Groundwater Research Report WR11R004

ESTABLISHING PALEOCLIMATE RECORDS FROM SPRING TUFA DEPOSITS IN THE DRIFTLESS AREA OF WISCONSIN

Maureen A. Muldoon, Ph.D. Susan K. Swanson, Ph.D.

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PROJECT SUMMARY

Title: ESTABLISHING PALEOCLIMATE RECORDS FROM SPRING TUFA DEPOSITS IN THE DRIFTLESS AREA OF WISCONSIN

Project I.D.: WR11R004

Investigators: Maureen A. Muldoon, Associate Professor of Geology, University of Wisconsin – Oshkosh; Susan K. Swanson, Associate Professor of Geology, Beloit College

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Background/Need: Water at two tufa-depositing springs in Grant County, Wisconsin emanates from stratigraphic positions similar to a laterally-extensive perched aquifer that was identified in the eastern Driftless Area and shown to be stable under current climate conditions (Carter et al., 2010). Due to the similarity in hydrogeologic setting, the tufa-depositing springs may be supplied by a similar shallow groundwater flow system. If geochemical records from the tufa deposits correlate with other proxy climate data in the region, this may suggest that tufa deposition, and therefore spring flow from the shallow flow system, has been continuous throughout the Holocene, even during climate regimes that differ from the present. Few domestic wells in the study area are installed at the stratigraphic interval of interest, but the headwaters of streams throughout the Driftless Area are fed by water discharging from the shallow groundwater flow system. Therefore, an understanding of the potential effects of climate change and variability on shallow groundwater levels and flow is important in maintaining aquatic diversity and stream habitat.

Objectives: The objectives of this study are 1) to gain a better understanding of how regional variations in the lithostratigraphy of the Sinnipee Group (Platteville, Decorah, and Galena Formations) affect shallow groundwater flow patterns in the southern Driftless Area of Wisconsin and, specifically, in the vicinity of the tufa-depositing springs and 2) to use the tufa-depositing spring systems to better understand changes in Holocene climate in this region and the effects that climate change had on groundwater levels and flow.

Methods: To address the first objective, detailed measurements and descriptions of a stratigraphic section near the Potosi spring were made, and borehole geophysical logs were collected from existing domestic wells that are in close proximity to each spring site and open to the appropriate stratigraphic interval. Measurements of outcrop natural gamma allowed correlation to subsurface geophysical and hydrogeological data. In order to assess which, if any, of the many lithologic contrasts observed in outcrop functions as a high-permeability flow feature in the subsurface, we also examined existing natural gamma and hydrologic logs from wells where the Decorah Formation, in particular, was saturated.

To address the second objective, it was necessary to first gain an understanding of seasonal variations in tufa deposition. If tufa is deposited year-round, geochemical signatures are likely to represent mean annual conditions, whereas if tufa is deposited seasonally, the record may reflect mean summer or mean winter conditions. Monthly water samples were collected from the spring orifice and the dripface of each tufa mound and analyzed for major ion concentrations. These data were used to calculate calcite saturation indices at each orifice and dripface throughout the year. Continuous measurements of fluid temperature, conductivity, and water level with Leveloggers® provided context for the monthly samples.

Three one-inch tufa cores, each approximately 4m in length, were used to develop a paleoclimatic record based on variations in stable isotopes (δ^{18} O and δ^{13} C) and elemental molar ratios (Mg/Ca).²³⁴U-²³⁰Th

dating was used to constrain the age of the tufa deposits. The paleoclimatic record developed from the tufa cores was then compared to existing proxy climate records for the region.

Results and Discussion: This distinct gamma signature of the Platteville and Decorah Formations is present in all of the logs we collected or examined and was used to correlate the units across the study area. The lithologic contrast between the shaley Spechts Ferry and the overlying Guttenberg limestone, which compose the Decorah Formation, seems to control the location of the tufa-depositing springs as well as seepage in the valley where the Potosi section was measured. Positions of seepage and vegetation growth in other nearby outcrops coincide with this interval and suggest that there are several additional discrete discontinuities that are in close stratigraphic proximity to the Spechts Ferry shale, have developed at zones of contrasting lithology, and may also function as high-permeability features in the subsurface.

