Spatial and temporal patterns in the hydrogeochemistry of a poor fen in northern Wisconsin

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Abstract. We studied the factors causing spatial and temporal patterning of interstitial water chemistry in Crystal Bog, a 7 ha northern Wisconsin kettle-hole peatland. Over the course of the snow-free season Crystal Bog exhibited spatial and temporal patterns in chemistry, especially hydrogen-ion, dissolved organic carbon, and specific conductance. The peatland contains a 0.5 ha pond that has water more dilute than the interstitial water of the surrounding peatland. The direction of groundwater flow between the lake and the peatland was seasonally dependent. In the spring and early summer, flow was from the lake into the peatland, especially on the eastern side of the lake. This flow resulted in a plume of relatively dilute surface interstitial water in the peatland. In mid and late summer direction of groundwater flow was from the peatland into the lake and the dilute plume was reduced in areal extent. By fall the direction of water flow was again from the lake to the peatland.

The spatial and temporal heterogeneity in water chemistry produced by the seasonal variation in the direction of horizontal water flow was substantial. Minimum and maximum observed concentrations of dissolved organic carbon (DOC) in the interstitial water of the peatland, for example, differed by more than a factor of three, and pH ranged between 3.8 and 5.0. Correlations of DOC with anion deficit and hydrogen ion concentration and experiments of photo-oxidation of water samples showed that organic acids were the primary cause of acidity in the peatland. Specific conductance was highly correlated with DOC, probably because of DOC's correlation with the very conductive hydrogen ion. In Crystal Bog it was possible to use the relatively simple measure of specific conductance to estimate the temporal and spatial distribution of the more difficult to determine DOC.

Introduction

The source and movement of water into and through peatlands are two of the primary determinants of peatland structure and function (Gorham 1957; Heinselman 1970; Ivanov 1981; Wilcox et al. 1986). Investigations of the hydrology of large, patterned peatlands have shown that the amount of water entering a peatland through groundwater discharge is a critical determinant of interstitial water chemistry, and indirectly, of plant community composition (Glaser et al. 1981; Siegel 1983; Siegel & Glaser 1987; Siegel 1988). In small peatlands, however, other hydrologic features can be equally important. For example, 'kettle-hole bogs' (Kratz & DeWitt 1986; Vitt & Slack 1975), which are common

throughout most of the glaciated parts of the eastern U.S., often have a central pond that exchanges water with the surrounding peatland (Heinselman 1970; Hooper & Morris 1982; Marin 1986; Vitt & Slack 1975). If the chemistry of the water in the central pond is markedly different from that in the interstitial water of the surrounding peatland, spatial gradients in water chemistry may occur in the peatland as a function of distance from the pond. In addition, temporal gradients may occur if the direction of horizontal water flow between the pool and the surrounding peatland changes with time.

Here, we describe spatial and temporal patterns in the surface (0–25 cm) interstitial water chemistry of Crystal Bog, a seven hectare, poor fen-lake system in northcentral Wisconsin. Because horizontal water flow in the peatland-lake system can create spatial patterning in chemistry, we focus on seasonal patterns of water movement, particularly between the lake and surrounding peatland.

The predominant biogeochemical feature of Sphagnum-dominated peatlands is their high level of acidity. The source of acidity has been a matter of some controversy (Gorham et al. 1985), but recent hydrogen-ion budgets have indicated that much of the acidity arises through the production of organic acids from the incomplete decay of organic matter (Hemond 1980; Urban et al. 1986). Despite the importance of organic acids to peatlands, there have been few studies of the temporal and spatial distribution of dissolved organic acids within peatlands or of the factors that might cause these distributions (Eshleman & Hemond 1985; McKnight et al. 1985). Accordingly, we pay special attention to the spatial and temporal distributions of hydrogen ion and dissolved organic carbon (DOC).

