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The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp

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Abstract. A seven year chemical budget of a minerotrophic conifer swamp located on the PreCambrian Shield, Ontario, Canada and subjected to anthropogenically acidified deposition is presented. Contrary to other published studies, this swamp retains sulphate during wet years and exports it during dry years. Alkalinity is always retained (acidity is exported) and base cations are almost always exported. It is predicted that if this pattern continues, the cation exchange sites of the swamp will become increasingly saturated with protons and aluminum ions, and the waters passing through the swamp will be increasingly acidified.

Introduction

Minerotrophic conifer swamps are common peatlands on the Precambrian Shield in Canada, with important impacts on down-stream and lake chemistry (Gorham et al. 1984; Dillon & LaZerte 1992). Recently there has been a resurgence of interest in the impact of peatlands on water chemistry (Gorham et al. 1984; Bayley et al. 1986; Bayley et al. 1987; DeVito et al. 1989; Urban et al. 1989a; DeVito & Dillon 1992). Traditional minerotrophic swamp inputs are non-acidic, however when the surrounding uplands have been anthropogentically acidified, elevated inputs of protons, aluminum and sulphate are introduced into the swamp. How peatlands transform and/or retain these compounds and their impact on other peatland processes is an important subject of study (Gorham et al. 1984). Also of interest is how climatic conditions, in particular the amount of rainfall, affect this transformation and/or retention in peatlands (Gorham et al. 1984).

Detailed long-term chemistry and input-output budgets are provided here for a representative minerotrophic conifer swamp (PC1) on the PreCambrian Shield in the Muskoka-Haliburton area of Ontario. Previous studies of this swamp have examined the hydrology (Shibitani 1988; Wels

& DeVito 1989), paleoecology (Warner et al. 1992), the transformation of nutrients from inorganic to organic forms (DeVito et al. 1989; DeVito & Dillon 1992) and the retention as well as transformation to organic form of some metals (Al, Pb, Cu; LaZerte 1989; LaZerte et al. 1989; LaZerte 1991). The hydrology and geochemistry of the surrounding uplands have also been analyzed (Wels et al. 1991; Kirkwood & Nesbitt 1991; Law 1991; Dillon & LaZerte 1992). Kirchner et al. (1992; Fig. 1) have described the effect of drought on the swamp's outflow chemistry in the context of testing a geochemical model of stream chemistry. DeVito & Dillon (1992) examine the role of hydrology on phosphorus and nitrogen dynamics in the PC1 conifer swamp. In this study, the role of hydrology (low swamp water level in particular) and upland acidification on the net retention of the base cations, sulphate, aluminum species and alkalinity is determined.

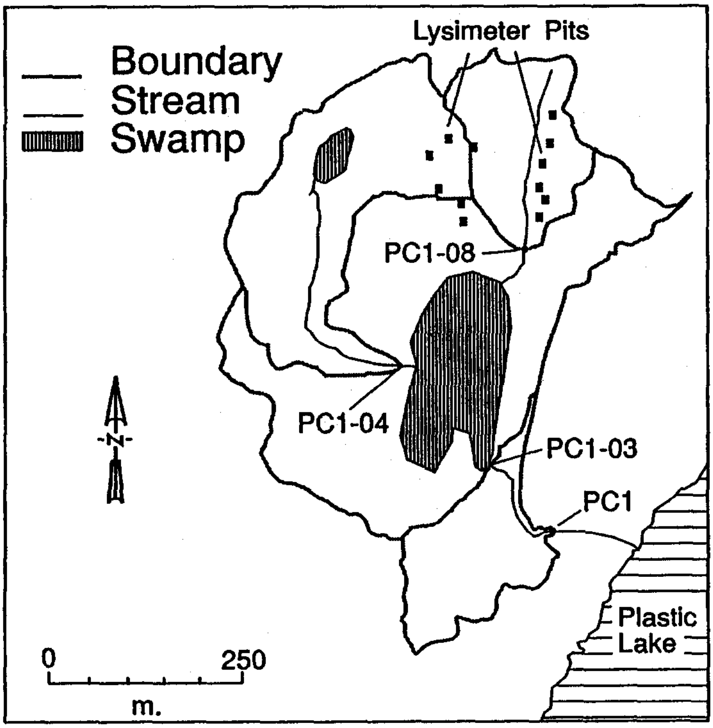

Fig. 1. Location of Plastic 1 swamp, major inflows, outflow and lysimeters.

Methods

The Muskoka-Haliburton region is located on a southern extension of the Pre-Cambrian Shield in Central Ontario. The sensivity of this area to acidic deposition, coupled with the relatively high historical deposition of acidity have made the Muskoka-Haliburton region one of the most acidified in Ontario (Neary & Dillon 1988). Precipitation depth in the Muskoka-Haliburton area averages about 1 m/yr (Dillon et al. 1988) with maximum precipitation depth usually in the fall (September to November) and minimum in the summer (June to August). Winter (December to February) precipitation accumulates as snow pack until spring (March—May) snowmelt.

The interior of the three largest basins draining into Plastic Lake are dominated by conifer swamps, of which the Plastic 1 (PC1) swamp and sub-catchment are the largest (Fig. 1). The upland soils of the PC1 catchment surrounding the swamp are sandy, shallow (~ 0.5 m) podzols underlain by granitic gneiss and amphibolite (Lozano 1987; Kirkwood & Nesbitt 1991; Law 1991). The upland forest cover is dominated by white pine, hemlock and soft maple. The conifer swamp soils are peaty, organic mucks and gleysols (mean depth 2—3 m; 7 m max. depth) dominated by white cedar and black spruce with sphagnum sp. as the dominant ground cover (Lozano & Parton 1986; DeVito 1989).

The PC1 basin above the swamp outflow (Fig. 1; PC1-03: 20.09 ha) was subdivided into three different sub-basins draining into the swamp and the swamp itself (PC1-08: 3.22 ha; PC1-04: 5.29 ha; other uplands: 9.46 ha; swamp: 2.12 ha). Of the three areas that drain into the swamp, PC1-08 discharges the greatest amount over the longest period of time. Chemical data from PC1-08 is available from March 1983. Discharge data is available from December 1986; prior to that, discharge was estimated by areal pro-rating discharge at PC1, a weir 50 m downstream from the swamp outflow.

The PC1-04 sub-basin is larger than PC1-08 but all possible sampling sites flow erratically and represent only a small portion of the total flow from this sub-basin. For chemical sampling a site was chosen that appears to have the greatest flow but a weir was not installed. Hydrological discharge from this area is computed by areal pro-rating the discharge from PC1-08 or PC1 (prior to December 1986 only). Chemical data from PC1-04 is available from March 1983.

