Biogeochemistry **43:** 17–41, 1998.

Peat characteristics and groundwater geochemistry of calcareous fens in the Minnesota River Basin, U.S.A. *

JAMES E. ALMENDINGER[1,*] & JEANETTE H. LEETE[2]
[1]*U.S. Geological Survey, Water Resources Division, 2280 Woodale Drive, Mounds View, MN 55112, USA;* [2]*Minnesota Department of Natural Resources, Division of Waters, 500 Lafayette Road, St. Paul, MN 55155, USA; (* Corresponding author: St. Croix Watershed Research Station, Science Museum of Minnesota, 16910 152nd St. N, Marine on St. Croix, MN 55047, USA, Telephone: 612-433-5953; Fax: 612-433-5924; E-mail: dinger@sci.mus.mn.us)*

Accepted 7 January 1998

Key words: calcareous fens, carbonate precipitation, groundwater geochemistry, peat composition, peat initiation, wetland drainage

Abstract. Calcareous fens in Minnesota are spring-seepage peatlands with a distinctive flora of rare calciphilic species. Peat characteristics and groundwater geochemistry were determined for six calcareous fens in the Minnesota River Basin to better understand the physical structure and chemical processes associated with stands of rare vegetation. Onset of peat accumulation in three of the fens ranged from about 4,700 to 11,000 ^{14}C yrs BP and probably resulted from a combination of climate change and local hydrogeologic conditions. Most peat cores had a carbonate-bearing surface zone with greater than 10% carbonates (average 27%, dry wt basis), an underlying carbonate-depleted zone with 10% or less carbonates (average 4%), and a carbonate-bearing lower zone again with greater than 10% carbonates (average 42%). This carbonate zonation was hypothesized to result from the effect of water-table level on carbonate equilibria: carbonate precipitation occurs when the water table is above a critical level, and carbonate dissolution occurs when the water table is lower. Other processes that changed the major ion concentrations in upwelling groundwater include dilution by rain water, sulfate reduction or sulfide oxidation, and ion adsorption or exchange. Geochemical modeling indicated that average shallow water in the calcareous fens during the study period was groundwater mixed with about 6 to 13% rain water. Carbonate precipitation in the surface zone of calcareous fens could be decreased by a number of human activities, especially those that lower the water table. Such changes in shallow water geochemistry could alter the growing conditions that apparently sustain rare fen vegetation.

Introduction

Calcareous fens in Minnesota are spring-seepage peatlands that harbor a rare vegetation assemblage tolerant of associated calcium carbonate (marl or tufa) deposits (Eggers & Reed 1987; MDNR 1993). Most of these fens are less than

10 ha and occupy in aggregate only about 730 ha at 100 known sites, accounting for less than 0.02% of wetland area in the state (Minnesota Department of Natural Resources, St. Paul, unpublished data, 1996). Calcareous fens typically are located in the western and southern parts of the state (Figure 1), thereby providing critical habitat to maintain regional biodiversity in a climatically warm and dry region where peatlands are otherwise nearly absent. Hydrogeologic settings include river-valley terraces, moraines with buried lenses of coarse ice-contact deposits, and abandoned beach ridges of Glacial Lake Agassiz, where topographic relief is sufficient to generate substantial groundwater discharge at these fens relative to that at most other wetlands. In this paper, the term “calcareous fen” is reserved narrowly for a peatland with surficial calcium-carbonate deposits and a distinctive calciphilic flora (MDNR 1995). The term “fen” is used broadly and variably in the literature, and most fens by far fall outside this definition of calcareous fen, despite the nearly ubiquitous discharge of calcareous groundwater in fens.

Most of the literature on calcareous fens as defined here comes from the midwestern United States and Great Britain, where such fens have been described as tufa mounds. Fens that are hydrogeologically similar to those in Minnesota have been described in Wisconsin (Curtis 1971; Kratz et al. 1981; Eggers & Reed 1987), Indiana (Wilcox et al. 1985, 1986; Shedlock et al. 1993), Iowa (van der Valk 1975, 1976; Thompson et al. 1992), North Dakota (Duxbury et al. 1986; Malterer et al. 1986, 1987, 1988), and Great Britain (Boyer & Wheeler 1989; Gilvear et al. 1993). Most of these studies focus on the general hydrologic setting or vegetation of calcareous fens, with only a few giving details of peat stratigraphy or water chemistry. Malterer et al. (1986, 1987, 1988) give example peat stratigraphies, emphasizing carbonate content. Wilcox et al. (1986) and Shedlock et al. (1993) discuss the chemistry of water in the studied fen and nearby aquifers to identify source waters supplying the fen, but did not model geochemical processes within the fen. Komor (1994) investigated both peat composition and geochemical reactions in Savage Fen, Minnesota, which is included as part of the present study. Boyer and Wheeler (1989) studied four calcareous fens in Great Britain, and provide an excellent discussion of the relation between geochemical processes and vegetation.

The purpose of this report is to determine peat characteristics and groundwater geochemistry of calcareous fens to better understand the physical and chemical setting associated with fen vegetation, thereby allowing inference of potential impacts on fens resulting from changes in that setting. Peat characteristics include radiocarbon age, composition, bulk density, and coarse particle content. Groundwater geochemistry includes composition of groundwater within and beneath the fens and processes that occur as water moves through the peat. The scope is limited to six calcareous fens studied during 1992–94

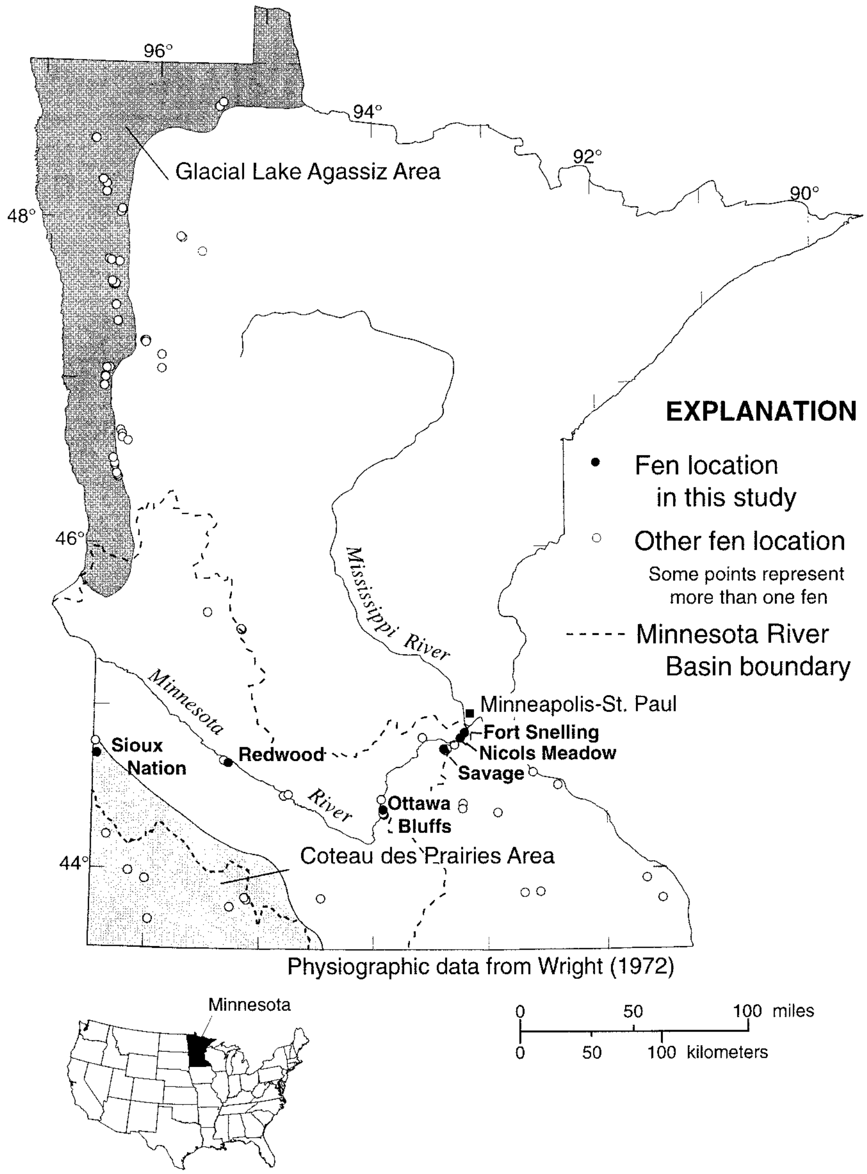

Figure 1. Calcareous fens in Minnesota, associated physiographic areas, and the Minnesota River Basin.

in the Minnesota River Basin. The principal findings of this study confirm that calcareous fens precipitate calcium carbonate at their surfaces, and that this carbonate-bearing surface zone often overlies a zone where carbonate is depleted. Geochemical modeling demonstrated that carbonate precipitation likely occurs when discharging groundwater is not substantially diluted by rain or snowmelt and when the water table is above a critical depth. While calcareous fens are rare end members along the mineral-richness spectrum of palustrine systems, discharge of calcareous groundwater is nearly ubiquitous in fresh-water ecosystems, and findings from this study improve understanding of carbonate dissolution, transport, and deposition.