Methods

Study site

Crystal Bog is located in the Northern Highland Lake District in northern Wisconsin (46°00′30″ N, 89°36′30″ W) (Fig. 1). The peatland is situated in Pleistocene glacial deposits of sandy tills ranging in thickness from 30–60 m (Trotta & Cotter 1973; Okwueze 1983), and contains peat ranging from 2 to 7 m thick. Deeper portions of the basin have a thin clay layer beneath the peat. The peatland has no stream inlets or outlets and overland runoff is assumed to be insignificant because of the sandy soils of the surrounding land. Kratz & Medland (in press) estimated that 2–15 cm of water (volume of water/surface area of the peatland), representing 3–17% of the total annual water inputs, enter the peatland by groundwater inseepage each year. The peatland encloses a 2.5 m deep, 0.54 ha pond, designated as unnamed lake 27-2 by the Wisconsin Department of Natural Resources (Black et al. 1963). Vegetation is typical of poor fens in the region (Vitt & Slack 1975; Schwintzer 1981; Kratz & DeWitt 1986) and is dominated by *Carex oligosperma*, *Chamaedaphne calyculata*, *Kalmia polifolia*, *Picea mariana*, and several species of *Sphagnum*, including *S. angustifolium*, *S.*
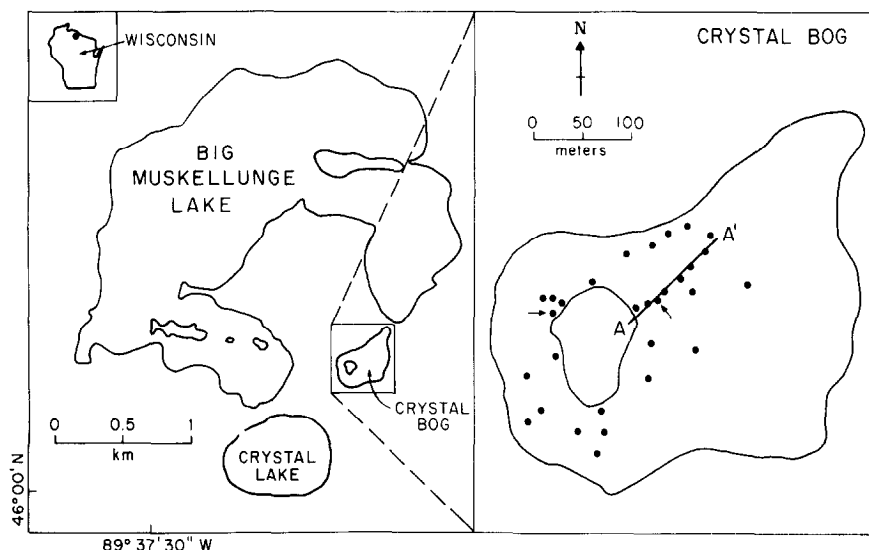
Fig. 1. Map of Crystal Bog and surrounding landscape indicating position of the central pond and the transect A–A′. Dots indicate the positions of water table wells. Arrow to east of pond indicates position of well used in gradient calculations used for Fig. 3. Arrow to northwest of pond indicates area containing closely spaced wells used for Table 3.

magellanicum, S. fuscum, and *S. nemoreum.* Voucher specimens of the *Sphagna* are deposited in the ALTA herbarium at the University of Alberta.

Hydrology

To measure horizontal hydraulic gradients of the peatland's water table, we hand drove 30 PVC water table wells (3.17 cm diameter i.d.) into the peatland. Each well was 1.5 m long, was capped at the bottom, and had a 15 cm slotted section that straddled the water level in the peatland. We measured water level in the lake using a staff gauge attached to a pipe whose bottom end was pounded into the mineral substrate beneath the lake. Occasionally throughout the study period, we used a surveyor's level to determine the elevation of the top of each well and the staff gauge relative to a permanent benchmark on the nearby upland. No movement of the staff gauge or of wells placed farther than 15 m from the lake edge was observed.

The peat mat responds to a person's weight, making water level measurements in the wells difficult. To minimize this problem, we made measurements as quickly as possible with a tape and 'popper', a small cylinder with a concave end attached to the end of the tape that makes a 'popping' sound when it contacts water. The observer stood at least 50 cm from the well while making a measurement. Experiments showed that, for wells more than 15 m from the lake edge, and with the observer at least 50 cm from the well, measured water levels were reproducible to within 3 mm and did not differ significantly from those measured using a portable boardwalk for support (Fig. 2). We used water level
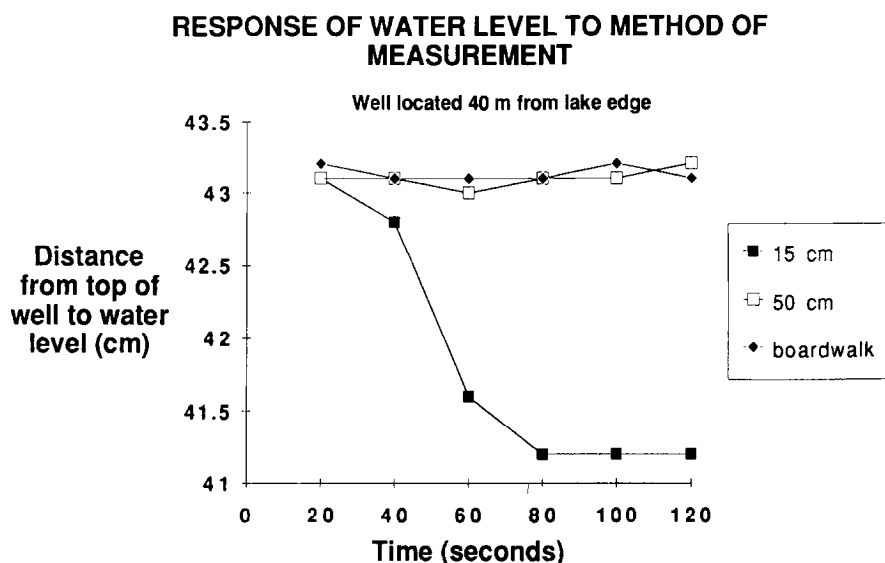
RESPONSE OF WATER LEVEL TO METHOD OF MEASUREMENT