The largest contributor to the PC1 conifer swamp is not channelized or surface flow at all, but macropore flow along the bedrock soil interface. The porous, sandy upland soils allow rapid vertical permeation of snowmelt and rainfall down to the bedrock interface. This is followed by gravitational, macropore flow along with bedrock soil/interface down to the swamp (Shibitani 1988; Wels et al. 1991; Renzetti et al. 1992). Areal pro-rating of the discharge from PC1-08 or PC1 (prior to December 1986 only) is used to estimate the hydrological discharge from these areas. Two possible estimates of the chemistry of the unchannelized macropore flow into the swamp are PC1-08 stream chemistry or ground water samples collected from 12 lysimeter pits installed in the northern section of the PC1 catchment (Fig. 1). The groundwater samples collected deep in the mineral soil horizon (usually under a Bf2 horizon) close to the bedrock interface should be the most similar to that leaching into the swamp. Only the four most recent years of data is available from these pits, so for longer term analysis, PC1-08 data is used.

The final input to the PC1 conifer swamp is direct precipitation to its surface. A bulk deposition collector and meteorological site located in the Plastic Lake catchment provide weekly chemistry and daily precipitation depth (Dillon et al. 1988; OME 1990). Data from this site is available from December 1983. Earlier data (March to December 1983) is obtained from a similar site located within 15 km. Empirical models were calibrated against three years of snowpack monitoring in PC1 catchment (Findeis et al. 1989; LaZerte, unpubl. results) to account for the substantial amounts of deposition collected in the swamp snowpack over winter and not released until spring snowmelt.

The hydrologic discharge at the swamp outflow (PC1-03) is calculated by areally prorating the discharge at the PC1 weir located about 50 m downstream. Chemical data from PC1-03 and hydrological data from PC1 are available from March 1983.

Samples were collected for chemical analyses more frequently during high flow periods (1—4 times per week in the spring and fall) than during low flood periods (once per week if water was available). All data was carefully examined for outliers using time trend plots and charge balance calculations. Linear interpolation was used to estimate the chemistry on days between sample collection. Sampling was frequent enough and discharge-concentration relationships weak enough that filling in missing data by interpolation was more accurate than using discharge-concentration relationships.

Chemical analyses were performed as described in OME (1983). All analyses were insensitive to DOC interference, including the ion chromatographic sulphate method. Aluminum species were estimated with a catechol violet/anion exchange method (LaZerte et al. 1988) and with the calculations described in LaZerte (1984). Oliver's model (Oliver et al. 1983) was used to estimate the organic anion contribution to charge balance. The model works well in these waters and elsewhere when corrected for iron and aluminum complexation (Oliver et al. 1983; LaZerte & Dillon 1984; Cantrell et al. 1990).

As Gran titrations are not adequate for aluminum or organic rich waters (see appendix), alkalinity was both titrated to a fixed endpoint of pH 3.8 and calculated at surface water sites. At groundwater sites, alkalinity was only calculated. For these calculations, alkalinity was defined to include bicarbonate alkalinity as well as the alkalinity generating portion of inorganic Al and weak organic acids. The latter was estimated as the fraction of Oliver's model organic acid (Oliver et al. 1983) that contributes to alkalinity titrations down to a pH of 3.8 ($Orgw^-$). This fixed endpoint alkalinity definition is quite different from the charge-balance definition (Reuss & Johnson 1986). For example, the attached hydroxyl groups of aluminum species, not the charges, are counted. Further details, and justification are provided in the appendix.

The start of each hydrological year was taken to be 1 September, before the fall rains began and when discharge from the swamp was usually zero. Input and output chemical fluxes per square metre of swamp surface were prepared on a daily basis, and then quarterly and annual sums computed. Input and output volume weighted concentrations on a quarterly basis were calculated by dividing quarterly chemical flux by the equivalent quarterly water flux and adjusting for the swamp area.

Errors and method checks

A regression (with an intercept of zero; $N = 15$) of the quarterly discharge of the PC1-08 inflow after December 1986 against the PC1 weir gives an R^2 of 0.99 and a slope of 0.16 ± 0.1 (2 S.E.). This slope compares favourably with the ratio of areas (0.15), confirming the use of areal prorating on a quarterly or annual basis for missing upland water fluxes. DeVito (1989) has also concluded that areal prorating works well in these catchments.

The major systematic error in these PC1 swamp budgets is probably the estimate of groundwater chemical concentrations. A rough estimate of this error can be obtained by comparing the total input fluxes to the swamp using PC1-08 stream chemistry for unmonitored areas with fluxes using lysimeter chemistry over the same period. The following slopes were obtained regressing (with an intercept of zero; $N = 16$) the PC1-08 estimate against the lysimeter estimate using the most recent four years of quarterly data where both estimates are available:

Variable	Coefficient	S.E.	P
Base Cations	0.91	0.01	0.0
Inorganic A1	0.85	0.02	0.0
H^+	1.09	0.01	0.0
Sulphate	0.93	0.01	0.0
$Orgw^-$	0.90	0.04	0.0
Other Anions	0.82	0.01	0.0

With the exception of H^+, the PC1-08 estimates of unchannelized groundwater chemistry are lower than estimates based on lysimeter data. The errors appear to be on the order of 8% lower for base cations and sulphate and 10—18% lower for the other ions.

Charge balances on the quarterly input and output volume weighted concentrations average −7% ± 6% (mean ± standard deviation, $n = 30$) and −1% ± 6% respectively, with maximum deviations of −24% and +16% respectively, for the long term budgets using PC1-08 chemistry for unchannelized input fluxes (Table 2).

Results

Base cations are the major cations entering the swamp with positively charged aluminum species and H^+ also important (Fig. 2; Table 1). Sulphate dominates the anion inputs with $Orgw^-$, bicarbonate, chloride and nitrate of lesser significance. The major inputs occur in the spring during snowmelt, with fall and occasionally early winter (December) influxes being somewhat important.

As chemical flux is the product of chemical concentration and water flux, changes in chemical flux are caused by changes in either one or both. Changes in surface water flux is a major determinant of the temporal pattern of chemical input flux to the swamp (Fig. 3; quarterly coefficient of variation, C.V. is 86%). The volume weighted input concentrations are comparatively stable (Table 2; quarterly C.V. are 23% and 18% for base cations and sulphate respectively). On an annual basis, both total cation inputs and total anion inputs have maximum and minimum annual fluxes (1984/85 and 1986/87 respectively) that correspond to maximum and minimum annual water fluxes (Figs. 2—3).