Description of study areas

The six studied fens are located along the east-west breadth of the Minnesota River Basin (Figure 1): Fort Snelling (44°51′17″ N, 93°11′00″ W, 219 m above mean sea level), Nicols Meadow (44°49′25″ N, 93°13′08″ W, 218 m), Savage (44°46′07″ N, 93°22′12″ W, 228 m), Ottawa Bluffs (44°21′36″ N, 93°55′49″ W, 233 m), Redwood (44°39′15″ N, 95°17′37″ W, 271 m), and Sioux Nation (44°41′14″ N, 96°26′09″ W, 504 m). All of the calcareous fens studied have open areas dominated by sedges and rushes; the rarer species tend to be associated with these areas, especially where the vegetation has a relatively short stature. *Carex sterilis* Willd., *Rhynchospora capillacea* Torr., *Eleocharis rostellata* Torr., *Scleria verticillata* Muhl., and *Valeriana edulis* var. *ciliata* (T. and G.) Cronq. occur frequently in calcareous fens and are listed by the State of Minnesota as threatened species (Eggers & Reed 1987; Coffin & Pfannmuller 1988). Calcareous fens are typically in complexes with other wetland types (rich fen, emergent marsh, shrub swamp, swamp forest, and so forth), which are discussed in MDNR (1993). Detailed floristic analysis was beyond the scope of this study. Consequently, vegetation was mapped at Fort Snelling and Sioux Nation fens according to simple physiognomic descriptors, and boundaries as shown between calcareous fens and other wetland types are provisional (Figure 2). Patches of shrubs composed of *Salix* spp. or *Cornus stolonifera* Michx. are common, as are patches of *Phragmites australis* (Cav.) Steudel and *Phalaris arundinacea* L. Expansion of these shrub and reed patches threatens the rare vegetation in the open areas, particularly at Fort Snelling and Savage fens.

The hydrogeologic settings of calcareous fens comprise factors affecting the movement of groundwater from recharge areas to the fens. As illustrated at Fort Snelling Fen (Figure 2a), five of the calcareous fens – Fort Snelling, Nicols Meadow, Savage, Ottawa Bluffs, and Redwood – form broad peat aprons overlying sand and gravel terraces along the Minnesota River, and the higher water table in the adjacent bluffs provides sufficient hydraulic gradient to cause groundwater to upwell and discharge in the fens. The sixth fen, Sioux Nation Fen (Figure 2b), is a peat dome overlying a small breach in a clay till unit that confines an artesian sand and gravel aquifer recharged in the adjacent

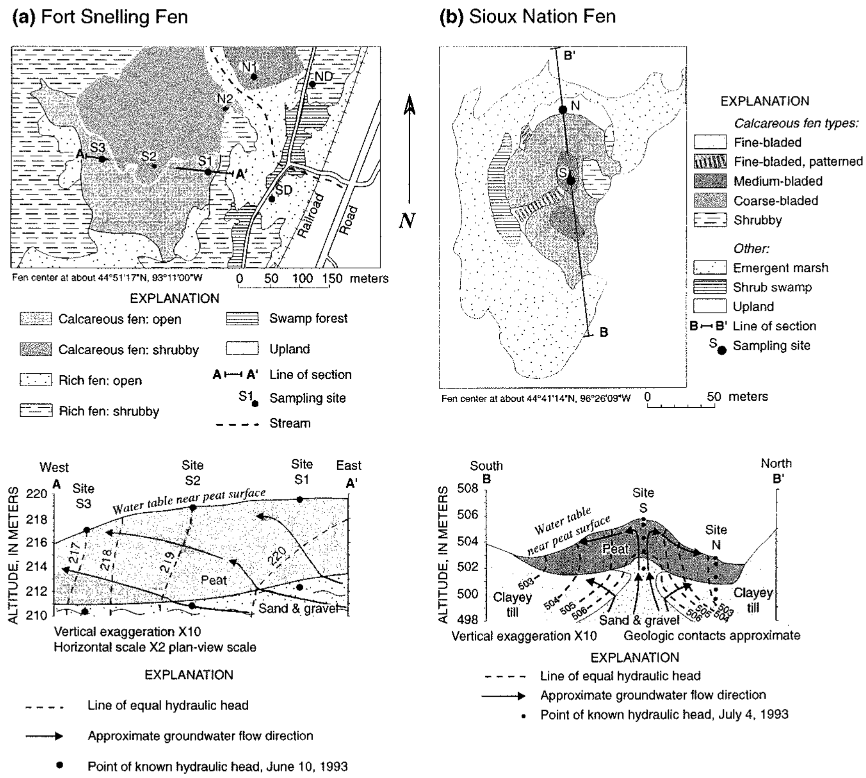

Figure 2. (a) Fort Snelling Fen, a peat-apron calcareous fen on a river terrace in the eastern Minnesota River Basin. (b) Sioux Nation Fen, a peat-dome calcareous fen in morainal topography on the flank of the Coteau des Prairies in the western Minnesota River Basin.

morainal highlands. Groundwater moved upward through peat sediments at all six fens during the period of study; the physical hydrogeology of the fens is discussed in greater detail in Almendinger & Leete (1998).

Sioux Nation Fen is in an area managed for wildlife and appears to be the most pristine of the six fens in the study. The other five fens have evidence of being affected at least in some areas by human activities. Fort Snelling and Ottawa Bluffs fens have highways at their upgradient margins and receive roadway runoff. Savage Fen receives some water that recharges from ponds with elevated chloride (Cl^-) concentrations on the adjacent bluffs (Komor 1994). Savage Fen also has fans of sand extending over the fen surface at its upgradient margin that may have formed because of activities on the bluffs that increased runoff and slope instability (SAIC 1988). Redwood Fen has ponds and ditches excavated along its margin that may have caused some local drainage of the peat, although other parts of the fen appear natural.

Nicols Meadow Fen was partially dewatered in 1989 by nearby groundwater pumping and appears to be the most disturbed of all fens studied. During the pumping, water levels dropped at least 1.3 m below seasonal norms, and the fen changed from being a site of groundwater discharge to one of groundwater recharge (Leete & Gullett 1989). Parts of the fen subsided between 0.5 and 1 m because of the pumping and have not recovered.

Methods

Two sampling sites were chosen in each calcareous fen along horizontal flow lines in areas of characteristic fen vegetation; additional sites were available at both Fort Snelling and Savage fens from other studies (viz., Komor 1994; Almendinger & Leete 1998). Peat was cored at each site to determine peat thickness and sampled at eleven selected sites for loss-on-ignition and fiber-content analyses. For simplicity in this paper, peat refers to all post-glacial sediments in the fens. Bulk density (dry wt per wet volume), organic matter content, and carbonate content (calcium-carbonate [$CaCO_3$] equivalent) were determined by loss on ignition at temperatures of 105 °C, 550 °C, and 925 °C, respectively (Bengtsson & Enell 1986). Sediment composition refers to the organic matter, carbonate, and residual non-carbonate inorganic matter content of the sediment on a percent dry weight basis. Coarse particles were isolated by soaking a peat sample in a dispersing solution and rinsing away the fine particles with a gentle stream of water on a screen with 0.25-mm openings. Because this coarse residue commonly contained a considerable fraction of carbonate particles, the samples were then washed in 10% hydrochloric acid to remove the carbonates and leave primarily plant fiber. Average values for peat composition, density, and coarse particle content were calculated so that each fen was given equal weight, despite different numbers of sites and samples among fens. Linear and polynomial regression models were fit to the data by using standard least squares methods (Snedecor & Cochran 1967). Goodness of fit and validity of underlying assumptions were evaluated by residual analysis; logarithmic transformations were used to improve linearity and homoscedasticity where appropriate (Helsel & Hirsch 1992).