Well located 40 m from lake edge

Distance
from top of
well to water
level (cm)

Fig. 2. Water level as a function of time for three methods of measurement. Boardwalk is a portable wooden platform that places observer's weight 2 m from well. 15 and 50 cm refer to distance of observer to well at time measurement was taken. Water level measured as distance from well top; smaller numbers indicate higher water levels.

data only from wells at least 15 m from the lake edge, although we used wells closer to the lake edge for water chemistry sampling.

Water levels in the wells and lake were measured 10 times between May and November 1985 (19, 30 May; 27 June; 18, 25 July; 1, 9, 16 August; 7 September; and 12 November). Using the water level measurements, we plotted equipotential lines by hand. If the upper layer of the peat is isotropic, then flow is perpendicular to these lines (Freeze & Cherry 1979).

Water chemistry

To determine overall spatial patterning in chemistry, water samples were taken from the entire network of wells on 5 June 1985. Additional samples were taken in 1985 (25 June; 19, 26 July; and 7 September) from the piezometers that lay along the transect A–A′ (Fig. 1). On each of these dates, samples for each of the parameters listed below were collected, except that on 19 July only samples for pH and specific conductance were taken. On 5 June we sampled three test wells that were placed within a circle of radius 0.5 m (Fig. 1) to estimate variance in interstitial water chemistry that occurs over a small spatial scale in the peatland.

Immediately before collecting water samples we removed 2–3 well volumes of water using a hand operated vacuum pump. Water samples were analyzed for pH, alkalinity, specific conductance, Ca^{2+}, Mg^{2+}, Fe, Na^+, K^+, Cl^-, SO_4^{2-}, SiO_2, DOC, and dissolved inorganic carbon (DIC). Samples for cation analyses were placed in acid washed, 125 ml polyethylene bottles and preserved with

Ultrex HCl; those for DOC, DIC, Cl^-, SO_4^{2-}, and SiO_2 were put into 125 ml polyethylene bottles that were previously washed only with deionized Milli-Q grade ultrapure water (Millipore Corporation). Finally, those for pH, alkalinity, and specific conductance were collected in a 25 ml polyethylene vial previously washed in ultrapure water.

All samples were kept cold and dark and were returned to the laboratory where water samples in the two 125 ml bottles were centrifuged at 15 000 rpm for 15 min and passed through a 0.4 μm Nuclepore filter to remove particulate material. Immediately after filtering, the anion sample was split: one portion was stored in glass vials for DOC/DIC analysis and the second portion was stored in a polyethylene bottle until analyzed for Cl^-, SO_4^{2-}, and SiO_2.

Analyses for pH, total alkalinity, and specific conductance were made within six hours of sampling. We measured pH using a Radiometer pH meter and a Radiometer electrode, total alkalinity using Gran titration, and specific conductance using a Markson IV meter on samples equilibrated to room temperature. We report specific conductance corrected to 25 °C.

We determined Ca, Mg, Na, and K using a Perkin–Elmer Model 503 Atomic Absorption Flame spectrophotometer (A.A.) within one month of collection. Iron was measured on the A.A. six months after collection. Chloride and SO_4^{2-} were determined on a Dionex Model 10 Chromatograph. We measured DOC/DIC using a wet potassium persulfate digestion with an O/I Corporation Model 700 TOC analyzer. Dissolved SiO_2 was analyzed using a colorimetric method with a Technicon II autoanalyzer.

Results

Hydrology

Equipotential lines indicate that the direction of water flow between the lake and surrounding peatland changed with season. Fig. 3 shows equipotential lines for four days at roughly monthly intervals from May to August. On the first two dates, 19 May and 27 June, water flowed out of the lake into the peatland. In contrast, on 25 July and 16 August, flow was mostly from the peatland into the lake. However, in the eastern part of the peatland, about 50 m from the lake, there was flow to the east away from the lake throughout the study period. Horizontal gradients along the transect A–A' (Fig. 1) demonstrate this seasonal pattern with a finer time resolution (Fig. 4). Water flowed from the lake into the peatland in spring and early summer and in fall. From mid-July to mid-September the direction of water flow was from the peatland into the lake.

