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Nitrogen isotopes in nitrate from surface water and shallow groundwater at Sixmile Creek, southeastern Colorado

by

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ABSTRACT

Dissolved nitrate in surface water and shallow groundwater draining cultivated areas in the Sixmile Creek watershed can exceed the U.S. EPA drinking water standard of 10 mg/L NO_3-N. Herein we report on a study of nitrate concentrations and N-isotopic compositions that was designed to identify the nature and origin of the nitrate contamination. In samples collected in August 1993, Sixmile Creek nitrate became isotopically heavier downstream increasing from $\delta^{15}N_{AIR}$=-1.8 to +1.6 permil over the final two miles of the creek. Springs and small tributaries feeding Sixmile Creek carried 9 to 29 mg/L NO_3-N with compositions of 3.6 to 5.6 permil. The isotopic and concentration data are in close agreement with a simple model in which creek water is modified by progressive inflow of high-nitrate, isotopically-heavy groundwater like that observed in springs and spring-fed tributaries. The isotopically-light nitrate contained in upstream Sixmile Creek waters is inferred to be fertilizer-derived. The isotopically-heavy nitrate emanating from springs and small tributaries is also inferred to be fertilizer-derived but to have undergone additional transformations. Applied nitrogen taken up by growing crops is later released to groundwater as isotopically heavier nitrate during mineralization of crop residues. Fertilizer-derived nitrate may also undergo isotopic modification as a result of bacterially-mediated denitrification occurring in shallow aquifers underlying the fields.

INTRODUCTION

Sixmile Creek is a small tributary of the Arkansas River in semi-arid southeastern Colorado (Fig. 1). The creek drains a cultivated area of some 14.2 km^2 that is fertilized and heavily irrigated during the summer growing season. Irrigation-return flow and overflow from an irrigation ditch are the important water sources for the creek. Natural flow from open rangeland at the headwaters of the creek is intermittent and is insignificant except perhaps during very strong summer rainstorms.

The Sixmile Creek drainage basin is of interest because it offers an opportunity to study the effects of agricultural practices on the quality of water discharging to the Arkansas River. In this report we focus on the behavior of nitrate. Cain and Edelmann (1980) and Cain (1985) demonstrated that in 1976 and 1978 Sixmile Creek waters contained 2-9 mg/L NO_3-N, significantly higher than nearby Arkansas River waters. For comparison, the U.S. EPA maximum contaminant level for drinking water (MCL) is 10 mg/L NO_3-N. In a separate report Zielinski et al. (manuscript in preparation) focus on the behavior of uranium, which is also higher than in nearby Arkansas River waters. This work is part of a larger study, underway since 1991, of land-use and geologic factors influencing the concentrations of dissolved uranium in the Arkansas River valley (Zielinski et al., 1995).

DESCRIPTION OF THE AREA

For the purposes of this study, Sixmile Creek (Fig. 1) begins at 4685 feet elevation where there is direct outflow from Bessemer irrigation ditch, a manmade diversion that takes water from the Arkansas River above Pueblo, Colorado. At higher elevations the creek flows only intermittently during infrequent rainstorms. The mean annual precipitation is 12 inches, three fourths of which falls during the growing season. Pan evaporation measurements indicate that evaporation in the area is 3.5 to 5 times precipitation (U.S. Department of Commerce, 1991).

Below the irrigation ditch Sixmile Creek flows through cultivated fields covering alluvial terraces of the Arkansas River. The soils are mostly well-drained and are calcareous ranging to 2 meters in thickness. Beneath the soils are alluvial gravels and colluvium and alluvium of Pleistocene and Holocene age (Scott et al., 1978). The unconsolidated deposits rest on the Pierre Shale, a calcareous marine sedimentary rock of Cretaceous age (Tweto, 1979).

The fields are planted mostly in corn and hay. Irrigation is intensive with water obtained from the Bessemer irrigation ditch. Supplemental water is obtained from local wells which tap the shallow unconfined aquifer beneath the fields. Irrigation waters percolate through the soil and flow down-gradient through unconsolidated gravels. Springs or seeps are common where erosion has exposed the contact between the gravels and the bedrock. Liquid fertilizer (10-34-0) and anhydrous ammonia are applied to the fields each spring at rates of 200-400 lbs/acre. Supplemental fertilization is carried out later in the growing season.