Base cations and sulphate also dominate the swamp outflow, but H^+ is more important than inorganic aluminum cations and organic anions are more abundant (Fig. 2; Table 1). Spring is very important to the output fluxes, but, in contrast to inputs and especially in the four years following

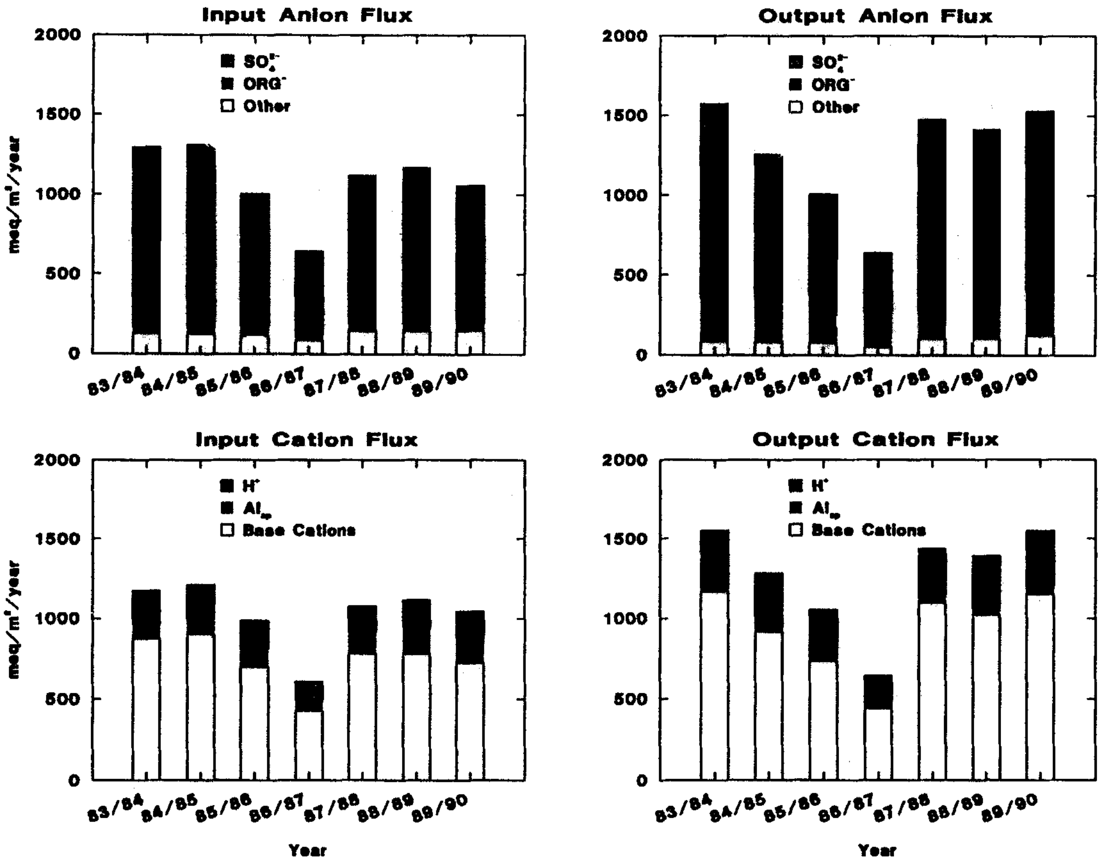

Fig. 2. Annual input and output cation and anion fluxes to Plastic 1 swamp.

Table 1. Inputs, outputs and retention per square metre of swamp surface. Units: discharge (m), all ions (meq/m2), DOC (g/m2).

Period	Discharge		Base Cations			Protons			Aluminum			Sulphate			Organic Anions			Other Anions			DOC		
	IN	OUT	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET
Unmonitored inputs estimated with PC1-08 data																							
Spring 83	3.61	3.23	462	399	63	101	160	−59	38	3	34	595	467	128	8	85	−77	52	19	33	9	19	−10
Summer 83	0.28	0.14	26	14	12	8	7	2	1	0	1	36	14	22	1	8	−7	6	1	5	0	2	−1
Fall 83	1.49	1.18	184	458	−274	48	105	−57	24	12	12	275	510	−235	10	72	−62	41	35	5	4	15	−11
Win 83/84	1.21	1.13	179	226	−47	47	82	−35	16	4	11	233	246	−13	5	42	−37	30	22	8	4	10	−7
Spring 84	3.29	2.99	444	432	12	85	153	−68	50	8	42	536	445	91	20	103	−83	44	22	22	10	22	−12
Summer 84	0.65	0.42	67	49	18	23	20	4	4	2	2	80	18	62	2	49	−47	15	6	9	2	9	−8
Fall 84	0.92	0.64	109	146	−37	35	44	−9	12	3	9	137	111	25	4	47	−44	24	19	4	2	10	−8
Win 84/85	1.28	1.25	196	223	−27	36	74	−38	24	13	11	247	235	12	7	59	−52	22	17	5	4	11	−7
Spring 85	4.34	3.98	540	515	25	119	207	−87	55	11	44	694	565	129	26	112	−86	60	38	22	12	25	−14
Summer 85	0.55	0.31	56	30	26	23	15	8	3	1	2	68	4	64	2	38	−36	17	8	9	1	7	−6
Fall 85	1.84	1.51	219	224	−5	51	83	−32	33	6	27	260	158	102	15	106	−90	32	32	0	5	21	−16
Win 85/86	0.53	0.61	74	92	−18	14	36	−22	13	3	10	88	95	−7	5	26	−21	9	12	−3	2	5	−4
Spring 86	2.65	2.66	346	348	−1	83	146	−63	61	11	50	412	370	42	29	100	−71	51	22	30	9	21	−12
Summer 86	0.71	0.58	57	68	−11	27	30	−2	7	2	4	76	11	65	5	64	−58	20	11	9	2	12	−11
Fall 86	1.31	1.60	136	166	−31	35	73	−38	19	2	17	158	96	61	15	121	−106	33	25	8	5	23	−18
Win 86/87	0.26	0.38	36	39	−3	5	16	−11	4	0	4	40	30	10	2	19	−17	5	6	−1	1	4	−3
Spring 87	2.00	1.97	237	228	10	59	98	−39	44	8	36	294	241	53	23	70	−48	36	18	18	7	15	−8
Summer 87	0.24	0.08	15	7	8	15	3	11	1	0	1	25	2	23	0	8	−8	10	2	8	0	1	−1
Fall 87	0.33	0.17	38	175	−138	17	24	−7	6	6	0	49	195	−146	2	12	−10	16	12	3	1	3	−2
Win 87/88	1.11	1.10	202	394	−193	35	96	−61	41	13	28	229	432	−203	12	54	−42	40	37	4	3	12	−8
Spring 88	3.47	3.03	530	520	10	93	177	−83	89	20	68	623	565	58	38	102	−64	80	54	26	11	22	−11
Summer 88	0.18	0.04	11	5	6	11	2	9	1	0	1	21	3	18	0	3	−3	7	0	7	0	1	−0