Radiocarbon ages of basal organic matter from three fens were obtained to estimate onset of organic matter accumulation in different parts of the state. Basal wood samples were collected at Fort Snelling and Savage fens in the eastern part of the state; basal peat was collected at Sioux Nation Fen in the western part of the state. Peat samples were sieved to retain only particles larger than 0.25 mm (fiber). All samples were rinsed with phosphoric acid to remove carbonates and oven-dried at 105 °C for at least 12 hours. The wood and peat fiber were presumed to have fixed carbon from the atmosphere, eliminating any need for correction due to incorporation of old carbon from dissolved carbonate sources. Samples were analyzed at the Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratory; graphite targets were prepared at the Limnological Research Center of the University of Minnesota. Dates are reported in radiocarbon years before present (yr BP), which refers to 1950 AD.

Samples for water-chemistry analysis were collected from water-table wells in the fen, sub-peat wells driven into the inorganic substrate under the fen sediments, and deeper wells drilled into the drift. Water-table and sub-peat wells were established in pairs at each of the two sites in each fen. Three additional pairs were available at Fort Snelling Fen, and two water-table and three sub-peat wells (unpaired) were also available at Savage Fen from previous studies. Deeper wells were installed with a rotary drill rig at two sites near the upgradient margin of Fort Snelling Fen and one site near the downgradient margin of Savage Fen to characterize groundwater chemistry outside the fens. All wells were constructed of polyvinyl chloride (PVC) casing. Water-table wells were 5 cm in diameter with 0.7- to 1-m-long PVC screens (0.25-mm slots), the tops of which were set at the peat surface. Sub-peat wells were 3.2 cm in diameter with 15-cm-long stainless-steel screens (0.25-mm slots) set about 50 cm below the base of the fen sediments. Mid-screen depths of sub-peat wells ranged from 3.2 to 8.2 m below the peat surface. Drilled wells were 5 cm in diameter with 75-cm PVC screens (0.25-mm slots) set 5.4, 13.2, and 22.2 m below land surface at site ND in Fort Snelling Fen (Figure 2a); 3.0, 6.6, 14.5, and 23.7 m below land surface at site SD in Fort Snelling Fen; and 2.2, 5.6, and 10.1 m below land surface at Savage Fen. Only the deepest two wells at each site were used to characterize groundwater outside the fen.

In this report, water sampled from water-table, sub-peat, and drilled wells is referred to as shallow, sub-peat, and aquifer water, respectively. During 1992–94, water was sampled at least once from each well, and two or three times from selected wells. Most wells were purged of three well-casing volumes of water before sampling; wells that recovered slowly were pumped dry and sampled as they recovered. Well water was sampled with a peristaltic pump and passed through a closed, flow-through chamber until stable readings of temperature, pH, specific conductance, and dissolved oxygen (DO) content were obtained. Separate filtered samples (cellulose-nitrate membrane filters, 0.45 μm pore diameter) were collected for cation, anion, and alkalinity determinations and chilled in the field. Samples for cation analyses were preserved with acid. Alkalinity was measured in the field by incremental titration to a variable end point. Anions were determined by ion chromatography, and cations by inductively-coupled plasma spectroscopy at the Research Analytical Laboratory of the University of Minnesota. Values of P_{CO_2} (partial pressure of dissolved carbon dioxide) and saturation indices for common minerals were calculated with the WATEQ program (Truesdell & Jones 1974).

The computer program NETPATH (Plummer et al. 1991), which incorporates algorithms developed by Truesdell and Jones (1974) and Parkhurst et al. (1982), was used to infer geochemical processes that could occur as sub-peat groundwater moves upwards to near the peat surface. Major ionic constituents considered include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), sulfate SO_4^{2-}, bicarbonate (HCO_3^{-}), and other species of dissolved inorganic carbon. The model considered the general case that shallow water was a mixture of sub-peat water and rain water:

$$(1 - x)\ \text{liters subpeat water} + x\ \text{liters rain water} \rightarrow 1\ \text{liter shallow water}$$

for $0 \leq x \leq 1$. In this paper, the term "rain water" comprises rain, snowmelt, and dilute surficial runoff to the fen, if any, from rain or snowmelt events. In addition to dilution by rain water, modeled processes included CO_2 dissolution or outgassing, calcite dissolution or precipitation, SO_4^{2-} reduction or S^{2-} oxidation, and cation adsorption or exchange. Evaporative concentration (i.e., where $-1 \leq x \leq 0$) was considered but not supported by the data. Plant biomass was ignored as a significant sink/source of major ions because the amounts sequestered/released by net primary productivity/decomposition typically were small compared to the amounts advected by discharging groundwater.

Results and discussion

Peat characteristics

Basal radiocarbon age

Basal radiocarbon ages at Fort Snelling Fen were 10,030±90 yr BP at site S1 (± one standard deviation; laboratory identification CAMS-13573) and 10,310±60 yr BP at site S2 (CAMS-13571). The basal radiocarbon age at Savage Fen site 1 was similar at 10,970±60 yr BP (CAMS-13572). Two basal radiocarbon ages at Sioux Nation Fen in the western part of the state were much younger: 4,740±60 yr BP (CAMS-13575) at site S at the fen center, and 3,270±60 yr BP (CAMS-13574) at site N near the fen margin. Basal radiocarbon ages were not obtained at any of the other fens.

The timing of the onset of organic matter deposition at these three fens was probably related to past climatic change. The terrace surfaces underlying Fort Snelling and Savage fens were geomorphically stable by about 12,000 yr BP, when Glacial Lake Agassiz formed in the northwest part of Minnesota, thus trapping sediment from the glacial meltwaters and halting significant downstream glacio-fluvial deposition (Wright 1972). Vegetation probably colonized the stabilized terraces at this time, but peat accumulation at Fort Snelling and Savage fens did not begin until one or two thousand years later (about 11,000 to 10,000 yrs BP). The ages of peat initiation in these two fens are about coeval with a shift in vegetation from spruce forest to birch and pine forest in the region at 10,230 yr BP, indicating a change to a warmer climate (Wright et al. 1963; Watts & Winter 1966). Initiation of peat accumulation may have been related to increased vegetation productivity spurred by the climatic warming.

The much later initiation of peat accumulation at site S in Sioux Nation Fen (about 4,700 yr BP) was probably related more to a change in effective moisture rather than to temperature. Before that time in the early to mid-Holocene, the midwestern United States had a climate more arid than at present (McAndrews 1966; Webb et al. 1983; Bartlein et al. 1984; COHMAP Members 1988). Subsequent increases in effective moisture evidently increased groundwater discharge at the fen enough to maintain saturated conditions, thus inhibiting organic matter decomposition and allowing peat accumulation. The peat mound grew not only vertically but apparently laterally outward from the center, reaching site N at about 3,270 yr BP.

Peat accumulation in calcareous fens in nearby states began at different times throughout the past 11,500 years. To the east of Minnesota in Wisconsin, basal radiocarbon ages range from about 7,500 yr BP (Kratz et al. 1981) to about 11,500 yr BP (F. Byrne, Wisconsin Department of Natural Resources, unpublished). Farther east in Indiana, Wilcox et al. (1986) reported an age of about 2,000 yr BP for basal peat from a calcareous fen within the Cowles Bog wetland complex. To the south of Minnesota in Iowa, basal radiocarbon ages range from about 1,240 to 10,900 yr BP, with most ages being younger than about 5,000 yr BP (Thompson & Bettis 1994). To the west in North Dakota, Malterer et al. (1988) reported a basal age of about 4,790 yr BP, essentially synchronous with the basal age of Sioux Nation Fen.

The scattered basal radiocarbon ages of calcareous fens demonstrate two points. First, calcareous fens are not relict plant communities from glacial times. Although some fens did originate before about 10,000 yr BP in late glacial times, many originated much later and did not require glacial conditions to initiate peat accumulation. Second, the onset of peat accumulation likely depends on both past climate and local hydrogeologic setting (Thompson & Bettis 1994). Hence, even under identical climatic conditions, different fens, or different areas within a fen/wetland complex, could begin peat accumulation at different times, depending on differences in local hydrogeology.