SAMPLING AND ANALYTICAL METHODS

Water samples were collected during April and August of 1993. The August sampling was unfortunately interrupted by a rainstorm, and two of the creek sites, Stealey Ranch and Hwy 50, were sampled after the storm had passed at a time when inflow to Sixmile Creek from the Bessemer ditch was substantially increased. Implications of the increased flow are discussed below.

Specific conductance, temperature, pH and dissolved oxygen were measured at the time of collection. The waters were then filtered using 0.45 micron cellulose acetate membranes, and an aliquot was bottled for nitrate, nitrite and ammonium analyses. During the August sampling, a larger 1 L aliquot was bottled and preserved with mercuric chloride for isotopic analysis. To test the necessity of the preservative for the isotope analysis, the filtered water collected at Stealey Ranch Spring #2 was stored in separate bottles with and without mercuric chloride. All water samples were stored under refrigeration until they were analyzed. Liquid fertilizer samples were collected directly from holding tanks and were stored in polyethylene bottles.

Nitrate concentrations were determined by ion chromatography with a reproducibility of ±10% or better based on replicate analyses of standards. Nitrite and ammonium were determined by colorimetry. In all cases the waters were at or below the minimum detection limits of 0.01 mg/L NO_2-N and 0.1 mg/L NH_4-N. The dissolved oxygen measurements have an estimated reproducibility of ±20%, somewhat larger than normal due to larger-than-normal instability in the instrument.

For the nitrogen isotopic analysis, nitrate was separated from water samples and ammonium from liquid fertilizers using standard steam distillation techniques (Keeney and Nelson, 1982; Knoke et al., 1993). The distillates were evaporated to dryness and the resulting solids were combusted to form N_2 gas following Kendall and Grim (1990). Nitrogen isotope ratios were determined by admitting the gases to a Finnigan MAT 252 mass spectrometer and comparing them to a pure N_2 reference gas that had been previously

calibrated against NIST standards. The compositions are given herein in δ-notation relative to air N_2 where

$$\delta^{15}N \text{ (in permil)} = \left(\frac{(^{15}N/^{14}N)_{sample}}{(^{15}N/^{14}N)_{air}} - 1 \right) \times 1000.$$

The values reported for each sample are averages of two or more separate distillations

The reproducibility of nitrate $\delta^{15}N$ measurements, based on repeated analysis of a standard solution, was ±0.4 permil (1-σ, n=9). Reproducibility of fertilizer ammonium $\delta^{15}N$ measurements was ±0.2 permil, based on repeated analysis of an ammonium standard solution (n=3). The nitrogen gases derived from nitrate standard solutions were consistently 0.7 permil lighter than the gases derived by direct combustion of the KNO_3 from which the solutions were prepared. We infer this to be the result of incomplete conversion of nitrate to ammonia during the distillation, and we have corrected our analyses of unknowns by this value. Nitrogen gases derived from ammonium standard solutions were isotopically indistinguishable from the gases derived by direct combustion of the starting $(NH_4)_2SO_4$.

RESULTS

The nitrate concentrations and $\delta^{15}N$ values are given in Table 1. For the August sampling the Stealey Ranch and Hwy 50 sites, both of which were sampled after the rainstorm, had specific conductance values about half that observed in creek samples collected prior to the rainstorm. The increased flow of low conductance ditch water undoubtedly led to substantial dilution of the creek, leading to lower observed nitrate concentrations. Nevertheless, the nitrogen isotopic composition of dissolved nitrate is unaffected by dilution because Bessemer ditch water carries very little nitrate.

Data for the April sampling indicate that the nitrate concentrations in Sixmile Creek waters are significantly lower than those in spring and tributary waters feeding the lower portion of the creek. The creek waters exceed the U.S. EPA MCL of 10 mg/L NO_3-N only at the Hwy 50 site whereas the spring and tributary waters are nearly twice the MCL. A contrast between creek waters and spring/tributary waters is also apparent in the data for the August sampling (Table 1).

Cain (1985) reported nitrate concentrations for Sixmile Creek samples collected in 1976 and 1978 at the same Hwy 50 site sampled for this work. A comparison of his results with ours is shown in Figure 2. Given the small number of analyses for 1993 and the apparent sensitivity of nitrate concentration to creek discharge, it is impossible to determine any significant change in nitrate in the creek from 1976 to 1993.

