



The role of critical zone processes in the evolution of the Prairie Pothole Region wetlands

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ABSTRACT

The Prairie Pothole Region, which occupies 900,000 km² of the north central USA and south central Canada, is one of the most important ecosystems in North America. It is characterized by millions of small wetlands whose chemistry is highly variable over short distances. The study involved the geochemistry of surface sediments, wetland water, and groundwater in the Cottonwood Lakes area of North Dakota, USA, whose 92 ha includes the dominant wetland hydrologic settings. The data show that oxygenated groundwater interacting with pyrite resident in a component of surficial glacial till derived from the marine Pierre Shale Formation has, over long periods of time, focused SO₄²⁻-bearing fluids from upland areas to topographically low areas. In these low areas, SO₄²⁻-enriched groundwater and wetlands have evolved, as has the CaSO₄ mineral gypsum. Sulfur isotope data support the conclusion that isotopically light pyrite from marine shale is the source of SO₄²⁻. Literature data on wetland water composition suggests that this process has taken place over a large area in North Dakota.

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1. Introduction

The Cottonwood Lake (CWL) wetlands are typical of the millions of wetlands in the larger Prairie Pothole Region (PPR; Fig. 1). The extent of the PPR broadly matches the maximum extent of Wisconsin glaciation, which was the last major southward advance of Pleistocene continental glaciers in North America. The melting glaciers left behind a blanket of till, an unstratified and heterogeneous mixture of materials deposited by ice without significant modification by water or wind. The till has low permeability and as a result, water tends to pond on the surface creating the wetlands (Winter, 2003a).

The CWL (Fig. 2) is a 92 ha parcel whose biology, hydrology and chemistry have been extensively studied (see Winter (2003b) for a recent summary). These studies reveal that wetland hydrochemistry is strongly controlled through interaction with groundwater (Winter, 2003a). The wetlands in the uplands (e.g. T8) only seasonally contain water. Seasonal wetlands recharge to the local groundwater flow system. Wetlands located at intermediate topographic positions (e.g. P6 and P7) are flow-through wetlands that both actively receive ground-water inputs and recharge groundwater to the local flow system. Discharge wetlands, which are located at

topographic low points (e.g. P1), dominantly receive ground-water inputs.

The study focuses on the origins of the extreme geochemical variability in both total dissolved solute concentration and chemical composition exhibited by individual wetlands that are spatially separated by short distances (hundreds of meters or less). For example, wetland T8, which has a total dissolved solids concentration of 150 mg/L, is only about 300 m from wetland P1 which contains over 3000 mg/kg total dissolved solids (LaBaugh and Swanson, 2003).

2. Methods

A Geoprobe® percussion core sampling device was used in August 2010 to obtain five cores of up to 13.4 m long. Samples of wetland waters were collected during August 2009, and again in August 2010. The water samples were filtered through 0.45 µm filters into acid cleaned bottles and were analyzed at US Geological Survey Laboratories for cations by ICP-AES, and ICP-MS and for anions by Ion Chromatography. Groundwater samples were obtained in 2009 and 2010 using a peristaltic pump to recover water from groundwater monitoring wells whose location is shown by the filled circles in Fig. 2. Field and laboratory procedures for analysis of groundwater samples were the same as for wetland water samples. The S isotope composition of selected water samples was determined at the USGS by precipitating the SO₄²⁻ as BaSO₄, converting this to SO₂ gas, and determining the isotopic composition of this gas by mass spectrometry.

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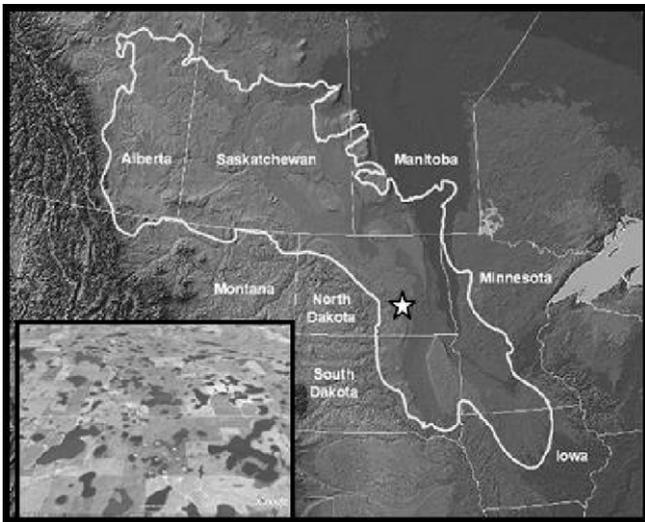


Fig. 1. The outline of the Prairie Pothole Region. The Cottonwood Lakes area is shown as a star. The inset is a Google Earth view of Stutsman County North Dakota looking north.