Fall 88	1.55	1.12	220	377	−157	51	105	−54	48	12	36	273	384	−112	16	77	−61	51	38	13	5	16	−12
Win 88/89	0.31	0.42	48	106	−57	9	32	−23	11	4	7	58	107	−49	3	20	−17	11	15	−4	1	4	−3
Spring 89	3.41	3.21	481	515	−34	94	194	−100	106	13	93	599	568	30	32	113	−81	73	52	21	10	25	−14
Summer 89	0.30	0.19	28	22	6	11	10	1	4	1	3	39	10	28	2	22	−21	9	2	7	1	4	−3
Fall 89	1.48	1.65	190	516	−326	48	141	−93	41	19	22	218	491	−273	17	125	−108	51	56	−5	5	25	−21
Win 89/90	0.66	0.76	102	168	−66	23	57	−34	24	6	18	119	173	−54	7	35	−27	23	19	3	2	7	−5
Spring 90	3.13	2.89	412	442	−29	79	158	−79	91	15	76	491	446	45	27	106	−80	65	46	19	9	22	−14
Summer 90	0.23	0.14	18	20	−1	12	7	5	3	0	2	28	18	10	1	9	−8	7	1	6	0	2	−1
Unmonitored inputs estimated with PC1-08 data																							
83/84	6.65	5.72	873	1165	−291	203	360	−156	93	26	68	1125	1219	−94	37	267	−230	130	86	44	19	57	−37
84/85	7.08	6.18	901	914	−13	213	339	−126	94	28	65	1146	916	231	39	257	−218	122	82	40	19	53	−34
85/86	5.73	5.36	697	732	−35	175	295	−120	114	22	92	836	634	202	55	296	−241	112	76	36	17	60	−43
86/87	3.81	4.03	425	441	−16	113	190	−78	68	10	58	518	370	148	40	218	−179	84	51	33	13	43	−30
87/88	5.09	4.34	780	1094	−314	156	299	−143	137	39	98	922	1195	−273	52	171	−120	144	104	40	15	37	−21
88/89	5.56	4.95	777	1020	−243	165	341	−176	169	30	139	969	1070	−102	53	232	−180	143	106	37	17	49	−33
89/90	5.49	5.43	723	1145	−422	162	363	−201	159	40	119	856	1128	−272	52	275	−223	146	123	23	16	56	−41
Unmonitored inputs estimated with lysimeter data																							
86/87	3.81	4.03	497	441	56	106	190	−84	81	10	72	550	370	180	47	218	−171	108	51	57	14	43	−29
87/88	5.09	4.34	834	1094	−260	146	299	−153	152	39	113	968	1195	−227	58	171	−113	170	104	66	16	37	−21
88/89	5.56	4.95	863	1020	−157	155	341	−186	199	30	169	1049	1070	−21	63	232	−169	171	106	64	18	49	−31
89/90	5.49	5.43	801	1145	−344	146	363	−217	179	40	138	919	1128	−209	59	275	−216	169	123	46	16	56	−40

Table 2. Volume weighted concentrations and charge balances. Units: ueq/L except mg/L for DOC.

Period	Base Cations		Protons		Aluminum		Sulphate		Organic Anions		Other Anions		DOC		Charge Balance		%Charge Balance	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT
Unmonitored inputs estimated with PC1-08 data																		
Spring 83	128	111	28	44	10	1	165	129	2	23	14	5	3	5	−15	−2	−9	−1
Summer 83	94	51	30	25	3	0	130	51	4	30	21	2	2	6	−28	−6	−20	−8
Fall 83	123	307	32	70	16	8	184	342	7	48	27	24	3	10	−47	−29	−24	−7
Win 83/84	147	186	39	67	13	3	192	203	4	35	25	18	3	9	−23	1	−11	1
Spring 84	135	131	26	47	15	2	163	135	6	31	13	7	3	7	−6	7	−4	4
Summer 84	103	75	36	31	6	3	122	27	3	75	23	9	2	14	−3	−3	−2	−3
Fall 84	119	159	38	49	13	3	149	122	4	52	26	21	3	11	−9	16	−5	8
Win 84/85	153	174	28	58	19	10	193	184	5	46	17	13	3	8	−15	−1	−7	−0
Spring 85	125	119	27	48	13	3	160	130	6	26	14	9	3	6	−15	4	−9	2
Summer 85	102	55	42	27	5	1	125	8	3	70	31	14	2	13	−10	−9	−7	−10
Fall 85	119	122	28	45	18	3	141	86	8	57	17	17	3	11	−2	10	−1	6
Win 85/86	141	175	26	68	24	5	167	180	9	49	17	22	3	10	−2	−3	−1	−1
Spring 86	131	131	31	55	23	4	155	140	11	38	19	8	3	8	−1	5	−0	2
Summer 86	80	96	39	42	9	3	107	15	7	89	27	15	2	17	−14	21	−10	16
Fall 86	104	127	27	56	14	1	120	73	11	92	25	19	3	18	−12	−1	−8	−1
Win 86/87	140	153	18	62	17	2	156	118	7	74	20	23	3	15	−9	2	−5	1
Spring 87	119	114	29	49	22	4	147	120	11	35	18	9	4	7	−6	2	−4	1
Summer 87	63	30	60	14	4	0	104	8	1	33	40	8	2	6	−18	−6	−13	−12
Fall 87	113	525	51	72	18	17	148	584	5	36	47	37	2	8	−17	−43	−9	−7
Win 87/88	182	356	32	87	37	12	206	390	11	49	36	33	3	11	−3	−17	−1	−4
Spring 88	153	150	27	51	26	6	180	163	11	29	23	16	3	6	−9	−2	−4	−1
Summer 88	63	27	62	12	6	1	117	18	2	18	42	2	2	3	−30	2	−20	5
Fall 88	142	243	33	68	31	8	176	248	10	50	33	24	3	11	−13	−3	−6	−1
Win 88/89	158	346	31	106	35	13	191	350	10	66	35	49	3	14	−12	0	−5	0
Spring 89	141	151	28	57	31	4	176	167	10	33	21	15	3	7	−7	−3	−3	−2

