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Variation in nitrate and calcium as indicators of recharge pathways in Nolte Spring, PA

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Abstract This study documents variations in calcium and nitrate concentrations that suggest changes in recharge pathways in a karst spring. The nitrate concentrations increased at the end of the growing season, showing the importance of the soil zone in the recharge pathway. The increase occurred over just a few days, which may be indicative of a change in contribution of baseflow in different seasons from deep to shallow groundwater. The calcium concentrations decreased several days after storm events. A change in the carbonate equilibrium

is hypothesized because chloride was not diluted during these events. The decrease in calcium could be due to outgassing and calcite precipitation in the recharge area when older, higher ionic strength matrix water mixes with stormwater in open conduits. The use of geochemical indicators to better understand recharge pathways benefited from long-term monitoring and periods of daily sampling.

Keywords Karst · Nitrate · Infiltration · Recharge

Introduction

Karst aquifers are vulnerable to contamination because of the rapid recharge through closed depressions and sinking streams and fast flow paths created by conduits. Recharge can be dispersed, through the soil zone and epikarst, or focused, entering through closed depressions and sinking streams. A combination of the two types of recharge can occur (Ford and Williams 1989). This variation makes it difficult to define protection areas for karst aquifers. Long-term geochemical monitoring is helping to unravel the different types of recharge and the likely causes for the variation.

Nitrate is a common groundwater contaminant in agricultural karst areas. A number of studies have looked at the variation in nitrate concentrations in spring discharge to better understand the sources and timing of nitrate contamination. Boyer and Pasquarell (1995) as well as an earlier study by Kastrinos and White (1986) found a linear correlation between nitrate con-

centration and percent agricultural land use in karst springs. When agricultural land use reached 79%, Boyer and Paquarell observed nitrate concentrations reached 16 mg/L in spring discharge in West Virginia. In cave systems in the same basin, the nitrate concentrations were higher and more variable beneath dairy farms than pastureland.

Nitrate concentration varies during storm events, providing evidence of flow paths. Peterson et al. (2002) sampled springs and soil core in an Arkansas karst region to study how nitrate moves through the regolith. They found that most (about 74%) of the nitrate is transported during baseflow, based on the steady concentrations, dilution during storms, and long time scales of transport. They sampled three storms and found the load in storm discharge was about six times lower in the growing season than the non-growing season (August vs February). Storm intensity can influence travel time and concentrations. In a carbonate aquifer in France (Riboldi et al. 2000), chloride and nitrate were used to

delineate baseflow and overland flow components of recharge. High intensity storms had 82% overland flow, but low intensity storms had only 12% overland flow.

Storage of nitrate in the soil zone can delay and prolong release of nitrate. Panno and Kelly (2004) found less seasonal variation of nitrate concentration in karst basins than non-karst basins due to storage. The long time scales of transport were also observed in cave drips in Slovenia that received septic tank discharge (Kogovsek and Sebelja 2004). A decade after the septic tanks were removed, nitrate was still observed in the discharge. A controlled tracer injection showed arrival times in different drips varied from a little over an hour to 17 days. The combination of fast flow paths shown by the tracer arrival and diffuse recharge shown by the long-term contamination makes it difficult to predict concentrations even in a controlled experiment.

Shifts in nitrate concentration were greater in the soil zone than in the groundwater samples in a study in Indiana (Iqbal and Krothe 1995). Lysimeter concentrations varied from 10 to 75 mg/L. In contrast, groundwater varied less (range of about 10 mg/L) and concentrations were typically lower. The more stable concentrations are attributed to dilution from lateral flow. Dilution along flow paths was also observed by Howard (1985).

Katz and others (2001) used isotope dating to evaluate the residence time of nitrate in Floridan Aquifer springs. The isotopes suggested residence times on the order of 10 to 20 years. In addition, increases in nitrate concentrations did not follow application rates, suggesting delayed release. However, discordant ages using alternate dating methods (CFCs, SF₆, ³H/³He) suggest mixing from different flow paths occurs (Katz 2004). Nitrogen isotopes have been used to indicate sources and timing of nitrate input. Wells and Krothe (1989) found large shifts downward in the nitrogen isotope signature from September to May; the change is attributed to macropore flow, which provides a slug rather than a diffuse input. Katz et al. (2004) distinguished artificial fertilizer from manure by its higher nitrogen isotope signature; the highest concentrations were also associated with the artificial fertilizer.