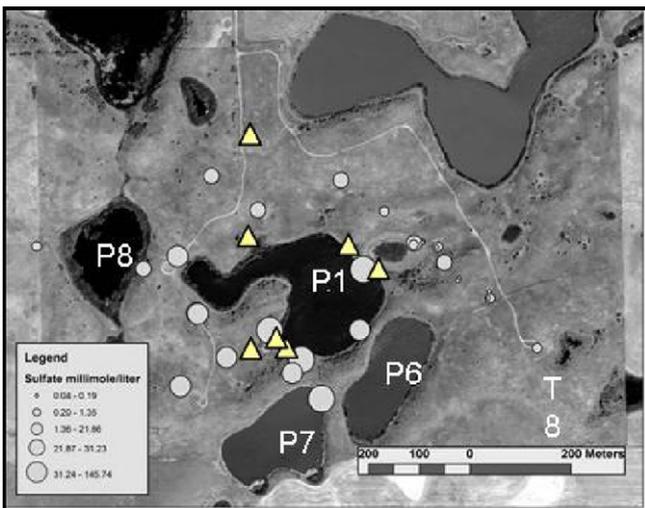


Fig. 2. Map view of the Cottonwood Lakes area, North Dakota. Circles are locations of groundwater monitoring wells whose size is proportional to sulfate concentration. Triangles are locations where gypsum has been reported in the till.

3. Results

The Geoprobe cores all had an upper brown zone underlain by a grey zone. This same color structure was also mapped previously during the drilling of the groundwater wells shown in Fig. 2 (Tom Winter, pers. comm., 2010). The brown–grey color transition occurs throughout Stutsman County with an average depth of 4 m (Winters, 1963).

Data for both wetland and groundwater compositions in the CWL area are plotted on a piper diagram in Fig. 3. On a relative basis, the anionic component of all wetland and groundwaters are systematically low in Cl^- and fall along a trend dominated by nearly pure HCO_3^- to nearly pure SO_4^{2-} . Thus, Cl^- represents a nearly constant and minor proportion of the total anionic charge. Fig. 4 is a log–log plot of the ratio of SO_4^{2-} to HCO_3^- versus total dissolved solids for CWL wetlands. Also plotted on this figure are literature data from 178 wetlands in Stutsman and adjacent Kidder Counties. This plot shows that SO_4^{2-} is increasingly dominant with

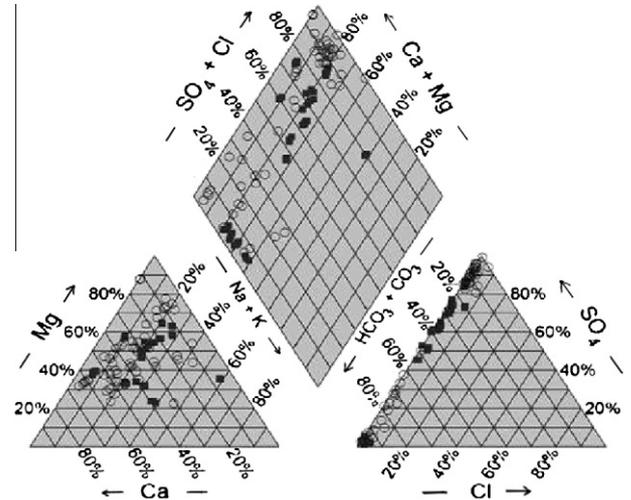


Fig. 3. Piper diagram of the major ion composition of wetland water (filled squares) and groundwater (open circles) in the Cottonwood Lakes area, North Dakota.