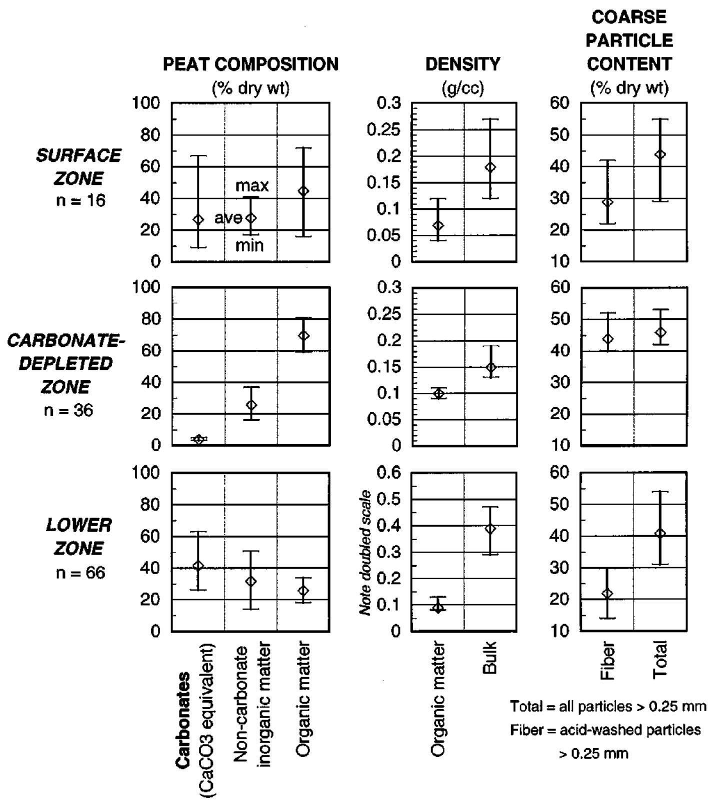

Figure 3. Average peat characteristics for studied calcareous fens in the Minnesota River Basin.

Peat composition

Peat composition commonly followed a distinctive stratigraphic pattern, especially in the carbonate content (Figures 3 and 4). Most cores (eight of eleven) had a surface zone with a carbonate content greater than 10% (average 27%), a middle carbonate-depleted zone with a carbonate content of 10% or less (average 4%), and a lower zone with a carbonate content again greater than 10% (average 42%). We emphasize that the term "carbonate-depleted" does not mean necessarily devoid of carbonates, only that the carbonate content is 10% or less and is depleted relative to the surface and lower zones. For two of the cores where a carbonate-depleted zone was not identified (both from Ottawa Bluffs Fen), peat was not collected at the 50-cm level because the peat was too loose and fibrous to be retained in the core barrel of the peat sampler. Similarly structured peat characterized the carbonate-depleted zone at the other sites.

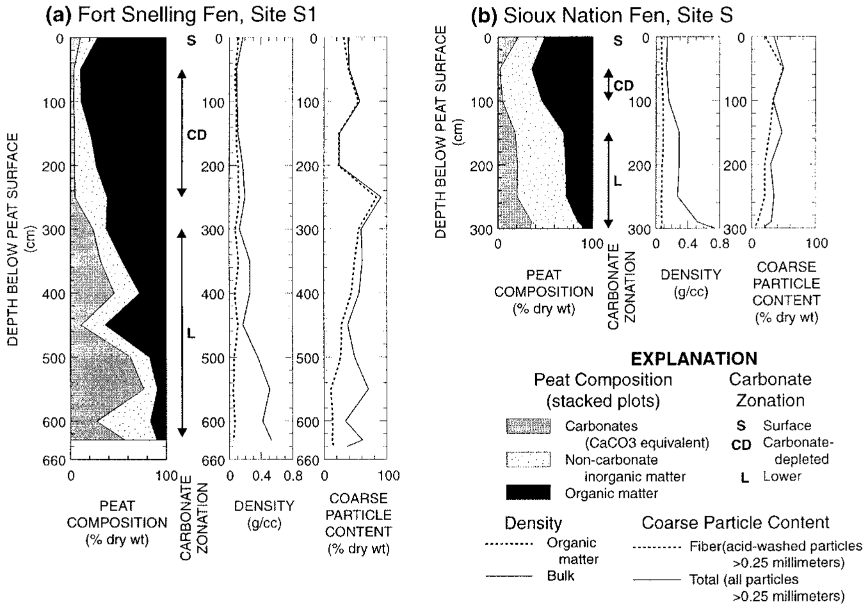

Figure 4. Example stratigraphies of peat composition, carbonate zonation, density, and coarse-particle content for selected sites in (a) Fort Snelling Fen and (b) Sioux Nation Fen.

Carbonate deposition was dominated by chemical and bio-mediated precipitation rather than by deposition of detrital clastics, and strata with carbonate contents exceeding about 25% had a smooth, silty texture typical of aquatically precipitated marl (Troels-Smith 1955). Larger carbonate particles (1 to 2 mm) were casts precipitated around plant fragments. Organic matter followed a pattern opposite that of carbonates, averaging 45% in the surface zone, 70% in the carbonate-depleted zone, and 26% in the lower zone. The content of non-carbonate inorganic matter was similar among the three zones, averaging 28%, 26%, and 32% in the surface, carbonate-depleted, and lower zones, respectively. Nicols Meadow Fen was excluded from these calculations because partial drainage may make it unrepresentative, even though its two cores followed this same distinctive zonation.

The carbonate content of calcareous fen peat results from the net balance between precipitation and dissolution. In particular, the boundary between the carbonate-bearing surface zone and the underlying carbonate-depleted zone is hypothesized to be affected by a critical water-table level relative to the peat surface, above which precipitation dominates and below which dissolution dominates. For shallow water in equilibrium with carbonates, primarily calcite, the critical water-table level is where the P_{CO_2} in the shallow water matches that in the unsaturated zone pore space. The P_{CO_2} in the unsaturated zone is likely controlled by production of CO_2 from aerobic decay of organic matter, loss of CO_2 by diffusion to the atmosphere, and dissolution or outgassing of CO_2 at the water table. When the water table is above the critical level, the P_{CO_2} of the unsaturated zone decreases because CO_2 loss exceeds production; CO_2 can outgas from the shallow water and cause carbonate precipitation in the surface zone. When the water table is below the critical level, the P_{CO_2} of the unsaturated zone increases because CO_2 production exceeds loss; CO_2 can dissolve in the shallow water and cause dissolution of carbonates, thus forming a carbonate-depleted zone. The critical water-table level is likely variable depending on temperature, shallow water chemistry, and direction of water-table movement. The net deposition of carbonates depends on the relative frequency and duration of periods when the water table is above, or below, the critical level. When shallow water has been diluted by enough rain water to reduce dissolved $CaCO_3$ concentrations below equilibrium with carbonates, then the concept of a critical water-table level loses value because outgassing of dissolved CO_2 from the shallow water will not cause carbonate precipitation.

The thickness of the carbonate-bearing surface zone, which at Savage Fen was about 8 cm (Komor 1994), may approximate the average critical water-table level. Peat cores at other fens were not sampled with enough vertical resolution to determine the thickness of the surface zone accurately. Because of the many variables hypothesized to affect the critical water-table depth, thickness of the surface zone is expected to differ among sites. The thickness of the carbonate-depleted zone, which ranged from about 5 to 250 cm, may differ among sites because of differences in local hydrogeological conditions during fen development. The lower boundary of the carbonate-depleted zone may originate from a time, different in each fen, when peat had accumulated to such a height that the water table was below the critical level with increasing frequency. Over time, the carbonate-depleted zone would increase in thickness by dissolving carbonates from the base of the surface zone, which would rise as the fen continued to accumulate peat. Carbonate precipitation would still occur in the surface zone, as long as the water table rose above the critical level for some portion of the year, which may occur less frequently as peat accumulation gradually raises the fen surface. A carbonate-depleted zone need not form if groundwater discharge maintains the water table above the critical level, and the carbonates in the lower zone are likely residual from an earlier time in the fen history when groundwater discharge was large enough so that a carbonate-depleted zone had not yet formed.

Carbonate precipitation in the surface zone could be reduced by at least five mechanisms. First, natural peat accumulation may decrease the frequency and duration of periods when the water table is above the critical level and carbonate precipitates in the surface zone, as discussed above. Second, a reduction in groundwater recharge caused by climatic or land-use changes also would reduce groundwater discharge and carbonate precipitation at the fen. Third, groundwater pumping near the fen could reduce hydraulic heads in the aquifer below the fen, reducing vertical head gradients and groundwater discharge. Fourth, land-use changes in the recharge area that reduce the P_{CO_2} in the soil atmosphere would reduce the amount of carbonates that could be dissolved by groundwater and moved to the fen. The P_{CO_2} in the soil atmosphere can be affected by changes in temperature, humidity, and organic matter content of the unsaturated zone (Hinkle 1994). Fifth, increases in atmospheric P_{CO_2} from human-caused and other emissions will decrease the amount of CO_2 that could be outgassed from discharging groundwater, decreasing carbonate precipitation. A doubling of atmospheric P_{CO_2} may occur within the next century (IPCC 1990) and would increase the solubility of calcite in pure water by about 25%. Reduction of carbonate deposition at the fen surface is important because it could alter growing conditions and cause a loss of rare vegetation at the expense of more aggressive common species.