Spring monitoring results suggest that physicochemical conditions do not vary widely at the springs, and the lack of variation in calcite saturation at each spring orifice and dripface supports the consistency of tufa deposition throughout the year. This indicates that geochemical results for the tufa deposits are more likely to represent mean annual conditions than seasonal conditions. Three of the seven ²³⁴U-²³⁰Th dates that were obtained are thought to be reliable on the basis of their lower levels of detrital thorium and/or higher levels of uranium. Subsequent correlation of geochemical results among the tufa cores and other proxy climate records for the region lends further support for the reliability of the dates. Oxygen isotopes do not show increasing or decreasing trends within the cores. However, carbon isotopic trends in the Platteville cores are similar, in that the δ^{13} C in each core decreased by about 2 per mil between 2.4 ka and 1.8 ka. The Potosi core also shows a 2 per mil decrease in δ^{13} C between 2.4 ka and 1.8 ka; however, because it represents a longer time period, it is clear that the positive $\delta^{13}C$ excursion existed prior to 2.4 ka. Mg/Ca excursions correspond to δ^{13} C excursions in all three cores. Knox (2000) shows an episode of especially small floods in rivers in southwestern Wisconsin from about 5.5 ka to 3.3 ka, which he attributes to warmer and drier conditions. This interval corresponds to the maximum positive δ^{13} C and Mg/Ca excursions in the Potosi core. Carbon isotopic trends in the Potosi core also generally correspond to the δ^{13} C records for the Coldwater Cave stalagmites from northeastern Iowa (Denniston et al., 1999).

Conclusions/Implications/Recommendations: Perched groundwater in the Driftless Area was shown to be laterally-extensive and broadly associated with the Decorah, Platteville, and Glenwood Formations, and it is thought to be stable over decadal time scales (Carter et al., 2010). We provide further evidence of the significance of the sequence to shallow groundwater flow in the region, but refine the interval to several high-permeability zones that are concentrated near the upper contact of the Spechts Ferry shale or within one unit above or below the shale. We also favor a conceptual model for the shallow groundwater flow system that includes perched groundwater beneath some ridges and fully saturated conditions beneath others. The low-resolution age control on the tufa cores does not allow for detailed paleoclimatic reconstruction, but broad patterns that agree with other proxy climate records for the region are evident, suggesting that tufa deposition, and therefore spring flow, has been mostly continuous for at least the last five thousand years. This implies that the shallow groundwater flow system has been stable over time frames of thousands of years, even during warmer and drier periods.

Related Publications:

Swanson, S.K., Muldoon, M.A., 2010, The geology and ecohydrology of springs in the Driftless Area of southwest Wisconsin, *in* de Wet, A., ed., Proceedings of the Twenty-third Annual Keck Research Symposium in Geology, Houston, Texas, pp. 96-102.

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INTRODUCTION

Project Objectives

Where groundwater dissolves limestone and dolomite and becomes saturated with calcium carbonate, CO_2 degassing can cause tufa deposition near a spring orifice. Paleoclimate records can be constructed from tufa depositional sequences using stable isotope ratios and major and trace element concentrations (Andrews, 2006). Used in association with hydrogeologic information, these records provide insights into the effects of climate change and variability on groundwater levels and flow patterns. Springs that deposit tufa and create mounds are rare in Wisconsin. However, at least two, one near Platteville and another near Potosi, are known to emanate from the Sinnipee Group in the southern Driftless Area of Wisconsin (Figure 1) (Heller, 1988). Both springs discharge at mid-slope positions, well above the level of the receiving streams (Figure 2).



Figure 1. (a.) The location of tufa-depositing and other springs in southwestern Wisconsin (Macholl, 2007) and (b.) the distribution of bedrock (WGNHS, 2006; Mudrey et al., 2007).



Figure 2. The Potosi tufa-depositing spring and the associated spring mound. Person for scale on left.

Water at the tufa-depositing springs emanates from stratigraphic positions similar to a laterallyextensive perched aguifer that was identified in the eastern Driftless Area and shown to be stable under current climate conditions (Carter et al., 2010). Due to the similarity in hydrogeologic setting, the tufadepositing springs may be supplied by a similar shallow groundwater flow system. If the geochemical records from the tufa deposits correlate with other proxy climate data in the region, this may suggest that tufa deposition, and therefore spring flow from the shallow flow system, has been continuous throughout the Holocene, even during climate regimes that differ from the present. The objectives of this study are 1) to gain a better understanding of how regional variations in the

lithostratigraphy of the Sinnipee Group affect shallow groundwater flow patterns in the southern Driftless Area of Wisconsin and, specifically, in the vicinity of the tufa-depositing springs and 2) to use the tufa-depositing spring systems to better understand changes in Holocene climate in this region and the effects that climate change had on groundwater levels and flow.

