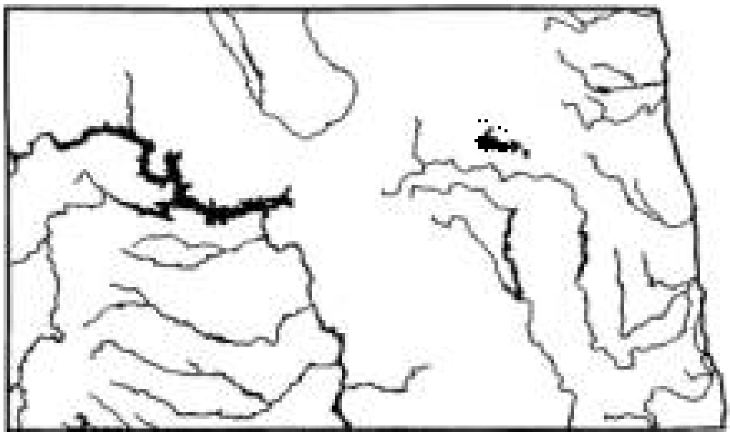


Technical Report No: ND07 - 01

Effect of Land Cover and Pattern on the Quality of Groundwater Discharged from Springs and Seeps at Pigeon Point, Southeastern North Dakota

Philip J. Gerla
Associate Professor
Department of Geology and Geological Engineering
University of North Dakota
Conservation Hydrologist, The Nature Conservancy
Minnesota-Dakotas Chapter

and

William Lenarz
Graduate Student, University of North Dakota
Department of Geology and Geological Engineering
University of North Dakota

June 2007

North Dakota Water Resources Research Institute
North Dakota State University, Fargo, North Dakota

Technical Report No: ND07-1

EFFECT OF LAND COVER AND PATTERN ON THE QUALITY OF GROUNDWATER DISCHARGED FROM SPRINGS AND SEEPS AT PIGEON POINT, SOUTHEASTERN NORTH DAKOTA

by

Philip J. Gerla[1]
William Lenarz[2]
Associate Professor[1] **and WRRI Graduate Research Fellow** [2]
Department of Geology and Geological Engineering
University of North Dakota
Grand Forks, ND 58202-8358

June 2007

The work upon which this report is based was supported in part by federal funds provided by the United States of Department of Interior in the form of ND WRRI Graduate Research Fellowship for the graduate student through the North Dakota Water Resources Research Institute.

Project Period: March 1, 2005 – February 28, 2007
Project Number: 2006ND125B

North Dakota Water Resources Research Institute
Director: G. Padmanabhan
North Dakota State University
Fargo, North Dakota 58105

Effect of Land Cover and Pattern on the Quality of Groundwater Discharged from Springs and Seeps at Pigeon Point, Southeastern North Dakota

Table of Contents

List of Figures

Appendix

Effect of Land Cover and Pattern on the Quality of Groundwater Discharged from Springs and Seeps at Pigeon Point, Southeastern North Dakota

Abstract

Pigeon Point hosts a large group of springs and seeps along Sheyenne River, where the river cuts deeply though underflow sediments deposited in glacial Lake Agassiz. The north-facing slope and abundant cold, mineralized groundwater discharging at the face creates a wetland that hosts unusual boreal species. The pattern of water quality in the springs appears reversed from that expected: discharge at the lowest elevation, indicating longest and deepest flow path, has the least mineralized water, while springs discharging at higher elevation reveal increasing mineralization and reducing conditions. We suggest that differences in land cover and infiltration processes across the groundwater capture zone lead to this apparent reversal. To test this hypothesis, we installed drive-point piezometers and soil-water samplers up-gradient from the springs within dunes, wet meadow, and pasture. Water samples from these instruments and the springs were collected seasonally and analyzed for major cations, anions, and dissolved carbon content.

Our observations indicate a trend of increasingly reducing conditions from southeast to northwest towards the springs, with perhaps the most reduced environment closest to the springs. Oxidation-reduction conditions control the variability in groundwater composition. The upper parts of the seepage face show discharge of groundwater with abundant iron and dissolved carbon, indicating reducing conditions. Slightly lower pH may explain greater mineralization. Flow path analysis suggests that recharge of these waters takes place within nearby wetlands and soils characterized by a well developed, organic-rich A-horizon. The lower springs, which are more oxidizing, receive water from the distant dunes, where there is rapid recharge and little interaction with soil organic matter. The results support the hypothesis that the water discharging from the higher elevation springs infiltrates and recharges groundwater in a more reduced environment, while recharge for the more oxidized lower springs occurs by rapid infiltration in the dunes. These results suggest that vadose and shallow phreatic conditions near Pigeon Point impart the composition of waters observed at the springs, in contrast with the more generally accepted view that prolonged time and deep flow processes control groundwater quality.

Acknowledgments

Funding for this project was generously provided by the Cox Family Fund for Science and Research, North Dakota Water Resources Research Institute, and the University of North Dakota. We thank the U.S. Forest Service, Sheyenne National Grassland for permission to access field sites and allow for the installation of monitoring equipment.

Introduction

This report focuses on the relationship between land use, infiltration processes, and the quality of water discharged along the expansive seepage face at Pigeon Point, an area of springs and fens in the Sheyenne delta aquifer in southeastern North Dakota. Interestingly, the lowest seeps, suggesting longest flow paths, have the least mineralized water (350 uS/cm) while springs and seeps at higher elevation reveal increasing mineralization (500 uS/cm) (Askin and Gerla, 2005) (Figure 1), which is reversed from what might be typically expected. Results of the work address the following questions:

- The Sheyenne delta aquifer constitutes an important source of high quality groundwater in southeast North Dakota and indirectly contributes water for Fargo and downstream communities by discharge into the Sheyenne River. To what extent does geomorphology and land cover influence infiltration, recharge, and groundwater quality in the Sheyenne delta aquifer?
- What are the vadose and phreatic processes that result in changes to hydrogeochemistry of water along a flow path?
- Why do shorter groundwater flow paths that discharge at the Pigeon Point seepage face produce more mineralized water? How is the greater mineralization reflected in relative concentrations of cations, anions, and saturation index of calcite?
- How might future land use changes influence the quality of groundwater discharged in the Pigeon Point nature preserve? How can other parts of the Sheyenne delta aquifer be managed to best protect groundwater quality?

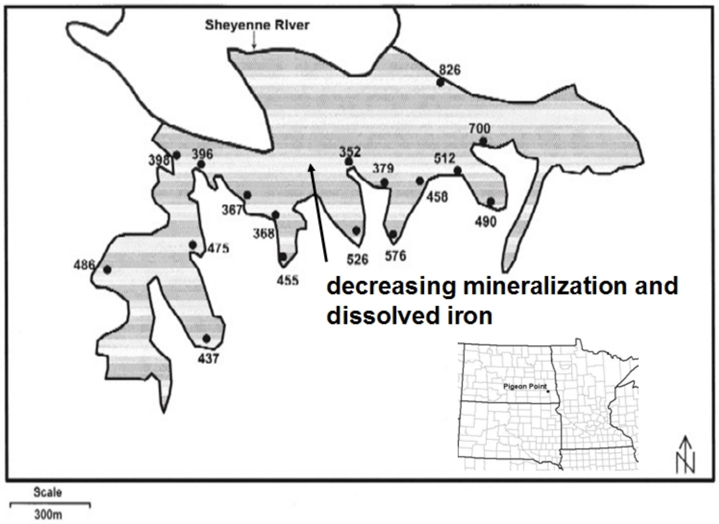


Figure 1. Map of the seepage face at Pigeon Point showing the electrical conductivity of spring and seep samples collected in August, 2004. The insert in the lower right corner shows the location of Pigeon Point in southeastern North Dakota.

Oxidation-reduction conditions likely exert significant control on the variability in groundwater composition. The upper parts of the seepage face shows discharge of groundwater with elevated Fe concentration, suggesting reducing conditions. Flow path analysis (Askin, 2004) strongly suggests that recharge of these waters takes place within nearby wetlands and soils with a well-developed, organic-rich A-horizon. Lower springs, which may be more oxidizing, receive water from dunes (Figure 2).