Summer 89	95	74	36	33	14	2	129	35	6	75	31	7	2	14		−21	−8	−14	−7
Fall 89	129	350	33	96	28	13	148	333	11	84	35	38	3	17		−4	3	−2	1
Win 89/90	155	255	34	86	36	9	181	263	11	53	34	30	3	11		−1	5	−0	1
Spring 90	132	141	25	50	29	5	157	143	9	34	21	15	3	7		0	5	0	3
Summer 90	80	85	52	30	12	2	119	76	4	40	32	6	2	7		−12	−5	−8	−4
C.V.	23	68	30	42	54	87	18	82	47	42	34	66	19	39	Mean	−12	−2	−7	−1
															S.D.	10	12	6	6
Unmonitored inputs estimated with PC1-08 data																			
83/84	131	175	31	54	14	4	169	183	6	40	20	13	3	9		−18	−3	−10	−1
84/85	127	129	30	48	13	4	162	129	5	36	17	12	3	8		−14	4	−8	2
85/86	122	128	30	51	20	4	146	111	10	52	20	13	3	10		−3	8	−2	4
86/87	111	116	30	50	18	3	136	97	10	57	22	13	3	11		−9	1	−6	0
87/88	153	215	31	59	27	8	181	235	10	34	28	20	3	7		−9	−7	−4	−3
88/89	140	183	30	61	30	5	174	192	10	42	26	19	3	9		−10	−3	−5	−1
89/90	132	208	30	66	29	7	156	205	9	50	27	22	3	10		−2	4	−1	1
C.V.	10	25	2	12	33	39	10	32	25	20	18	27	6	17	Mean	−9	0	−5	0
															S.D.	6	5	3	2
Unmonitored inputs estimated with lysimeter data																			
86/87	130	116	28	50	21	3	144	97	12	57	28	13	4	11		−5	1	−3	0
87/88	164	215	29	59	30	8	190	235	11	34	33	20	3	7		−12	−7	−5	−3
88/89	155	183	28	61	36	5	189	192	11	42	31	19	3	9		−12	−3	−5	−1
89/90	146	208	27	66	33	7	167	205	11	50	31	22	3	10		−4	4	−2	1
C.V.	10	25	3	11	21	41	12	33	6	22	7	21	9	19	Mean	−8	−2	−4	−1
															S.D.	4	5	2	2

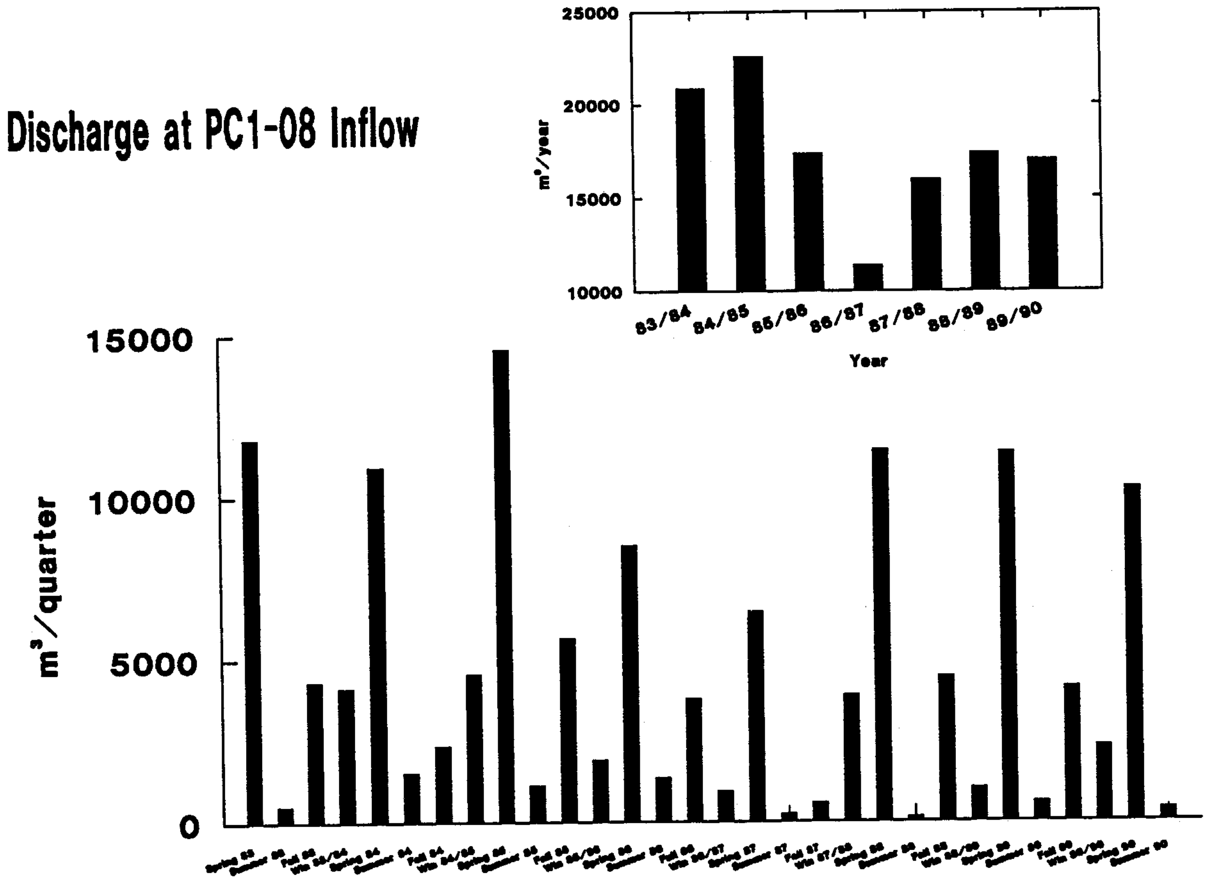

Fig. 3. Quarterly and annual discharge at PC1-08 inflow to Plastic 1 swamp.

the dry summers of 1983, 87, 88 and 89, Fall + Winter is even more important.

Summer drought conditions have a major impact on wetland chemical concentrations and consequently on chemical output fluxes. The average daily summer precipitation depth is correlated with the number of days with zero discharge from the PC1 swamp (Fig. 4). A lowered water table and exposed muck soils are found during these periods of zero discharge in the summer. In the years following an extended summer period of zero discharge, concentrations of most chemical parameters become elevated and, in particular, with the onset of fall rains the first flush of water from the swamp is very concentrated (Table 1; see also Kirchner et al. 1992, Fig. 1). The variability of output water flux is similar to the inflow (quarterly C.V. is 88%), but the equally variable base cation and sulphate concentrations (Table 2; quarterly C.V. of 68—82%) also have an substantial impact on the temporal variability of chemical fluxes from the swamp.

It is in the Fall + Winter quarters following the dry summers that the most substantial negative retentions (net export; Table 1; Fig. 5) of base cations and sulphate occur. The annual pattern of sulphate and base

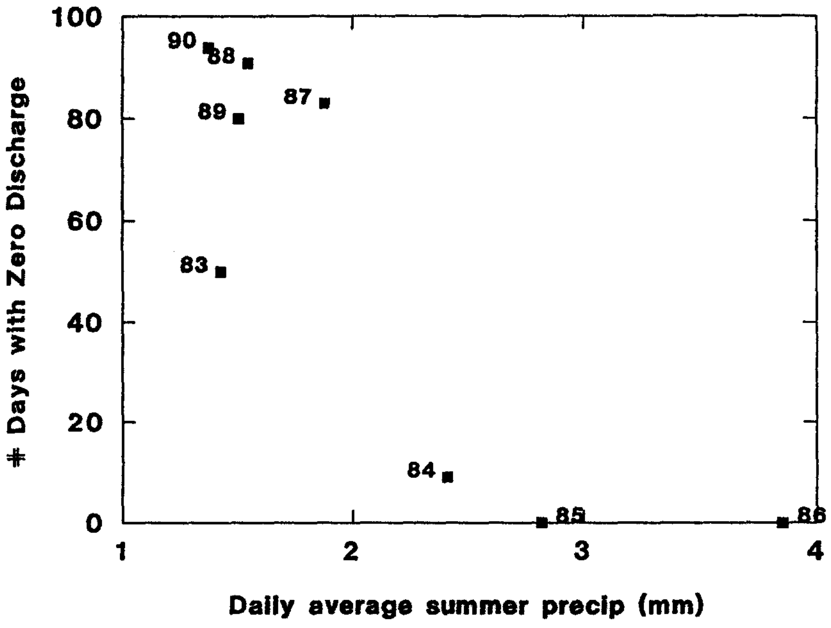

Fig. 4. Relationship between the daily average summer precipitation depth and number of days of the year with zero discharge from the Plastic 1 swamp.