Background

Hydrogeologic Setting

Cambrian and Ordovician age strata generally thicken to the west and south in southwestern Wisconsin. They are deeply dissected and regularly exposed in narrow valleys (Figure 1). The Sinnipee Group, composed of the Platteville, Decorah and Galena Formations (Figure 1), is the uppermost bedrock unit in much of Grant County and is highly heterogeneous with abundant dissolution voids, horizontal and vertical fractures, and zones of shale strata. Pleistocene deposits are absent except for layers of loess on ridges, hillslope sediment on valley sides, and stream sediment in valley bottoms (Clayton and Attig, 1997; Mudrey et al., 2007). Local flow systems, with short groundwater flow paths, are common in the layered bedrock uplands. Perched aquifers, some of which may be laterally-extensive, also occur in the region (Krohelski et al., 2000; Hunt et al., 2003; Runkel et al., 2003; Carter et al., 2010). Therefore, the potential for complex groundwater flow paths exists.

Springs provide evidence of heterogeneity of permeability and discrete groundwater flow. As such, their occurrence can reveal important hydrogeologic controls on groundwater flow (Manga, 2001). Although thousands of springs occur in southwestern Wisconsin, the relationship of springs to the groundwater flow system is not well understood. Groundwater is generally thought to flow preferentially along bedding plane fractures or along lithologic contacts between units with differing hydraulic conductivity. Where these features intersect stream valleys, groundwater is discharged at contact springs. De Geoffroy et al. (1967; 1970) note that many of the springs in the historic lead-zinc mining district of southwestern Wisconsin (Iowa, Grant, and Lafavette Counties) emanate from fractures and along zones of contrasting permeability in the Platteville, Decorah, and Galena Formations (Sinnipee Group) (Figure 1). In Iowa County, Wisconsin, approximately 60% of 407 historically-mapped springs are thought to emanate from the Sinnipee Group (Swanson et al., 2007), and recent work suggests that some of these springs may be supplied by a laterally-extensive aguifer that is stable under current climate conditions and perched above the Decorah, Platteville, and Glenwood Formations (DPG aquitard) (Carter et al., 2010). An improved understanding of the hydrostratigraphic positions of springs in other parts of the Driftless Area may lend further evidence to the regional nature and stability of shallow groundwater flow systems under current climate conditions. Geochemical records from tufa deposits may extend the evidence to climate conditions that differ from the present.

Paleoclimatic Reconstructions

The Holocene climatic history of the upper midwestern United States has been reconstructed using a variety of physical and biological data sets including, for example, the analysis of cave stalagmites in northeastern Iowa (Dorale, 1992; Denniston et al., 1999), varved sediments from lakes in central Minnesota (Dean et al., 1984), floods reconstructed from the alluvial records of rivers in southwestern Wisconsin (Knox, 2000), and pollen from across the region (Webb et al., 1983; Bartlein et al., 1984; Baker et al., 1996; Clark et al., 2001; Williams et al., 2009). These studies generally agree that, due to changes in the frequency and duration of the Pacific, Gulf of Mexico, and Arctic air masses, an increase in mean July temperature and a reduction in mean annual precipitation took place from the early to mid-Holocene. Proxy climate data suggest that from the mid Holocene to present, the region became cooler and wetter, with some areas experiencing abrupt changes in temperature and moisture (Knox, 2000; Williams et al., 2009). While a large variety of Holocene proxy records exist for the upper midwestern USA (Williams et al., 2010), relatively few are available for the Driftless Area of Wisconsin. This is largely due to the lack of lakes and bogs typically used in pollen studies (Baker et al., 1996).

Stable isotope and elemental variation in active tufa-depositing systems and accumulated tufa deposits have been shown to reveal paleo-temperature and -moisture conditions (e.g., Andrews et al., 1997; Ihlenfeld et al., 2003; Garnett et al., 2004). Therefore, tufa sequences offer an opportunity not only to better understand current and past groundwater flow conditions, but also to augment climate reconstructions for this region. Variability in the δ^{18} O of tufa deposits reflects changes in temperature and the δ^{18} O of water that recharges the aquifer and flows to the spring . Variability in the δ^{13} C of tufa deposits reflects the sources of carbon that contribute to dissolved inorganic carbon (DIC) in groundwater. CO₂ with lower δ^{13} C is often derived from soil organic matter, whereas higher δ^{13} C is often derived from the dissolution of the carbonate aquifer. Variation in δ^{13} C can also reflect the dominant type of plant metabolism. Where C3 plants dominate, δ^{13} C is typically lower. In drier regions, where C4 plants dominate, δ^{13} C is higher (Andrews, 2006). Ratios of Mg to Ca, or other elements such as Sr and Ba, in groundwater are known to increase with aquifer residence time due to differences in dissolution rates of dolomite versus calcite. Low Mg to Ca ratios in tufa have been shown to be associated with short residence times during wet periods and high Mg to Ca ratios with longer residence times during dry episodes (Garnett et al., 2004).