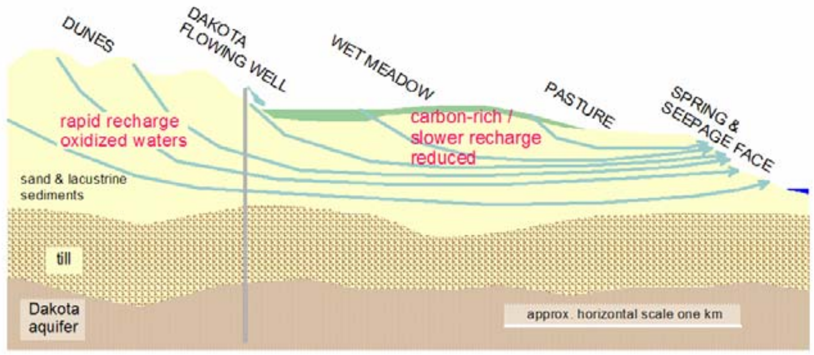


Figure 2. Conceptual model of the geochemical processes along a groundwater flow path at Pigeon Point.

Therefore, we suggest that land cover in the recharge capture zone of the springs and seeps (Figure 3), the latter of which was delineated by Askin (2004), affects the quality of groundwater discharged. Water infiltrated in areas of low carbon content, large permeability, and a deep water table will likely have significantly different oxidation-reduction characteristics and reactivity than waters recharged in organic-rich meadows. If this relationship is observed, then protection of the ecological resources at Pigeon Point will depend not only on sustaining the water budget, but may also require that land cover types and distribution not be altered.

Research Objectives

The goal of this research project is to determine changes in groundwater quality along aquifer flow paths that discharge at the seepage face. The objectives are: (1) characterize the infiltration characteristics of soils in the recharge/capture zone, (2) document the changes in the composition of infiltrating water as a function of depth, soil type/geomorphology, and land cover, and (3) explain the reason for spatial variability of hydrogeochemistry across the site.

The study area covers about six square kilometers within the recharge/capture zone of Pigeon Point, which lies along the south side of the Sheyenne River where it transects the

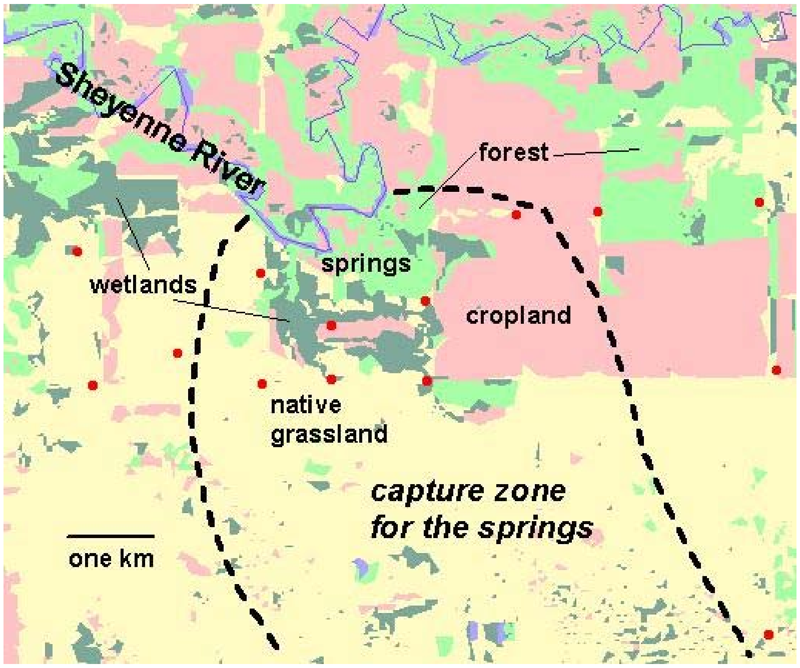


Figure 3. Land cover map of the Pigeon Point area, interpreted from satellite imagery. The map also shows the approximate eastern and west edge of the recharge capture zone for the seepage face. Red dots indicate the locations of monitoring wells used to delineate the recharge capture zone (Askin, 2004).

Sheyenne delta aquifer (Figure 3). The landscape and surficial geology of this area was developed by glacial deposition during the Wisconsinan glacial period, especially due to the formation, deposition, and eventual draining of glacial Lake Agassiz. During the period of time that glacial Lake Agassiz was at the Herman and Campbell levels, approximately 11,000 to 13,000 years ago, the Sheyenne Delta formed in eastern Ransom County. The delta likely resulted from large load deposition as the Sheyenne River emptied into glacial Lake Agassiz. Well-sorted sand dunes comprise the southern portion of the Pigeon Point site, with fluvial-lacustrine fine sands lying northward, which are eroded and exposed along the Sheyenne River. Till underlies most of the site at a depth ranging from 20 to 30 meters (Baker, 1967; Bluemle, 1979).

Eight major springs along the extensive seepage face coalesce to form four small, perennial streams that flow into the Sheyenne River. Fens, or groundwater-fed wetlands, occur along nearly the entire seepage zone (Askin 2004). These wetlands slope northward and host several rare and unusual boreal plant species, which do not occur elsewhere in North Dakota or at any locations farther south than Pigeon Point (J. Challey, personal communication, 2004). Fens in the Midwestern U.S. have been recognized as unusual and an important host for botanical diversity (Amon and others, 2001)

Methods and Analysis

Six shallow wells and eleven soil-water samplers in three nests across the study area have been installed along a single selected flow path (Figure 4). Two additional wells were installed at an earlier date. One of the nests was placed in the dunes toward the southern border of the study area, while the other two nests were placed in the pasture and restored prairie down-gradient near the seepage face and the Sheyenne River. The placement of the three nests allows for synoptic collection of the soil water and groundwater within spring and seep capture zone. The study site lies within land owned by The Nature Conservancy and the U.S. Forest Service. There is privately owned land to the west and east, but this study was conducted without accessing these areas.

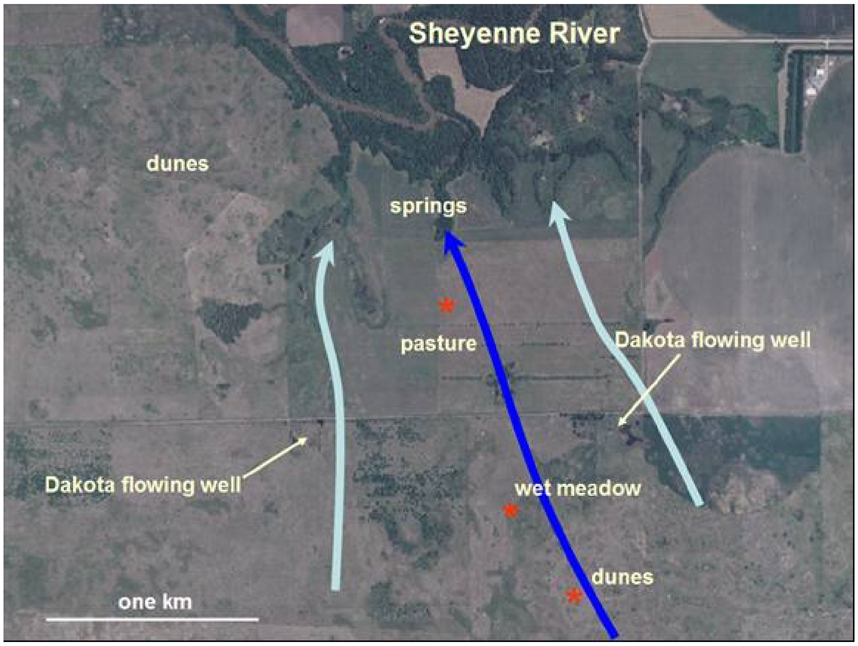


Figure 4. Air photograph of the Pigeon Point area showing predicted flow paths (blue) (Askin, 2004) and infiltration monitoring sites (red).

