

ROLE OF IRON-RICH GEORGIA SOILS IN CONTROLLING NITRATE CONTAMINATION OF GROUND WATER

D.M. Endale¹, J.W. Washington², and L. Samarkina²

AUTHORS: ¹USDA-ARS, J. Phil Campbell, Sr., Nat. Res. Cons. Center, 1420 Experiment Station Road, Watkinsville, GA 30677-2373.

²US EPA, National Exposure Research Laboratory, 960 College Station Road, Athens, GA 30605-2700.

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Abstract. Nitrate contamination of ground water is widespread in the USA, and is often associated with nutrient losses from grazing and row-crop agriculture. Studies in Georgia find, however, generally lower levels of nitrate in ground water than in many other parts of the country. The mechanisms controlling the fate of nitrate and related N compounds in groundwater are poorly understood, but the commonality of iron minerals in Georgia soils suggests iron may play a role. We monitored ground water for several solutes for a year and examined the data thermodynamically. The redox states quantified as electron activity pE between couples of N-species (NO_3^- , NO_2^- , NH_4^+) were found to lie on the intersection of the stability field of freshly precipitated $\text{Fe}(\text{OH})_3$ with Fe^{2+} on a Pourbaix (pE-pH) diagram. More over, the evident redox potential relationship between these couples seems stable through time as well. This strongly suggests that the energy-generating nitrification and denitrification reactions are being drawn toward equilibrium with $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ redox couple. These observations support the hypothesis that nitrate reduction proceeds largely by oxidation of Fe^{2+} to an amorphous solid that subsequently recrystallizes to a meta-stable ferric hydroxide. An inverse relationship between $[\text{Fe}^{2+}]$ and $[\text{NO}_3^-]$ in GA waters noted in other studies, suggests that this phenomenon might exercise a regional control on $[\text{NO}_3^-]$ in ground waters of the southeastern USA.

INTRODUCTION

The concern about contamination of water resources with nitrate to levels detrimental to human, animal and ecosystem health is well documented and accepted (Hallberg, 1989; Nolan et al., 1997, 1998; Kellogg et al., 1992, etc.). Consequently, a great deal of energy is invested by private and public institutions and researchers, in trying to understand processes that lead

to contamination and to develop ways and means to contain the problem.

Patterns of nitrate contamination differ across regions in the USA. Nolan et al. (1997) compiled a national map showing the risk of nitrate contamination of shallow ground water. The risk was grouped into four degrees based on low and high N input, and low and high aquifer vulnerability. Based on this criterion, the Midwest and parts of the western and northeastern USA were shown to have a high risk of ground water contamination by nitrate. The contamination risk in the southeastern USA was put as low to moderate. On the other hand, a national map compiled by Kellogg et al. (1992) showed high potential for ground water contamination by N fertilizer in the Southeast, although this did not consider the potential for nitrate attenuation by natural processes. Nolan et al. (1998) statistically verified their 1997 national risk map with nitrate data from a 1993-1995 sampling of more than 1400 wells and found that contamination risks and ground water nitrate concentrations were lower than expected in the Southeast considering the high N inputs in the region and a good deal of well-drained soils.

Groundwater studies in the humid southern USA and the Piedmont and Coastal Plain of Georgia have found nitrate and iron concentrations in ground waters to be inversely correlated or mutually exclusive (Steele et al., 1996; Nolan, 1999; Vendrell et al., 2001). Georgia soils, especially those in the Piedmont, have high iron content characterized by the typical yellow to red colors. These facts, coupled with the comparatively low nitrate concentrations reported by Nolan (1998) in agricultural areas in the Southeast, suggests nitrate attenuation by natural processes involving iron.

The potential role of iron in nitrate attenuation has been reported (Hansen et al., 1996; Cheng et al., 1997), but not extensively. Most reports deal with anaerobic environments in limited lab scale research setting.

The objective of this study was to monitor ground water for several solutes at a spring at the base of a small typical Southern Piedmont pasture watershed and examine these data thermodynamically in order to determine the role of iron in nitrate attenuation around a nitrate-rich and oxic ground water environment.