Water chemistry

Crystal Bog is a poor fen, with weakly ionic surface water. Interstitial water samples ranged in pH from 3.8 to 5.0. DOC was between 15 and 56 mg/L, and
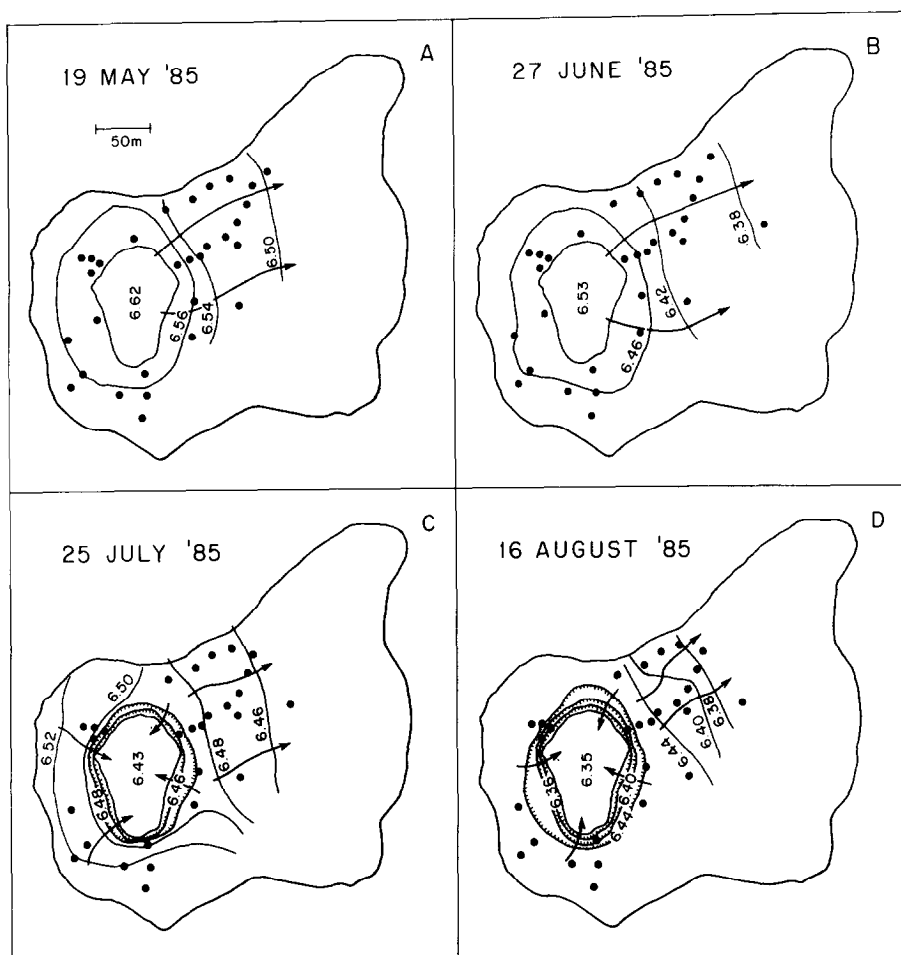
Fig. 3. Equipotential maps of the surface of Crystal Bog at roughly monthly intervals from May through August. Note that contour intervals are not consistent among dates. Elevations are in meters relative to an arbitrary benchmark. Lines with arrows indicate flow paths of surface interstitial water.

specific conductance ranged from 15 to 58 μS. Total dissolved solids ranged between 4–20 mg/L. Values for other chemical constituents are given in Table 1. Compared to the interstitial water of the peatland, water in the central pond had a lower concentration of all chemical parameters except sulfate.

Several lines of evidence suggest that the pH in the peatland is determined primarily by organic acids. First, interstitial water in the peatland had sizeable inorganic anion deficits and the magnitude of the inorganic anion deficit was correlated positively with the concentration of DOC (Fig. 5). Second, DOC was also positively correlated with hydrogen ion concentration (Fig. 6). Finally, the pH increased as much as two units, and alkalinity increased from 0 to about
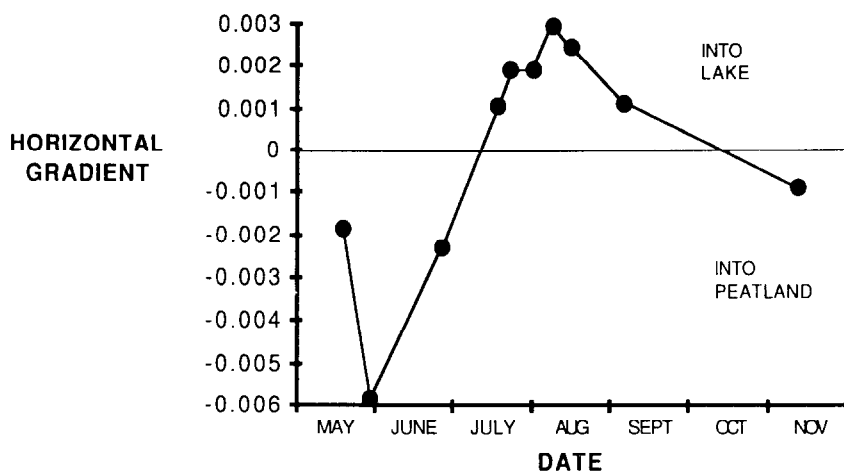
Fig. 4. Horizontal gradient in water level between the lake and a well 40 m from the lake along transect A–A' (Fig. 1) as a function of time of year. Positive values indicate flow from peatland into lake, negative values indicate the opposite direction of flow.

