

Effects of Dry and Wet Periods on Water Chemistry of Two Springs in Dewey County, Oklahoma

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INTRODUCTION AND METHODS

Springs occur when water emerges from the ground; their water chemistry should reflect the combined complex effects of precipitation, regional geology and biological processes in the terrestrial ecosystem and groundwater (system). A major perturbation to the system could occur when precipitation is abnormally high or low, but such major changes might be discernable in the water chemistry of spring water only when dry periods are directly juxtaposed with wet periods. This study reports changes in spring water chemistry between two years with very large differences in annual precipitation, a situation that often occurs on the Great Plains. The objective of the research was to learn if changes occurred in spring water chemistry between dry and wet years with the expectation that such changes could give insight into biogeochemical processes in the system that are sensitive to precipitation. An advantage was taken of a very dry and wet period to investigate nitrogen (N) cycling in such a system. The following parameters were measured: specific conductance, a measure of salinity, chloride (Cl⁻), a conservative tracer, nitrate (NO₃⁻), a pivotally important ion in the N cycle, and $\delta[^{15}\text{N}]\text{NO}_3^-$. In a previous study at this same site, local pollution of shallow groundwater (4-10 m) below the waste spray area of a concentrated animal feeding operation (CAFO) was demonstrated using the three latter parameters (Toetz, 2006).

Medusa's spring (MS) and West spring (WS) are located in Dewey County (Oklahoma) in the Canton Wildlife Management Area of the Oklahoma Department of Wildlife Conservation (Oklahoma City, OK). The

CAFO (elevation 513 - 534 m) was located about 4.3 and 2.2 km north of MS and WS, respectively. The elevation of both springs was about 499 m, and consequently, the gradient in elevation between the CAFO and the spring suggested that surface water flow and perhaps groundwater was north to south. During the study, water from the springs flowed perennially from the base of the 6 - 8 m bluff through small basins with black sediments; watercress (*Rorippa spp.*) was the dominant emergent plant in both. Toetz (2006) provides more details on the site.

Four samples of MS and WS, respectively, were obtained on February 2, May 13, and September 12, 2006 and February 20, 2007. Six samples were also collected on April 16, June 3, July 7, September 16, and December 3, 2007 and February 9, 2008. More samples were taken in 2007 when it became clear that high precipitation events were occurring. Grab samples of running water from MS were taken just upon its point of emergence from the ground. Because the sediment was soft and points of exit from the ground were not visible, samples were taken about 10 m downstream from the apparent sources of WS where water ran in a single channel. Discharge was not measured, although discharge was visibly higher on July 7, 2007 and thereafter.

Water samples were stored on ice in the field and filtered the same or one day later through pre-rinsed 0.8 μm Millipore filters before analyses. Nitrate and Cl⁻ were analyzed colorimetrically with a flow injection analyzer (Lachat Quik-Chem 8000) (ALPHA, 1995). Specific conductance was measured with an Accumet meter and probe. Stable isotope methodology is briefly described below. Further details can be found in Sulz-

man (2007). The ammonia diffusion method of Sigman et al. (1997) as modified by Toetz (2006) was used to prepare NO_3^- for mass spectrometry.

Samples were analyzed at the Marine Biological Laboratory, Woods Hole, MA) with an Europa 20-20 stable isotope mass spectrometer. Analytical precision was $\pm 0.2 \text{ ‰}$. The mass spectrometer was used to determine the $^{15}\text{N}:$ ^{14}N ratios slightly different than the standard, which is atmospheric N_2 . The difference between the standard ratio and that of the material of interest, when multiplied by 1000 and divided by the standard is called delta (δ) and is expressed in per mil or ‰ units.

Precipitation data were obtained for Fairview, Oklahoma (about 26 km northeast of the springs) from the Oklahoma Climatological Survey. Total annual precipitation was 8.72, 7.69, and 16.16 cm in 2005, 2006, and 2007, respectively. The difference between annual precipitation during 2007 and the previous two years was +46.0%

and 52.2%, respectively. The dry period is operationally defined as 2006 and the first two months of 2007; the wet period is defined as the remainder of 2007 and the first two months of 2008. These definitions are consistent with a report that the 2005-2006 drought in central Oklahoma ended during March, 2007 (Garbrecht, et. al. 2007).

Statistical analyses were performed with Excel 2003. Data were normalized to base 10 logarithms, prior to conducting two-tailed t-tests, because of lack of both normality and equal variance.

RESULTS AND DISCUSSION

Mean specific conductance in MS was 485.9 in the dry period and 563.5 $\mu\text{S}/\text{cm}$ in the wet period; the difference was significant ($t=3.62$, $P=0.01$ $df=8$) (Table 1). Mean specific conductance in WS was 475.7 in the dry period and 533.2 $\mu\text{S}/\text{cm}$ in the wet period: the difference was also significant ($t=3.58$, $P=0.01$, $df=8$). In MS water the mean concentration

Table 1. Water chemistry of Medusa's spring and West spring during dry (n=r) and wet (n=6) periods.