Within each of the three nests, soil-water samplers were installed at different depths depending on the water table depth and the thickness of the root zone (Figure 5). Because of large infiltration and recharge rates in the dunes, the water table tends to be very shallow (< 1.5 m) in intra-dune basins. Samplers were placed at depths of 0.7, 1.0, and 1.5 m. In all cases, samplers were placed beneath the densest root zone to help assure collection of deeply infiltrating water. The ceramic cup of the samplers was packed with 200-mesh silica flour and when water samples were collected, the sampler was pumped to a suction of approximately -0.4 MPa (-60 psi) and sampled 6 to 12 hours later.

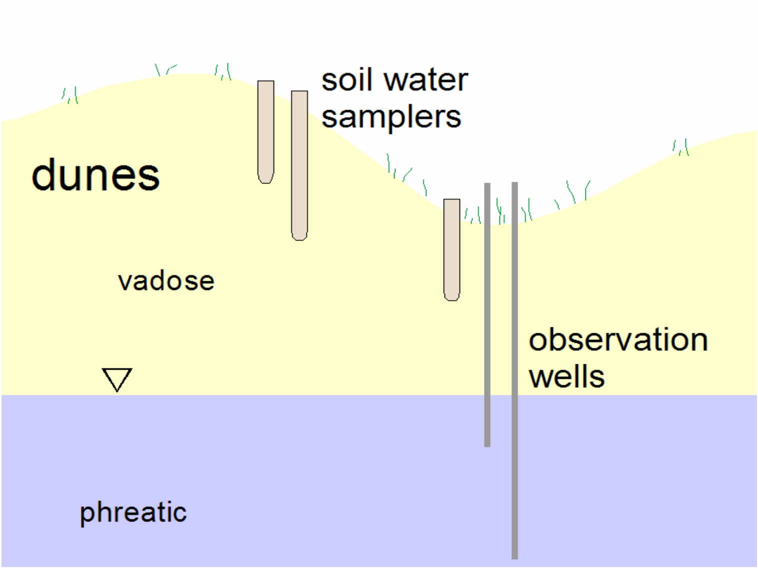


Figure 5. Schematic diagram showing the arrangement of instruments at the dunes soil infiltration monitoring site.

One-inch diameter stainless steel well points connected to galvanized steel casing were driven approximately one to two meters below the water table for sampling groundwater. In addition to the samples that are collected from the three nests, each of the two wells already in place supplemented the samples collected from each nest. To complete the water sample collection, samples from each of the six largest springs along the seepage face and directly down-gradient from the nests were also collected for analysis.

During the course of the research project, there were three sampling periods. Each of these sampling periods took place during a different season to determine if groundwater quality and chemical transport vary temporally within the study area. The first sampling round took place in October 2005. The second round of sampling followed in May 2006 to sample water influenced by the spring thaw and winter run-off. The final sampling was carried out in July 2006, following relatively dry antecedent conditions.

During each sampling period, standard operating procedures for the collection and preservation of groundwater samples for chemical analysis were followed, as set forth by the North Dakota State Department of Health (field sampling protocol report published in 1995). These methods were supplemented with the following ASTM standard guides:

D4696-92(2000) Pore-Liquid Sampling from the Vadose Zone
D5903-96(2001) Planning and Preparing for a Groundwater Sampling Event
D6517-00 Field Preservation of Ground-Water Samples
D6564-00 Field Filtration of Ground-Water Samples
D6634-01 Purging and Sampling Devices for Ground-Water Monitoring Wells

While in the field, samples were measured for temperature, pH, conductivity, and dissolved oxygen. After collection, the samples were transported to and analyzed at the Environmental Analytical Research Laboratory (EARL) at the University of North Dakota campus in Grand Forks.

The analytical work done in the EARL laboratory comprised a large portion of the project time and expense. The three main analytical methods used were flame atomic absorption spectrometry (FAAS), total organic carbon (TOC) analysis, and ion chromatography (IC). The flame atomic absorption spectrometer was used to analyze samples for major cations, including calcium, magnesium, and sodium. The ion chromatograph was used to analyze chloride, sulfate, and nitrate, while the TOC carbon analyzer provided concentrations of both total organic carbon and inorganic carbon, which enabled us to determine the concentration of bicarbonate.

Because of disequilibrium and multiple redox couples, redox probes were unlikely to have little value (e.g. Lindberg and Runnells, 1984). Instead, we tracked oxidation-reduction conditions qualitatively at the sample site by analyzing directly pumped and filtered groundwater for DO, nitrate, iron, and manganese using a portable spectrophotometer. Results provided sufficient data to interpret the spatial variability of oxidation-reduction conditions using pE-pH diagrams.

Finally, in conjunction with soil water and groundwater sampling and analysis, work to better understand the physical conditions of infiltration and recharge were completed during the project. Soil permeability was estimated using a disk infiltrometer near the recharge monitoring sites. This instrument provides an estimate of variably saturated hydraulic conductivity, the results of which were used to predict differences in recharge rates.

Results and Discussion

Soil Permeability

Results from the infiltrometer tests reveal that most of the sites have similar hydraulic characteristics (Figure 6) with saturated hydraulic conductivity ranging from about 12 cm/hr in the wet meadow to about 55 cm/hr in the dunes. Although not measured, the pasture site is underlain by slightly coarser soils and sediments, so is likely to have a larger hydraulic conductivity. The dune top and blow out show a steeper curve, indicating that hydraulic conductivity decreases rapidly under drier conditions. Bluestem sod areas in the meadow show larger hydraulic conductivity at greater soil tensions, suggesting more heterogeneous soil structure than other soils and a greater capacity to moderate soil moisture conditions under both dry and wet conditions.

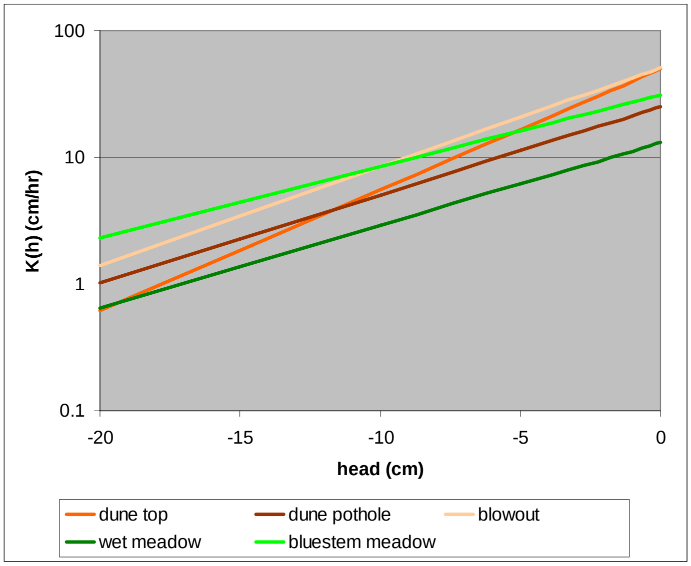


Figure 6. Graph of soil hydraulic conductivity (cm/hr) as a function of tension head (cm) for soils in the Pigeon Point recharge capture zone, based on disk infiltrometer measurements.

Groundwater Composition

Groundwater discharged from the springs and seeps at Pigeon Point and the recharge capture zone are Ca-Mg and HCO_3- type of a homogeneous composition (Appendix and Figure 7); little variation in major ions exists for any of the sample sites. The major ion composition of the Dakota flowing well southeast of Pigeon Point is also shown (Figure 7). There is no apparent trend connecting the position of the waters on the trilinear diagram, suggesting that none of the shallow wells or springs along the flow path have mixed to any extent with the deeper bedrock water.