Sixmile Creek waters also contrast with spring/tributary waters in the isotopic composition of nitrate. In August 1993 the creek waters were -1.8 to 1.6 permil whereas the spring and tributary waters were several permil heavier at 3.6 to 5.6 permil. The two liquid fertilizer samples have ammonium nitrogen isotopic compositions near zero permil (Table 2). This is a composition typical of commercial fertilizers inasmuch as they are synthesized from atmospheric nitrogen which has a δ-value of zero permil (c.f., Heaton, 1986).

Dissolved oxygen concentrations for Sixmile Creek waters were 6-11 mg/L, in close agreement with the 7-12 mg/L range observed by Cain (1985) at the Hwy 50 site. Spring waters were slightly less oxygenated at 3-7 mg/L. To determine the degree of oxygenation of waters within the shallow aquifers underlying the study area, dissolved oxygen was measured in standing water some 20 feet below the ground surface in a well above Bessemer ditch (Fig. 1). The concentration was found to be below the detection limit of 0.2 mg/L.

DISCUSSION AND CONCLUSIONS

A plot of nitrate concentrations along Sixmile Creek shows a dramatic increase downstream from Bessemer irrigation ditch (Fig. 3). Samples collected during April show a 100-fold increase over a distance of about 5.5 miles. There is a slight decrease in nitrate as the creek flows through a small slough, probably reflecting bacterial denitrification. Nitrate commonly becomes an electron acceptor in anoxic stagnant waters, and it is transformed to N_2 or N_2O which are dispersed as gases (Hallberg and Keeney, 1993). Nitrate begins to increase rapidly at about three miles from the ditch. At this point the stream emerges from a narrow valley, some two miles wide, onto a broad plain underlain by an alluvial terrace of the Arkansas River. The transition corresponds to a change ir ground- and surface water inflow to the creek. Above the transition irrigation-return is derived only from fields immediately adjacent to the creek. Surface runoff is more rapid than farther downstream inasmuch as the fields are more steeply sloping. Below the transition irrigation-return is derived from a much larger area and subsurface flow is more efficiently focussed toward the creek in a well-developed unconfined aquifer in terrace gravels.

The nitrogen isotopic composition of nitrate also increases downstream (Fig. 3). The increase is 3.4 permil over the lower 2 miles of the creek, more than 8 times the analytical error for an individual measurement. The -1.8 permil value at South Road is somewhat lower than the value determined for ammonium in the liquid fertilizer samples (Table 1). The negative fractionation may indicate that oxidation of the applied ammonium was not yet complete when the nitrate was flushed out of the soils (e.g., Heaton, 1986). On the other hand, -1.8 permil is within the range reported for fertilizers by other workers (Heaton, 1986; Hübner, 1986). It is entirely possible that fertilizers somewhat lighter than those analyzed for this work were also applied to the fields. A negative and/or small fractionation with respect to the fertilizer is consistent with the hypothesis that delivery of fertilizer-derived nitrate to the creek was rapid enough to prevent any significant transformations from occurring along the flowpaths.

The progressive increase in $\delta^{15}N$ downstream is undoubtedly due to inflow of high-nitrate, isotopically-heavy spring waters, such as those sampled at Stealey Ranch, and tributary waters, such as those sampled at Stealey Ranch and the pond outlet. Figure 4 shows a comparison of the data with a simple two-component mixing model. For the purpose of the model, the creek water component was assumed to have the same nitrate concentration and $\delta^{15}N$ value as the South Rd sample collected in August, 2.7 mg/L NO_3-N and -1.8 permil, respectively. The spring/tributary component was assumed to have a nitrate concentration of 20 mg/L NO_3-N and a $\delta^{15}N$ value of 4.5 permil; both figures are averages of the four analyzed samples. Surface runoff and groundwater return to the creek from irrigated fields is clearly variable in nitrate concentration and isotopic composition, and the model represents a simplification. However, changes in the nitrate concentration and isotopic composition of the spring/tributary component do not result in substantial changes in the shape of the mixing hyperbola or in the position of its lower end. The principal change is in the amount of inflow water required for a given shift in the isotopic composition of the creek water. The agreement of the data with the model curve is fairly good and it would improve for the creek waters if one were to double the nitrate concentrations for the two downstream data points to account for the roughly 50 percent dilution effect discussed earlier. The agreement strongly supports the hypothesis that shallow groundwater inflow from fields covering the Arkansas River terrace are responsible for the rise in nitrate in lower Sixmile Creek.