Bulk density and coarse particle content

Average bulk density was about the same in the surface (0.18 g cm^{-3}) and carbonate-depleted (0.15 g cm^{-3}) zones, but much greater in the lower zone (0.39 g cm^{-3}; Figure 3). Average organic matter density differed little among the zones, being only slightly greater in the carbonate-depleted zone (0.10 g cm^{-3}) than in the surface (0.07 g cm^{-3}) and lower (0.09 g cm^{-3}) zones. These values of bulk and organic matter density may overestimate the true values because of peat compression during coring. Average fiber content was greatest in the carbonate-depleted zone (44%), and smaller in the surface (29%) and lower (22%) zones.

Because organic matter content is commonly measured in peats, the equations relating bulk density, organic matter density, and fiber content to organic matter content in the studied fens may be useful in estimating these variables at other sites (Figure 5). However, the scatter in the plots indicates substantial potential errors. Some of these relations are commonly found in other peatlands, whereas others are not. For example, bulk density is commonly inversely related to organic matter content (Figure 5a) because of the greater density of the inorganic matter component. Also, as in other peatlands, the fiber content of calcareous fen peat increases with organic matter content (Figure 5c). However, the unimodal relation between organic matter content and organic matter density (Figure 5b) is not commonly described in the

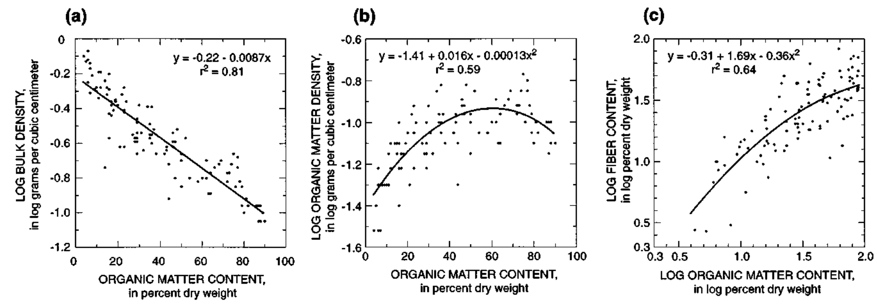

Figure 5. Selected peat characteristics at the studied fens plotted as functions of organic matter content: (a) bulk density, (b) organic matter density, and (c) fiber content.

literature. This curvilinear relation becomes evident only when the full range of organic matter contents from calcareous fen peats is used for analysis. At organic matter contents above 20%, organic matter density shows little relation to organic matter content (and hence bulk density), and averages about 0.1 g cm^{-3}, the same value found by Sjörs (1961) for many other peats. Calcareous fen peats have a wider range of organic matter contents than most other peatlands as a consequence of the potentially large amounts of intermixed carbonate and other mineral precipitates. Indeed, at organic matter contents below 20%, as can be found in calcareous fen peats, one may question whether the material can be termed “peat.”

Groundwater geochemistry

Fens were categorized into two groups based on water chemistry (Table 1). Eastern fens included Fort Snelling, Ottawa Bluffs, and Savage fens, and western fens included Sioux Nation and Redwood fens. These two groups are likely points on a continuum, and differences between them may become less distinct as more fens are sampled. Nicols Meadow Fen, in the eastern part of the state, has been so altered by nearby groundwater pumping that its water chemistry is no longer representative of natural calcareous fens, and selected data are provided to contrast those from other studied fens.

The purpose of the geochemical models developed with NETPATH (Plummer et al. 1991) was to describe the general geochemical functioning of calcareous fens as water moves upward through the peat column. Consequently, only average major-ion chemistries from the eastern and western groups of fens were modeled, rather than detailing processes at any one site. These models can explain only the net change in water chemistry from initial (sub-peat) to final (shallow) water, and model results are not unique. That is, NETPATH generates alternative models when the same data can be explained by alternative processes, which need not be mutually exclusive. Nonetheless, the modeling exercise is important because quantification of geochemical processes may be valuable in distinguishing calcareous fens from other wetlands. The same processes certainly may occur in other wetlands, but perhaps not to the same extent as in calcareous fens. Furthermore, modeling helps identify where additional research is most needed.

Eastern fens

Shallow water in eastern fens was characterized by lower specific conductance, SO_4^{2-}, Ca^{2+}, and Mg^{2+} values, relative to western fens (Table 1). In terms of milliequivalents, the Ca^{2+}:Mg^{2+} ratio was about 2.0, and the Ca^{2+}-plus-Mg^{2+}:alkalinity ratio about 1.0, indicating strong control by calcium and magnesium carbonate mineral equilibria. The Cl^- concentration in shallow water was higher than that in western fens, probably because of road-salt runoff from upgradient highways near several of the eastern fens. Neither nitrate nor phosphate was detected in most of the samples. Dissolved oxygen (DO) was less than saturation with respect to atmospheric oxygen (about 0.67 mM at average altitude and temperature of the eastern fens), demonstrating the influence of low-DO groundwater upwelling from below. The P_{CO_2} was greater than that of the ambient atmosphere ($10^{-3.5}$ atm); hence CO_2 could outgas from the water if exposed near the fen surface. Shallow water was slightly undersaturated with respect to calcite, and more so with respect to dolomite and gypsum.

Average Ca^{2+}, alkalinity, and P_{CO_2} values were slightly lower in sub-peat water than in shallow water, and average pH, Mg^{2+} content, and SO_4^{2-} contents slightly greater. Variability (range) of sub-peat water chemistry was less than that of shallow water for most constituents, both within and among fens. In contrast to sub-peat water, aquifer water had lower average values of specific conductance and most other constituents, notably Ca^{2+}, alkalinity, and P_{CO_2}. These differences indicate that sub-peat water originated at least partly from a different, probably shallower, source than from the deeper aquifer water alone.

The following model plausibly represents conversion of average sub-peat water to average shallow water in the three eastern fens:

$$\underbrace{870\text{ ml sub-peat water} + 130\text{ ml rain water}}_{\text{dilution by rain water}} + \underbrace{1.2\text{ mmol } CO_2}_{CO_2\text{ dissolution}} + \underbrace{0.51\text{ mmol } CaCO_3}_{\text{calcite dissolution}} + \underbrace{0.14\text{ mmol } CH_2O}_{\text{organic matter conversion}} \rightarrow 1\text{ L shallow water} + \underbrace{0.07\text{ mmol } H_2S}_{H_2S\text{ production}} \quad (1)$$

According to model (1), sub-peat water (87%) mixes with rain water (13%), CO_2 and calcite dissolve, and organic matter converts to HCO_3^- during reduc-

Table 1. Average chemistries of water samples from wells in or near five calcareous fens in the Minnesota River Basin, 1992–94. Eastern fens comprise Fort Snelling, Savage, and Ottawa Bluffs fens; western fens comprise Sioux Nation and Redwood fens.

			Field parameters				Cations						
Type of well (N)	n	[Reporting limit →]	T (°C)	SC (μS cm^{-1})	pH	DO (mM) [6×10^{-2}]	Ca (mM) [1×10^{-3}]	Mg (mM) [8×10^{-3}]	Na (mM) [8×10^{-3}]	K (mM) [2×10^{-2}]	Fe (mM) [3×10^{-4}]	Mn (mM) [7×10^{-5}]	NH_4 (mM) [1×10^{-3}]
							Eastern fens						
Water-table wells (11)	22	Average	11.1	643	7.0	0.16	2.43	1.23	0.74	0.06	0.005	0.014	0.024
		Range	3.3	212	0.4	0.15	1.30	0.37	1.81	0.08	0.012	0.014	0.059
Subpeat wells (11)	19	Average	9.7	688	7.1	<0.06	2.20	1.41	0.55	0.07	0.008	0.012	0.019
		Range	1.6	464	0.3	na	0.97	0.52	1.17	0.06	0.017	0.017	0.038
Drilled wells (6)	14	Average	10.2	478	7.3	0.08	1.73	1.14	0.22	0.05	0.011	0.005	0.003
		Range	2.2	60	0.1	0.04	0.37	0.18	0.07	0.02	0.005	0.006	0.003
							Western fens						
Water-table wells (4)	6	Average	14.4	1057	7.1	0.11	3.85	2.05	1.01	0.12	0.006	0.006	0.046
		Range	4.6	554	0.4	0.04	0.67	1.01	1.03	0.02	0.009	0.009	0.080
Subpeat wells (3)	4	Average	17.2	1216	7.0	0.07	4.21	2.27	1.24	0.14	0.017	0.008	0.026
		Range	5.8	414	0.0	0.02	1.11	1.14	1.38	0.01	0.007	0.010	0.031

Table 1. Continued.