The US Geological Survey (Hall et al. 1997) mapped nitrate in soils and compared the timing of applications and well concentrations near Ephrata, Pennsylvania (same region as the spring used in this study). They measured application rates of 0.4–8 kg/ha/cm (1–18 lbs/acre/in) as nitrogen, with as much as a factor of six variation from year to year and a factor of two variation from fall to spring. There was no relationship between monthly precipitation and concentration of nitrate, which indicates the importance of the source term in determining concentrations. The lag between nitrate peaks in application and nitrate peaks in well concentration was between 4 and 19 months. The leaching

appeared to be diffuse based on the lag time and the spread in nitrate concentrations in groundwater.

These studies indicate that nitrate concentrations will be difficult to predict because they vary both in source term and type of recharge. Variations in ion data help reveal how infiltration occurs and how it changes over time.

Methods

Nolte Spring is in the karst region of southeastern Pennsylvania in Lancaster County. It is a former public water supply in Brownstown, PA, 6.5 km NE of Lancaster on the Ephrata quadrangle (Fig. 1). The bedrock is the Ordovician Epler Formation (interbedded limestone and dolomite). The Epler is prone to sinkhole development aligned with north-northeast trending fracture traces. Although the conduit system has not been mapped, elsewhere in the Epler conduits are on the order of 1 m.

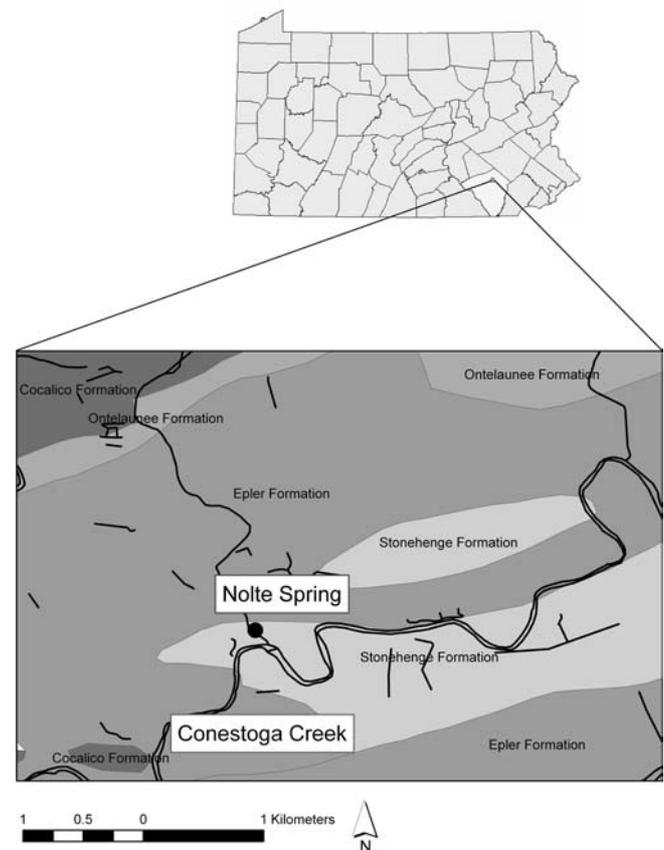


Fig. 1 Location of Nolte spring in SE Pennsylvania. Capture zone is in the Epler formation (carbonate rocks). Stonehenge Formation is also present in the valley. The spring discharge drains to the Conestoga Creek

The spring discharges from two conduits about 10 cm diameter, and forms a pool in the basement of the water treatment building. The spring was used as a public water supply from the late 1950s until 1998, when it was abandoned because of high turbidity and replaced with a well. The spring discharge at baseflow is about 25 L/s to a tributary that joins the Conestoga Creek about 0.3 km downstream.

