



Using stable isotopes to understand hydrochemical processes in and around a Prairie Pothole wetland in the Northern Great Plains, USA

Christopher T. Mills*, Martin B. Goldhaber, Craig A. Stricker, JoAnn M. Holloway, Jean M. Morrison, Karl J. Ellefsen, Donald O. Rosenberry, Roland S. Thurston

US Geological Survey, Denver, CO 80225, United States

ARTICLE INFO

Article history:

Available online 22 March 2011

ABSTRACT

Millions of internally drained wetland systems in the Prairie Potholes region of the northern Great Plains (USA and Canada) provide indispensable habitat for waterfowl and a host of other ecosystem services. The hydrochemistry of these systems is complex and a crucial control on wetland function, flora and fauna. Wetland waters can have high concentrations of SO_4^{2-} due to the oxidation of large amounts of pyrite in glacial till that is in part derived from the Pierre shale. Water chemistry including $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^2\text{H}_{\text{H}_2\text{O}}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ values, was determined for groundwater, soil pore water, and wetland surface water in and around a discharge wetland in North Dakota. The isotopic data for the first time trace the interaction of processes that affect wetland chemistry, including open water evaporation, plant transpiration, and microbial SO_4 reduction.

Published by Elsevier Ltd.

1. Introduction

The Prairie Potholes region is an approximately 715,000 km² area that extends from Alberta (Canada) to Iowa (USA) (Euliss et al., 1999). Retreat of Pleistocene glaciers from this landscape left pothole-like depressions that now comprise millions of internally drained wetland systems that provide many important ecosystem services including indispensable waterfowl habitats. These wetland systems typically consist of topographically high recharge wetlands, intermediate flow-through wetlands, and topographically low discharge wetlands (Euliss et al., 2004). Recharge wetlands depend exclusively on precipitation (mainly snow-melt) and are relatively fresh and seasonal. Discharge wetlands are fed by precipitation and groundwater and tend to be semi-permanent and more saline. The major anion in discharge wetlands is often SO_4^{2-} , which originates from Pierre Shale-derived pyrite in the glacial till. Sulfate is liberated during pyrite oxidization and is subsequently transported to and concentrated in wetlands during infiltration, groundwater discharge, and evapotranspiration.

The chemistry of discharge wetlands is complex and depends on a number of processes including overland flow, groundwater input, open-water evaporation, mineral precipitation and dissolution, and biogeochemical processes. Understanding how these processes interact is important because water chemistry is a primary control wetland of function, flora and fauna in these systems (Euliss et al., 1999, 2004). It is important to be able to predict how

climate and land use change will affect hydrochemical processes and, in turn, ecosystem services provided by the wetlands.

One little-studied hydrochemical process is the concentration of salts at the wetland edge by plant transpiration (Arndt and Richardson, 1993) although it is known that the hydrologic gradients in this zone can change during intense summer plant transpiration (Rosenberry and Winter, 1997). This study used $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^2\text{H}_{\text{H}_2\text{O}}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ values of soil pore waters in this zone to investigate the hydrochemical complexity of a semi-permanent discharge wetland, designated P1, in the Cottonwood Lake (CWL) study area near Jamestown, North Dakota (USA).

2. Methods

Groundwater wells were purged before samples were collected in August 2010. Wells were allowed to recharge overnight and a second sample was then collected. Values for these field duplicates were typically within analytical error and were averaged. Soil pore waters were collected from drive point lysimeters installed at two transects separated by a few meters along the edge of P1 (Fig. 1). Lysimeters were installed at two depths (60 and 150 cm for transect 1 and 90 and 150 cm for transect 2) at each of 3 sites proximal, middle, and distal from the wetland edge within both transects (Fig. 1). Exceptions were that water could not be collected from either the proximal deep lysimeter at transect 2 or the distal shallow lysimeter at transect 1. The proximal site was at the edge of the wetland under ~2 cm of water and the middle and distal sites were on dry land. Pore water was extracted by applying a vacuum to a filter flask. Two collections were typically made for each

* Corresponding author. Address: MS 964, Building 20, Denver Federal Center, Denver, CO 80225, United States. Tel.: +1 303 236 5529.

E-mail address: cmills@usgs.gov (C.T. Mills).