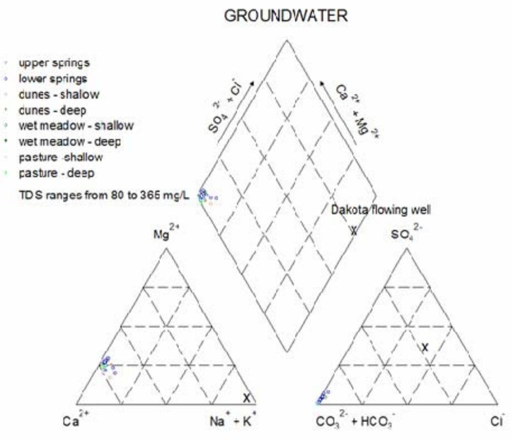


Figure 7. Trilinear diagram showing the composition of groundwater sampled at the Pigeon Point seepage face and within the recharge capture zone.

Geochemistry of Infiltrating Precipitation

Unfortunately, the coarseness of the sediment and soils at the pasture site precluded our ability to extract soil water at this site. Notwithstanding, pore water extracted from soils at the other infiltration monitoring sites shows more compositional variability than groundwater (Figure 8), as might be expected. The dune waters show a trend from initial infiltration being very dilute waters with a relatively greater concentration of alkalis (Na and K) and chloride (Cl) in comparison to the wet meadow where the waters evolve from dilute water characterized by greater proportions of magnesium (Mg) and sulfate (SO_4).

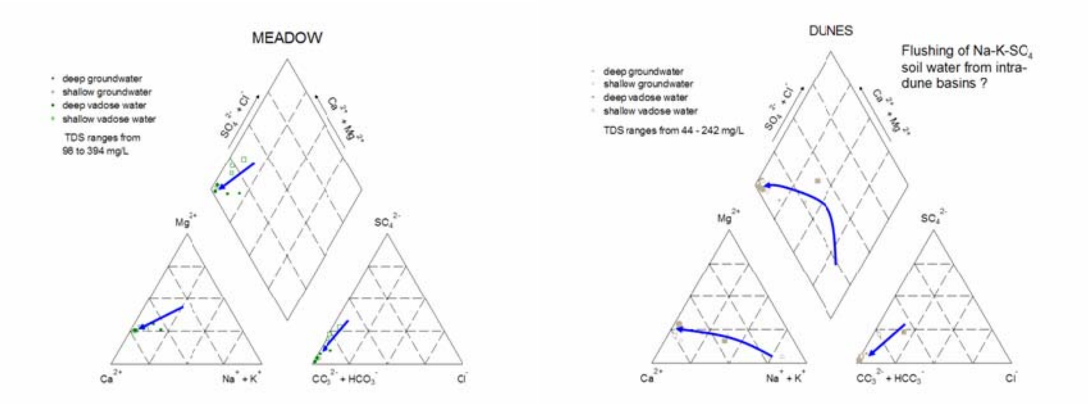


Figure 8. Trilinear diagram showing the composition of groundwater and soil water at the meadow and dunes monitoring sites. Blue arrows show the trajectory of soil water composition during infiltration.

The trend for the wet meadow waters was modeled using the USGS hydrogeochemical code PHREEQC (Parkhurst and Appelo, 1999; Appelo and Postma, 2005). In the model, one kilogram rain water with a typical Midwest US composition (Nilles and Conley, 2001) is reacted with 0.001 g (10^{-5} moles) of calcite ($CaCO_3$) in each of five steps. Figure 9 shows that the pattern is very similar to the compositional trend of natural water as it percolates through the sediments at the wet meadow (Figure 8), suggesting that the somewhat acidic precipitation reacts quickly with solid carbonate rock fragments in the meadow soils and sediments.

Although this process probably occurs in the dunes too, the contrasting pattern on the trilinear diagram suggests an additional, different process. Although not monitored, small intra-dune basins are likely to be hydrodynamic. Under long-term dry weather conditions, these basins can create small zones where groundwater is rapidly lost to evapotranspiration, thereby increasing the concentration of dissolved minerals that originally occurred in precipitation and shallow groundwater. During wet periods, perhaps on an annual basis, recharge flushes salts into the groundwater system that has built up in the shallow soil during dry periods. Depression-focused recharge was recognized as an important process in mid-continent, semi-arid wetland potholes (e.g.

Lissey, 1971; Derby and Knighton, 2001). As will be shown later, the vertical variation of composition in the seepage face corroborates with this process.

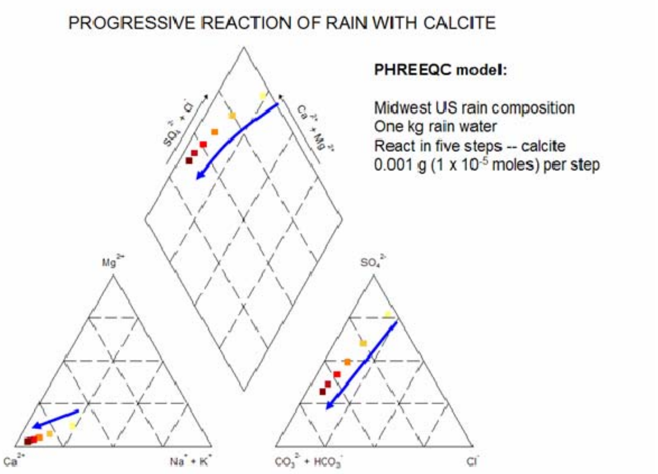


Figure 9. Results from the PHREEQC geochemical model applied to infiltrating water at the meadow monitoring site (plotted on a trilinear diagram).

Calcite Saturation and Precipitation

PREEQC (Parkhurst and Appelo, 1999) was also used to estimate the saturation index or log (IAP/ Keq) for calcite (Figure 10), where IAP is the ion activity product and Keq the equilibrium constant for the following reaction:

$Ca^{2+} + 2HCO_3^- = CaCO_3 \text{ (calcite)} + H_2O + CO_2$

Results show that nearly all the groundwater samples analyzed are saturated or slightly supersaturated, which is corroborated by abundant calcite cement on the well screens (Figure 11). In contrast, vadose pore waters are unsaturated (Figure 8), but results show that deeper pore water and pore water from the wet meadow approach saturation, as would be expected from reaction of infiltrating water with carbonate rock fragments. In the wet meadow, reaction of infiltrating water with organic matter likely leads to increased dissolved carbonate (and hence an approach to calcite saturation) through the reaction given above.

Significantly, the composition of water analyzed from the seepage face shows a decrease in saturation downward along the seepage face, suggesting three possible reasons:

1. *Enhanced dissolution of $CaCO_3$ occurs in nearby carbon-rich recharge areas, thereby leading to waters that are saturated and supersaturated in calcite in the upper part of the seepage face*. In contrast, the more rapid infiltration of recharge and lower soil CO_2 in the dunes leads to deeper groundwater with unsaturated conditions. Lower CO_2 may result from less organic matter and aerobic decomposition in the dunes.

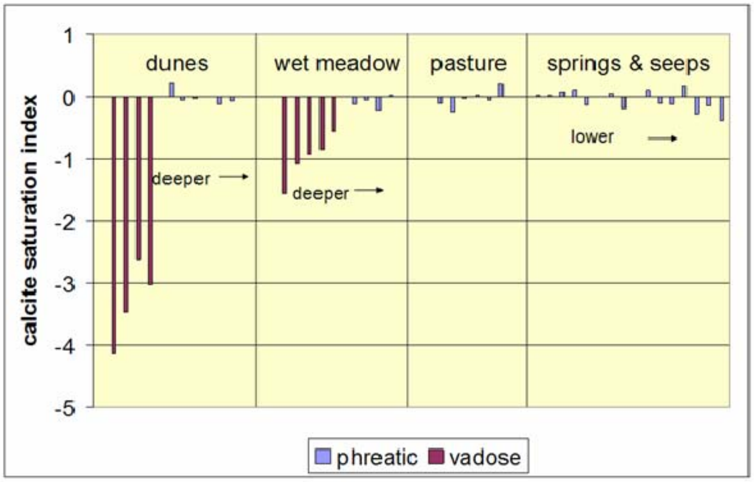


Figure 10. Distribution of calcite saturation index along the monitored Pigeon Point flow path.