The nitrate flux from fields along the lower section of Sixmile Creek is undoubtedly due to agricultural activity, but the heavy isotopic compositions indicate that the fertilizer

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nitrogen has undergone transformations which fractionated the isotopes. There are two possible origins for the isotopically heavy nitrate, either or both of which may apply to the study area. First, the nitrate may be derived from mineralization of soil organic compounds. The organics most likely are crop residues inasmuch as these fields have a long history of cultivation and any leachable native organics are sparse and probably long removed. Organic-derived nitrate varies in $\delta^{15}N$, but a number of studies have shown that mineralization can produce nitrate with $\delta^{15}N$ values of 5-6 permil (see Heaton, 1986 for review). The predominance of organic-derived nitrate in the lower portion of the creek may reflect the vastly larger area of cultivation compared to the upper portion of the creek, and may reflect longer residence times for irrigation-return waters in the soils of more flat-lying fields.

The second possible origin for isotopically-heavy nitrate is denitrification in the shallow unconfined aquifer. This bacterially-mediated process has been documented in previous studies of aquifers similar to those underlying the Sixmile Creek watershed (see Trudell et al., 1986 and references therein). Denitrification can proceed only in anoxic waters. The single well water sample in which dissolved oxygen was measured demonstrates that anoxic conditions can be attained at least locally in the aquifers underlying the area. The extent to which this single measurement is representative of the entire area is unknown. Denitrification is characterized by a large kinetic isotope fractionation of some 25 to 35 permil (Heaton, 1986). The large fractionation implies that nitrate loss of some 15 percent would be sufficient to shift the $\delta^{15}N$ value of the remaining fertilizer-derived nitrate to the 5-6 permil range observed in the spring and small tributary waters. Denitrification is likely to be more important for waters that have longer residence times in the aquifer. The mean groundwater flowpath beneath the Arkansas River terrace is undoubtedly longer than at higher elevations where the drainage basin is narrower and steeper-sided. If flowpath length correlates with the residence time of groundwater within the aquifer, then the downstream increase in $\delta^{15}N$ is what would be predicted for denitrification.

In summary, there is a strong positive correlation between intensity of agricultural activity and concentration of dissolved nitrate in the Sixmile Creek drainage. The nitrogen isotope data support the conclusion that fertilizer is responsible for the high levels, but they indicate that the nitrate is delivered to the creek by more than one pathway. In the upper portions of the irrigated drainage, relatively small amounts of fertilizer-derived nitrate are delivered directly to the creek with little opportunity for isotopic modification. In the lower portions of the irrigated drainage, much greater amounts of fertilizer-derived nitrate are delivered to the creek but only after isotopic modification by either of two mechanisms. First, fertilizer nitrogen may be taken up by growing crops and then released to groundwater as nitrate during mineralization of crop residues. Second, fertilizer-derived nitrate may be transported directly to the creek through aquifers in which bacterially-mediated denitrification is proceeding.

ACKNOWLEDGEMENTS

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Table 1. Concentration (in mg/L NO_3-N) and nitrogen isotopic composition (in permil) of nitrate in water samples

Sample Location	NO^{3-} 4/93	NO^{3-} 8/93	$\delta^{15}N_{AIR}$ 8/93
Sixmile Creek:			
Bessemer Ditch	0.1		
Above Slough	0.19		
Below Slough	0.04		
South of Olson Rd	0.27		
Olson Rd	0.08	0.9	
South Rd	2.1	2.7	-1.8
Stealey Ranch	8.1	2.0*	0.7
Hwy 50	13	3.3*	1.6
Springs/Seeps:			
Stealey Ranch Spg #1	21	16	3.6
Stealey Ranch Spg #2 w/ $HgCl_2$	22.6	24	5.5
Stealey Ranch Spg #2 w/o $HgCl_2$	22.6	24	5.6
Surface Runoff:			
Side Drainage, Stealey Ranch		29	4.0
Pond Outlet	20	9.0	4.4

*Concentrations are artificially low compared with other samples collected in August because water collection followed a rainstorm that substantially increased Bessemer ditch overflow to the creek. See text for discussion.