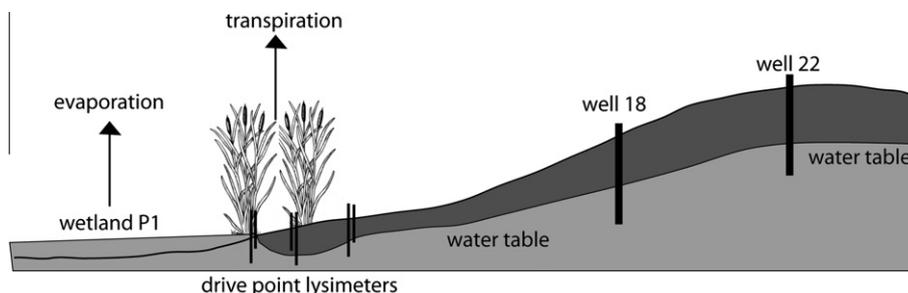


Fig. 1. Schematic of water sampling transect and processes around wetland P1. A hypothesized cone of depression in the groundwater table that results from plant transpiration at the edge of the wetland is shown.

lysimeter. One was collected in the afternoon a few hours after installation and the second the next morning. Water from the wetland was collected ~15 m from shore with a 1-m long tube designed to collect a representative water column sample. Shallow water from the wetland edge near the proximal lysimeter sites was also collected. All samples were filtered (0.45 μm) in the field and transported and stored at 5 $^{\circ}\text{C}$. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$ values were determined by a cavity ringdown spectrometer and $\delta^{34}\text{S}_{\text{SO}_4}$ values were determined by elemental analysis-isotope ratio mass spectrometry of BaSO_4 precipitates.

3. Results and discussion

Groundwater sampled around wetland P1 in August 2010 had a relatively narrow range of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (-12.6‰ to -14.6‰ VSMOW) and fell close to the meteoric water line (Fig. 2). Water column samples from two different areas of P1 in August 2010 had identical $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (-4.6‰) and fell well below the meteoric water line (Fig. 2). In contrast, P1 water column samples collected in July 2009 and April/May 2010 were less evaporated (Fig. 2). Saturated soil pore water samples from the lysimeter transects in August 2010 had a wide range of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (-14.2‰ to -7.1‰) with some pore waters appearing to be a mixture of groundwater of meteoric origin and evaporated water from P1.

Both SO_4^{2-} concentrations (700–8400 mg L^{-1}) and $\delta^{34}\text{S}_{\text{SO}_4}$ values (-18.2‰ to -4.1‰ VCDT) for all samples covered wide ranges. In Fig. 3, SO_4^{2-} concentrations and $\delta^{34}\text{S}_{\text{SO}_4}$ values are plotted against the ^2H offset ($[8 * \delta^{18}\text{O}_{\text{H}_2\text{O}} + 10] - \delta^2\text{H}_{\text{H}_2\text{O}}$), a measure of how far the sample departs from the meteoric water line. More positive

values indicate more evaporation. These plots highlight several processes occurring in the P1 wetland system.

3.1. Concentration of sulfate by plant transpiration

Samples from many of the soil pore water transect sites are not evaporated, but have much higher concentrations of SO_4^{2-} than found in either two up gradient groundwater wells (22 and 18) or P1. This suggests a concentration mechanism in these soils that does not result in deviation from the meteoric water line. Transpiration by plants at the wetland edge is a likely mechanism. Plants pump water to the atmosphere without the isotopic fractionation characteristic of open water evaporation.

3.2. Sulfur recycling in soil pore waters

A relatively tight range of $\delta^{34}\text{S}_{\text{SO}_4}$ values (-14.6‰ to -18.2‰) was observed for non-evaporated soil pore water and the two upgradient groundwater samples (wells 22 and 18) (Fig. 3). This suggests that either microbial SO_4 reduction is negligible in these soils or that a net loss of the sulfide (either by precipitation or volatilization) produced during SO_4 reduction is minimal. Isotopically light sulfide produced in these soils is likely re-oxidized to SO_4^{2-} by O_2 or Fe(III) . More positive $\delta^{34}\text{S}_{\text{SO}_4}$ values determined for some other groundwater near P1 could indicate SO_4 reduction or may result from isotopic variation in the source S in the glacial till. A wide range of $\delta^{34}\text{S}_{\text{SO}_4}$ values have been reported for pyrite in the Pierre Shale (-35‰ to $+16\text{‰}$) (Gautier, 1985).

3.3. Net sulfate reduction and sulfide sequestration or volatilization in P1

The $\delta^{34}\text{S}_{\text{SO}_4}$ values for samples collected from the water column of P1 (mean 4.2 ± 0.1) were very consistent over a 1-a period (Fig. 3). These values are more positive than those for nearby groundwater and indicate SO_4 reduction with net sequestration (precipitation) or loss (volatilization) of the resulting sulfide. During this same period $\delta^{34}\text{S}_{\text{SO}_4}$ values for samples collected from other semi-permanent wetlands in the CWL study area were also relatively enriched (range -5.6‰ to 1.7‰) compared to more temporary flow-through wetlands (-13.6‰ to -8.0‰) (data not shown).

