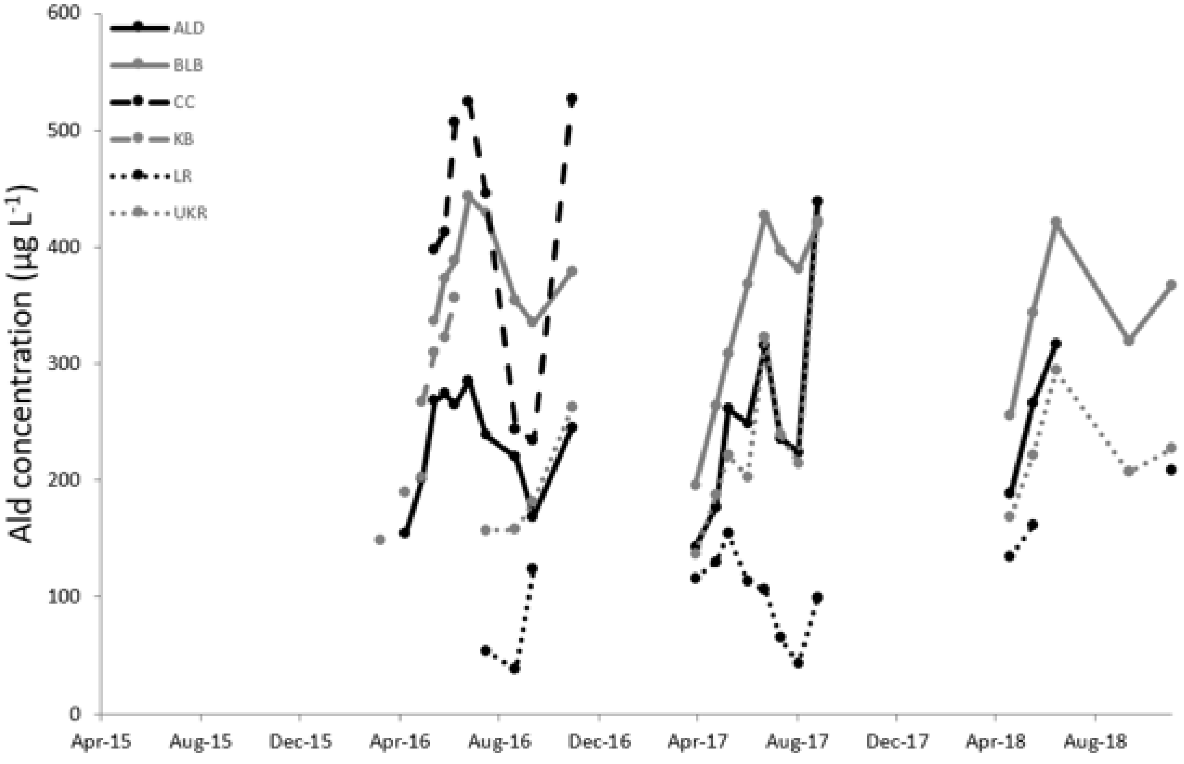


Figure S2.20 Time series of Al_d concentration between 22 April 2015 and 23 November 2018.

Section S3. Scripts

S3.1. Linear regression

```
    """Linear regression calculation script
    :author: Lobke Rotteveel
    :email: lobke.rotteveel@dal.ca
    """

    # Import modules
    from scipy import stats
    import pandas as pd
    import csv

    # Import data
    df = pd.read_csv('Input.csv')

    # Run Mann Kendall test on site-variable groups and create table of results
    results = []
    results.append(['site_id', 'variable', 'tau', 'pvalue', 'slope', 'std error of slope'])
    grouped = df.groupby('Site')
    for name, group in grouped:
        chem_groups = [group['Ald'], group['Ca'], group['DOC_TOC'], group['CalibpH'],
group['Tw'], group['RunOff']]

        Ali = group['Ali']
        for i in chem_groups:
            pair = {'i':i,'Ali':Ali}
            pair = pd.DataFrame(pair)
            pair = pair.dropna()
            if not pair.empty:
                ken_tau = stats.kendalltau(pair['i'], pair['Ali'])
                slope = stats.linregress(pair['i'], pair['Ali'])
                result_row = [name, i.name, ken_tau.correlation, ken_tau.pvalue, slope.slope,
slope.stderr]
                results.append(result_row)

    with open('LinearRegression_Out.csv', 'w') as f:
        writer = csv.writer(f)
        writer.writerows(results)
```