Table 2. Nitrogen isotopic composition (in permil) of ammonium in liquid fertilizer samples

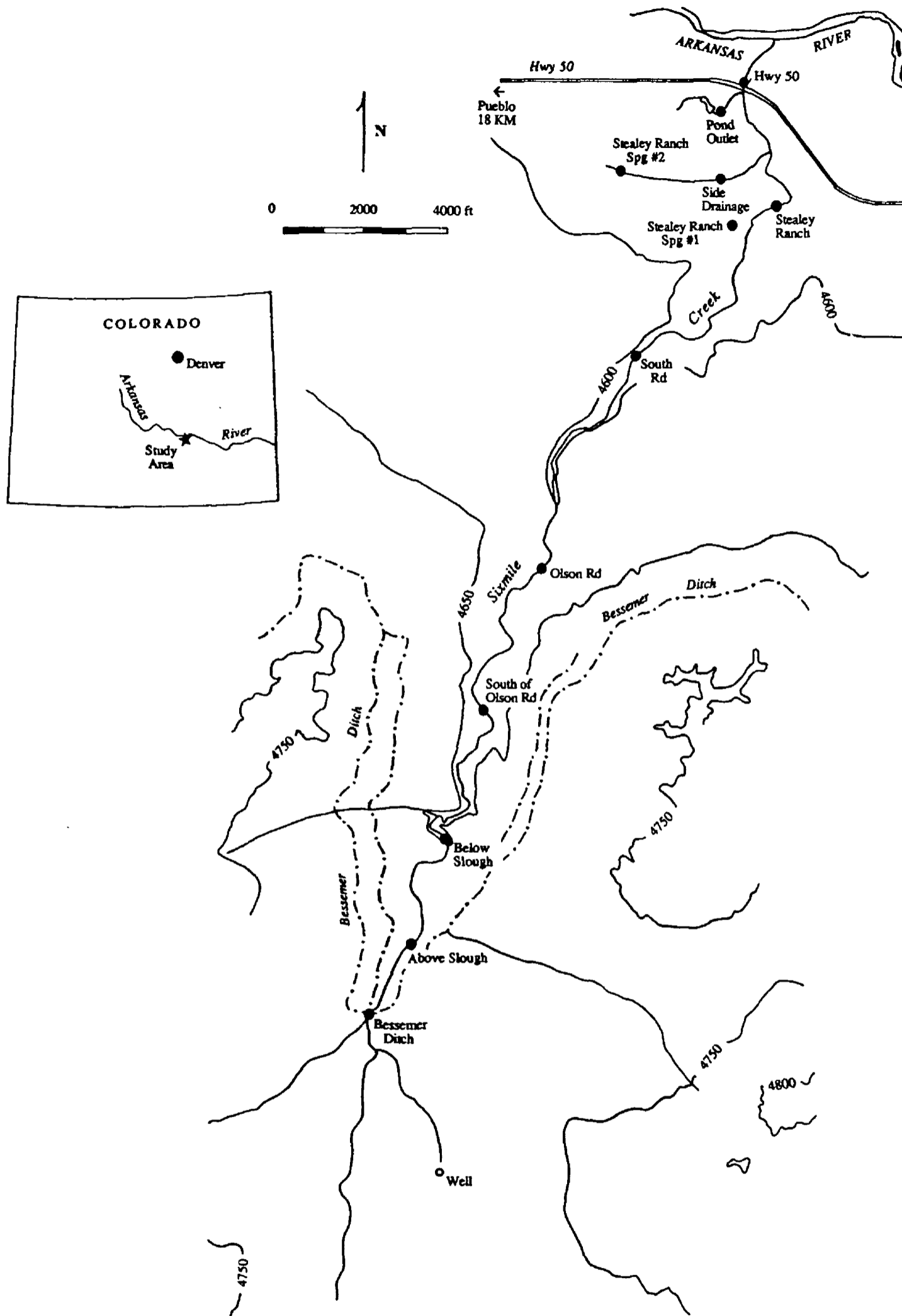| Sample	$\delta^{15}N_{AIR}$	Comments
10-34-0	0.1	Collected 8/93
10-34-0	-0.2	Collected 4/93