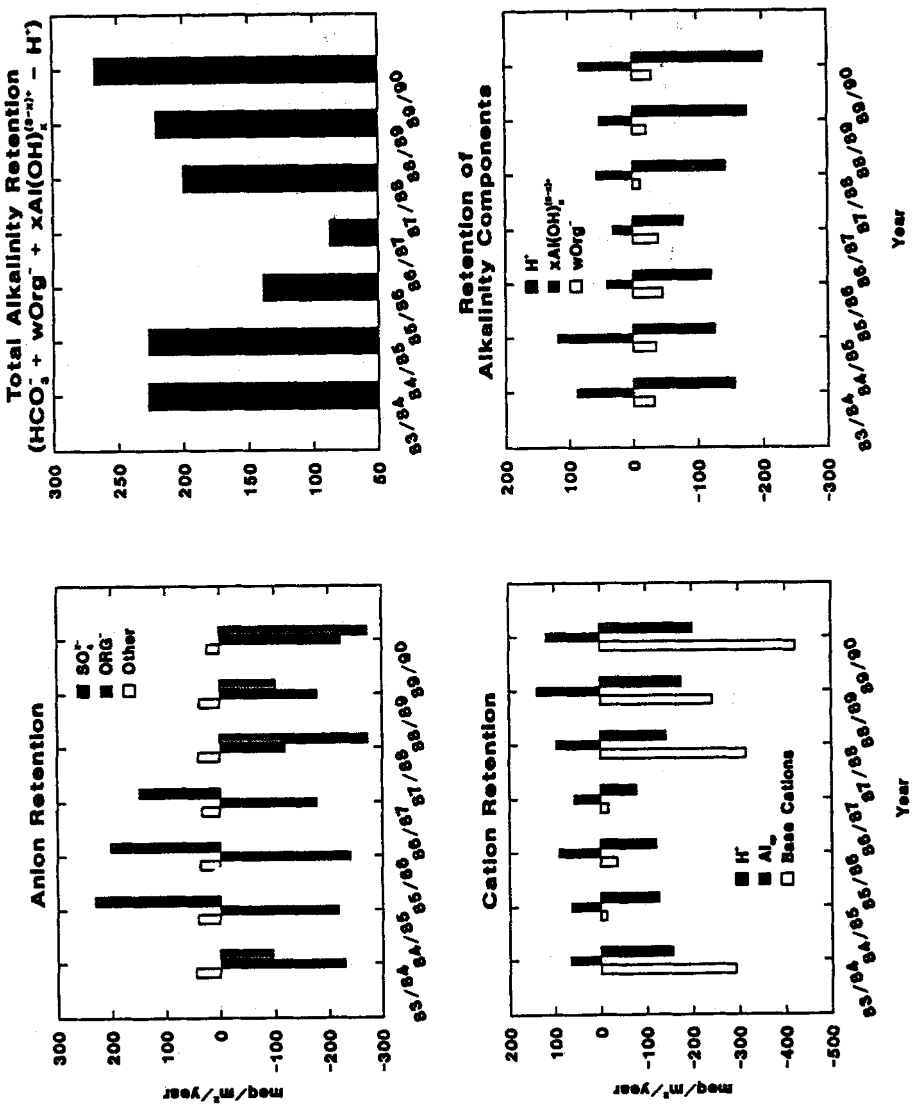

Fig. 5. Annual retention of cations and anions and alkalinity (total and by components) in Plastic 1 swamp.

cations is also revealing: only in the years following dry summers is there a net export of sulphate (negative retention). In all other years, including those years with the highest and lowest water fluxes through the swamp (1984/85 and 1986/87 respectively), suphate is retained. Base cations are never positively retained on an annual basis (when using the PC1-08 estimate for ungauged area; Table 1, Fig. 5); they are approximately in balance after a normal summer and exported after drought, even through the highest and lowest water flux years. Clearly summer drought conditions have a substantial impact on the retention of these major ions, primarily by releasing larger quantities of them in the subsequent fall and winter discharge periods.

The negative retention (net export) of H^+ shows an annual pattern that may have as much to do with annual water flux as summer drought. Large net exports in the spring dominate the annual budgets. Although the pH drops dramatically, most of the fall export of sulphate following summer drought is balanced by base cations, not protons. Nonetheless, the three years of minimum proton export do correspond to the three years of positive sulphate retention. The seasonal and annual retentions of aluminum cations, $Orgw^-$ and other anions show less pattern, although the three latest drought years do have elevated aluminum retentions relative to the three previous wet years.

H^+ and aluminum hydroxide species are the two dominant components of alkalinity retention in the PC1 conifer swamp and consequently the temporal pattern of alkalinity retention is similar to theirs (Fig. 5; Table 3). Annually, alkalinity is retained; only in the summer are small amounts of alkalinity exported. This is the result of H^+ retained from summer rainfalls (the only time when direct deposition is important to these budgets) and $Orgw^-$ export. If the contribution of alumimum hydroxides and weak organics to alkalinity were ignored, the estimates of alkalinity retained by the swamp would be less but the pattern would be similar.

Net DOC fluxes from this peatland range from 21 to 43 g m^{-2} yr^{-1} (Table 1).

Discussion

One of the most significant results of this research is the net export of base cations from the PC1 swamp over the current seven year study period. Other budget studies, although rare, indicate that both ombrotrophic and minerotrophic peatlands retain base cations (Hemond 1980; Gorham et al. 1984; Urban & Bayley 1986). The lack of base cation retention at this acidified site may be the result of competition for new exchange sites by

Table 3. Input, output and retention per square metre of swamp surface of fixed endpont alkalinity (meq/m2).