Figure 11. Photograph of one-foot stainless steel well screens pulled from the meadow (upper two screens) and dune (lower screen) monitoring site. Note the strong precipitation of calcite cement on the meadow points; points were in place for about 18 months.

2. *Dissolution and precipitation of $CaCO_3$ along the groundwater flow path might result from differences in recharge timing*. As with many carbonates, calcite exhibits retrograde solubility and is therefore more soluble at cooler temperatures. The dunes likely experience more summer recharge, thereby introducing warmer water with less calcite solubility.

3. *Loss of CO_2 gas preferentially occurs along the lower part of the seepage face, resulting in calcite precipitation.* Greater loss of CO_2 gas farther down the seepage face through the reaction

$$HCO_3^- = CO_2 \text{ (gas)} + H_2O$$

would decrease HCO_3^-, drive the previous reaction to the right, and cause calcite precipitation. But the lack of tufa or marl deposits suggests that this hypothesis is unlikely.

Regardless of the process, discharge that occurs at lower elevations along the seepage face results from water that was either very rapidly recharged and not brought into equilibrium with calcite, or the product of some geochemical process along the groundwater flow path that leads to decreasing concentrations of HCO_3^-, Ca, or both.

Dissolved Iron

Concentration of dissolved iron provides information on the oxidation-reduction of groundwater and soil pore water. Figure 12 and the appendix shows that total dissolved Fe concentrations are at or below the analytical detection limit of 0.05 mg/L in nearly all of the soil water samples, suggesting a pE of at least zero in most recharge zone soils, including those in the wet meadow. More reducing conditions, however, are found in the phreatic zone and increasing concentrations of dissolved iron (Fe^{2+}) occur in deeper groundwater at the meadow and pasture sites.

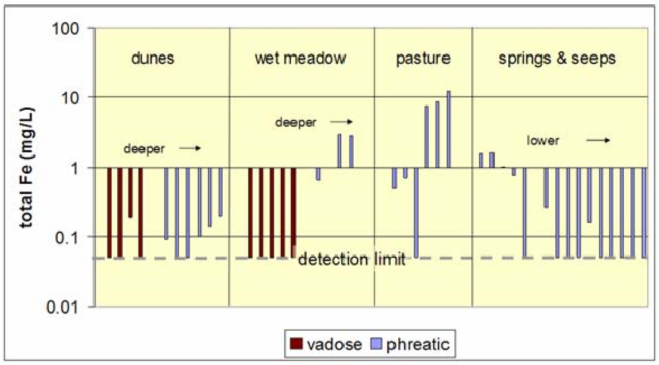


Figure 12. Distribution of total dissolved iron concentration along the monitored flow path.

Geochemical Trends at the Seepage Face

The variation of dissolved iron across the seepage is striking; only springs in the upper part of the face have detectable dissolved iron (Figure 12). On contact with the atmosphere, this dissolved iron quickly precipitates as iron hydroxide, likely mediated by iron oxidizing bacteria. When circumneutral-pH, anoxic water with a large concentration of ferrous iron flows into an oxic zone, a community of "iron bacteria" commonly develops at the oxic-anoxic interface and an ochreous mass of amorphous FeOOH precipitates (Figure 13). Although the bacterial species are difficult to identify, neutrophilic bacteria such as *Gallionella* spp., *Leptothrix ochracea*, and species in the family *Siderocapsaceae* commonly occur (Emerson and Revsbech, 1994).

Figure 13. Ferric hydroxide precipitation in the upper springs at the discharge end of the groundwater flow path.

The concentration of dissolved calcium has an inverse relationship to sulfate concentration --- both temporally and spatially --- at the seepage face (Figure 14). Dissolved calcium and bicarbonate both generally decrease from top to bottom across the seepage face, which also establishes the decreasing calcite saturation index. Although this may also partly explain the similar decrease in total dissolved solids, sulfate increases downward across the face. Based on the results from the three samplings, sulfate and calcium show an inverse temporal relationship.

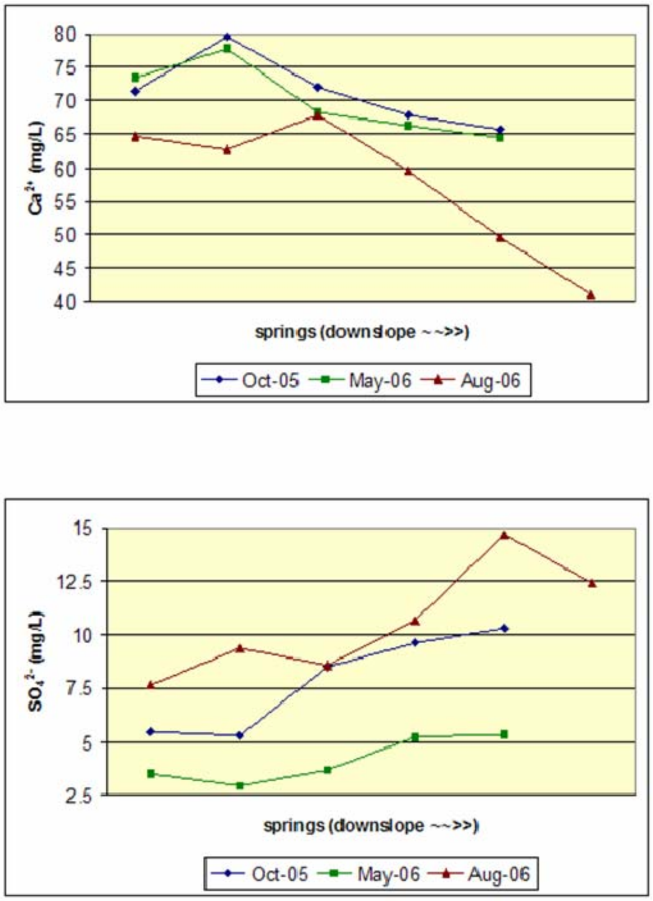


Figure 14. Trends of dissolved sulfate and calcium concentration from the top (left) to the bottom (right) of the spring / seepage face.

This may result from recharge dynamics. During extended periods of wet weather, and perhaps during spring recharge, salts built up because of evapotranspiration in the intra-dune basins are flushed into the groundwater system. During these periods of wet weather, recharge through the wet meadow and pasture sediments is enhanced and a pulse of water that is not calcite saturated enters the groundwater system. Although there is a time lag of an unknown length, after a wet period, dissolved sulfate concentrations rise and calcium diminishes across the face. The reverse will occur following a dry period.

It would take considerably longer and more detailed monitoring to show this conclusively, but the water levels observed in nearby wells corroborate this explanation. Figure 15 shows that the October 2005 and August 2006 samplings followed a relative dry period, as indicated by a declining water table in the aquifer. May 2006 followed a period in which the water table rose steadily for a period of about six months. Note that the May 2006 sampling and analysis show the greatest concentration of sulfate for the three samplings (Figure 14), perhaps reflecting a flushing and surge of salts from the intra-dune basins. Similarly, calcium shows the lowest concentrations (Figure 14), which may indicate a relatively more rapid infiltration of precipitation in the wet meadow and pasture. Longer monitoring and more sampling would need to be carried out to confirm this possibility.

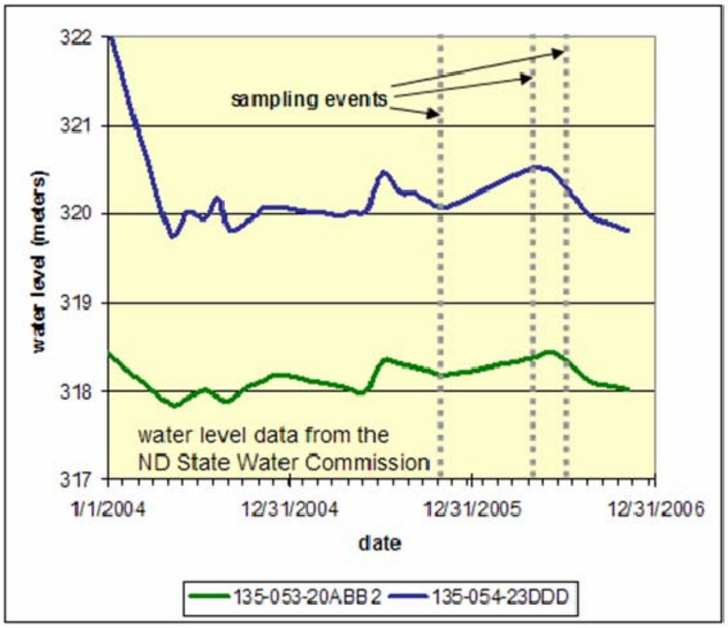


Figure 15. Water table hydrographs from the vicinity of Pigeon Point. Well 135-053-20ABB2 and 135-054-23DDD lie approximately five km (two miles) east-northeast and west of Pigeon Point, respectively.