METHODS AND MATERIALS

Location

A spring instrumented for flow measurement located within the North Unit of the USDA-ARS J. Phil. Campbell Sr., Natural Resource Conservation Center, Watkinsville, Georgia, was the primary site for this study (Fig.1). This spring that we designate as W2-spring is located at the base of watershed W2, a 10-ha pasture, through which about 200 head of cattle, 100 cow-calf pairs, are rotated roughly one week in six. The pasture receives inorganic fertilizer twice a year at a rate of about $78\text{kg N ha}^{-1}\text{yr}^{-1}$. A saprolite derived from granitic to grandioritic gneiss that is about 8 to 21 m thick acts as the near surface aquifer. For comparison purposes, a monitoring well (NU18) located within W2, a second spring (Spring-two) located about one km NNW of W2-spring in the North Unit, and a second well (Hillcrest) that is a municipal well located about 3.5 km west of W2 were also sampled. NU18, located about 30 m ENE of W2-spring, extends 11 m to bedrock and is screened over the bottom 3 m. Hydraulic head measurements established groundwater flow path between NU18 and W2-spring. The hydraulic conductivity of the saprolitic W2 aquifer was estimated as 2 to $3 \times 10^{-5} \text{ cm s}^{-1}$ at NU18. This suggests that a large fraction of water leaves W2 as surface water from the spring as opposed as groundwater. Spring-two is in an area used less intensively for agriculture and in which no cattle are grazed. The municipal well is drilled into grandioritic gneiss to a depth of about 177 m.

Water sample collection and analysis

Details for collection, preservation and protocols for analysis are given in Washington et al. (2003). All analysis were done at USEPA, National Exposure Research Laboratory in Athens, GA. Water samples were collected from W2-spring approximately once a month for about 12 months. The other sites were sampled less often and analysis is presented for only two sampling for Spring-two and NU18 and one for

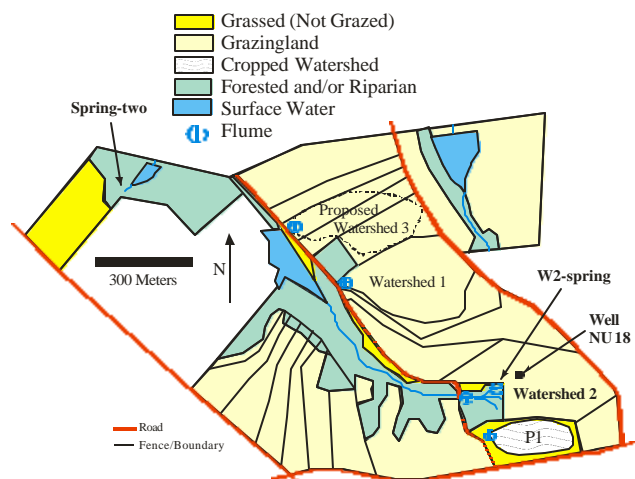


Fig. 1: Study location. North Unit, USDA-ARS, Watkinsville, GA

Hillcrest well. Spring samples were collected from near the source into bottles with inlet at the bottom and an overflow at the top to avoid sample contact with air. For wells, samples were collected similarly but only after stable readings were achieved for temperature, pH, specific conductance and dissolved O_2 . The Hillcrest well was sampled from a tap on the well-head during its normal, continuous-production pumping of about 340 L min^{-1} . Alkalinity and nitrite were also measured on-site. All field measurements were done on duplicate samples until consistent readings were obtained. Careful protocol was also followed in water sampling for iron analysis so that water samples were not exposed to air before complete acidification to $\text{pH} < 2$ nor until immediately before analysis in the lab. Three replicate samples were collected for major-anion analysis (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and H_2PO_4^-) and preserved in the lab by freezing until analysis. These samples were also used for ammonium analysis. Samples for dissolved N_2O and N_2 gas analysis in the lab were obtained and preserved with specially designed sample collector glass jars. Organic N (N_{org}) was analyzed using the June 6, 2001 W2-spring anion samples.

Saprolitic borehole cuttings were carefully collected and preserved during auger drilling of a new monitoring well at W2 about 80 m south of NU18. The cuttings represent an interval of about 7-11 m below ground level and about 1 m below static water level in the monitoring well. Samples were later subjected to dissolution to evaluate the solubility controlling phase for Fe^{3+} .