PROCEDURES AND METHODS

Stratigraphic Sections

The lithostratigraphy of the Sinnipee Group has been well characterized, as these strata serve as the host rock for the lead-zinc deposits within the tri-state mining district. Detailed descriptions of the members of the Platteville, Decorah, and Galena Formations can be found in numerous publications (e.g., Agnew et al., 1956; Heyl et al., 1959; Agnew, 1963; Agnew, 1966). One of the goals of this project was to investigate how lithostratigraphic variations affect groundwater flow patterns within the vicinity of the tufa-depositing springs. To accomplish this goal we 1) measured a detailed stratigraphic section of the rocks outcropping near the Potosi spring, 2) collected outcrop natural gamma measurements at both spring sites, and 3) used these data to correlate the outcrop lithostratigraphy near the springs to the regional subsurface stratigraphy. Poor exposure near the Platteville spring precluded measuring a detailed stratigraphic section at that site.

At the Potosi site, the stratigraphic units are exposed along the Grant River and in a small gully that cuts the hillside near the tufa mound. The exposed section extends from the upper St. Peter Formation through the base of the Galena Formation. Unit thicknesses were measured using a Jacob staff, and lithologic units were described noting composition, bedding characteristics, texture, Munsell color, and presence of fossils. These data were used to construct a detailed stratigraphic column. Location of groundwater seepage was also noted. Natural gamma measurements were collected approximately every 0.5 m at the Potosi exposure using a GF Instruments GRM-260 hand-held gamma-ray spectrometer. Additional gamma measurements were taken approximately every 0.1 m within the Decorah Formation which contains the Spechts Ferry and Guttenberg Members.

Borehole Geophysics

We examined well constructions reports (WCRs) located within several miles of each spring site in order to identify existing domestic wells that were open to the Sinnipee Group, and specifically the Decorah Formation. For both the Potosi and Platteville sites we were able identify a suitable well and obtain permission from the owners. We hired certified pump installers to pull the pumps from the wells prior to logging and then reinstall the pumps and disinfect the well upon completion of the logging process. In order to minimize inconvenience to the well owners, the logging was conducted immediately after the pump was pulled. Geophysical logs were collected using the Mount Sopris Matrix wireline logging system owned by the Wisconsin Geological and Natural History Survey (WGNHS). Geophysical data collected from each well include caliper, which measures borehole diameter and can help identify fractures and dissolution zones; natural gamma, which measures natural radiation and can be used for stratigraphic correlation as well as to identify zones with shale or clay; and single-point resistivity, normal resistivity, and spontaneous potential, which are useful for stratigraphic correlation. We also collected optical borehole image (OBI) and acoustic borehole image (ABI) logs for each well. In both wells, the static water level was well below the Decorah Formation, thus precluding the collection of any borehole flow measurements within that unit.

Geochemistry of Spring Water

Paleoclimate information is recorded only during times of active tufa deposition. If tufa is deposited yearround, geochemical signatures are likely to represent mean annual conditions, whereas if tufa is deposited seasonally, the record may reflect mean summer or mean winter conditions. To assess the seasonal consistency of tufa deposition, springs were sampled at the orifice and dripface on a monthly basis for one year. Temperature, specific conductance, pH, alkalinity, and dissolved oxygen were measured in the field, and samples were collected and sent to the University of Wisconsin - Stevens Point Water and Environmental Analysis Laboratory for analysis of major ions. These data were used to calculate monthly calcite saturation indices for each spring orifice and dripface. Lack of variation in the level of calcite saturation would support consistency in tufa deposition throughout the year.

Leveloggers® installed in the pool at each spring orifice were used to record water level, fluid temperature, and fluid conductivity at 30-minute intervals to provide additional context for the monthly water samples. Measurements of water levels in the spring pool allowed assessment of the seasonal variability in spring flow in lieu of actual discharge measurements, which are not possible due to shallow water depths and complex flow patterns across the mounds. A Barologger® installed at the Potosi site recorded barometric pressure and air temperature, allowing correction of water levels for barometric fluctuations. Hourly precipitation measurements for the duration of the study were obtained from the National Climate Data Center for the National Weather Service Cooperative Station at Cuba City, WI.

Geochemistry of Tufa Deposits

Three cores were collected from the two tufa mounds, two from the Platteville mound (3.85 m and 4.13 m) and one from the Potosi mound (3.95 m), using a handheld Tanaka 262DH Engine Drill with a oneinch diameter, diamond-encrusted bit. Each core was sampled at approximately 5 cm intervals using a Dremel drill. Samples were analyzed for stable isotopes of oxygen and carbon using an automated carbonate preparation device (KIEL-III) coupled to a gas-ratio mass spectrometer (Finnigan MAT 252) at the Environmental Isotope Laboratory in the Department of Geosciences at the University of Arizona . The cores were also cut and sampled at approximately 10 cm intervals. These samples were analyzed by X-ray Fluorescence (XRF) for 10 major and 19 trace element abundances at the GeoAnalytical Laboratory at Washington State University.