Conclusions

These results strongly support the hypothesis that groundwater discharged within the upper part of the seepage face is more reduced and that infiltration and recharge of these waters occurs within an environment that leads to greater reduction. The recharge zone for groundwater discharged from the lower springs is likely derived from a more distal source in the dunes, where conditions are more oxidizing. Other conclusions include the following:

* Subtle but persistent geochemical trends occur across the seepage face, with striking visual difference evident in the transport and deposition of dissolved iron.

* Similarity of groundwater composition at all sample points suggests no interaction or mixing with Dakota water, although monitoring and sampling points were specifically chosen along a groundwater flow line that would not be affected by the unregulated flowing wells. In other parts of the seepage face, shallow groundwater is likely to be

influenced by elevated concentrations of dissolved minerals in water from the Dakota aquifer.

* The upper springs, derived from longer flow paths, discharge groundwater with relative greater dissolved solids, ferrous iron, calcium, and bicarbonate, whereas sodium, potassium, and sulfate increase downward. This contrasts with the more generally accepted view that prolonged time and deep flow processes control regional groundwater quality (e.g., Gerla, 1992).

* Although the springs and seeps reveal an “integrating” effect on water quality, seasonal and long-term changes occur, suggesting that the residence time of groundwater in the system is short, up to a few years. Isotope and other tracer work would likely confirm this conclusion.

* Infiltrating precipitation quickly reaches equilibrium with calcite at the dune and wet meadow monitoring sites, but most rapidly at the wet meadow site where there is apparently greater oxidation of labile organic carbon. This oxidation of soil organic carbon also leads to recharge of more reduced water at the wet meadow site, which is reflected in the occurrence of the most reduced groundwater discharged at the seepage face.

Implications for Conservation

* Land cover controls the geochemical pattern observed along the seepage face and may have implications for subtle ecological differences within the wetlands at Pigeon Point.

* Changes in land cover are likely to affect not only water quantity (Askin, 2004), but water quality. For example, conversion of pasture and meadow to irrigated crops may increase recharge and oxidizing conditions, or otherwise disrupt the natural geochemical processes that control the composition of groundwater discharged along the seepage face.

* Swales in the dunes may be “point sources” of sodium and sulfate, flushing and dilution are likely to occur during climate variability. Although the small fluctuation that was observed in the study would have little effect on ecology, long periods of drought or deluge may change the pattern and ecological conditions along the seepage face. Furthermore, future climate change will likely change both the quality and quantity of water discharged at Pigeon Point

Finally, the springs at Pigeon Point and similar groundwater discharge zones along the Sheyenne River contribute a significant volume of flow to the river; many communities downstream in the Red River basin depend on surface water from sources such as this for their municipal supply. Should the need for groundwater diversion in the Sheyenne delta aquifer arise, it would be important to recognize that groundwater discharge by wells up-gradient would decrease water discharged to the river, thus altering the natural wetland function and resource at Pigeon Point and decreasing the volume of water conveyed by the river to downstream points.

Recommendations for Further Investigation

Further monitoring and analytical work at Pigeon Point can lead to a better understanding of the hydrogeochemical system. Additional questions that can be asked and investigated include:

* Advection likely transports mineral and boron-rich Dakota waters, with little dispersion. Are the narrow points of discharge discernable and do they affect ecology?

* Can nitrogen isotopes be used to distinguish sources of nitrate and serve as a strong indicator of land cover in different parts of the recharge capture zone?

* Records of oxygen and hydrogen isotopes may reveal contrasting times and locations of recharge in the capture zone. These data would be very important in predicting how climate change will alter both the water quality and overall water budget.

References

Amon, J. P., C. A. Thompson, Q. J. Carpenter, and J. Miner. 2002. Temperate zone fens of the glaciated Midwestern USA: Wetlands 22:301-317.

Appelo, C.A.J. and D. Postma (2005) Geochemistry, Groundwater and Pollution, Second Edition. Francis and Taylor, 649 p.

Askin, C.W. 2004. Determination of the Relationship Between The Hydrology of the Sheyenne Delta Aquifer and Ground Water Discharge from Fens at Pigeon Point, Ransom County, North Dakota: University of North Dakota, Grand Forks, North Dakota Masters Thesis, 79 p.

Askin, C.W. and P.J. Gerla. 2005. Hydrology of the Springs, Seeps, and Fens at The Nature Conservancy's Pigeon Point Preserve, Ransom County, North Dakota. 2nd International Water Conference, Red River Water Institute, Winnipeg, Manitoba.

Baker, C.H., Jr. 1967. Geology and Ground Water Resources of Richland County: North Dakota Geological Survey Bulletin 46 and North Dakota State Water Commission County Ground Water Studies 7, 45 p.

Bluemle, J. P. 1979. Geology of Ransom and Sargent Counties, North Dakota: North Dakota Geological Survey Bulletin 69 and North Dakota State Water Commission County Ground Water Studies 31, 79 p.

Derby, N. E. and R. E. Knighton. 2001. Field-Scale Preferential Transport of Water and Chloride Tracer by Depression-Focused Recharge. Journal of Environmental Quality 30:194-199.

Emerson, D. and N. P. Revsbech. 1994. Investigation of an Iron-Oxidizing Microbial Mat Community Located near Aarhus, Denmark: Field Studies. Applied and Environmental Microbiology 60:4022-4031.

Gerla, P. 1992. Pathline and geochemical evolution of groundwater in the Red River Valley, North Dakota: Ground Water 30:743-754.

Lindberg R.D. and D.D. Runnells. 1984. Ground-water redox reactions: an analysis of equilibrium state applied to Eh measurements in geochemical modeling: Science 255:925-927.

Lissey, A. 1971. Depression-focused transient ground water flow patterns in Manitoba. Geological Association of Canada Special Paper 9:333–341.