Type of well (N)	n	[Reporting limit →]	Anions and nutrients Alk (meq L^{-1}) [2×10^{-2}]	SO_4 (mM) [3×10^{-3}]	Cl (mM) [6×10^{-3}]	F (mM) [1×10^{-2}]	NO_3 (mM) [7×10^{-3}]	Others Si (mM) [3×10^{-3}]	TOC (mM) [4×10^{-2}]	log P_{CO_2}	Saturation indicies Cal	Dol	Gyp
						Eastern fens							
Water-table wells (11)	22	Average	7.25	0.35	0.58	0.03	0.008	0.35	0.55	−1.43	−0.13	−0.62	−2.27
		Range	2.61	0.80	1.45	0.01	0.003	0.08	0.57	0.55	0.17	0.38	1.48
Subpeat wells (11)	19	Average	7.20	0.48	0.24	0.02	0.008	0.36	0.17	−1.54	−0.10	−0.48	−2.00
		Range	3.48	0.89	0.40	0.00	0.002	0.04	0.08	0.48	0.01	0.06	0.95
Drilled wells (6)	14	Average	5.59	0.19	0.16	0.02	0.019	0.27	0.27	−1.92	0.02	−0.23	−2.28
		Range	1.02	0.01	0.10	0.00	0.025	0.02	0.38	0.16	0.02	0.03	0.09
						Western fens							
Water-table wells (4)	6	Average	7.03	3.28	0.08	0.04	0.008	0.52	0.49	−1.62	0.20	0.10	−0.96
		Range	0.85	2.13	0.09	0.02	0.001	0.00	0.07	0.37	0.17	0.12	0.25
Subpeat wells (3)	4	Average	7.29	3.89	0.10	0.04	<0.007	0.48	0.44	−1.45	0.12	0.00	−0.87
		Range	2.48	1.78	0.12	0.01	na	0.15	0.18	0.17	0.28	0.75	0.19

Notes: Concentrations of the following were below reporting limits in most samples (reporting limit in mM follows element or compound name): As, 5×10^{-4}; B, 2×10^{-3}; Be, 3×10^{-4}; Br, 2×10^{-3}; Cd, 6×10^{-5}; Cr, 3×10^{-4}; Cu, 4×10^{-4}; Li, 3×10^{-3}; Mo, 1×10^{-4}; Ni, 4×10^{-4}; NO_2, 7×10^{-3}; Pb, 4×10^{-4}; PO_4, 6×10^{-3}; Rb, 3×10^{-2}; Sr, 5×10^{-5}; Ti, 3×10^{-4}; V, 4×10^{-4}; Zn, 1×10^{-4}.

Abbreviations: N, number of wells; n, number of samples used in calculating average and range; T, water temperature; SC, specific conductance; DO, dissolved oxygen; Alk, alkalinity; TOC, total organic carbon; log P_{CO_2}, base-10 logarithm of carbon dioxide partial pressure, in atmospheres; Cal, calcite; Dol, dolomite; Gyp, gypsum; °C, degrees Celsius; $\mu S\ cm^{-1}$, microsiemens per centimeter; mM, millimoles per liter; meq L^{-1}, milliequivalents per liter; na, not applicable, for ranges with only one sample or with all sample values below reporting limit.

tion of SO_4^{2-} to S^{2-} in the form of hydrogen sulfide (H_2S) gas. The dissolution of calcite is supported by equilibrium modeling results, which indicate undersaturation of shallow water with respect to calcite (Table 1). The added CO_2 originates from aerobic decay of peat, especially in the unsaturated zone when the water table is below the critical level. Increased CO_2 enhances carbonate dissolution, apparently from the lower part of the surface zone when inundated by a rising water table. The P_{CO_2} in shallow water was greater than that of the atmosphere, however, and CO_2 eventually would outgas if the water table rose above the critical level near the peat surface.

Dilution by rain water was quantified based on reduction in Mg^{2+}, which has been used successfully as a conservative tracer in other systems (Stauffer 1985). Mg^{2+} appears useful in fens as well, although it is not an ideal tracer because of potentially nonconservative behavior caused by mineral equilibria and ion-exchange reactions. Na^+ and Cl^- are more conservative but were excluded from model calculations because of probable contamination by road salt. Mineral equilibria reactions involving Mg-carbonates are unlikely to be significant in fens because the Ca^{2+}: Mg^{2+} ratio is too high (about 2.0); Mg-carbonates do not form unless the Ca^{2+}:Mg^{2+} ratio is less than about 0.5 (Kelts & Hsu 1978). Calcite near the surface of Savage Fen is nearly pure $CaCO_3$, and calcite deeper in the peat column contains only about 3 mole-percent $MgCO_3$ (Komor 1994).

Ion desorption and exchange reactions, however, do appear potentially significant for Mg^{2+} in peat, which commonly has a high cation-exchange capacity (Mitsch & Gosselink 1993) proportional to pH (Clymo 1983). Dilution by rain water and reduction in pH could cause desorption of Ca^{2+} and Mg^{2+} from the peat. If desorption occurred, then dilution by rain water would be greater than shown in model (1), and calcite dissolution and SO_4^{2-} reduction would be less. Alternatively, dissolution of calcite could cause exchange of Ca^{2+} for $Mg_{adsorbed}$ because of increasing Ca^{2+}:Mg^{2+} ratios in solution. If Ca^{2+}-Mg^{2+} exchange had occurred, then dilution by rain water and calcite dissolution would again be greater than shown in model (1), and SO_4^{2-} reduction would be less. Model (1) is in error to the degree that ion desorption and exchange are operating, and the error appears to be in underestimating the amount of dilution. No plausible model was found that discounted dilution.

The hydrologically-altered Nicols Meadow Fen had the highest shallow-water values of specific conductance, most ionic constituents, and P_{CO_2} of all fens sampled. Average values of specific conductance (2,190 μS cm^{-1}), Ca^{2+} (9.35 mm), and Mg^{2+} (4.56 mM) were over three times higher than those of other eastern fens. The dominant anion was SO_4^{2-}, with an average concentration (10.46 mM) about 30 times higher than that in other eastern fens, and yet the upwelling sub-peat water had an average SO_4^{2-} concentration of only 0.18 mM. Geochemical evolution of upwelling groundwater at Nicols Meadow Fen was not adequately explained by modeling because of violation of the model assumption that peat decomposition was not a significant source of major ions. Simple model runs indicated that dissolution of calcite, dissolution of CO_2, and oxidation of S^{2-} (thereby creating additional acidity) were occurring as water moved upward through the peat. However, the model could not simulate increases in Mg^{2+} concentrations, which likely resulted from aerobic decay organic matter. Peat is known to contain significant quantities of inorganic ions that are released upon decay of the peat (Dasberg & Neuman 1977; Heathwaite 1991). Calcareous fen peat from Savage Fen, for example, contained about 2,500 to nearly 4,000 ppm Mg^{2+} (Komor 1994).

Western fens

Shallow water in western fens had a greater average specific conductance, SO_4^{2-}, Ca^{2+}, Mg^{2+}, and Na^+ values than that in eastern fens, but slightly lower alkalinity (Table 1). In terms of milliequivalents, the Ca^{2+}:Mg^{2+} ratio was about 1.9, and the Ca^{2+}-plus-Mg^{2+}:alkalinity ratio was about 1.7, indicating the influence of minerals other than calcium and magnesium carbonates. Shallow water was oversaturated with respect to calcite and dolomite, and undersaturated with respect to gypsum, which is a likely source for the larger Ca^{2+} and SO_4^{2-} values relative to those in eastern fens. Sub-peat water in western fens had slightly greater average values of specific conductance, most ionic constituents, and P_{CO_2} than shallow water did, and slightly lower average values of pH and DO.

The following model plausibly represents the conversion average sub-peat water to average shallow water in the two western fens:

$$\underbrace{940\text{ ml sub-peat water} + 60\text{ ml rain water}}_{\text{dilution by rain water}} + \underbrace{0.72\text{ mmol } CH_2O}_{\text{organic matter conversion}} + \underbrace{0.15\text{ mmol } Ca_{\text{adsorbed}}}_{Ca^{2+}\text{ desorption}} \rightarrow$$

$$1\text{ L shallow water} + \underbrace{0.39\text{ mmol } CO_2}_{CO_2\text{ outgassing}} + \underbrace{0.24\text{ mmol } CaCO_3}_{\text{calcite precipitation}} + \underbrace{0.36\text{ mmol } H_2S}_{H_2S\text{ production}} + \quad (2)$$

$$\underbrace{0.15\text{ mmol } Na_{\text{adsorbed}} + 0.08\text{ mmol } Mg_{\text{adsorbed}}}_{Na^{+}\text{ and } Mg^{2+}\text{ adsorption}}$$

According to model (2), sub-peat water (94%) mixes with rain water (6%); CO_2 outgasses, causing calcite precipitation; organic matter is converted to HCO_3^- in reducing SO_4^{2-} to S^{2-} in the form of H_2S; and Ca^{2+} is exchanged for both Na^+ and Mg^{2+}. Dilution by rain water was calculated based on both Na^+ and Mg^{2+}. Calcite precipitation is in accordance with the equilibrium modeling results; an alternative model that calculated a greater dilution based on Na^+ alone was rejected because results indicated calcite dissolution rather than precipitation. A problem with model (2) is that the ion exchange reactions are not well constrained. In particular, replacement of the divalent Ca^{2+} at exchange sites by the monovalent Na^+ seems unlikely given the prevalence of Ca^{2+} and Mg^{2+} in solution.