²³⁴U-²³⁰Th dating was used to constrain the age of the tufa deposits. U and Th isotopes for seven samples were measured using a Thermo Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at the University of New Mexico Radiogenic Isotope Laboratory. Although seven samples were analyzed, only three yielded reasonable ages. High levels of detrital Th and/or low levels of U rendered the other four samples questionable.

RESULTS AND DISCUSSION

Stratigraphic Controls on Shallow Groundwater Flow

The stratigraphic section from the Potosi site is presented in Figure 3; a more detailed section is presented in Appendix B. The section exposes 1.7 m of St. Peter Sandstone which is conformably overlain by 0.3 m of Glenwood Shale. The section extends through the Platteville, Decorah, and Galena Formations of the Sinnipee Group. The Pecatonica Member consists of 6.0 m of irregularly bedded dolomite that is overlain by 7.25 m of limestone of the McGregor Member. The Quimbys Mill Limestone, as well as part of the overlying Spechts Ferry Member, are covered by talus. By digging into the gully walls, we were able to expose the base of the Quimbys Mill Member which we estimated as 0.2 m thick. The upper Spechts Ferry, exposed under a resistant ledge of the overlying Guttenberg Limestone Member, consists of interbedded gray-green shale layers and thin, fine-grained limestone layers. There is considerable groundwater seepage at the top of the Spechts Ferry Member (18.1 m in Figure Y) and we believe that this stratigraphic contact controls the location of the tufa-depositing springs. The Spechts Ferry Member

is overlain by 4.9 m of the irregularly bedded Guttenberg Limestone Member of the Decorah Formation. The section extends 2.0 meters into the base of the Galena Formation.



Figure 3. Measured stratigraphic section near the Potosi spring with outcrop natural gamma values.

The domestic well (WUWN GR1541), located near the Potosi spring and logged as part of this project, illustrates the natural gamma profile that is characteristic for the Ancell and Sinnipee Group stratigraphic units. The St. Peter Formation near the base of the log has a characteristically low gamma signature followed by the distinct gamma peak caused by the Glenwood shale. The Platteville Formation exhibits a somewhat variable natural gamma signature that is elevated above St. Peter values. The distinctive peak that extends from ~155 to 180 ft marks the location of the shaley Spechts Ferry Member of the Decorah Formation. This distinct gamma signature is present in all of the logs in Figure 4 and can be used to correlate this stratigraphic unit across the study area. In well GR1541 the Guttenberg lies directly above the Spechts Ferry and it is characterized by generally low gamma values, whereas the Ion submember of the Galena Formation has elevated gamma near the base that decreases as it grades into the overlying Galena members, which have quite low natural gamma signatures.

The lithologic contrast between the shaley Spechts Ferry and the overlying Guttenberg limestone seems to control the location of both tufa-depositing springs as well as the seepage in the valley where the Potosi section was measured. Doherty (2010) notes that the lithology of the backwall at each spring is composed of limestone with brown shale interbeds (Guttenberg) and that at some locations green shale (Spechts Ferry) is visible beneath the limestone. Positions of seepage and vegetation growth in outcrops along Highway 151 and the nearby Church Road quarry coincide with this interval and suggest that there are several additional discrete discontinuities, often developed at zones of contrasting lithology, that may also function as high-permeability features in the subsurface. Specifically, seepage is seen at the contact of the McGregor with the overlying Quimbys Mill, a zone of enhanced vegetation growth was noted in the Church Road quarry at the base of Spechts Ferry, and a large discontinuity with significant seepage was noted at the contact between the Guttenberg and the overlying Ion submember, which lie above the Spechts Ferry.

In the OBI logs collected from both domestic wells near the tufa springs (GR1541 and AD099) we noted that the borehole walls appear wet (dashed line, Figure 4) well above the static water level in the well (solid line, Figure 4). These observations could indicate one of the following hydrogeologic conditions: 1) a strong downward hydraulic gradient where the static water level in the well is not representative of the water table or 2) a perched water table that lies above the regional water table. It is impossible to assess which of these hydrogeologic conditions is present without installing short-interval piezometers at several depths; which was beyond the scope of this project. Logs for both wells are included in Appendix C.