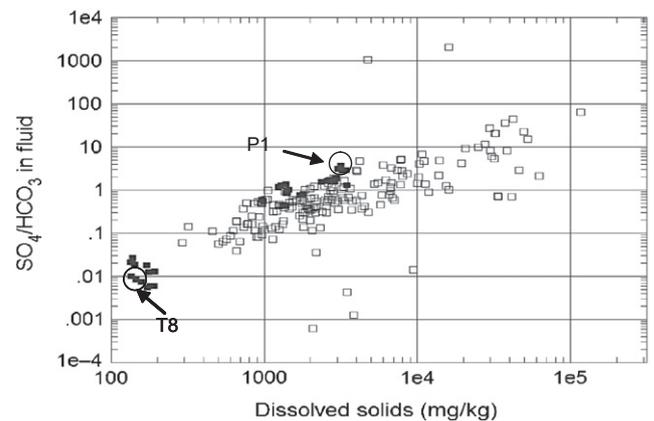


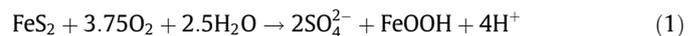
Fig. 4. Plot of the ratio of SO_4^{2-} to HCO_3^- versus total dissolved solids in wetland waters. Solid squares are data from the Cottonwood Lakes area. Open squares are literature values from Swanson et al. (1988).

increasing total salt content. On this figure, the data for wetlands T8 (recharge wetland) and P1 (discharge wetland) are identified. Fig. 5 shows that over the approximately 9400 km² area represented these two counties, geochemical evolution of the wetlands is associated with increasing SO_4^{2-} domination of the fluids.

4. Discussion

4.1. Role of the till in controlling Prairie Pothole wetland characteristics

Fig. 4 demonstrates that a key process increasing dissolved constituents in wetlands is linked to addition of SO_4^{2-} . Several lines of evidence indicate that this process is pyrite oxidation. Pyrite oxidation occurs via interaction with atmospheric O_2 .



The pyrite bearing Pierre Formation that underlies the study area is a significant component of the glacial till (Winters, 1963). It is hypothesized that pyrite oxidation is the major source of SO_4^{2-} to the wetlands. Pyrite oxidation generates Fe oxyhydroxides (Eq. (1)) that are brown in color. Previous research has established that the origin of the brown–grey transition, present elsewhere in the

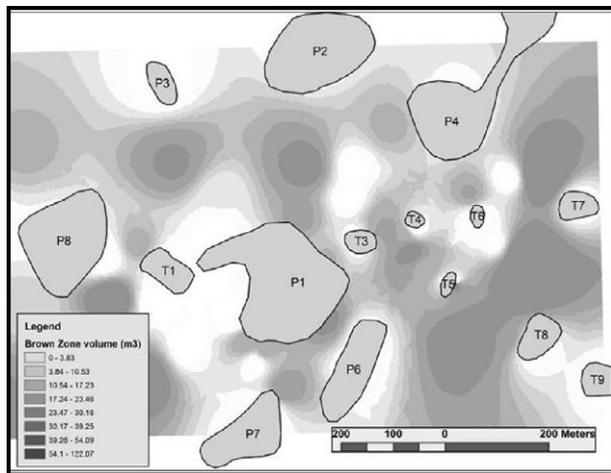


Fig. 5. Modeled volumetric contour map of the brown oxidized zone in the Cottonwood Lakes area. The map was constructed based on the thickness of this zone derived from lithologic logs made during the drilling of the groundwater wells whose location is shown in Fig. 2.

PPR (Van Stempvoort et al., 1994), and recognized in the CWL area (Section 3), is the interaction of atmospheric O_2 with pyrite in the upper layers of the till.

Sulfur isotope data on SO_4^{2-} in groundwater support oxidation of shale-pyrite as the source for the dissolved SO_4^{2-} . The S isotopic data for SO_4^{2-} in groundwater shows enrichment in the light isotope and ranges between -7.5‰ and -18‰ VCDT ($n = 26$). These negative isotopic values overlap the isotopically light S in the Pierre Shale, which ranges from -35‰ to $+16\text{‰}$ with a median of approximately -20‰ (Gautier, 1985).