Processes affecting the chemical evolution of major ions in groundwater moving upward through fen peat appear to be essentially identical in eastern and western fens. Carbonate solubility is sensitive to small changes in water chemistry caused by atmospheric exchanges of CO_2 (dissolution or outgassing) and water (rainfall or evaporation). Because these exchanges are variable and reversible, carbonate precipitation and dissolution are likewise variable and reversible. Rainfall during the sampling months was greater than normal by about 20% in 1992 and about 70% in 1993. Perhaps in drier months, or years, geochemical models would indicate evaporative concentration rather than rain-water dilution. The composition of the peat column represents integration of the time-variability and demonstrates net carbonate precipitation in the surface zone and net carbonate dissolution in the carbonate-depleted zone. However, the relative amounts of time when carbonate is precipitating or dissolving are not known. Calcareous fens require a certain balance in climate: the climate must be moist enough to produce substantial groundwater discharge, thereby allowing peat accumulation and carbonate precipitation, yet not so moist such that rain water dilutes the shallow water continuously below the solubility of calcite. The characteristically sloped surfaces of calcareous fens help shed rain water, thus limiting dilution of upwelling groundwater and enhancing carbonate precipitation.

Relations between hydrology and vegetation

The input of dissolved minerals to peatlands by groundwater (or runoff) has long been inferred as the primary cause of vegetation distinctions among peatland types, ranging from bogs with no appreciable input through all categories of fens with differing inputs. Fens may be termed “poor” or “rich” according to the amount of dissolved mineral input, and by this criterion calcareous fens are one of the “richest” types of fens. However, as Bridgham et al. (1996) rightly point out, mineral richness does not necessarily correlate with abundance of all nutrients required for plant growth. Vegetation is stunted in primary discharge zones of calcareous fens (van der Valk 1976), implying conditions stressful for plant growth. Potential causes of physiological stress are low concentrations of phosphate because of co-precipitation with carbonate (Boyer & Wheeler 1989), reduced aeration of the rooting zone (van der Valk 1975, 1976), and iron toxicity (Snowden & Wheeler 1993). Studies in other types of fens have likewise concluded that input of calcareous groundwater can limit nutrient availability, especially phosphorus (Verhoeven & Arts 1987; Koerselman et al. 1993).

Changes in fen hydrology are a primary cause of changes in fen vegetation. A chemical change resulting from a shift in groundwater sources (e.g., Wassen & Joosten 1996; Boeye et al. 1996) or change in recharge conditions (Verhoeven et al. 1983; Verhoeven & Arts 1987; Schot & Wassen 1993) can change mineral loading and nutrient availability, and consequently the vegetation. Even if the chemistry of discharging groundwater remains constant, a decline in rate of discharge may lower water levels and consequently change aeration and nutrient release from decomposing surface peats (Heathwaite 1991). Water-table lowering can allow invasion by opportunistic woody species (Bradof 1992), which may contribute to the loss of rare species such as *Cypripedium candidum* Muhl. ex Willd. by shading (Curtis 1971; Falb & Leopold 1993). Likewise, raising the water level can cause expansion of dense monocultures of other aggressive species such as *Typha* spp. (Wilcox et al. 1985).

Calcareous fens are sensitive to reductions in groundwater discharge, particularly if water levels decline enough to promote aerobic decay of the alkaline surface peat and consequent release of sequestered nutrients. Our study demonstrated dramatic differences in the shallow water chemistry of the partially de-watered Nicols Meadow Fen relative to other studied fens. In this and other nearby fens (Fort Snelling and Savage), aggressive common species have colonized the drier parts of the wetland complex and are poised to expand if given the opportunity by continued declines in groundwater discharge and water-table levels. Abstraction of groundwater from nearby wells caused the hydrologic and vegetation changes in Nicols Meadow Fen and has been demonstrated to cause similar changes in British calcareous fens (Harding 1993; Fojt 1994). However, a reduction in groundwater discharge may still cause vegetation change, even if the surface peat does not dehydrate substantially. Calcareous fen vegetation is associated with the precipitation of calcium carbonate and therefore may be affected by any reduction in groundwater discharge that lowers the supply of dissolved calcium carbonate and reduces the time that the water table is above the critical level for calcite precipitation.

Summary and conclusions

Calcareous fens are rare peatlands with a distinctive calciphilic vegetation associated with carbonate-bearing peat. Peat accumulation began from about 4,700 to 11,000 yrs BP in the studied fens. The surface peat commonly has a carbonate content greater than 10% and overlies a zone of carbonate-depleted peat with 10% or less carbonates. Geochemical modeling demonstrated that shallow water in the studied fens was a mix of groundwater with 6 to 13% rain water at the times of sampling, and indicated that carbonate precipitation was sensitive to CO_2 exchanges across the water table. Because of these exchanges, carbonate precipitation occurs when the water table is above a critical level, and carbonate dissolution occurs when the water table is lower.

While calcareous fens are rare in spatial distribution, they appear to be persistent once established, although paleoecological studies would be needed for confirmation. Persistence of such spring fens probably results from groundwater discharge smoothing fluctuations in regional climate and maintaining flows above a threshold amount that keeps water levels near the peat surface. This persistence is limited, however, and calcareous fens can be altered when groundwater discharge falls below the required threshold, or when other factors that reduce carbonate precipitation occur. Furthermore, persistence does not imply resilience, and once a fen is altered by a reduction in groundwater discharge, vegetation may not recover even if discharge is restored. The threshold amount of groundwater discharge required to maintain fen vegetation probably differs among fens, depending on local hydrogeologic settings. Whatever the threshold amount is for any one fen, our study suggests that it must be great enough to raise the water level above the critical level at times when the shallow water is not substantially diluted by rain water, thus allowing precipitation of carbonates associated with the rare vegetation that distinguishes calcareous fens from more common types.

Acknowledgements

B. Delaney, J. Frischman, R. Kelsey, K. Knoke, M. Macbeath, M. Menheer, and T. Ward provided help in the field. W. Anderson, J. Kennealy, and C. Mines kindly allowed access to calcareous fens on their property. Two anonymous reviewers offered many suggestions that significantly improved the manuscript.

References

Almendinger JE & Leete JH (1998) Regional and local hydrogeology of calcareous fens in the Minnesota River Basin, USA Wetlands 18: (in press)

Bartlein PJ, Webb T III & Fleri E (1984) Holocene climatic change in the northern Midwest: Pollen-derived estimates. Quat. Res. 22: 361–374

Bengtsson L & Enell M (1986) Chemical analysis. In: Berglund B (Ed) Handbook of Holocene Palaeoecology and Palaeohydrology (pp 423–451). Wiley, New York

Boeye D, Van Haesebroeck V, Verhagen B, Delbaere B, Hens M & Verheyen RF (1996) A local rich fen fed by calcareous seepage from an artificial river water infiltration system. Vegetatio 126: 51–58

Boyer MLH & Wheeler BD (1989) Vegetation patterns in spring-fed calcareous fens – Calcite precipitation and constraints on fertility. J. Ecol. 77: 597–609

Bradof KL (1992) Ditching of Red Lake peatland during the homestead era. In: Wright HE Jr, Coffin BA & Aaseng NE (Eds) The Patterned Peatlands of Minnesota (pp 263–284). Univ. Minnesota Press, Minneapolis

Bridgham SD, Pastor J, Janssens JA, Chapin C & Malterer TJ (1996) Multiple limiting gradients in peatlands: A call for a new paradigm. Wetlands 16: 45–65

Clymo RS (1983) Peat. In: Gore AJP (Ed) Ecosystems of the World 4A: Mires – Swamp, Bog, Fen and Moor. General Studies (pp 159–224). Elsevier, New York

Coffin B & Pfannmuller L (1988) Minnesota's Endangered Flora and Fauna. Univ. Minnesota Press, Minneapolis