Figure 1. Map of the study area showing the lower portion of the Sixmile Creek drainage. All the land below Bessemer irrigation ditch is in cultivation, whereas the land above the ditch is undeveloped rangeland. Filled circles show the location of water sampling sites. Modified from the Vineland quadrangle 7.5' topographic map.
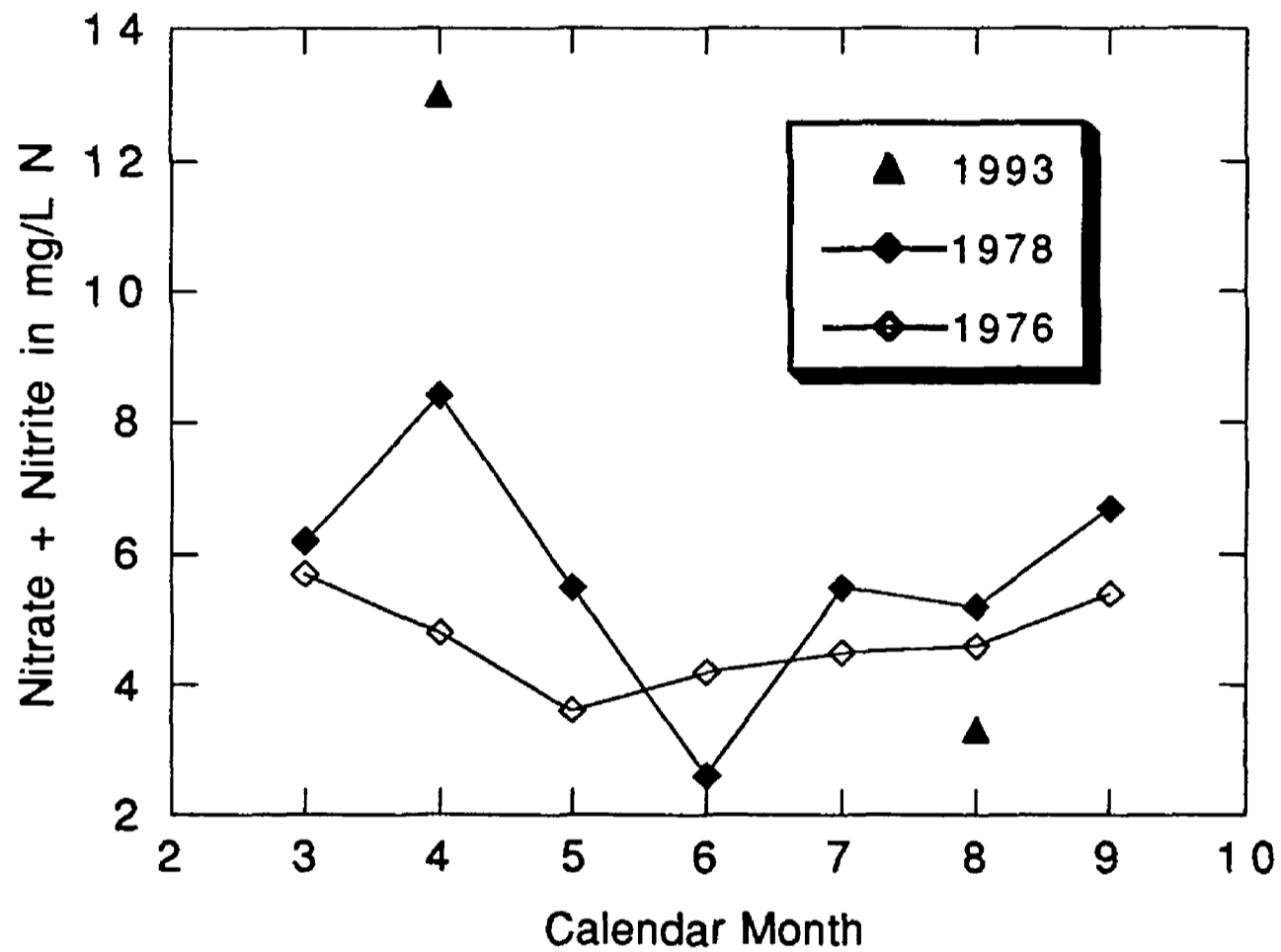
Figure 2. Concentration of nitrate+nitrite in Sixmile Creek at the Hwy 50 sampling site near the confluence with