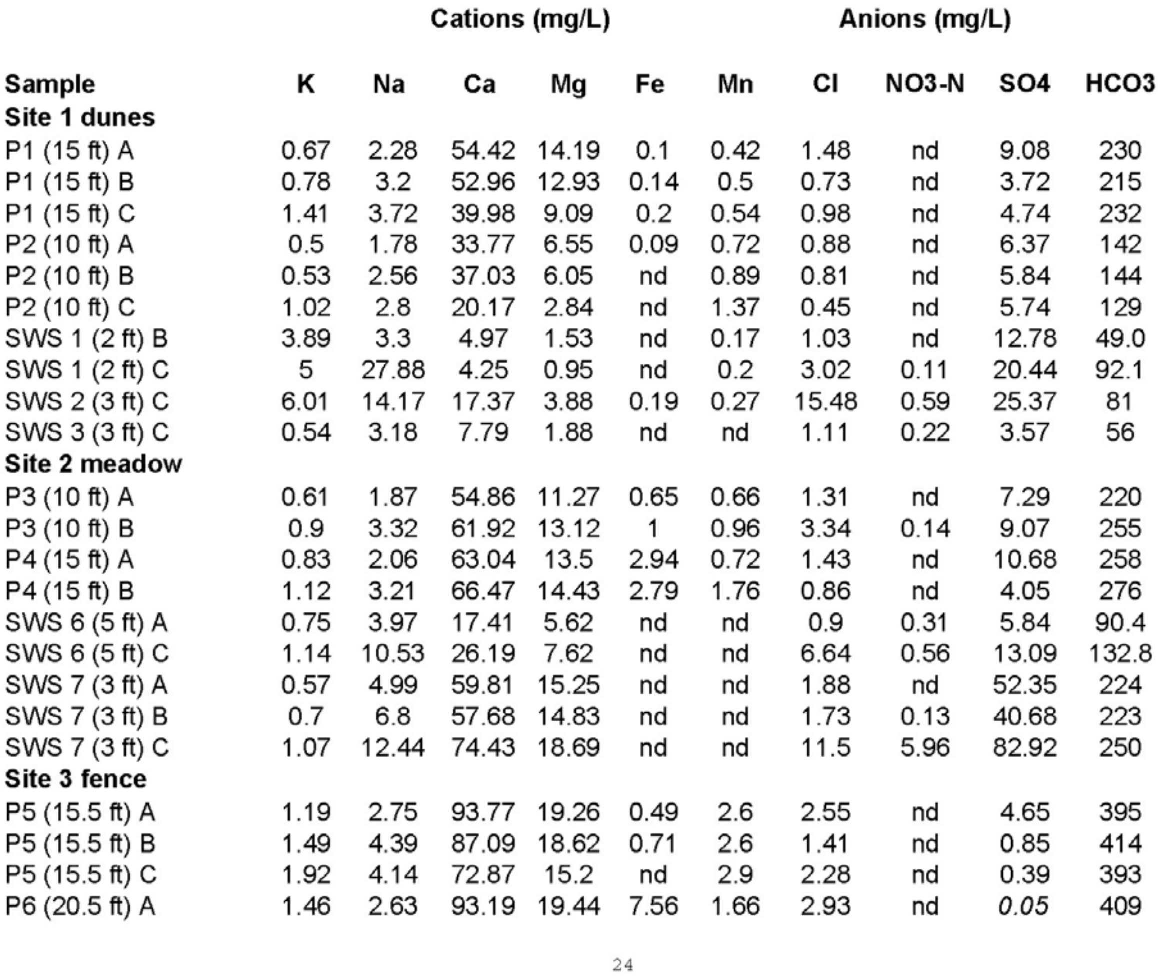
Nilles, M.A. and B.E. Conley 2001. Changes in the chemistry of precipitation in the United States, 1981-1998. Water, Air, and Soil Pollution 130(1-4 II):409-414.

Parkhurst, D.L. and C.A.J. Appelo. 1999. User's guide to PHREEQC (Version 2) - A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigation Report 99-4259.

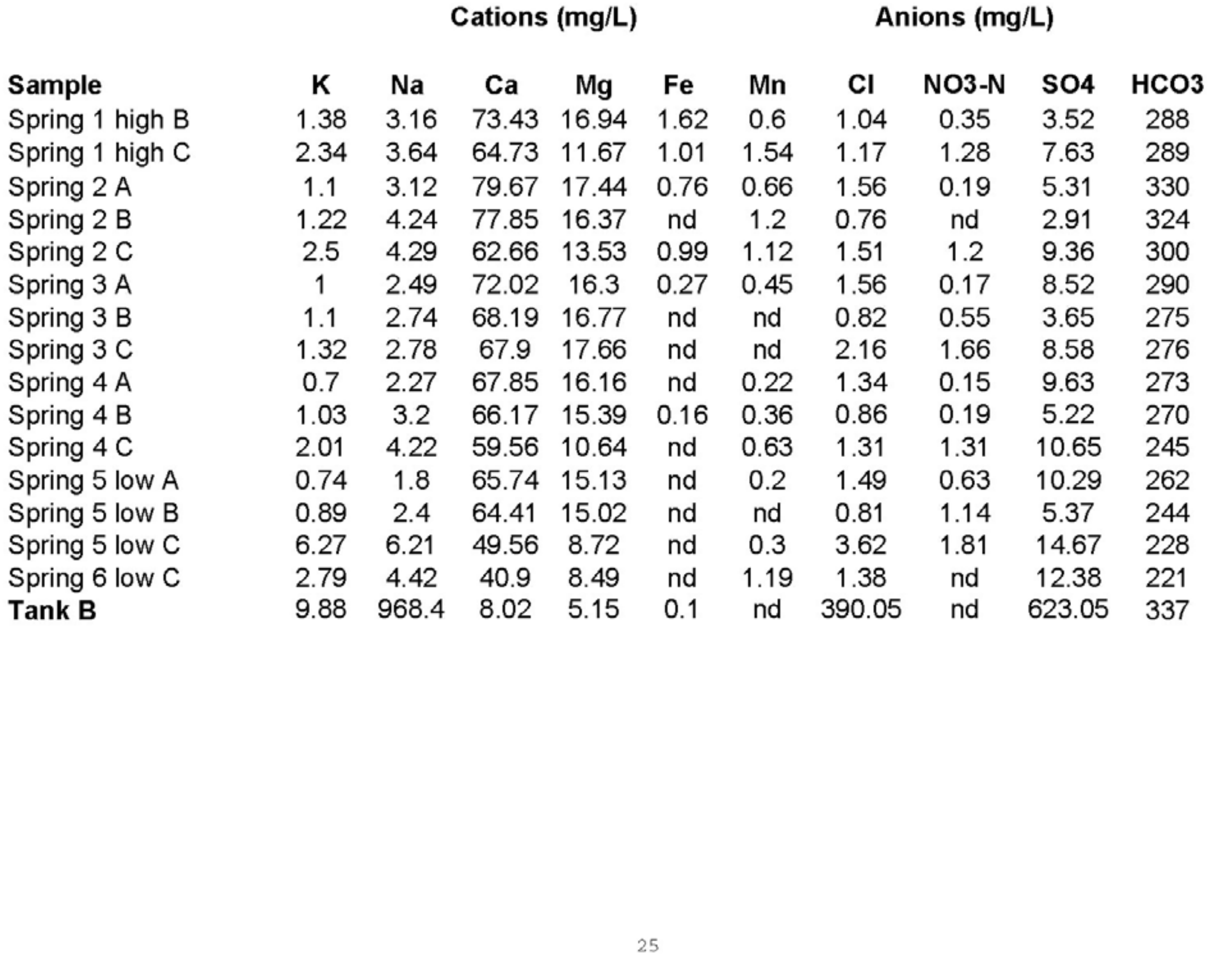
Appendix - Analytical Results (A = 13 Oct. 2005, B = 11 May 2006, C = 15 Aug. 2006 sample dates)

					EC	TOC		
Sample	**pH**	**D.O. (%)**	**D.O. (mg/L)**	**Temp (ºC)**	**(µS/cm)**	**TC (mg/L)**	**IC (mg/L)**	**TOC (mg/L)**
Site 1 dunes								
P1 (15 ft) A	7.72	10.3	1.05	14.5	369.9	47.68	45.31	2.37
P1 (15 ft) B	7.51	7.4	0.86	8.9	352.0	43.34	42.34	1
P1 (15 ft) C	7.75	17.4	1.93	10.6	403.9	47.64	45.67	1.97
P2 (10 ft) A	7.91	6.5	0.66	14.2	238.5	30.8	28.01	2.79
P2 (10 ft) B	7.79	4.3	0.50	8.9	250.0	29.25	28.41	0.84
P2 (10 ft) C	8.28	47.8	5.06	12.1	133.7	25.83	25.33	0.50
SWS 1 (2 ft) B	5.39	26.9	2.93	11.5	73.3		9.64	
SWS 1 (2 ft) C	5.62	45.6	4.95	11.7	168.1		18.13	
SWS 2 (3 ft) C	5.93	38.20	4.12	12.00	251.12		15.90	
SWS 3 (3 ft) C	6.03	43.90	4.60	13.10	82.45		10.94	
Site 2 meadow								
P3 (10 ft) A	7.39	14.3	1.50	13.0	347.2	45.19	43.23	1.96
P3 (10 ft) B	7.43	13.7	1.57	9.1	400.0	51.84	50.29	1.55
P4 (15 ft) A	7.22	11.3	1.22	11.8	413.5	52.33	50.8	1.53
P4 (15 ft) B	7.42	10.7	1.22	9.1	433.0	55.88	54.38	1.5
SWS 6 (5 ft) A	6.70	66.2	5.99	20.2	163.8		17.79	
SWS 6 (5 ft) C	7.01	60.0	6.38	12.6	266.7		26.15	
SWS 7 (3 ft) A	6.50	11.3	1.22	20.7	418.2		44.19	
SWS 7 (3 ft) B	6.69	24.4	2.64	11.7	404.0		43.97	
SWS 7 (3 ft) C	6.93	41.3	4.48	11.6	656.8		49.24	
Site 3 fence								
P5 (15.5 ft) A	6.96	10.5	1.11	14.5	585.0	80.75	77.81	2.94
P5 (15.5 ft) B	6.94	9.1	1.05	9.3	559.0	82.3	81.53	0.77
P5 (15.5 ft) C	7.27	26.5	2.97	10.4	514.9	81.48	77.28	4.20
P6 (20.5 ft) A	7.09	46.9	4.86	13.2	608.0	87.8	80.5	7.3