3.4. Mixing of P1 water and deeper soil pore waters

Some shallow soil pore water samples fall on a mixing line between deeper soil pore water and P1 surface water (Fig. 3). Mixing is evident in both the SO_4^{2-} concentration and $\delta^{34}\text{S}_{\text{SO}_4}$ data. Shallow pore water at the proximal site is expected to have a mixture of deeper pore water and wetland surface water. However, the

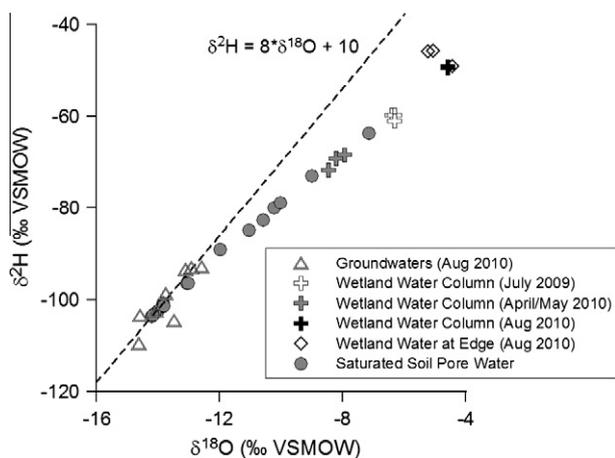


Fig. 2. Plot of $\delta^2\text{H}_{\text{H}_2\text{O}}$ versus $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ for groundwater, soil pore water, and wetland water collected in and around wetland P1 in the CWL study area. The dashed line indicates the global meteoric water line.