S3.2. Laboratory comparison

```
"""Laboratory result comparison script
:author: Lobke Rotteveel
:email: lobke.rotteveel@dal.ca
"""

# Import modules
import pandas as pd
import numpy as np
import scipy as sp
from scipy import stats
import warnings

warnings.simplefilter('ignore', np.RankWarning)

# Importing data
df = pd.read_csv('SampDat_CompareInput_LimSur_171105_LR.csv', ',', header=0)
#print (df.head(n=5))

# Run comparisson
with open('SampData_Compare_LimSur.txt', 'w') as f:

    x = df.filter(regex='B_.*').columns
    y = df.filter(regex='A_.*').columns

    for x_col, y_col in zip(x,y):
        Sig = sp.stats.wilcoxon(df[x_col],df[y_col])
        f.write('x: {}, y: {}, sig:{}\n'.format(x_col, y_col, Sig))
```

S3.3. Script for GLMM model

```
#setwd
setwd("C:\\Users\\50nlo\\Documents\\Research\\MS_AliPatterns\\Data")

#load packages
#require(lme4)
require(car)
require(MASS)

#Read in Data
ALiDatDF<-as.data.frame(read.csv("GLMM_Input_V2.csv",header=T))
```

```
ALiDat<-ALiDatDF$Ali_ugL

#Exploratory data analysis of ALi data
hist(ALiDat) #data are skewed

#Test goodness-of-fit of lognormal data

#Normal QQ plot for comparison
qqnorm(ALiDat)
qqline(ALiDat)

qqp(ALiDat, "norm")

#lognormal QQ plot
fit_params <- fitdistr(ALiDat,"lognormal")

quants <-seq(0,1,length=length(ALiDat))[2:138]
fit_quants <- qlnorm(quants,fit_params$estimate['meanlog'],
fit_params$estimate['sdlog'])
data_quants <- quantile(ALiDat,quants)

plot(fit_quants, data_quants, xlab="Theoretical Quantiles",
ylab="Sample Quantiles")
title(main = "Q-Q plot of lognormal fit against data")
abline(0,1)

qqp(ALiDat, "lnorm")

#Gamma QQ plot
gamma <- fitdistr(ALiDat, "gamma")
qqp(ALiDat, "gamma", shape = gamma$estimate[[1]], rate =
gamma$estimate[[2]])

#Exponential QQ plot
exp <- fitdistr(ALiDat, "exponential")
qqp(ALiDat, "exp", rate = gamma$estimate[[1]])


Site<-ALiDatDF$Site
Season<-ALiDatDF$Season
ALd<-scale(ALiDatDF$Ald_ugL)
Ca<-scale(ALiDatDF$Ca_ugL)
DOC<-scale(ALiDatDF$DOC_mgL)
pH<-scale(ALiDatDF$Calib_pH)
SO4<-scale(ALiDatDF$SO4_ugL)
Tw<-scale(ALiDatDF$Tw_C)
F<-scale(ALiDatDF$F_ugL)
NO3<-scale(ALiDatDF$NO3_ugL)
Dis<-scale(ALiDatDF$Disch_m3s)
```

```
#ALd and Season cause a singular fit (overfit)
#This means that the effect structure is too complex to be supported
by the data
#ALd is likely due to it being a function of ALi
#Season is due to limited seasonal data at each site.
Models <- glmer(ALiDat ~ DOC + Tw + Ca+ pH + SO4 + F + NO3 + (1 |
Site), family = gaussian(link = "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ DOC + SO4 + NO3 + (1 | Site), family =
gaussian(link = "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ DOC + NO3 + DOC*NO3+(1 | Site), family =
gaussian(link = "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ DOC +(1 | Site), family = gaussian(link =
"log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ Tw +(1 | Site), family = gaussian(link =
"log"))
summary(Models)

Models <- glmer(ALiDat ~ DOC + Tw +(1 | Site), family = gaussian(link
= "log"))
summary(Models)

Models <- glmer(ALiDat ~ DOC + Tw + DOC*Tw + (1 | Site), family =
gaussian(link = "log"))
summary(Models)



#pH and Tw causes a singular fit (overfit)
Models <- glmer(ALiDat ~ ALd + DOC + Ca + SO4 + F + NO3 + (1 |
Season), family = gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ ALd + DOC + (1 | Season), family =
gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ ALd + DOC + ALd*DOC + (1 | Season), family =
gaussian(link = "log"))
```

```
summary(Models)

Models <- glmer(ALiDat ~ ALd + (1 | Season), family = gaussian(link =
"log"))
summary(Models)

Models <- glmer(ALiDat ~ DOC + (1 | Season), family = gaussian(link =
"log"))
summary(Models)

Models <- glmer(ALiDat ~ DOC + SO4 + NO3 + (1 | Season), family =
gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ DOC + NO3 + DOC*NO3+(1 | Season), family =
gaussian(link = "log"))
summary(Models)

#################################For
testing##############################
#95% confidence intervals
fm1W <- confint.merMod(Models, method="Wald")

#Check for singularity
tt <- getME(Models,"theta")
ll <- getME(Models,"lower")
min(tt[ll==0])

#Use penalized quazilikelihood to estimate non-normal parameters
PQL <- glmmPQL(ALiDat ~ ALd + DOC + pH + SO4+ Tw + NO3 + Ca, ~1 |
Site, family = gaussian(link = "log"), verbose = FALSE)

#Fluoride is confounded, remove from model.

summary(PQL)

#At the 5% sig. level, pH, SO4, NO3, and Ca are not significant
effects

#Use penalized quazilikelihood to estimate non-normal parameters
PQL <- glmmPQL(ALiDat ~ ALd + Tw + DOC + ALd*pH + Tw*pH, ~1 | Site,
family = gaussian(link = "log"), verbose = FALSE)
summary(PQL)

resid<-as.matrix(PQL$residuals[,1])
#Explore the model residuals
acf(resid) #good
```