Figure 4. Correlation of natural gamma profiles from outcrop measurements and boreholes logs. The red line indicates the base of the Spechts Ferry Member. For the spring locations, the dashed blue lines indicate spring position whereas the solid blue line indicates the stream level which is assumed to represent the regional water table. For the wells, the solid blue line is the static water level whereas the dashed line indicates the position in the borehole where the walls appeared wet (as seen in the OBI logs).

In order to assess which, if any, of these lithologic contacts functions as a high-permeability flow feature in the subsurface, we also examined existing natural gamma and hydrologic logs from wells where the Decorah Formation was saturated. The WGNHS collected fluid temperature/resistivity data from wells GR-172 (UW-Platteville campus) and LF-465 (UW-Platteville Farm). In addition, an OBI log is available for hole GR-172 and a spinner flowmeter log is available for well LF-465. Sharp changes in a fluid temperature/resistivity profile have been used to identify high-permeability flow features in the subsurface (Muldoon and others, 2001). In GR172, there is a sharp inflection in both fluid temperature and resistivity at 106 ft depth, which lies just above the elevated natural gamma values that characterize the Spechts Ferry. Examination of the OBI log, indicates that this high-permeability feature lies between the Spechts Ferry and the Guttenberg. In LF-465 the fluid temperature and resistivity values showed little variation, however, an inflection in the spinner flow log at about 170 ft depth suggests that a highpermeability feature may be present at the base of the Spechts Ferry in this borehole.

Geochemistry Results

Geochemistry of Spring Waters

Spring monitoring results suggest that physicochemical conditions do not vary widely at the tufadepositing springs. Concentrations of major ions were consistent throughout the sampling period. Between sampling events, the specific conductance of the spring waters decreased after some large or extended precipitation events, but consistently returned to just below 800 μ S/cm within a few days of an event. Fluid temperature was consistent at both springs, with a slight (< 0.3 °C) decrease and increase lagging behind the seasonal transitions to winter and summer, respectively. Furthermore, the water depth in the Potosi spring pool did not vary widely over the monitoring period, averaging 3.7 cm. The water depth in the Platteville spring pool appears to have varied more; however, because these water levels were corrected using atmospheric data recorded at the Potosi mound, some of the variation in the recorded values is clearly due to uncorrected barometric pressure fluctuations. Therefore, it appears as though spring pool water depths do not vary widely at either mound, suggesting that discharge is also fairly consistent at these springs. Records of physicochemical conditions for both springs for the duration of the monitoring period are included in Appendix D.

Throughout the sampling period and at each mound, calcite saturation indices and pH values increased, from spring orifice to dripface whereas the calcium concentration, alkalinity, and partial pressure of CO_2 decreased (Appendix E). These results provide support for CO_2 off-gassing as the driving mechanism for tufa precipitation at the Platteville and Potosi mounds, although mosses that cover the mounds probably enhance precipitation of tufa by providing a substrate that aids calcite nucleation (Andrews, 2006).



Figure 5. Calcite saturation indices at the (a.) Potosi and (b.) Platteville mounds.

Geochemistry of Tufa Deposits

Calcite saturation indices did not vary widely over the sampling period, aside from the January and February results for the Potosi dripface (Figure 5). Challenging winter field conditions at the Potosi dripface and cold air temperatures influenced the reliability of pH measurements for these samples. Water was collected at the dripface and then carried across the Grant River prior to measuring pH. Because it was necessary to traverse the river slowly, the pH meter was exposed to cold temperatures for a longer time period than at other sampling sites. To account for suspect measurements from a malfunctioning pH meter, the average of the pH values for December and March was used to calculate a second calcite saturation index for January and February. These indices are more in line with results for other dates. The overall lack of variation in the level of calcite saturation at each spring orifice and dripface, as well as the lack of variation in monthly differences between orifice and dripface calcite saturation indices, support the consistency of tufa deposition throughout the year. This indicates that geochemical results for the tufa deposits are more likely to represent mean annual conditions than seasonal conditions.

Three of the seven 234 U- 230 Th dates are thought to be reliable on the basis of their lower levels of detrital thorium and/or higher levels of uranium (Appendix F). Subsequent correlation of geochemical results among the three cores and other proxy climate records for the region lends further support for the reliability of these 234 U- 230 Th dates. Figure 6 shows the temporal variation of carbon and oxygen isotopic compositions and elemental ratios in the Platteville (PLC3, PLC4-5) and Potosi (POC8) tufa cores. Oxygen isotopes do not show increasing or decreasing trends throughout the depth of the cores. However, carbon isotopic trends in the two Platteville cores are similar, in that the δ^{13} C in each core decreased by approximately 2 per mil between 2.4 ka and 1.8 ka. The similarity of the δ^{13} C trends for the two Platteville cores suggests that water infiltrating the soil zone had time to reach isotopic equilibrium with soil CO₂ and/or that groundwater reached equilibrium with bedrock carbonate. The carbon isotopic trend in the Potosi core also shows a 2 per mil decrease between 2.4 ka and 1.8 ka. Because this core represents a longer time period, it is clear that the positive δ^{13} C excursion existed prior to 2.4 ka.