Table 1. Statistical summary of analytical results*

	Flow rate (mL/min)	Spec. Cond. (uS)	pH (SU)	Temp (C)	Alkalinity (mgCaCO3/L)	Dis. O2 (mg/L)	[NO3-N] (mg/L)	[NO2-N] (mg/L)	[NH4+] (mg/L)	Dis.[Norg] (mg/L)	Sus.[Norg] (mg/L)	[N2O] (nM)	[Fe2+] (mg/L)
W2-Sprg													
Mean	12656	76.4	4.74	17.3	14	6.51	3.51	0.006	0.014	0.64	0.13	244.2	0.141
STDEV	21929	8.5	0.21	4.4	4	1.45	1.11	0.008	0.017			141.6	0.112
Median	6600	76.4	4.68	18.3	13	6.65	3.68	0.003	0.009	0.64	0.13	221.6	0.127
MIN	118	64.8	4.45	6.1	10	4.52	1.79	0.003	0.001	0.64	0.13	88.0	0.003
MAX	90000	98.2	5.18	21.7	19	8.52	5.44	0.03	0.05	0.64	0.13	466.4	0.344
COUNT	15	12	12	12	12	10	13	10	12	1	1	5	13
Spring-2													
Mean	2000	32.1	5.38	14.2	19	5.94	1.23	0.005	0.050	nd	nd	37.5	0.131
MIN	2000	31.8	5.34	14.1	19	5.64	0.86	0.004	0.050	nd	nd	37.0	0.090
MAX	2000	32.3	5.41	14.3	19	6.24	1.60	0.006	0.050	nd	nd	38.1	0.1720
COUNT	2	2	2	2	2	2	2	2	2	nd	nd	2	2
NU18													
Mean	140	51.7	5.57	21.1	18	4.35	2.55	0.007	0.007	nd	nd	643	0.320
MIN	140	45.6	5.34	20.1	10	2.66	1.34	0.004	0.007	nd	nd	236	0.131
MAX	140	57.8	5.80	22.0	26	6.03	3.76	0.010	0.007	nd	nd	1050	0.509
COUNT	2	2	2	2	2	2	2	2	2	nd	nd	2	2
Hillcrest													
7/23/02	1.10E+06	2.33E+02	7.09	18.7	71	0.28	0.05	0.003	0.072	nd	nd	1.98	1.354

* nd means not determined

Table 2. Statistical summary of electron activity pE for various redox couples*

	O2 H2O	NO3- N2O	NO2- N2O	pE for NO3- NO2-	Redox NO3- NH4+	Couple NO2- NH4+	NO3- N2	Fe(OH)3 Fe2+	Fe2O3 Fe2+
W2-Sprg									
Mean	16.47	12.78	14.36	10.98	9.84	9.70	15.24	10.05	5.00
STDEV	0.22	0.25	0.34	0.24	0.21	0.31	0.26	1.02	1.00
Median	16.48	12.78	14.38	11.06	9.87	9.66	15.34	9.93	4.87
MIN	16.08	12.40	13.93	10.48	9.49	9.36	14.66	8.68	3.68
MAX	16.75	13.10	14.73	11.27	10.06	10.11	15.57	12.20	7.14
COUNT	10	5	4	9	6	4	12	11	11
Spring-2									
Mean	15.85	12.20	13.93	10.07	nd	nd	14.39	8.040	3.05
MIN	15.81	12.19	13.91	10.06	nd	nd	14.37	7.80	2.80
MAX	15.89	12.21	13.95	10.07	nd	nd	14.40	8.28	3.29
COUNT	2	2	2	2	nd	nd	2	2	2
NU18									
Mean	15.62	11.89	13.42	9.95	nd	nd	14.21	7.14	2.15
MIN	15.34	11.50	13.10	9.50	nd	nd	13.89	6.73	1.75
MAX	15.89	12.27	13.74	10.39	nd	nd	14.53	7.54	2.54
COUNT	2	2	2	2	nd	nd	2	2	2
Hillcrest									
7/23/2002	13.81	nd	nd	nd	nd	nd	nd	1.94	-3.14

* nd means not determined

To examine these solute data thermodynamically, activity coefficients were calculated and redox states quantified in terms of the electron activity pE , which is analogous to pH .

RESULTS AND DISCUSSION

Only summarized results are presented here. See Washington et al. (2003) for detailed results, analysis and discussion. Statistical summary of analytical results are presented in Table 1. Water quality of the spring during the 12-months period was characterized by mean specific conductance of 76.4 μS , pH of 4.74, temperature of 17.3 $^{\circ}C$, and $[O_2]$ of 6.51 $mg L^{-1}$. Mean N speciation in $mg L^{-1}$, was 3.51 for $[NO_3-N]$, 0.006 for $[NO_2-N]$, and 0.014 for $[NH_4^+]$. Mean $[Fe^{2+}]$ concentration was 0.141 $mg L^{-1}$. Temperature varied in an annual sinusoidal pattern. At higher flows conductance appeared to have increased and pH decreased. These changes might be reflections of increased subsurface microbial activity during times of high water recharge when leached cattle manure fuels the subsurface environment.