Period	Protons			Weak Organics			Aluminum			Bicarbonate			Total Alkalinity		
	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET	IN	OUT	RET
Unmonitored inputs estimated with PC1-08 data															
Spring 83	101	160	−59	8	20	−12	46	0	46	15	6	10	−31	−134	103
Summer 83	8	7	2	0	2	−2	2	0	2	1	0	1	−4	−5	0
Fall 83	48	105	−57	4	8	−5	34	0	34	6	2	5	−4	−94	90
Win 83/84	47	82	−35	4	8	−4	13	0	13	5	3	2	−26	−71	46
Spring 84	85	153	−68	10	23	−13	37	1	36	12	7	5	−27	−123	97
Summer 84	23	20	4	1	12	−10	6	0	5	4	1	3	−13	−7	−5
Fall 84	35	44	−9	2	9	−7	8	0	8	4	1	3	−21	−34	13
Win 84/85	36	74	−38	3	10	−7	18	0	18	6	2	4	−8	−61	52
Spring 85	119	207	−87	11	25	−14	89	1	88	16	8	8	−3	−172	169
Summer 85	23	15	8	1	9	−8	5	0	5	4	1	4	−13	−5	−8
Fall 85	51	83	−32	5	23	−17	29	0	29	10	2	9	−7	−59	52
Win 85/86	14	36	−22	2	5	−4	3	0	3	4	1	3	−5	−30	24
Spring 86	83	146	−63	9	21	−12	9	1	8	13	4	9	−52	−120	68
Summer 86	27	30	−2	2	15	−13	1	0	1	5	1	4	−19	−4	−5
Fall 86	35	73	−38	5	29	−24	8	0	8	13	3	10	−9	−41	31
Win 86/87	5	16	−11	1	5	−4	3	0	3	3	1	2	2	−10	12
Spring 87	59	98	−39	8	16	−9	20	0	20	8	4	4	−23	−78	55
Summer 87	15	3	11	0	2	−2	1	0	1	1	0	1	−12	−1	−11
Fall 87	17	24	−7	0	0	0	2	0	2	1	0	1	−13	−23	10
Win 87/88	35	96	−61	4	6	−3	11	0	10	5	1	3	−16	−88	72
Spring 88	93	177	−83	12	20	−8	45	1	44	12	6	6	−25	−150	126
Summer 88	11	2	9	0	1	−1	1	0	1	1	0	1	−10	−2	−8

Fall 88	51	105	−54	5	8	−3	17	0	17	6	1	5	−23	−95	72
Win 88/89	9	32	−23	1	3	−2	4	0	4	2	1	1	−3	−28	26
Spring 89	94	194	−100	11	22	−11	30	1	30	13	7	6	−40	−165	125
Summer 89	11	10	1	1	5	−4	2	0	2	2	0	2	−6	−5	−2
Fall 89	48	141	−93	4	15	−11	30	1	30	5	2	3	−9	−124	115
Win 89/90	23	57	−34	2	5	−3	9	0	9	4	2	2	−8	−50	42
Spring 90	79	158	−79	9	22	−14	44	1	43	14	6	7	−13	−128	115
Summer 90	12	7	5	0	2	−2	1	0	1	1	0	1	−10	−5	−5
Unmonitored inputs estimated with PC1-08 data															
83/84	203	360	−156	19	50	−32	89	1	88	27	12	15	−69	−296	227
84/85	213	339	−126	18	53	−35	120	1	119	30	12	18	−46	−273	227
85/86	175	295	−120	18	63	−46	42	1	41	32	8	24	−83	−222	139
86/87	113	190	−78	13	53	−39	32	1	32	25	7	18	−42	−130	88
87/88	156	299	−143	16	27	−11	59	1	57	18	7	11	−64	−263	200
88/89	165	341	−176	17	38	−21	53	1	52	23	9	14	−71	−292	221
89/90	162	363	−201	15	45	−30	84	1	83	23	10	13	−39	−307	267
Unmonitored inputs estimated with lysimeter data															
86/87	106	190	−84	18	53	−34	33	1	32	36	7	28	−19	−130	110
87/88	146	299	−153	21	27	−7	81	1	80	32	7	25	−13	−263	250
88/89	155	341	−186	22	38	−16	85	1	84	37	9	28	−11	−292	281
89/90	146	363	−217	18	45	−27	110	1	109	39	10	29	21	−307	328

incoming protons and aluminum ions. In the past, there may have been sufficient incoming base cations (and fewer competing protons and Al ions) to populate many of the sites. Under current conditions, however, with the loss of base cations and the increase of aluminum ions, the cation exchange sites in the swamp are likely becoming more acidified as predicted by Gorham et al. (1984), Urban & Bayley (1986) and Bayley et al. (1986).

Another important result is the greater retention of sulphate relative to base cations. Currently, the swamp retains sulphate during normal and wet summers, and then exports it after dry summers. A similar pattern has been observed in this swamp for phosphorus and nitrogen (DeVito & Dillon 1992). It is likely that the exposure and oxidation of reduced sulphur compounds is responsible for these chemical fluctuations (Gorham et al. 1984; Bayley et al. 1986; Bayley et al. 1987; Urban et al. 1989b; DeVito & Dillon 1992); DeVito (unpubl. results) has documented increased rates of sulphur mineralization as the result of summer drought in PC1 swamp. This pulsed export of sulphate from the PC1 swamp is mostly balanced by an export of cations, presumably via an exchange reaction between the proton from the sulphur oxidation reaction and the base cations on the peat exchange sites. The retention of sulphate after wet summers, however, is not balanced by a retention of cations but by their reduced net export and, in part, by decreased proton export and increased aluminum retention. Geochemically, this is consistent with sulphate reduction increasing peat pH which reduces proton export but incresaes aluminum precipitation or adsorption. Eventually, if current conditions persist, the exchangeable pool of base cations in the swamp will be depleted by the periodic export of sulphate and more protons and some aluminum ions will be exported to compensate. This will increase acidity export (alkalinity retention) primarily by directly increasing the proton export and indirectly reducing $Orgw^-$ export.

Net sulphate retention has been observed in other peatlands as has post-drought release (Hemond 1980; Gorham et al. 1984 and references therein; Bayley et al. 1986; Urban & Bayley 1986; Urban et al. 1989b), but no investigator, to my knowledge, has reported an annual net export of sulphate (or of base cations) from an undisturbed minerotrophic peatland, as occurs in this wetland following dry summers. Bayley et al. (1986) hypothesize that, other conditions being equal, peatlands with historically less anthropogenic sulphur deposition should currently have greater base cation neutralization capacity and hence less proton export coupled with sulphate export. Their results and this study are consistent with this hypothesis.

The net export of acidity (retention of alkalinity) observed in this study is expected. Gorham et al. (1985) and Urban et al. (1989a) have documented the role of peatland organic acid exports in the acidification of stream water. In the PC1 swamp, organic acids increase the acidity of already acidified water passing through the swamp (LaZerte & Dillon 1984). This is especially the case in wet years (e.g. 87/88; Table 1) when the relative proportion of organic anions to sulphate anions in the swamp outflow approaches one. Conversely, after dry summers the large release of sulphate from the swamp reduces the relative importance of organic acids. More generally, the increased acidity of water passing through the swamp may be the result of high water yield (4—7 m of water m^{-2} of swamp yr^{-1}) which increases organic acid leaching from many peatlands, although the total net flux (21 to 43 g m^{-2} yr^{-1}) of organic carbon from the wetland is not unusual (Urban et al. 1989a). Another likely cause is the gradual loss of exchangeable base cations from the PC1 conifer swamp; these base cations would normally neutralize some of the internally generated organic acidity as well as mineral acidity from sulphur oxidation.