First line = mean; variance in parentheses. Range is in bold.

Period	n	Cl^- mg/l	NO_3^- mg/l	$\text{Cl}^-:\text{NO}_3^-$ mol/l:mol/l	Specific conductance $\mu\text{S}/\text{cm}$	$\delta [^{15}\text{N}]\text{NO}_3^-$ ‰
MEDUSA'A						
Dry	4	24.3 (3.1) 22.0-26.3	47.5 (0.7) 46.9-48.7	0.89 (0.00) 0.81-0.98	485.9 (2360.1) 437.1-533.4	+4.9 (0.4) +3.9 to +5.0
Wet	6	27.7 (8.7) 24.6-32.4	54.6 (21.6) 45.6-57.9	0.89 (0.01) 0.74-1.05	563.5 (23=23.0) 548.2-588.3	+5.3 (0.6) +3.9 to +6.0
WEST						
Dry	4	18.6 (1.4) 17.0-19.4	36.5 (0.2) 36.3-37.2	0.89 (0.00) 0.80-0.96	475.7 (1007.7) 429.7-500.5	+4.1 (0.0) +4.0 to +4.5
Wet	6	18.0 (2.1) 16.3-20.0	34.5 (0.2) 31.9-37.6	0.89 (0.00) 0.80-0.96	533.2 (340.4) 521.3-596.3	+4.5 (0.8) +3.8 to +6.2

of NO_3^- was 47.5 during the dry period and 54.6 mg/l during the wet period; the difference was significant ($t=2.91$, $P=0.02$, $df=8$). In MS water the mean concentration of Cl^- was 24.3 during the dry period and 27.7 mg/l during the wet period. The difference was almost significant ($t=2.07$, $P=0.07$, $df=8$). However, in WS the mean concentration of NO_3^- in the dry and wet periods were 36.5 and 35.4 mg/l, respectively (Table 1). The mean concentrations of Cl^- for the dry and wet period were 18.6 and 18.0 mg/l, respectively. In neither case was the difference significant ($t=1.08$, $P=0.31$, $df=8$ and $t=0.67$, $P=0.52$, $df=8$, respectively).

In MS mean values of $\delta [^{15}\text{N}]\text{NO}_3^-$ were $+4.9\text{‰}$ in the dry period and $+5.3\text{‰}$ in the wet period; in WS mean values were $+4.1\text{‰}$ and $+4.5\text{‰}$, respectively (Table 1). In neither spring was there a significant difference between dry and wet periods ($t=0.80$, $P=0.44$, $df=8$ and $t=0.66$, $P=0.53$, $df=8$, respectively). The $\delta [^{15}\text{N}]\text{NO}_3^-$ values observed are all within the lower end of the range for soils, $+4\text{‰}$ to $+8\text{‰}$ (Heaton, 1986).

In MS and WS the mean molar ratios of $\text{Cl}:\text{NO}_3^-$ were identical (0.89) during dry and wet periods (Table 1). In fact for all samples from both springs the mean ratio was also 0.89 (variance=0.00, $n=10$). A paired t -test revealed no significant difference between wet and dry periods in the mean molar ratios of $\text{Cl}:\text{NO}_3^-$ for MS and WS ($t=0.14$, $P=0.89$, $df=8$ and $t=-0.29$, $P=0.98$, $df=8$, respectively). However, the invariance of the mean ratios may be misleading, since they were as low as 0.80 and as high as 1.05 (Table 1).

Higher solute concentrations observed in the wet period in MS are consistent with the higher specific conductance also observed at the same time. Failure of solute concentrations in WS to increase with specific conductance may be attributed to a failure of NO_3^- and Cl^- alone to reflect salinity of spring water; other ions were involved.

In a study of Tallgrass Prairie soils near El Reno, OK (about 120 km to the south of the springs) Garbrecht et al. (2007) found

that the soil profile below 50 cm was essentially dry during the 2005-2006 drought while the top 50 cm was not affected by the lack of precipitation. After March 2007, when precipitation increased, the lower soil profile was recharged. In the present study it is reasonable to conclude that solutes were held in the system, perhaps in the upper soil profile, during the dry period and flushed from the system during the wet period.

CONCLUSIONS AND ACKNOWLEDGEMENTS

By measuring spring water chemistry during a dry and wet period, it was possible to infer flushing of the system using specific conductance. The molar $\text{Cl}:\text{NO}_3^-$ ratio was almost constant. The $\delta [^{15}\text{N}]\text{NO}_3^-$ was characteristic of soils.

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