The recharge area for the spring is gently rolling pastureland (Fig. 2), inhabited by old order Amish and Mennonite families. In Lancaster County, land use is about 65% cropland or pasture, about 25% forested, and about 10% urban. The capture zone for Nolte spring is pastureland. Precipitation is a little over a meter annually and recharge is estimated to be 30–40 cm annually. Precipitation records were obtained from the Lancaster airport, about 7.5 km west of Nolte spring.

The spring was sampled at the conduits approximately biweekly for 2 years. Unstable parameters (pH, temperature) were measured at the spring mouth, and water samples were collected there for major ions and alkalinity.

In addition, daily samples were collected with an automatic sampler mid-October to mid-November of the second year. This period was selected for additional sampling because increasing nitrate was observed in the first year of study. The sampler was set to collect at 10 a.m. and used a peristaltic pump with the intake in the spring conduit. The samples were left in open bottles (but inside the closed sampler) until the visit for bi-weekly sampling. Unstable parameters were not measured for these open bottles. A second period of daily sampling was programmed in the second year in January and February, the period when decrease in nitrate concentrations was observed in the first year of study.



Fig. 2 Photo of springhouse and surrounding pasture

Samples were analyzed for major cations and anions using ion chromatography. For the biweekly samples, alkalinity was measured by titration. The US Geological Survey geochemical model PHREEQC (Parkhurst and Appelo, 1999) was used to calculate the partial pressure of CO_2 (P_{CO_2}) in the biweekly samples. Modeling was not conducted for the daily samples due to the lack of pH and alkalinity data since the samples were not collected immediately after sampling.

Results

Nitrate concentrations varied from 8 to 10 mg/L in the summer of 2002 and 15 to 20 mg/L in the following fall and early winter (Fig. 3). The concentrations declined in January 2003 from 20 to 8 mg/L and remained low until fall, then rose again. The increase in concentrations occurred in October both years of the study. This increase in concentration was fairly abrupt, occurring over three or four days based on the daily sampling conducted the second year of the study (Fig. 4). When the automatic sampler was set up, the nitrate concentration was already 11 mg/L, then increased to 15 mg/L by the next day.

The nitrate dropped between January 9 and February 5 of the first year from almost 20 to 8 mg/L (Fig. 3). During the second year of the study, nitrate only dropped from 18 to 14 mg/L. This period of time was also selected for daily sampling the second year, but the concentrations decreased only slowly, typically 0.1 to 0.2 mg/L in a day.

The calcium concentrations varied from day to day in response to precipitation events, varying from 76 to 104 mg/L. The calcium dropped as much as 15 mg/L after precipitation (Fig. 5). There was less variation in periods without precipitation (e.g., the second week of

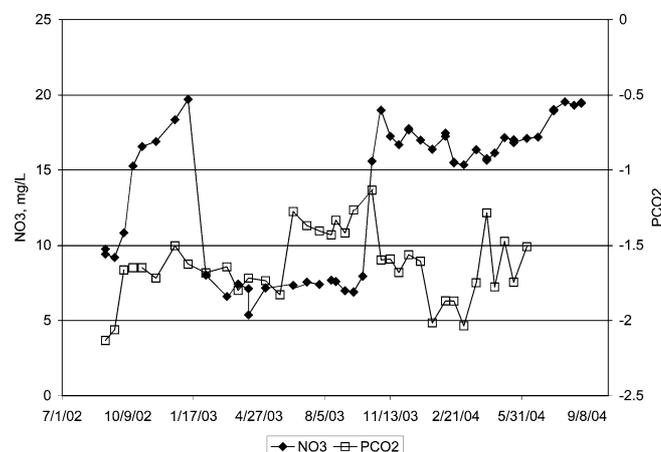


Fig. 3 Seasonal variation in nitrate concentration and P_{CO_2}

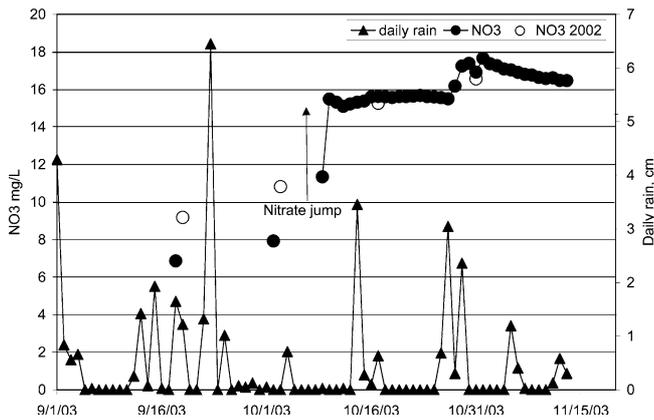


Fig. 4 Daily variation in nitrate concentration in year 2 with monthly concentrations for year 1, showing an increase in October for both years