If tufa δ^{13} C is influenced by bedrock carbon and groundwater residence time, then trends in molar ratios of Mg to Ca should be similar to carbon isotopic trends. In all three cores, the molar ratios of Mg to Ca mimic the trends in δ^{13} C. Although the δ^{13} C records may also be influenced by regional vegetation changes, changes in contributions to DIC from bedrock carbon due to variations in groundwater residence times likely occurred, suggesting that the records can be used to infer paleo-moisture conditions.

Regional Paleoclimatic Records

The low-resolution age control on the tufa cores does not allow for detailed paleo-climatic reconstruction, but broad patterns that agree with other proxy climate records for the region are evident. The results in Figure 6 suggest that the region experienced conditions that were drier than the present until approximately 1.8 ka. Using alluvial records of rivers in southwestern Wisconsin, Knox (2000) shows an episode of especially small floods from about 5.5 ka to 3.3 ka, which he attributes to warmer and drier conditions. This interval corresponds to the maximum positive $\delta^{13}C$ and Mg/Ca excursions in POC8 (Figure 6). Carbon isotopic trends in POC8 also generally correspond to the $\delta^{13}C$ records for the Coldwater Cave stalagmites from northeastern Iowa (Figure 7) (Denniston et al., 1999). Overall agreement with these well-established records suggests that tufa deposition, and therefore spring flow, has probably been continuous for at least the last 5,000 years, even during warmer and drier periods.



Figure 6. Temporal variation of carbon and oxygen isotopic compositions and elemental ratios in the Platteville (PLC3, PLC4-5) and Potosi (POC8) tufa cores.

CONCLUSIONS AND RECOMMENDATIONS



Figure 7. Temporal variation of carbon isotopic compositions in Coldwater Cave, IA stalagmite 1S (CWC-1S) (Denniston et al., 1999) and the Potosi tufa core (POC8).

Used in association with the hydrogeologic data, the tufa records from the Platteville and Potosi mounds provide new insights into shallow groundwater flow conditions under climate regimes that differ from the present. Perched groundwater in the Driftless Area has recently been shown to be laterally-extensive and broadly associated with an Ordovician carbonate-siliciclastic sequence (Decorah, Platteville, and Glenwood Formations). Groundwater levels are thought to be stable over decadal time scales (Carter et al., 2010). This study provides further evidence of the significance of the sequence to shallow groundwater flow in the region, but we refine the interval to several high-permeability zones that are concentrated near the upper contact of the Spechts Ferry shale or within one unit above (Guttenberg limestone) or below (Ouimbys Mill limestone) the shale. The increasing thickness of the Spechts Ferry shale to the west and southwest in southern Wisconsin (Agnew et al., 1956) may account for its greater relative influence on shallow groundwater flow within the study area. Although both tufa-depositing springs are associated with the high-permeability zone at the top of the Spechts Ferry shale and both discharge well above the level of the receiving streams, without short-interval piezometers, we cannot definitively say that shallow groundwater is perched above the Spechts Ferry shale near the springs. Furthermore, although the static water level lies below this unit in some open boreholes, it lies above this unit in others, so it is unlikely that a laterally-extensive perched system exists. It is more likely that perched systems do exist beneath some of the narrow ridges in the region where wedge-shaped unsaturated zones associated with one or more seepage faces extend to groundwater divides beneath the layered uplands (Rulon et al., 1985), but that fully saturated conditions across the interval have developed in wider ridges. Therefore, the shallow groundwater flow system is best characterized as one that is complex and influenced by the laterally-extensive lithostratigraphy and by the existing topography.

Few domestic wells in the study area are installed at this stratigraphic interval, but the headwaters of streams throughout the Driftless Area are fed by water discharging from the shallow groundwater flow system. Therefore, an understanding of the potential effects of climate change and variability on shallow groundwater levels and flow is important in maintaining aquatic diversity and stream habitat. All three tufa cores show similar isotopic trends and trends in molar ratios of Mg to Ca. Furthermore, the tufa δ^{13} C records are similar to well-established proxy climate records from elsewhere in the Driftless Area, suggesting that tufa deposition, and therefore spring flow, has been mostly continuous for at least the last five thousand years. This implies that the shallow groundwater flow has been stable over time frames of thousands of years, even during warmer and drier periods.

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APPENDIX A: Awards, Publications, Reports, Patents, and Presentations.