the Arkansas River. Data for 1976 and 1978 are from Cain (1985). The August 1993 sampling spanned a rainstorm which led to substantial dilution of the sample collected at the Hwy 50 site (see text for discussion).
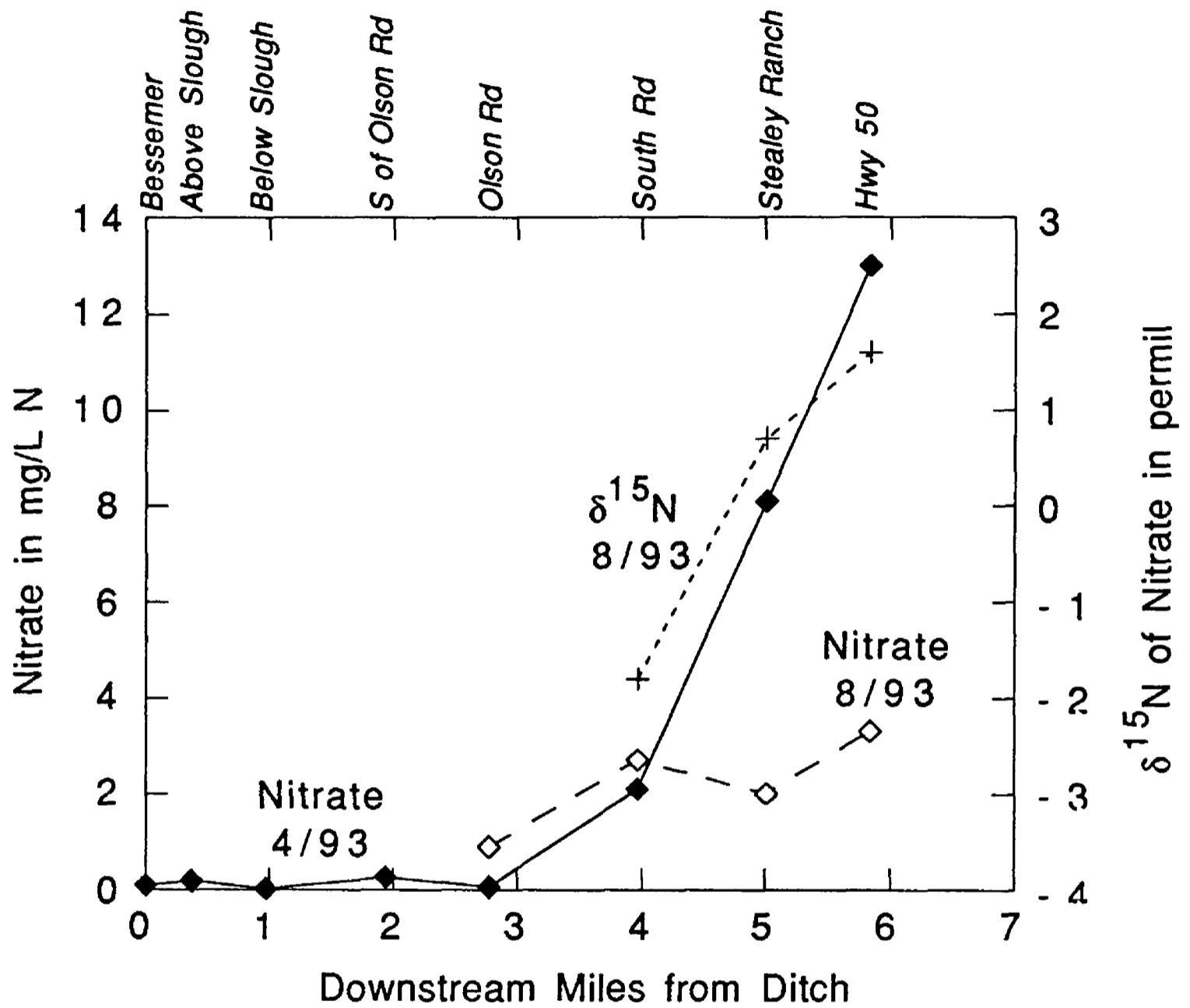
Figure 3. Concentration and nitrogen isotopic composition of nitrate in Sixmile Creek
waters collected in April and August 1993. Isotopic data were obtained only for
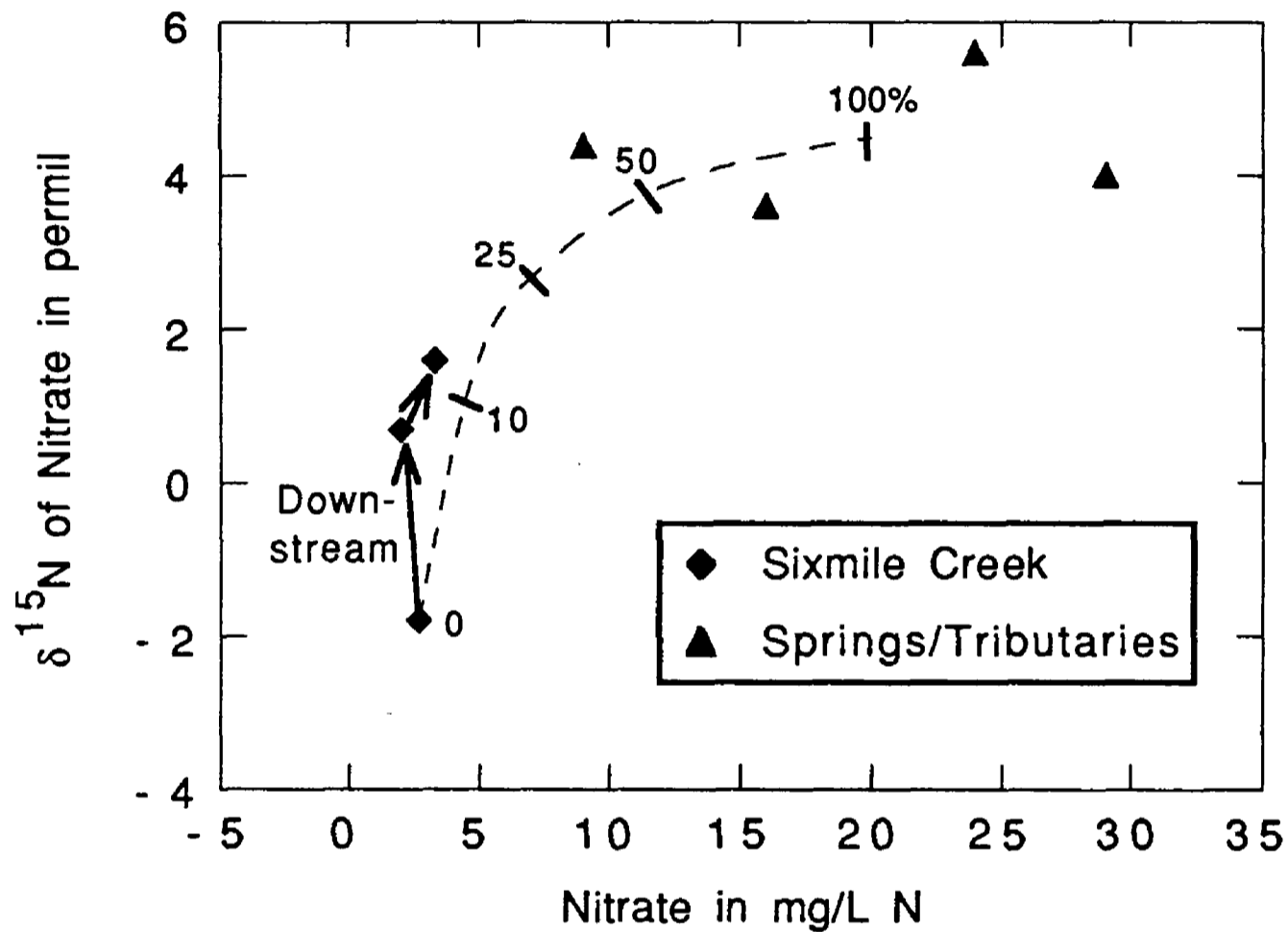the August sampling.

Figure 4. Nitrate concentration and nitrogen isotopic composition for creek and spring/tributary waters collected during August sampling. The dashed curve is a mixing model which describes progressive addition to the creek of waters like those emanating from the sampled springs and tributaries. Percentages are the amount of water added. The rapid downstream increase in $\delta^{15}N$ is what is expected for inflow of high-nitrate, isotopically-heavy spring/tributary waters.