Cattle grazing had impact on water quality based on differences between samples from W2-spring and well NU18 on one hand, and Spring-two and Hillcrest well on the other. NO_3-N was higher in grazed-source samples. The conductance was also higher in grazed-source samples suggesting higher dissolved solids in these samples. Higher microbial activity due to high flux of organic substrate from manure in W2 may have also led to higher H_2CO_3 and consequently lower pH in water samples from W2-spring than elsewhere. Hillcrest well, drawing water from the deeper and consolidated-rock aquifer, had much higher specific conductance, pH , alkalinity and $[Fe^{2+}]$, and lower $[O_2]$, $[N_2O]$ and $[NO_3^-]$ than saprolitic sample sources. The higher conductance, pH , alkalinity probably are the consequence of the presence of carbonate minerals in the rock. The lower $[O_2]$, $[N_2O]$ and $[NO_3^-]$ values likely reflect the deeper flow pattern of the rock aquifer. Calculations of approximate N balance for W2, based on the cattle and nutrient management, and spring flow and N speciation in spring flow, suggest significant N transformations in the subsurface system. Approximately 2,600 kg N are applied on W2 yearly from inorganic fertilizers and animal waste. We could account for only 15 kg NO_3-N total annual flow from W2-spring. And conservatively assuming $[N_{org}]$ about

equal to $[NO_3-N]$, then estimated total annual flow of N from W2-spring becomes 30 kg – well below that which was applied on W2; hence our conclusion of significant N transformation. Active NO_3^- reduction in W2 was also confirmed based on analysis of NU18 sample in September 2002 for N_2 and compared to that for deionized water that had been saturated with atmospheric air. The N_2 peak ratio for NU18 headspace to that of air-saturated water was 1.43.

The redox state for various redox couples, quantified in terms of the electron activity, pE , are given in Table 2 as statistical summaries. Detection limit constraints prevented calculation of pE for all redox couples. The pE_{O_2/H_2O} are higher than other values. Values of pE calculated with N_2O and N_2 also tend to be relatively high. For W2-spring, values of pE_{NO_3-/NO_2-} , pE_{NO_3-/NH_4+} and pE_{NO_2-/NH_4+} are in close agreement with each other and with $pE_{Fe(OH)_3ppt/Fe^{2+}}$. When these values are plotted on $pE-pH$ (Pourbaix) diagram (figure not shown) they lie on the intersection of the stability field for freshly precipitated $Fe(OH)_3$ with Fe^{2+} . This strongly suggests that the energy-generating nitrification and denitrification reactions are being drawn toward equilibrium with the $Fe(OH)_3/Fe^{2+}$ redox couple.

More over, the evident relationship of pE_{NO_3-/NO_2-} , pE_{NO_3-/NH_4+} , pE_{NO_2-/NH_4+} and $pE_{Fe(OH)_3ppt/Fe^{2+}}$ seems stable through time as well (figure not shown). After large rain events in which flow rate was at a short-term high and $[Fe^{2+}]$ was very low and variable among replicates, the $pE_{Fe(OH)_3ppt/Fe^{2+}}$ line showed slight offset from the general stable line. This long-term internal consistence among N and Fe redox couples underpins that these couples are mutually linked on an ongoing basis.

Additionally, the NH_4^+ couples also plot essentially on the line for stability field for freshly precipitated $Fe(OH)_3$ (figure not shown). Based on $Fe(OH)_3$ chemistry, it seems likely that the possible relationship of pE_{NO_3-/NH_4+} and pE_{NO_2-/NH_4+} with $pE_{Fe(OH)_3ppt/Fe^{2+}}$ is a consequence of nitrification of NH_4^+ with O_2 as the electron acceptor with subsequent denitrification of NO_3^- and NO_2^- to an endpoint defined by Fe^{2+} precipitating as $Fe(OH)_3$.

CONCLUSIONS

Our analysis coupled with the observations by several researchers of the geographically wide inverse relationship between $[NO_3^-]$ and $[Fe^{2+}]$ in well-waters in

the southeastern USA, including in Georgia, suggest that the process of NO_3^- reduction by Fe^{2+} might be the regional process controlling/checking $[\text{NO}_3^-]$ in ground waters of this part of the US.

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