- Swanson, S.K., and Muldoon, M.A., March 2012. Evaluating the persistence of perched groundwater using the stratigraphic position and geochemistry of spring tufa deposits in the Driftless Area of Wisconsin, American Water Resources Association – Wisconsin Section Annual Meeting, Wisconsin Dells, Wisconsin.
- Swanson, S.K., and Muldoon, M.A., October 2011. Hydrostratigraphic and climate controls on spring flow and perched groundwater in the Driftless Area of Wisconsin, Geological Society of America Annual Meeting, Minneapolis, Minnesota.

APPENDIX B. Detailed stratigraphic section near the Potosi spring.



APPENDIX C. Geophysical logs for GR1541 and AD099



GR1541





APPENDIX D. Records of physicochemical conditions at the tufa-depositing springs.



Water levels and barometric pressure records for the Platteville spring.



Precipitation, temperature, and conductivity records for the Platteville spring.



		Potosi orifice	Potosi dripface	Platteville orifice	Platteville dripface
Calcium	Mean	88.1	75.4	89.1	73.1
(mg/L)	Std. Dev.	3.1	5.9	5.3	14.9
Magnesium	Mean	45.9	45.4	48.3	48.1
(mg/L)	Std. Dev.	1.2	1.2	2.1	1.9
Potassium	Mean	1.1	1.1	0.5	0.6
(mg/L)	Std. Dev.	0.1	0.4	0.2	0.1
Sodium	Mean	5.7	5.5	7.8	7.5
(mg/L)	Std. Dev.	0.4	0.4	0.6	0.7
Chloride	Mean	7.9	7.9	16.3	16.3
(mg/L)	Std. Dev.	0.3	0.3	1.2	1.3
Nitrate	Mean	3.7	3.7	1.1	1.1
(mg/L)	Std. Dev.	0.1	0.3	0.1	0.1
Sulfate	Mean	18.5	18.3	23.6	23.7
(mg/L)	Std. Dev.	0.7	0.5	1.6	1.4
Alkalinity	Mean	386	348	393	349
(mg/L CaCO ₃)	Std. Dev.	7	9	19	38
	Mean	7.05	7.98	7.10	8.09
рп	Std. Dev.	0.36	0.66	0.41	0.42
Conductivity	Mean	755	707	795	718
$(\mu S/cm, 25^{\circ}C)$	Std. Dev.	12	14	44	63
Temperature	Mean	9.8	10.9	9.2	10.2
(°C)	Std. Dev.	0.1	3.4	0.9	4.3
SI _{calcite}	Mean	0.12	0.94	0.17	1.02
	Std. Dev.	0.36	0.59	0.39	0.32
DCO	Mean	5.0E-02	7.0E-03	4.6E-02	3.9E-03
PCO_2	Std. Dev.	6.5E-02	7.1E-03	4.9E-02	3.5E-03

APPENDIX E. Summary of spring water geochemistry results.

Sample	²³⁸ U (ppb)	²³² Th (ppt)	²³⁰ Th/ ²³² Th activity	²³⁰ Th/ ²³⁸ U activity	Measured δ ²³⁸ U	Initial δ ²³⁴ U	Uncorrected age	Corrected age
			ratio	ratio	(‰)	(‰)	(yr B.P.)	(yr B.P.)
PLC3- 308A	137.3±0.1	1126±29	15.994±0.468	0.0429±0.0006	719±2	725±2	2755±37	2617±78
PLC3- 389A	119.1±0.1	1549±40	11.288±0.371	0.0480±0.0010	719±2	655±2	3222±67	2993±132
POC8- 368A	141.5±0.1	8800±38	4.443±0.044	0.0904±0.0008	791±2	801±2	5637±52	4629±506
PLC5- 101	79.0±2.4	102,413±419	1.384±0.099	0.5875±0.0453	1632±67	1689±78	26873±2442	12053±7495
PLC4- 220A	80.3±0.1	1964±23	11.311±0.214	0.0905±0.0013	763±2	775±2	5735±87	5334±219
PLC4- 220	79.4±0.1	6907±22	2.337±0.028	0.0665±0.0008	599±2	606±2	4629±55	3838±399
PLC4- 347	117.8±0.1	12,397±15	1.971±0.012	0.0679±0.0004	1452±2	1459±4	3058±19	1807±624

Notes:

Corrected ages use a calculated initial 230 Th/ 232 Th atomic ratio 4.4 ppm ±50%.

Years before present = yr B.P., where present is AD 2011.

All errors are absolute 2σ .

Subsample sizes range from 50 to 250 mg.

Bold = samples that were more carefully selected to insure visually clean, nonporous carbonate.