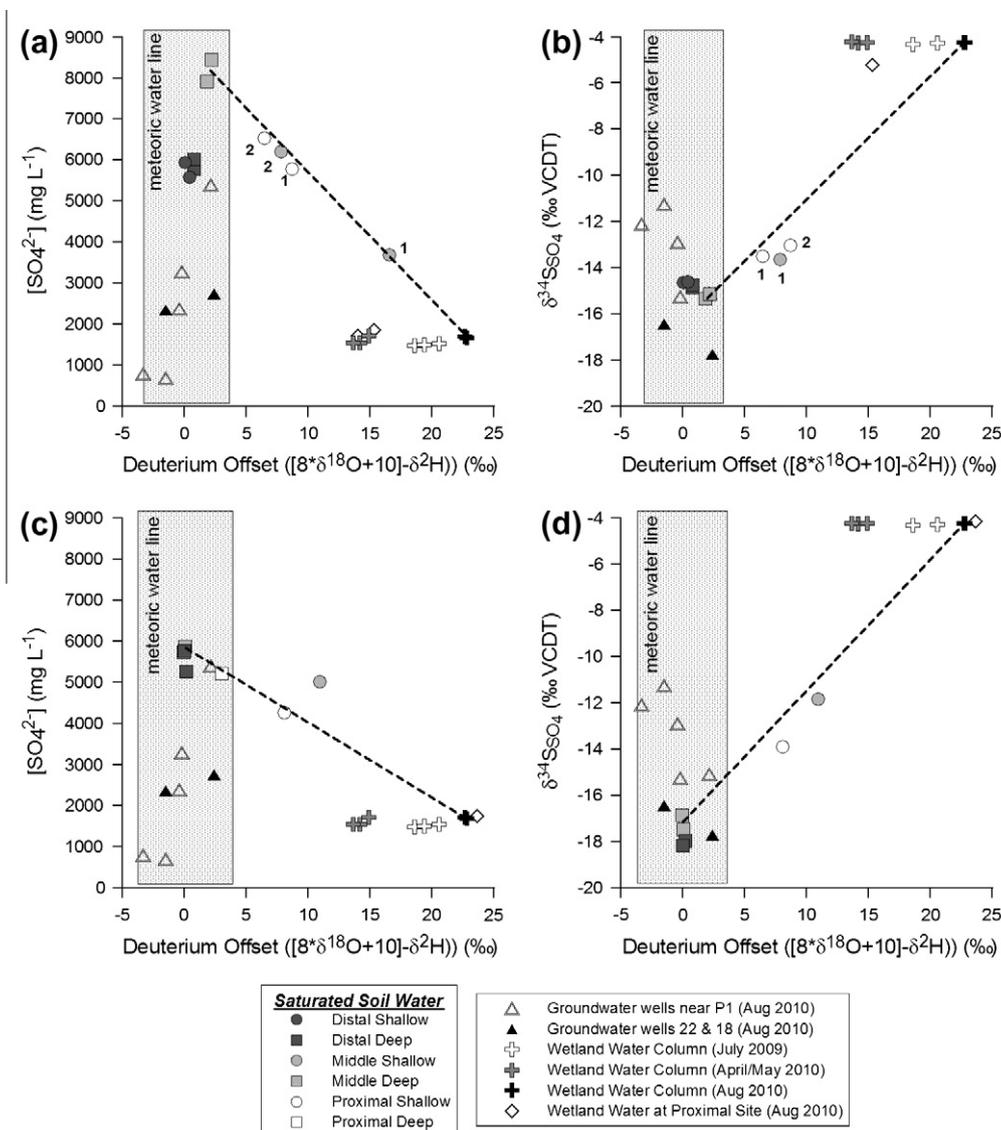


Fig. 3. Plots of, SO_4^{2-} concentrations (a and c) and $\delta^{34}\text{S}_{\text{SO}_4}$ values (b and d) versus the deuterium offset for groundwater, wetland water, and soil pore water from lysimeter transect 2 (a and b) and transect 1 (c and d). The shaded rectangle indicates samples that fall very close to the meteoric water line. The dashed line represents mixing between the middle shallow samples and the wetland water column August 2010 samples. Wells 18 and 22 were upgradient of the lysimeter sites and other groundwater wells were located in the vicinity of P1. The numbers next to the middle shallow and proximal shallow lysimeter samples in (a) and (b) indicate the order in which they were collected. A $\delta^{34}\text{S}_{\text{SO}_4}$ value was not determined for the second middle shallow sample.

substantial component of wetland water at the middle shallow site of both transects suggests a favorable hydrological gradient for wetland water to flow away from the wetland edge and is consistent with a transpiration-driven cone of depression around the wetland reported by others (Rosenberry and Winter, 1997). The second sample collected from the middle shallow site of transect two had a much smaller fraction of P1-derived water than the first sample collected from this site (Fig. 3a). The first sample was collected in the afternoon on a hot day and the second in the morning after a night time rain event. Thus, the second sample likely reflected a period of decreased plant transpiration and a potentially smaller hydraulic gradient away from P1. The $\delta^{34}\text{S}_{\text{SO}_4}$ value (−5.2%) of a surface water sample collected at the proximal location of lysimeter transect 2 is significantly more negative than any of the $\delta^{34}\text{S}_{\text{SO}_4}$ values determined for water from the P1 wetland water column (Fig. 3b). This may be a signal of seepage of groundwater at the wetland edge.

4. Conclusions

Groundwater, soil pore water, and wetland water in and around wetland P1 in the CWL study area have $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^2\text{H}_{\text{H}_2\text{O}}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ values that clearly document previously hypothesized processes important for controlling wetland chemistry. These types of data characterize the interplay of complex hydrochemical and biogeochemical processes that occur at the edges of Prairie Pothole wetlands. Such knowledge is important for being able to predict how natural climate variation, climate change, and land use changes may affect the chemistry of wetlands and, in turn, the many services provided by these ecosystems.

Acknowledgments

We thank David Mushet, Caleb Balas, and Chip Euliss for sampling support and helpful discussions.

References

- Arndt, J.L., Richardson, J.L., 1993. Temporal variations in the salinity of shallow groundwater from the periphery of some North Dakota wetlands (USA). *J. Hydrol.* 141, 75–105.
- Euliss Jr., N.H., LaBaugh, J.W., Fredrickson, L.H., Mushet, D.M., Laubhan, M.K., Swanson, G.A., Winter, T.C., Rosenberry, D.O., Nelson, R.D., 2004. The wetland continuum: a conceptual framework for interpreting biological studies. *Wetlands* 24, 448–458.
- Euliss Jr., N.H., Mushet, D.M., Wrubleski, D.A., 1999. Wetlands of the Prairie Pothole region: invertebrate species composition, ecology, and management. In: Batzer, D.P., Rader, R.B., Wissinger, S.A. (Eds.), *Invertebrates in Freshwater Wetlands of North America: Ecology and Management*. John Wiley & Sons, New York, pp. 471–514 (Chapter 21).
- Gautier, D.L., 1985. Sulfur/carbon ratios and sulfur isotope composition of some Cretaceous Shales from the Western Interior of North America. US Geol. Surv. Open-File Rep. 85–514.
- Rosenberry, D.O., Winter, T.C., 1997. Dynamics of water-table fluctuations in an upland between two prairie-pothole wetlands in North Dakota. *J. Hydrol.* 191, 266–289.