The total amount of pyrite oxidized, and, therefore, the total amount of SO_4^{2-} produced was approximated from the integrated thickness of the brown oxidized zone in the CWL area. This calculation assumes that there was originally 0.1 wt.% pyrite in the till (a conservative estimate), and that pyrite in the upper brown zone has been oxidized to SO_4^{2-} as previously demonstrated elsewhere in the PPR by (see Van Stempvoort et al., 1994). The thickness of the brown zone was contoured on the basis of the depth of the brown–grey transition in the area and a total brown zone volume of $2.7 \times 10^6 \text{ m}^3$ (Fig. 5) obtained from which a total of $1 \times 10^{12} \text{ g}$ of SO_4^{2-} was generated. This amount can be compared to a total SO_4^{2-} content in the discharge wetland P1 of about $6 \times 10^6 \text{ g}$ based on concentration wetland stage data from August 2009 and stage volume relationships for this wetland from Carroll et al. (2005). Thus, much more SO_4^{2-} was generated by pyrite oxidation than is currently stored in the local discharge wetland. The SO_4^{2-} not present in the wetland itself can be accounted for in one of four ways.

- Considerable SO_4^{2-} is stored in groundwater in the area surrounding wetland P1. The SO_4^{2-} concentration in groundwater is illustrated in Fig. 2. Dissolved SO_4^{2-} in groundwater is elevated in the topographically low area surrounding wetland P1 compared to upland values.
- Geochemical calculations show that groundwater in the area surrounding wetland P1 is saturated with gypsum. Gypsum has been recognized in the till from this area. The locations where gypsum occurs are plotted as triangles in Fig. 2.
- Bacterial SO_4^{2-} reduction may lead to pyrite formation in the wetland sediments, removing SO_4^{2-} to the solid phase.
- Sulfate may be lost to groundwater from wetland P1. By one estimate (Carroll et al., 2005), groundwater losses from wetland P1 are on the order of 15% of the total water loss from the wetland (the remainder is by evaporation).

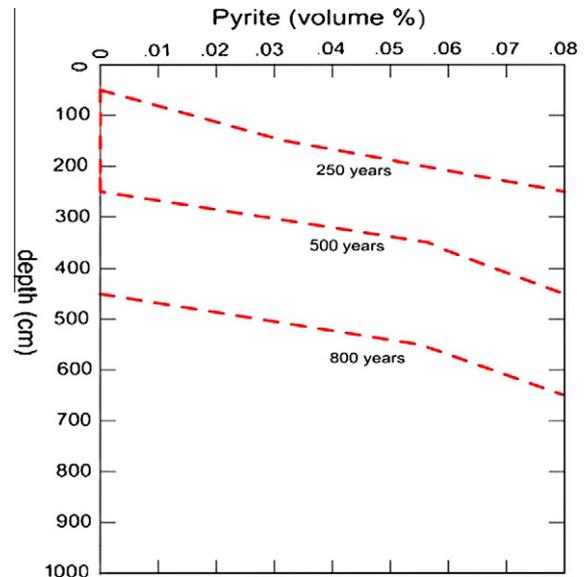


Fig. 6. Plot of the modeled abundance of pyrite as a function of depth and time calculated using the computer code X1T. The model assumes addition of O_2 saturated rainwater by diffusion and infiltration into fractures in the till (fractures are known to be present).

4.2. Oxidation of the till to form the brown zone is a slow process

Fig. 6 shows a model calculation using the computer program Geochemist's Workbench X1T. The dashed lines show the time required to oxidize pyrite in the till with a starting concentration of 0.08 vol.%. The results show that times approaching a 1000 years are required to form the upper brown zone over the depths observed in the field. Thus, the oxidation process is very slow and limited by the kinetics of competing rates of O_2 input to the till and its consumption by oxidation of pyrite and organic matter. Given the large reservoir of SO_4^{2-} -rich fluids in wetland P1 and its surrounding gypsum-bearing sediments and groundwater and the slow rate of pyrite oxidation. It is concluded that the CWL wetlands have evolved geochemically over a long period of time, and potentially over many thousands of years since the retreat of the Wisconsin glaciers.

5. Conclusions

The geochemical evolution of the CWL wetlands is closely tied to the area's geologic history and local topography. Glacial till, the material underlying the area, is the source of pyrite whose oxidation produces SO_4^{2-} . Sulfate-enriched waters produced by pyrite oxidation slowly migrate to topographically low portions of the area. The evolution of wetland waters to high SO_4^{2-} values is likely widespread in the geographic area surrounding the Cottonwood Lakes and previous studies have likewise identified the comparable processes elsewhere in the PPR.

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