Section S4. Additional methods

S4.1 Laboratory analysis methods

Samples were analyzed at Maxxam Analytics Laboratory, Health and Environmental Research Centre (HERC), and AGAT Laboratories. Samples from MR, MPB, PMB, MB, KB, and CC were analyzed at Maxxam and HERC labs only. Samples from BLB, ALD, UKR, and LR were analyzed at all three labs.

S4.1.1 Maxxam Laboratory

The protocol at Maxxam Laboratory in Bedford, NS, adheres to methods approved by the United States Environmental Protection Agency (US EPA) for identifying trace elements in water (US EPA, 1994) and analyzing samples using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (US EPA, 1998). Cations and anions were analyzed using ICP-MS, while a Continuous Flow Analyzer was used to measure DOC. pH was measured using a standard hydrogen electrode and reference electrode.

S4.1.2 HERC Laboratory

SO_4^{2-} samples were analyzed at HERC Laboratory in Halifax, NS, due to lower detection limits at the Maxxam laboratory. Once delivered to the laboratory, samples were filtered using a 0.45 µm glass fiber filter and analyzed using an Ion-Chromatography System (ICS) 5000 Dionex detector.

S4.1.3 AGAT Laboratory

Samples collected in the West River, Sheet Harbour area (UKR, ALD, LR, BLB, KB, CC) were analyzed at the AGAT laboratory in Dartmouth, NS. This laboratory holds the

9001:2015 and 17025:2005 International Organization for Standardization accreditations. Cation samples were analyzed using ICP-MS, laboratory pH was measured using a standard hydrogen electrode and reference electrode, and SO_4^{2-} and anions were measured using ICS. Samples analyzed at AGAT were analyzed for total organic carbon (TOC) as opposed to DOC and were analyzed using Infrared Combustion (IR Combustion).

S4.2 Data quality assurance and control

Blanks were used to assess contamination during the Al_o extraction procedure. Blanks were collected on 10% of samples, taken on arbitrary sampling events. Triple deionized water was collected before passing through filter and column (“Blank Before”), and after (“Blank After”). The triple-deionized water had traces of chemicals below the laboratory detection limits, providing “Not Detectable” results for the Blank Before sample. If chemicals were detected in the Blank After sample, this would have indicated leaching of chemicals from the column.

Duplicates were collected and analyzed for 10% of the samples; on arbitrarily selected sampling events, Al_o and $Al_{filtered}$ or $Al_{unfiltered}$, were analyzed twice, independently, by Maxxam laboratory. All laboratories also conducted additional duplicate, blank, reference material, and matrix spike testing, in addition to instrument calibration in adherence to industry standards for quality control and assurance.

Spiked blank samples were conducted using ICP Al standard, 1000 ug/mL, HNO_3 (SCP Science). Three types of measurements were taken. The ‘total’ measurement was an unaltered sample of the diluted solution created above. The ‘dissolved’ measurement was a sample of the above solution passed through a 0.45um PES filter. The ‘organic’ measurement as a sample of the above solution passed through a 0.45um PES filter and a cation exchange column.

The spiked column blanks show that the columns are performing well; the cation exchange column removed virtually all of the Al in the solution (detection limit = 4 ug/L). Additional blanks were conducted in the Dalhousie hydrology lab that was used to prepare the sampling equipment before field collection. The blanks showed no contamination.