1 meq/L after DOC in the samples was removed by irradiation with ultra-violet light (Table 2). Interestingly, there was also a tight relationship between specific conductance and DOC (Fig. 7). When we subtracted the conductivity due to hydrogen ions (Sjörs 1950) there was no relationship between the modified conductivity and DOC, suggesting that the relationship between the un-modified conductivity and DOC is due to the highly conductive hydrogen ion (Levine 1978).

Chemical parameters in the three wells placed near each other were very similar (Table 3), indicating that small scale spatial variation in water chemistry may not be important in this peatland.

However, larger scale spatial patterns in certain aspects of interstitial water

Table 1. Surface water chemistry in the peatland and lake. Means for pH were calculated using pH, not H^+. Concentration is in μmols unless otherwise specified.

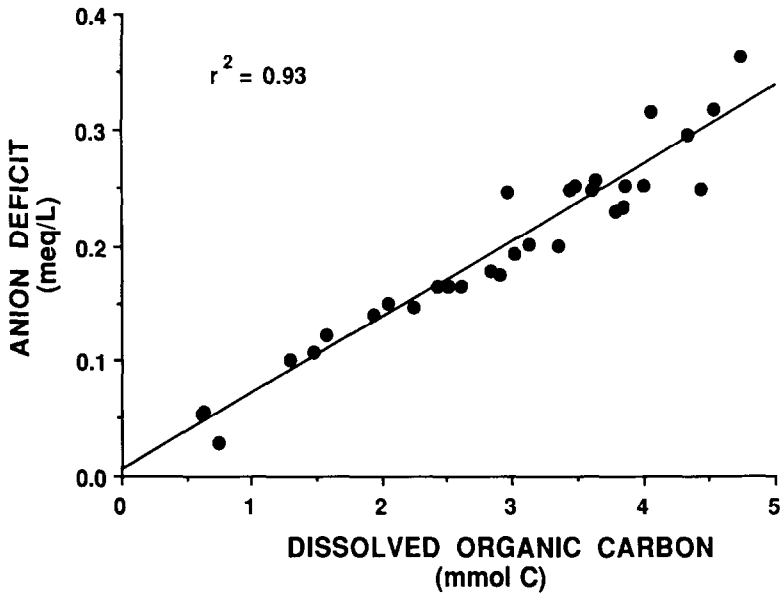| Parameter	Peatland			Lake		
	Mean	Range	n	Mean	Range	n
pH	4.1	3.8–5.0	67	4.9	4.8–5.1	5
Ca^{2+}	24.3	8–90	57	13	12–14	4
Mg^{2+}	12.5	3–52	57	8.8	8–10	4
Fe	11.3	2–21	43	1.7	0–2	3
Na^+	9.0	4–19	56	5.8	3–8	4
K^+	9.0	0–47	54	4.8	3–6	4
Cl^-	8.4	0–19	57	5.8	3–13	4
SO_4^{2-}	0.6	0–4	57	13	12–14	4
SiO_2	35.4	6–91	57	2.0	1–4	4
DOC (mg/L)	37.7	15.4–56	28	7.9	7.4–8.9	3
Conductance (μS)	38.4	15–58	67	11	9–12	5

Fig. 5. Inorganic anion deficit as a function of DOC concentration. Data are from interstitial water samples taken on 25 June, 26 July, and 7 September. Equation for the regression line is: DEF = 0.005 + 0.066*DOC; N = 31.
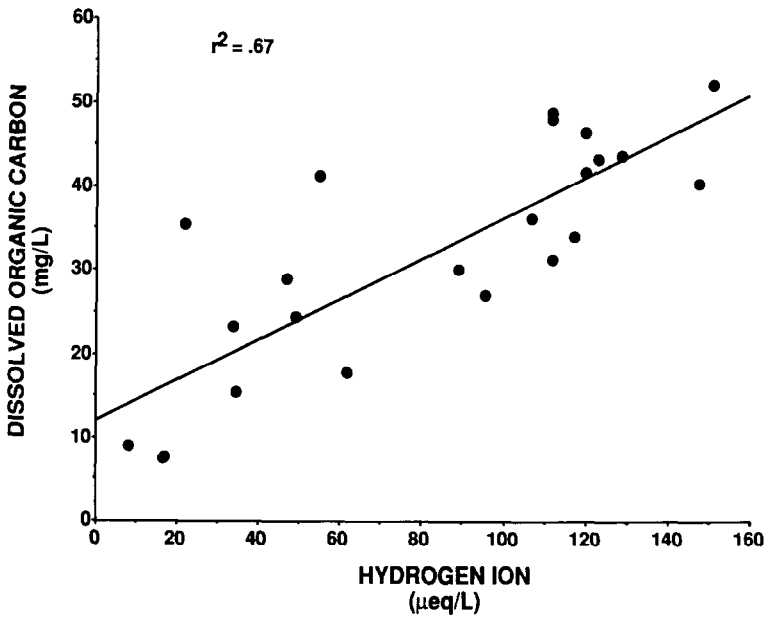