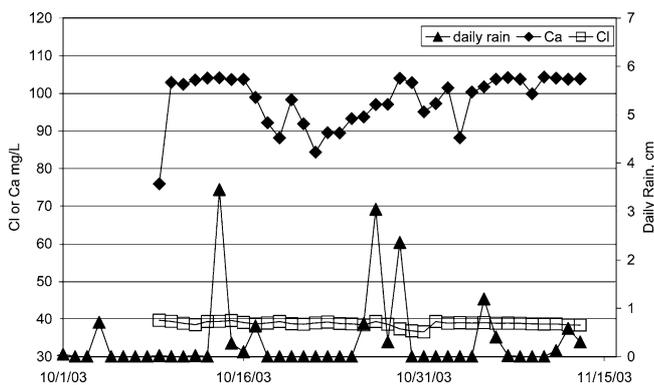


Fig. 5 Daily variation in calcium and chloride concentrations (year 2), showing steady chloride and declines in calcium after storm events

October). Although the calcium concentration varied, the water at the spring mouth remained undersaturated with respect to calcite during this sampling period, based on the bimonthly samples. The saturation index for calcite was -0.75 on October 16, 2003 and -0.31 on October 30, 2003.

In contrast, the chloride showed little seasonal or storm response. The chloride concentrations were nearly constant over each season, between 35 and 40 mg/L in the fall of the second year (Fig. 5) and between 40 and 45 mg/L in the winter. In the daily sampling the chloride varied little, sometimes showing a dilution of a 1–3 mg/L after a precipitation event (e.g. late October) and sometimes no change (e.g. early November). The only large change in chloride concentration was observed in the first year of the study when the concentration reached 90 mg/L in September during a drought. Over the fall the water levels rose, and the concentration gradually decreased to 50 mg/L by winter.

Modeling using PHREEQCI showed that the P_{CO_2} variation was related to the growing season (Fig. 3). High P_{CO_2} was observed during the growing season, beginning in mid-June and continuing until mid-October in 2003. The P_{CO_2} was between $10^{-1.5}$ and 10^{-1} , typical of values with high soil gas from plant growth. The P_{CO_2} fell to 10^{-2} and $10^{-1.5}$ at the end of the growing season in October. The decrease in P_{CO_2} was slightly later than the nitrate increase observed in October. Note that the P_{CO_2} in the growing season during the first year of the study in 2002 was the lowest observed; the two samples collected then were less than 10^{-2} . The region was under a severe drought, and it is believed that dewatered conduits led to outgassing.

Discussion

The ion variations through time suggest that changes in recharge patterns and the growing season affect concentrations. The variations to be considered are calcium, nitrate which varied seasonally, and chloride which remained relatively constant compared to calcium and nitrate. These contrasts suggest that both the source term and recharge are factors in ion variation, and the patterns can vary from one year to the next depending on climate.

The calcium variation in the daily samples reflects the influence of stormwater recharge. The variation is not due to simple dilution because the other ions (e.g., chloride) do not decrease concurrently. Equilibrium with respect to calcite is a likely controlling factor. Since water at the mouth of the spring is undersaturated with respect to calcite, precipitation of calcite (and decrease in calcium) is not likely to be occurring there but rather earlier in the flow pathway. Nonetheless, calcite has been observed in the sediment of spring discharge both at baseflow and during storms (Tancredi 2004). This decrease in calcium provides clues as to whether matrix flow or conduit flow is dominant. It furthermore indicates the type of recharge (dispersed versus focused).