More detailed study is required to determine the exact layers of peat involved in the cycle of sulphate accumulation and export, and whether these same layers are also responsible for the cation export. Presumably reduced sulphur is immobile and can only be exported when swamp water levels drop to the point where oxygen can diffuse to is location. However, the protons released by sulphur oxidation are mobile, and it may be that the depth of peat available for proton/cation exchange is greater than that available for the sulphur oxidation. In addition, possible internal sources of base cations diffusing up from deep sediments (as has been postulated for iron; LaZerte 1991) should be considered. Similarly, the role of different regions of the swamp (e.g. the PC1-08 lagg on the eastern side of the swamp; see DiVito & Dillon 1992) should be examined. The crucial question is the amount of residual sulphur available and the size of cation storage in the swamp available to neutralize these pulsed sulphur oxidation events.

Climatic changes in temperature and rainfall have been shown to influence lake chemistry in unexpected ways (Webster et al. 1990; Psenner & Schmidt 1992). With respect to peatland behaviour, it may nonetheless be possible to extrapolate the effects of the drought conditions observed in this and other studies (e.g. Bayley et al. 1986) to wetland behaviour under the longer-term reduced rainfall conditions predicted for some regions. It should be emphasized that only long-term studies can provide the perspective and data needed for long term predictions.

Acknowledgements

Lem Scott very capably supervised the field work providing the data for this study.

Appendix – alkalinity method

The formula for calculating the fixed endpoint alkalinity defined in the Methods section follows from the proton balances of the individual acids that are as weak or weaker than the arbitrarily defined weak organic acids at pH 3.8 (Stumm & Morgan 1981). These are:

$H_2O = H^+ + OH^-$
$HOrgw = H^+ + Orgw^-$
$H_2CO_3 = H^+ + HCO_3^-$
$H_2CO_3 = 2H^+ + CO_3^{2-}$
$Al(H_2O)_6^{3+} + H_2O = H_3O^+ + AlOH(H_2O)_5^{2+}$
$Al(H_2O)_6^{3+} + H_2O = 2H_3O^+ + Al(OH)_2(H_2O)_4^+$ (the H_2O terms will be dropped below)
etc.

which lead to:

$$\text{(1) Alkalinity} = [Orgw^-] + 2[CO_3^{2-}] + [HCO_3^-] + [AlOH^{2+}] + 2[Al(OH)_2^+] + 3[Al(OH)_3] + 4[Al(OH)_4^-] + [OH^-] - [H^+]$$

$Al(OH)_3$ includes monomeric, polymeric and colloidal forms in solution that respond to the titration.

To test whether the calculated alkalinity (1) proposed above agrees with the actual fixed end point alkalinity titration to pH 3.8, a regression using all samples was performed; an approximate 1:1 relationship ($R^2 = 0.81$; $N = 886$) was obtained. Equally important, a multiple linear regression (with zero intercept) of titrated alkalinity versus the three major components also reveals approximate 1:1 relationships for each component ($R^2 = 0.81$; $N = 886$):

Variable	Coefficient	S.E.	P
$2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$	0.94	0.02	0.0
$[Orgw^-]$	1.15	0.05	0.0
$[AlOH^{2+}] + 2[Al(OH)_2^+] + 3[Al(OH)_3] + 4[Al(OH)_4^-]$	1.06	0.05	0.0

The first term is the traditional definition of (bicarbonate) alkalinity; in all of these samples, its major component is $[H^+]$.

The fixed pH 3.8 endpoint used in this definition of alkalinity is arbitrary, but it does happen to be the pH in the Oliver model (Oliver et al. 1983) where 50% of the organic acids are dissociated and where all carbonates are protonated and inorganic aluminum is not hydrolysed. Also, at this proton reference level the dissociation of carbonic acid and HOrgw and the hydrolosis of $Al(H_2O)_6^{3+}$ are alkalinity neutral: their addition to or subtraction from solution does not change the alkalinity (Stumm & Morgan 1981) although the pH may change. However the dissolution of calcium carbonate and aluminum trihydroxide do increase alkalinity by an amount equivalent to the introduction.

Both Cantrell et al. (1990) and Urban et al. (1989a) recommend a similar fixed endpoint alkalinity titration when organic acids and aluminum hydrolysis species are important, as the usual Gran alkalinity titration fails when applied to non-bicarbonate dominated waters. Hemond (1990) has presented an alternative approach that uses a correction factor applied to Gran alkalinity titrations in the presence of DOC; but it is unclear how titratable aluminum species would be corrected for. Others have defined alkalinity differently (e.g. Reuss & Johnson 1986; Hemond 1990):

(2) Alkalinity $= C_B - C_A$ (Sum strong base cations — Sum strong acid anions)

Then using charge balance, they obtain:

(3) Alkalinity $= [Org^-] + 2[CO_3^{2-}] + [HCO_3^-] + (Al(OH)_4^-] + [OH^-] - [H^+] -$
$3[Al^{3+}] - 2[AlOH^{2+}] - [Al(OH)_2^+]$

where $[Org^-]$ is the concentration of ALL dissociated organic acids, both weak as defined above and strong. Thus the addition and dissociation of the strong organic acids at pH's less than 3.8 do not reduce alkalinity in this formation (3) whereas they would in (1). Also it is the dissolution of $Al(OH)_3$ that is alkalinity neutral, not the hydrolysis of Al^{3+}. Although this definition (2) works well for bicarbonate dominated waters, it does not agree well with any actual alkalinity titration with strong acid (fixed end point or Gran) when inorganic aluminum, organic acids or $CaCO_3$ are abundant. Even though the organic acid discrepancy can be corrected by including the strong acid portion of organic acids in C_A, a more difficult problem with the charge balance approach (2) is that it does not account for the weak acidic hydrolysis of positively charged metals (e.g. Al^{3+}), nor does it handle any uncharged species that may contribute to alkalinity such as $CaCO_3$ or polymeric or colloidal $Al\,(OH)_3$.

Because of these discrepancies, the two methods give quite different results, as can be shown by setting Strong Acids Anions in equation (2) to Sulphate + (Org Anions − Weak Org) + (Other − Bicarb) from Tables 1 and 2. On an annual basis, there is usually a net export of charge balance alkalinity whereas the fixed end point alkalinity is always retained (i.e. there is a net export of acidity). As noted by Morel (1983):

> Although convenient, the conceptualization of alkalinity as a charge balance is not strictly correct; the proper concept is that of an acid-base balance.

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