Fig. 6. DOC as a function of hydrogen ion concentration for surface interstitial water samples. Equation for regression line is: DOC = 12.1 + 0.241*[H$^+$]; N = 23.

Table 2. pH and alkalinity of samples before and after irradiation with ultra-violet light. Samples were taken from 3 wells on September 7, 1985.

pH		Alkalinity (meq/L)	
Before	After	Before	After
4.05	6.10	0.0	1.05
3.95	5.91	0.0	0.95
4.33	6.01	0.0	0.99

chemistry did occur. On all sampling dates both specific conductance and DOC increased as a function of distance from the lake edge along transect A–A'. Data for two example dates are shown in Figs. 8, 9. To test whether the steepness of the gradient was a function of the direction of water flow, we computed the slopes of linear regressions of specific conductance or DOC as a function of distance. During the time of year when water flows into the peatland from the lake, the spatial gradient of specific conductance was significantly lower than when water flows into the lake from the peatland (Wilcoxon signed-rank test, $p < 0.05$) (Fig. 10). For DOC the pattern was similar, but there were too few sampling dates to perform statistical tests.
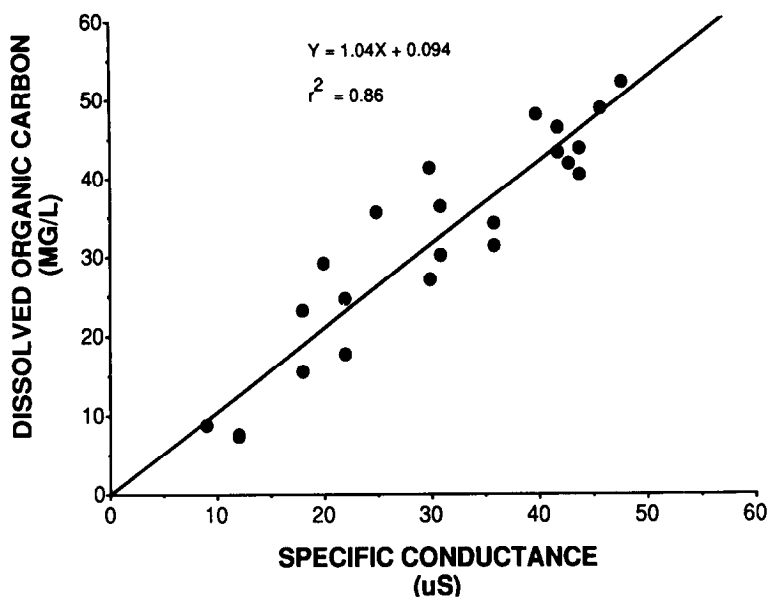

Fig. 7. DOC concentration as a function of specific conductance for surface interstitial water samples; $N = 23$.

Table 3. Chemical concentrations in three closely spaced wells sampled on June 5, 1985. Location of wells is indicated in Fig. 1. Means for pH were calculated using pH, not H^+. Data are in μmols unless otherwise indicated.

Parameter	Mean	Range	St. Dev.
pH	3.83	3.82–3.84	0.01
Conductance (μS)	43	41–44	2
Ca^{2+}	22	17–28	6
Mg^{2+}	13	10–16	3
Na^+	11	9–14	3
K^+	6	4–8	2
Cl^-	7	4–8	2
SO_4^{2-}	0	0	0
SiO_2	35	31–39	4