Matrix water is often considered to be an “old” component of storm water, with a higher ionic strength. Conduit water, with faster flow paths, tends to have lower ionic strength. The stormwater pulse observed in the daily samples has more dilute calcium, but it is constant in concentration of other ions. One hypothesis is that matrix water with higher calcium gets pushed into open conduits during the storm. This leads to supersaturation and outgassing. Where are conduits likely to be open during storms? Probably these open conduits would be in the recharge area, not further down the flow path where the passages are full. Mixing in the recharge area would explain why there is a significant delay be-

tween rainfall and the dip in calcium (about 4–5 days). The timing issue is more complicated than this simple explanation because there are variations in the conductivity immediately after storms (Toran et al. 2005). Thus, the mixing of matrix and conduit water occurs throughout the flow system, but the daily variation in calcium concentrations provides evidence of mixing in the *recharge area*. The “conduits” in the recharge area are likely narrow passages, or macropores.

The variations in nitrate concentration are likely due to a combination of changes in the source term and the flow path. The source term influence is evidenced by the relationship between nitrate concentrations and the growing season. Nitrate in groundwater increased after the growing season ended and there was less uptake of nitrate by plants. This increase occurred roughly the same time that the P_{CO_2} fell in year two, also indicating end of the growing season. Based on the daily sampling using the automatic sampler, nitrate increased 4 mg/L in just one day. The high nitrate is evidence of recharge through the soil zone where nitrate was stored.

A somewhat different pattern occurred in year one. The area was under a drought emergency and water levels were unusually low. The end of the growing season did not show a decrease in the P_{CO_2} ; P_{CO_2} was low all summer. The lower P_{CO_2} could be due to lower soil gas, but it could also be low because outgassing occurred in open conduits exposed when water levels declined during the drought. Nonetheless, a large increase in the concentration of nitrate also occurred in October as the region was recovering from a drought. The increase could be a change in the source term related to the end of the growing season (as in year two), but there may be a change in the flow path. During the drought, the baseflow at the spring may have changed from mostly deep groundwater as the source, to baseflow from dispersed recharge and shallower groundwater as the source. Evidence for the shift from deep to shallow groundwater as the source of baseflow is seen in the chloride concentrations. The chloride concentration dropped from 94 to 60 mg/L from late September to early October 2002. The deep groundwater would be expected to have lower nitrate than shallow groundwater, but higher chloride.

Nitrate declined sharply in February of year one, but gradually in year two. The decline is probably related to flushing. Several studies have found storage of nitrate in the soil zone maintains concentrations for months after application. The difference in flushing rates may be due to the heavy snowfall in year one (109 cm) and cold temperatures (below freezing). The frozen ground at the end of January and early February prevented diffuse recharge through the soil zone, and thus nitrate concentration dropped. When snowmelt occurred, a very large influx of water occurred, as

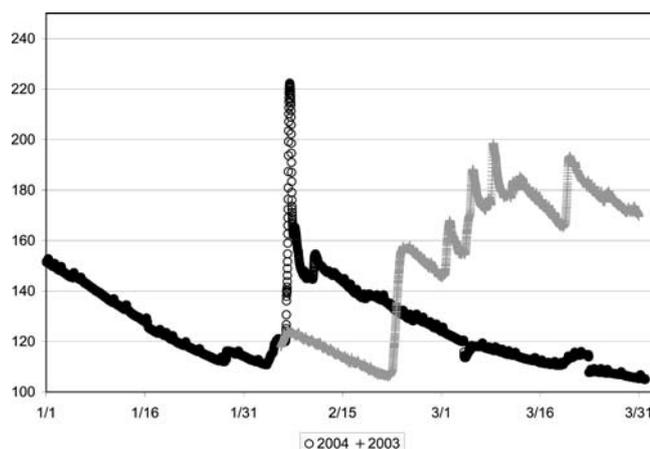


Fig. 6 Water level variation for winter (and early spring) of both sampling years. Base level shifted upward in 2003 in response to snowmelt and storm events. A large storm event occurred in 2004, but base level remained below 120 cm