To verify that sample analysis results from the Maxxam/HERC laboratory combination were comparable to AGAT, three sets of duplicate samples were collected for ALD, BLB, UKR, and LR (19 April 2017, 14 May 2017, and 30 May 2017) and analyzed by both laboratories. Laboratory results were compared using Wilcoxon Rank Sum statistical test in Python 3.6.5 using the SciPy Stats module (version 0.19) (Appendix C.2). Results indicated a significant difference in pH values between laboratories (T = 1, p = 0.04), therefore, statistical analysis on pH data was conducted on the calibrated YSI Pro Plus sonde field data. Al_o, $Al_{filtered}$, and $Al_{unfiltered}$ results were found to be comparable between laboratories (T = 8.5, p = 0.674; T = 5.0, p = 0.249; and T = 8.0, p = 0.600, respectively). After adjusting for detection limits (Table S1.6), Ca results were also found to be comparable between laboratories (T = 4.0, p = 0.173). However, due to the large difference in SO_4^{2-} detection limits between HERC and AGAT (10 µg L^{-1} and 2 mg L^{-1}, respectively), results for SO_4^{2-} are not comparable between laboratories. Lastly, organic carbon analyzed at Maxxam was analyzed for DOC, while AGAT analyzed for TOC, therefore these results cannot be compared. For dates where duplicate data is present, AGAT data was used to maintain data source consistency, apart from SO_4^{2-} data, for which HERC data was used due to superior detection limits. Analysis for BLB and ALD transitioned from Maxxam to AGAT 19 April 2017 and consequently DOC is approximated as TOC for these two sites after this date.

The YSI Pro Plus sonde was calibrated within 36 hours of in-stream data collection.

S4.3 Toxic thresholds of Al_i

Identified toxic thresholds of Al_i for *Salmo salar* vary in the literature. Based on toxicological and geochemical studies on Al and *Salmo salar*, the EIFAC suggested an Al_i toxic threshold of 15 ug L^{-1} for Atlantic salmon in freshwaters for pH between 5.0 and 6.0, and 30 ug L^{-1} in pH <5 (Howells et al., 1990). The lower threshold at higher pH is to account for the increased fraction in the $Al(OH)_2^+$ species. At pH > 6, the toxic effects of Al_i to *Salmo salar* are considered negligible, and toxic effects are dominated by other dissolved and precipitated forms (Gensemer et al., 2018), due to the decreased solubility of Al at pH > 6 (Dennis and Clair 2012). However, in colder rivers, the pH-toxicity threshold may be higher, closer to pH 6.5 (Lydersen, 1990). For the purposes of this study, we use the toxic threshold of Al_i at 15 ug L^{-1}, as the majority of our pH observations were greater than or equal to 5.0 (Table S1.2).

S4.4 Calibration of pH measurements

In situ pH measurements were taken using a YSI Pro Plus sonde and confirmed with a YSI Ecosense pH Pen. It was found that measurements taken with the YSI Pro Plus sonde deviated from the YSI Ecosense Pen, which is known to measure pH accurately (0.47 ± 0.44 pH units below in-stream pH as measured by YSI Ecosense Pen). Therefore, a calibration curve was created based on simultaneous side-by-side measurements of both instruments (n = 69 pairs) and the in situ pH data were adjusted accordingly (Eq. 1).

$$YSI\ Ecosense\ Pen\ pH = 0.595 + 2.3868 \qquad (1)$$

References for Section S4

Dennis, I. F. and Clair, T. A.: The distribution of dissolved aluminum in Atlantic salmon (Salmo salar) rivers of Atlantic Canada and its potential effect on aquatic populations, Can. J. Fish. Aquat. Sci., 69, 1174-1183, 2012.

Gensemer, R. W., Gondek, J. C., Rodriquez, P. H., Arbildua, J. J., Stubblefield, W. A., Cardwell, A. S., Santore, R. C., Ryan, A. C., Adams, W. J. and Nordheim, E.: Evaluating the effects of pH, hardness, and dissolved organic carbon on the toxicity of aluminum to freshwater aquatic organisms under circumneutral conditions, Environmental Toxicology and Chemistry, 37, 49-60, 2018.

Howells, G., Dalziel, T., Reader, J. P. and Solbe, J. F.: EIFAC water quality criteria for European freshwater fish: report on aluminium, Chem. Ecol., 4, 117-173, 1990.

Lydersen, E.: The solubility and hydrolysis of aqueous aluminium hydroxides in dilute fresh waters at different temperatures, Hydrology Research, 21, 195-204, 1990.

US EPA: Method 6020A (SW-846): Inductively coupled plasma-mass spectrometry, 1998.

US EPA.: “Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry,” Revision 5.4, 1994.