COHMAP (Cooperative Holocene Mapping Project) Members (1988) Climatic changes of the last 18,000 years: Observations and model simulations. Science 241: 1043–1052

Curtis JT (1971) The Vegetation of Wisconsin. Univ. Wisconsin Press, Madison

Dasberg S & Neuman SP (1977) Peat hydrology in the Hula Basin, Israel: I. Properties of peat. J. Hydrol. 32: 219–239

Duxbury AJ, Heidel BL & Malterer TJ (1986) Rare flora of North Dakota's calcareous fens. Proc. North Dakota Acad. Sci. 40: 50

Eggers SD & Reed DM (1987) Wetland Plants and Plant Communities of Minnesota and Wisconsin. US Army Corps of Engineers, St Paul

Falb DL & Leopold DJ (1993) Population dynamics of *Cypripedium candidum* Muhl. ex Willd., small white ladyslipper, in a western New York fen. Natural Areas J. 13: 76–86

Fojt WJ (1994) Dehydration and the threat to East Anglian fens, England. Biol. Conserv. 69: 163–175

Gilvear DJ, Andrews R, Tellam JH, Lloyd JW & Lerner DN (1993) Quantification of the water balance and hydrogeological processes in the vicinity of a small groundwater-fed wetland, East Anglia, UK. J. Hydrol. 144: 311–334

Harding M (1993) Redgrave and Lopham fens, East Anglia, England: A case study of change in flora and fauna due to groundwater abstraction. Biol. Conserv. 66: 35–45

Heathwaite AL (1991) Solute transfer from drained fen peat. Water, Air, and Soil Poll. 55: 379–395

Helsel DR & Hirsch RM (1992) Statistical Methods in Water Resources. Elsevier, New York

Hinkle ME (1994) Environmental conditions affecting concentrations of He, CO_2, O_2 and N_2 in soil gases. Applied Geochem. 9: 53–63

IPCC (Intergovernmental Panel on Climate Change) (1990) Climate Change. Cambridge Univ. Press, Cambridge

Kelts K & Hsü KJ (1978) Freshwater carbonate sedimentation. In: Lerman A (Ed) Lakes – Chemistry, Geology, Physics (pp 295–323). Springer-Verlag, New York

Koerselman W, van Kerkhoven MB & Verhoeven JTA (1993) Release of inorganic N, P and K in peat soils; effect of temperature, water chemistry and water level. Biogeochemistry 20: 63–81

Komor SC (1994) Geochemistry and hydrology of a calcareous fen within the Savage Fen wetlands complex, Minnesota, USA. Geochim. Cosmochim. Acta 58: 3353–3367

Kratz TK, Winkler MJ & DeWitt CB (1981) Hydrology and chronology of a peat mound in Dane County, southern Wisconsin. Trans. Wisconsin Acad. Sci., Arts, & Letters 69: 37–45

Leete JH & Gullett T (1989) Innovative approach to fen protection – Irrigate! Minnesota Ground Water Assoc. Newsletter 8: 6–7

Malterer TJ, Bluemle JP, Duxbury AJ, Heidel BL & Godfread C (1988) Peat initiation and accumulation during the Holocene, Denbigh Fen, McHenry County, North Dakota. Proc. North Dakota Acad. Sci. 42: 30

Malterer TJ, Duxbury AJ & Richardson JL (1987) Soil characteristics of three calcareous fens in North Dakota and Minnesota. Proc. North Dakota Acad. Sci. 41: 65

Malterer TJ, Richardson JL & Duxbury AL (1986) Peatland soils associated with the Souris River, McHenry County, North Dakota. Proc. North Dakota Acad. Sci. 40: 103

McAndrews JH (1966) Postglacial history of prairie, savanna, and forest in northwestern Minnesota. Mem. Torrey Bot. Club 22: 1–72
MDNR (Minnesota Department of Natural Resources) (1993) Minnesota's Native Vegetation – A Key to Natural Communities, version 1.5. Minnesota Dept. Nat. Resourc., St Paul
MDNR (Minnesota Department of Natural Resources) (1995) Technical Criteria for Identifying and Delineating Calcareous Fens in Minnesota. Minnesota Dept. Nat. Resourc., St Paul
Mitsch WJ & Gosselink JG (1993) Wetlands. Van Nostrand Reinhold, New York
Parkhurst DL, Plummer LN & Thorstensen DC (1982) BALANCE – A computer program for calculating mass transfer for geochemical reactions in ground water. US Geol. Surv. Water-Resourc. Invest. Rep. 82-14
Plummer LN, Prestemon EC & Parkhurst DL (1991) An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH. US Geol. Surv. Water-Resourc. Invest. Rep. 91-4078
SAIC (Science Applications International Corporation) (1988) Savage Fen project. Report to US Environ. Prot. Agency, Contract 68-04-5035, DO 18 (SAIC 1-834-06-193-18)
Schot PP & Wassen MJ (1993) Calcium concentrations in wetland groundwater in relation to water sources and soil conditions in the recharge area. J. Hydrol. 141: 197–217
Sjörs H (1961) Some properties of the humus layer in Swedish natural soils. Bull. Royal School Forest., Stockholm, No. 37
Shedlock RJ, Wilcox DA, Thompson TA & Cohen DA (1993) Interactions between ground water and wetlands, southern shore of Lake Michigan, USA. J. Hydrol. 141: 127–155
Snedecor GW & Cochran WG (1967) Statistical Methods. Iowa State Univ. Press, Ames
Snowden RED & Wheeler BD (1993) Iron toxicity to fen plant species. J. Ecol. 81: 35–46
Stauffer RE (1985) Use of solute tracers released by weathering to estimate groundwater inflow to seepage lakes. Environ. Sci. Technol. 19: 405–411
Thompson CA & Bettis EA III (1994) Age and developmental history of Iowa fens. J. Iowa Acad. Sci. 101: 73–77
Thompson CA, Bettis EA III & Baker RG (1992) Geology of Iowa fens. J. Iowa Acad. Sci. 99: 53–59
Troels-Smith J (1955) Characterization of unconsolidated sediments. Geological Survey of Denmark, IV Series 3(10): 39–73
Truesdell AH & Jones BF (1974) WATEQ, a computer program for calculating chemical equilibria of natural waters. US Geol. Surv. J. Res. 2: 233–274
van der Valk AG (1975) Floristic composition and structure of fen communities in northwest Iowa. Proc. Iowa Acad. Sci. 82: 113–118
van der Valk AG (1976) Zonation, competitive displacement and standing crop of northwest Iowa fen communities. Proc. Iowa Acad. Sci. 83: 51–54
Verhoeven JTA & Arts HHM (1987) Nutrient dynamics in small mesotrophic fens surrounded by cultivated land – II. N and P accumulation in plant biomass in relation to the release of inorganic N and P in the peat soil. Oecologia 72: 557–561
Verhoeven JTA, van Beek S, Dekker M & Storm W (1983) Nutrient dynamics in small mesotrophic fens surrounded by cultivated land – I. Productivity and nutrient uptake by the vegetation in relation to the flow of eutrophicated ground water. Oecologia 60: 25–33
Wassen MJ & Joosten JHJ (1996) In search of a hydrological explanation for vegetation changes along a fen gradient in the Biebrza Upper Basin (Poland) Vegetatio 124: 191–209
Watts WA & Winter TC (1966) Plant macrofossils from Kirchner Marsh, Minnesota – A paleoecological study. Bull. Geol. Soc. Am. 77: 1339–1360
Webb T III, Cushing EJ & Wright HE Jr (1983) Holocene changes in the vegetation of the Midwest. In: Wright HE Jr (Ed) Late Quaternary Environments of the United States. 2. The Holocene (pp 142–165). Univ. Minnesota Press, Minneapolis
Wilcox DA, Apfelbaum SI & Heibert RD (1985) Cattail invasion of sedge meadows following hydrologic disturbance in the Cowles Bog Wetland Complex, Indiana Dunes National Lakeshore. Wetlands 4: 115–128

Wilcox DA, Shedlock RJ & Hendrickson WH (1986) Hydrology, water chemistry and ecological relations in the raised mound of Cowles Bog. J. Ecol. 74: 1103–1117

Wright HE Jr (1972) Physiography of Minnesota. In: Sims PK & Morey GB (Eds) Geology of Minnesota – A Centennial Volume (pp 561–578). Minnesota Geol. Surv., Minneapolis

Wright HE Jr, Winter TC & Patten HL (1963) Two pollen diagrams from southeastern Minnesota: Problems in the regional late-glacial and postglacial vegetational history. Bull. Geol. Soc. Am. 74: 1371–1396