Discussion

The hydrology and chemistry of Crystal Bog are tightly coupled. Seasonal changes in water flow give rise to substantial seasonal patterns in the peatland's interstitial water chemistry, particularly the spatial distribution of DOC. Our conceptual model of the spatial and temporal dynamics of the hydrology and water chemistry is as follows. In the spring and early summer, snowmelt and minimal evaporation from the lake lead to high water levels in the lake and the peatland, and result in water flow from the lake into the surrounding peatland. Because water in the lake is relatively dilute with respect to hydrogen ion and
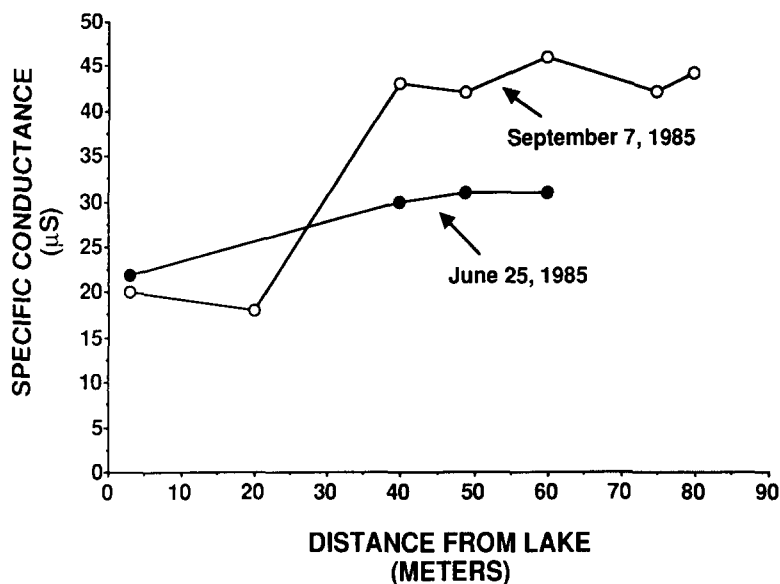

Fig. 8. Gradient of specific conductance along A–A' on two dates. On June 25, flow was from the lake into the peatland. On September 7, flow was in the opposite direction.
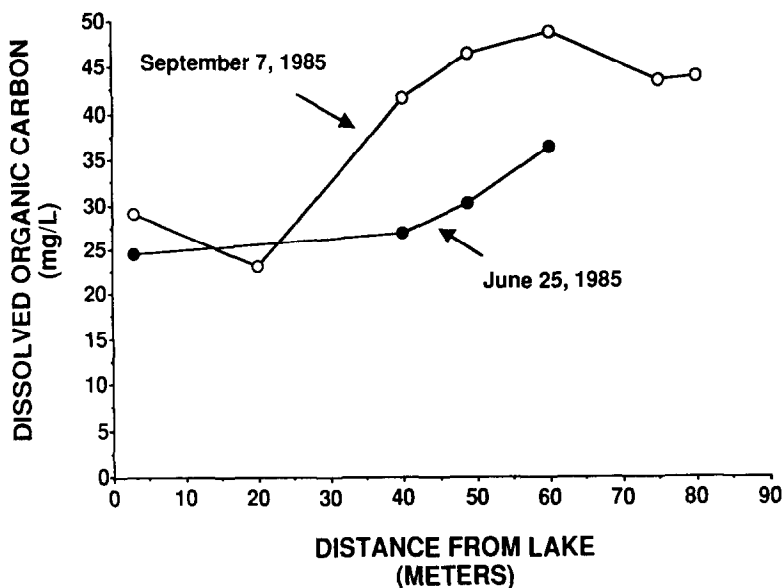
Fig. 9. Gradient of DOC along A–A' on two dates. On June 25, flow was from the lake into the peatland. On September 7, flow was in the opposite direction.

DOC, lake water entering the peatland dilutes the interstitial water of the peatland. This dilution causes a plume of water lower in DOC to appear, especially on the eastern side of the lake. The plume changes in spatial extent and magnitude depending on the hydraulic gradient from the lake into the
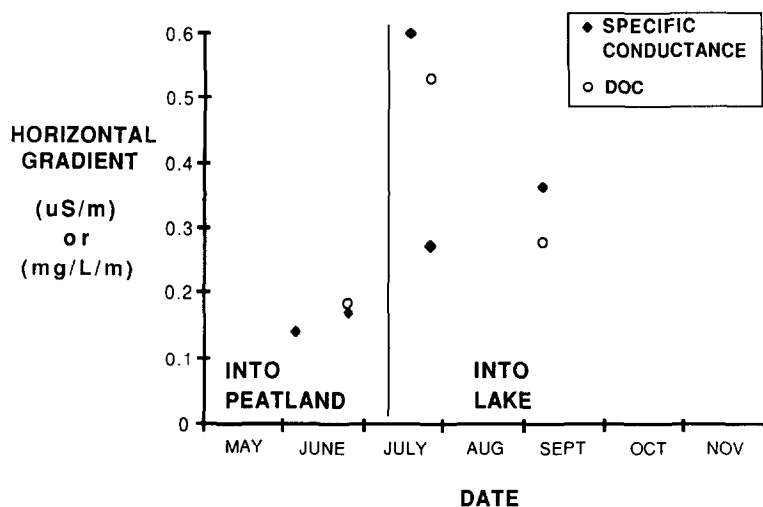