					EC			TOC
Sample	**pH**	**D.O. (%)**	**D.O. (mg/L)**	**Temp (ºC)**	**(µS/cm)**	**TC (mg/L)**	**IC (mg/L)**	**TOC (m**
Spring 1 high B	7.33	37.1	4.21	9.7	477.0	55.89	56.6	-0
Spring 1 high C	7.52	38.0	4.32	9.6	247.2	57.45	56.82	0
Spring 2 A	7.30	66.2	6.63	15.1	499.3	70.12	64.87	5
Spring 2 B	7.13	25.5	2.88	10.1	485.0	61.82	63.82	
Spring 2 C	7.46	45.9	5.21	9.6	*2.5*	59.57	59.12	0
Spring 3 A	7.32	66.6	6.70	15.0	460.3	59.73	57.08	2
Spring 3 B	7.20	41.5	4.70	9.8	232.0	52.01	54.21	-
Spring 3 C	7.40	52.4	5.93	9.6	521.1	53.44	54.28	-0
Spring 4 A	7.41	51.5	5.08	15.7	440.1	53.26	53.81	-0
Spring 4 B	7.29	23.5	2.65	10.0	431.0	51.97	53.11	-1
Spring 4 C	7.41	33.9	3.85	9.6	339.7	47.59	48.25	-0
Spring 5 low A	7.52	74.8	7.28	16.0	426.2	50.93	51.56	-0
Spring 5 low B	7.15	73.3	8.26	10.0	422.0	46.34	47.97	-1
Spring 5 low C	7.52	45.1	5.13	9.6	482.4	45.49	44.94	0
Spring 6 low C	7.43	65.7	7.44	9.6	441.5	43.40	43.45	-0
Tank B	8.38	5.8	0.61	12.2	4350.0	67.31	66.3	1



	Cations (mg/L)						Anions (mg/L)			
Sample	**K**	**Na**	**Ca**	**Mg**	**Fe**	**Mn**	**Cl**	**NO3-N**	**SO4**	**HCO3**
Site 1 dunes										
P1 (15 ft) A	0.67	2.28	54.42	14.19	0.1	0.42	1.48	nd	9.08	230
P1 (15 ft) B	0.78	3.2	52.96	12.93	0.14	0.5	0.73	nd	3.72	215
P1 (15 ft) C	1.41	3.72	39.98	9.09	0.2	0.54	0.98	nd	4.74	232
P2 (10 ft) A	0.5	1.78	33.77	6.55	0.09	0.72	0.88	nd	6.37	142
P2 (10 ft) B	0.53	2.56	37.03	6.05	nd	0.89	0.81	nd	5.84	144
P2 (10 ft) C	1.02	2.8	20.17	2.84	nd	1.37	0.45	nd	5.74	129
SWS 1 (2 ft) B	3.89	3.3	4.97	1.53	nd	0.17	1.03	nd	12.78	49.0
SWS 1 (2 ft) C	5	27.88	4.25	0.95	nd	0.2	3.02	0.11	20.44	92.1
SWS 2 (3 ft) C	6.01	14.17	17.37	3.88	0.19	0.27	15.48	0.59	25.37	81
SWS 3 (3 ft) C	0.54	3.18	7.79	1.88	nd	nd	1.11	0.22	3.57	56
Site 2 meadow										
P3 (10 ft) A	0.61	1.87	54.86	11.27	0.65	0.66	1.31	nd	7.29	220
P3 (10 ft) B	0.9	3.32	61.92	13.12	1	0.96	3.34	0.14	9.07	255
P4 (15 ft) A	0.83	2.06	63.04	13.5	2.94	0.72	1.43	nd	10.68	258
P4 (15 ft) B	1.12	3.21	66.47	14.43	2.79	1.76	0.86	nd	4.05	276
SWS 6 (5 ft) A	0.75	3.97	17.41	5.62	nd	nd	0.9	0.31	5.84	90.4
SWS 6 (5 ft) C	1.14	10.53	26.19	7.62	nd	nd	6.64	0.56	13.09	132.8
SWS 7 (3 ft) A	0.57	4.99	59.81	15.25	nd	nd	1.88	nd	52.35	224
SWS 7 (3 ft) B	0.7	6.8	57.68	14.83	nd	nd	1.73	0.13	40.68	223
SWS 7 (3 ft) C	1.07	12.44	74.43	18.69	nd	nd	11.5	5.96	82.92	250
Site 3 fence										
P5 (15.5 ft) A	1.19	2.75	93.77	19.26	0.49	2.6	2.55	nd	4.65	395
P5 (15.5 ft) B	1.49	4.39	87.09	18.62	0.71	2.6	1.41	nd	0.85	414
P5 (15.5 ft) C	1.92	4.14	72.87	15.2	nd	2.9	2.28	nd	0.39	393
P6 (20.5 ft) A	1.46	2.63	93.19	19.44	7.56	1.66	2.93	nd	*0.05*	409



	Cations (mg/L)						Anions (mg/L)			
Sample	**K**	**Na**	**Ca**	**Mg**	**Fe**	**Mn**	**Cl**	**NO3-N**	**SO4**	**HCO3**
Spring 1 high B	1.38	3.16	73.43	16.94	1.62	0.6	1.04	0.35	3.52	288
Spring 1 high C	2.34	3.64	64.73	11.67	1.01	1.54	1.17	1.28	7.63	289
Spring 2 A	1.1	3.12	79.67	17.44	0.76	0.66	1.56	0.19	5.31	330
Spring 2 B	1.22	4.24	77.85	16.37	nd	1.2	0.76	nd	2.91	324
Spring 2 C	2.5	4.29	62.66	13.53	0.99	1.12	1.51	1.2	9.36	300
Spring 3 A	1	2.49	72.02	16.3	0.27	0.45	1.56	0.17	8.52	290
Spring 3 B	1.1	2.74	68.19	16.77	nd	nd	0.82	0.55	3.65	275
Spring 3 C	1.32	2.78	67.9	17.66	nd	nd	2.16	1.66	8.58	276
Spring 4 A	0.7	2.27	67.85	16.16	nd	0.22	1.34	0.15	9.63	273
Spring 4 B	1.03	3.2	66.17	15.39	0.16	0.36	0.86	0.19	5.22	270
Spring 4 C	2.01	4.22	59.56	10.64	nd	0.63	1.31	1.31	10.65	245
Spring 5 low A	0.74	1.8	65.74	15.13	nd	0.2	1.49	0.63	10.29	262
Spring 5 low B	0.89	2.4	64.41	15.02	nd	nd	0.81	1.14	5.37	244
Spring 5 low C	6.27	6.21	49.56	8.72	nd	0.3	3.62	1.81	14.67	228
Spring 6 low C	2.79	4.42	40.9	8.49	nd	1.19	1.38	nd	12.38	221
Tank B	9.88	968.4	8.02	5.15	0.1	nd	390.05	nd	623.05	337