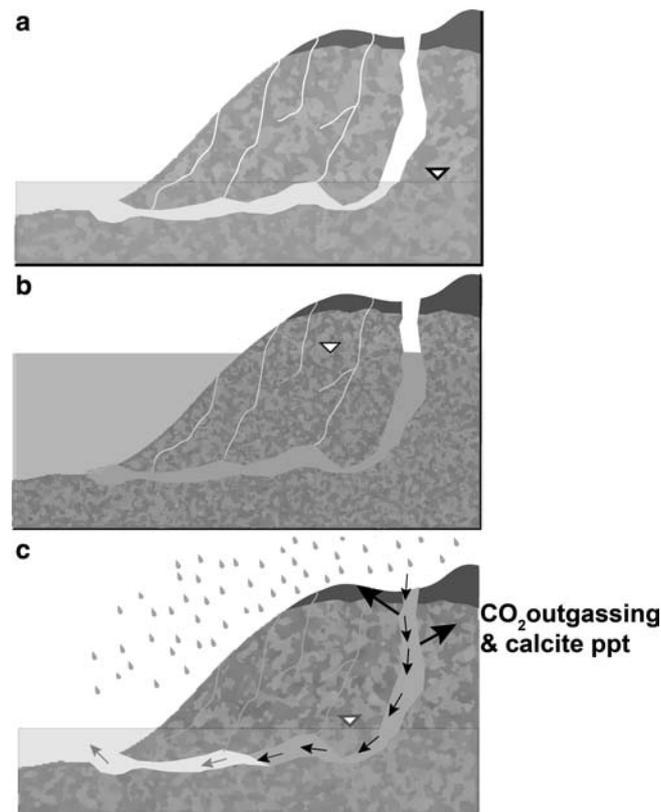


Fig. 7 Conceptual diagram of different types of recharge events observed at Nolte Spring. **a** Late summer 2002 baseflow from deep groundwater dominates spring discharge. Nitrate is low, chloride is high. **b** Oct 2002, water levels rise, nitrate from soil zone enters spring. At even higher stage (winter 2003) the nitrate is diluted during snowmelt. **c** During storms, matrix water mixes with conduit water. Outgassing and calcite precipitation can occur in open conduits

shown by the 100 cm increase in water level beginning the last week of February 2003 and a rise in the base level from 120 to 165 cm (Fig. 6). This large influx of water may have diluted and flushed the nitrate in the soil zone, so that the nitrate concentration remained low the following spring and summer. Snowfall was lower in year two (63.5 cm), and the ground was intermittently covered with snow. In year two, the water level rose in response to storm events (especially one large event in early February), but baseflow remained constant around 110 cm, unlike year one (Fig. 6). The concentrations fell gradually as the nitrate in the soil zone declined, but the drop was not large because nitrate in the soil zone continued to be gradually flushed. Thus, the recharge changed from year one when a large influx of snowmelt occurred, to year two when the soil zone was flushed more gradually.

In summary, ion variations were used to reveal types of recharge occurring in a karst system (Fig 7). The recharge can be a mixture of fast and slow paths, and the spring chemistry not only reflects this but also contributions from groundwater along the flow path. The high P_{CO_2} levels observed were evidence of a large component of recharge through agricultural soils with very little direct input from sinkholes or open throats. The steady concentration of nitrate and the increase at the end of the growing season also suggest that dispersed recharge is occurring. If conduit flow is an important component,

then more frequent changes in concentration would be observed in response to source term variations. The increase in concentration at the end of the growing season suggested that nitrate was stored in the soil zone, and then it was flushed through dispersed flow (Fig. 7b). Another change observed is the relative contribution of deep versus shallow groundwater to baseflow, which affected nitrate concentrations after a drought (Fig. 7a vs b).

Although dispersed flow seems to dominate in this system, the changes in the contribution of conduit (or macropore) flow are apparent in the variation in calcium concentrations. The decrease in calcium concentration after storms may indicate mixing of fast and slow flow paths in the recharge area, resulting in outgassing and precipitation of calcite (Fig. 7c). Dilution of nitrate also occurred, both rapidly through snowmelt and more gradually through dispersed infiltration.

Understanding of type and variation in recharge became apparent during long-term monitoring. Additional information was gained from periods of daily sampling.

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