Fig. 10. Horizontal gradients of specific conductance and DOC as a function of time of year. Gradients were calculated as slopes of linear regression of concentration vs distance. Vertical line indicates when direction of water flow changed from into the peatland to into the lake.

peatland. During periods of high hydraulic gradient, the plume is more exten-
sive and during periods of low gradient, the plume is less extensive or virtually
disappears. By mid summer, reduced precipitation and increased evaporation
from the lake cause the hydraulic gradient to reverse and water flows from the
peatland into the lake. The water table mound occurring about 50 meters east
of the lake is due perhaps to a lowering lake level that leaves this area relatively
high. Alternatively, this area could be a site of reduced evapotranspiration for
some unknown reason, or a site with groundwater inflow (Siegel 1988), although
the water chemistry data suggest this is unlikely. The reversal of the hydraulic
gradient causes a reduction in the plume of low DOC water. By mid fall the
hydraulic gradient reverses again, probably owing to reduced evaporation from
the lake because of lower air and water temperatures, and water flow is from the
lake to the peatland. Presumably this reversal causes the plume to increase its
extent in the fall, but we have no chemical data for this time of year.

The relationship between dissolved organic carbon, inorganic ion deficits, and
hydrogen ion concentration found in this study and elsewhere (Gorham et al.
1985; Urban et al. 1986) demonstrates that DOC is one of the most important
influences on interstitial water chemistry of peatlands. By regressing DOC (units
of moles of C) against inorganic anion deficit, we calculated there are 0.066
equivalents of organic acids per mole of organic carbon (Fig. 5). Our estimate
for Crystal Bog agrees closely with estimates for other peatlands (Eshelman &
Hemond 1985; Gorham et al. 1985, McKnight et al. 1985) and is roughly two
times the amount reported in lakes (Cook et al. 1987). However, the spatial and
temporal distribution of organic acids in peatlands remains poorly understood
(McKnight et al. 1985). One reason for the poor understanding is that measure-
ment is relatively difficult, time consuming, and expensive. The remarkably tight
relationship between DOC and specific conductance, a parameter that can be
measured essentially instantaneously in the field, allows us to use specific
conductance as a proxy for DOC, at least in Crystal Bog.

In an exploratory study of Crystal Bog in 1984, the year before the more
intensive study reported here, we measured specific conductance in the surface
interstitial waters throughout the peatland on two dates, 15 June and 9 August.
Using the relationship between DOC and specific conductance shown in Fig. 7,
we converted the specific conductance values to estimates of DOC. Contour
lines of DOC on these two dates showed substantial differences in the plume of
low DOC water between the two dates, consistent with the patterns found in
1985 (Fig. 11).

It remains to be seen whether the relationship between DOC and specific
conductance found in Crystal Bog can be applied to other peatlands in the area.
If it can, it may be possible to increase rapidly our understanding of the
temporal and spatial distribution of DOC and organic acids in peatlands. To the
extent that specific conductance can be used as a qualitative tracer of water flow
from the lake to the peatland, it may also be possible to use this simple
measurement to increase our understanding of the factors causing spatial and
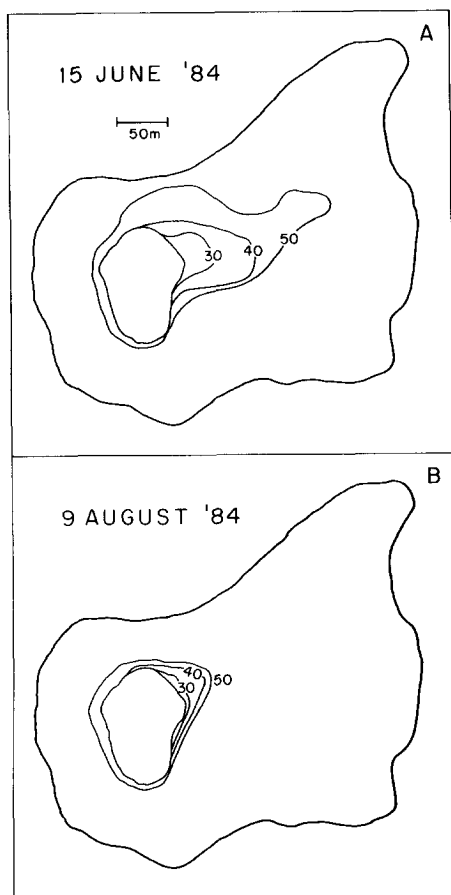temporal patterning of interstitial water chemistry of small peatlands.

Fig. 11. Spatial distribution of surface DOC concentration on (*a*) 15 June 1984 and (*b*) 9 August 1984, as inferred from specific conductance measurements.

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