Evaluating Nitrate Sources in Nested Agricultural Sub-Basins Using Nitrate Stable Isotopes

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H51C-05

INTRODUCTION

The U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program began a pilot study to investigate the transport and fate of fertilizer and other agricultural contaminants into streams and groundwater. The $\delta^{15}N$ and $\delta^{18}O$ of NO_3 were used to track NO_3 as it moved through an agricultural or urban dominated basin or a large integrator site. Samples were collected from four storms to measure water quality: (1) in the spring prior to fertilizer application and planting, (2) after fertilizer application, (3) early summer during peak growing season, and (4) late summer/early fall during the growing season. Questions we hope to answer in this pilot study are:

1.Are there significant differences in isotopic composition between sites with different land use?

2. Is there temporal variability within a site and is this related to agricultural practices, i.e. fertilizer application, peak growing season?

3. Are there event related shifts in isotopic values and hence nitrate sources?

4.Can the isotopic fingerprint be lost as the drainage basin increase?

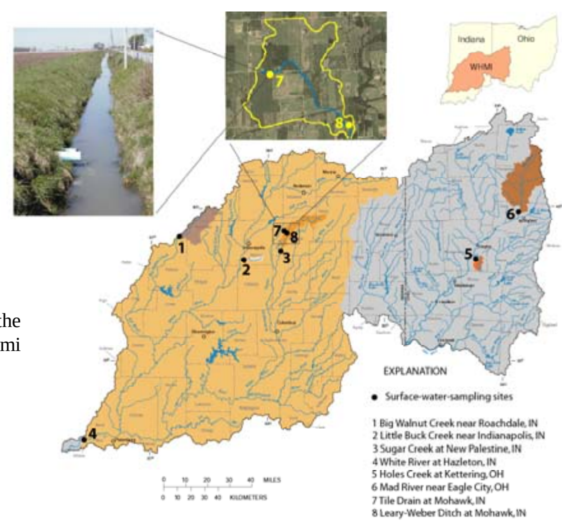

Fig. 1. Site locations in the White – Miami River Basin

Site Name	Basin Area (km^2)	Land Use (%) Urban	Ag	Undev.	Forest	Other
Tile Drain at Mohawk, IN	0.04	--	100	--	--	--
Leary Weber Ditch at Mohawk, IN	7.2	--	93	--	2	5
Sugar Creek At New Palestine, IN	246	3	95	1	1	< 1
Little Buck Creek Near Indianapolis, IN	45	57	42	< 1	< 1	< 1
White River At Hazleton, In	29,291	7	69	23	22	1

Table 1. Basin information including basin area, and land use.

Site Description and Methods

Nutrient and stable isotope data were collected at **Sugar Creek, IN** and two sites nested within the Creek, a **tile drain and Leary-Weber Ditch** (Fig. 1 & Table 1). **Sugar** Cr. drains **soy and corn fields---** a small amount of manure is applied only at Sugar. Samples were also collected at **Little Buck Creek** near Indianapolis, a small intermittent urban stream and **White River at Hazleton**, a large river site that integrates all of the West and East Fork White River. There are no wastewater treatment facilities at either of these sites.

Typically, anhydrous ammonia is applied to corn in early spring (April), depending upon weather and field conditions and prior to planting. 2003 was a typical water year and fertilizer was applied on different fields in Leary-Weber Ditch on April 15, and April 23-24. Some fields have a second application applied as a side dressing once the crops have emerged. In this manner, less N is lost to denitrification and leaching because N is applied closer to the time crops are actively growing and taking up N. Also, by measuring the amount of NO3 in the soil prior to application, it is possible to target the amount of N needed.

Stable isotopes (methods ref 1,2,3,4,5) used in conjunction with other data can be used to determine NO3 sources. This is because the isotopic fingerprints of atmospheric, fertilizer, soil, and manure-derived NO3 are often sufficiently distinct to permit separation (Fig. 5).

$\delta^{15}N$, $\delta^{18}O$ of NO3 top panel   Discharge and NO3 concentrations bottom panel

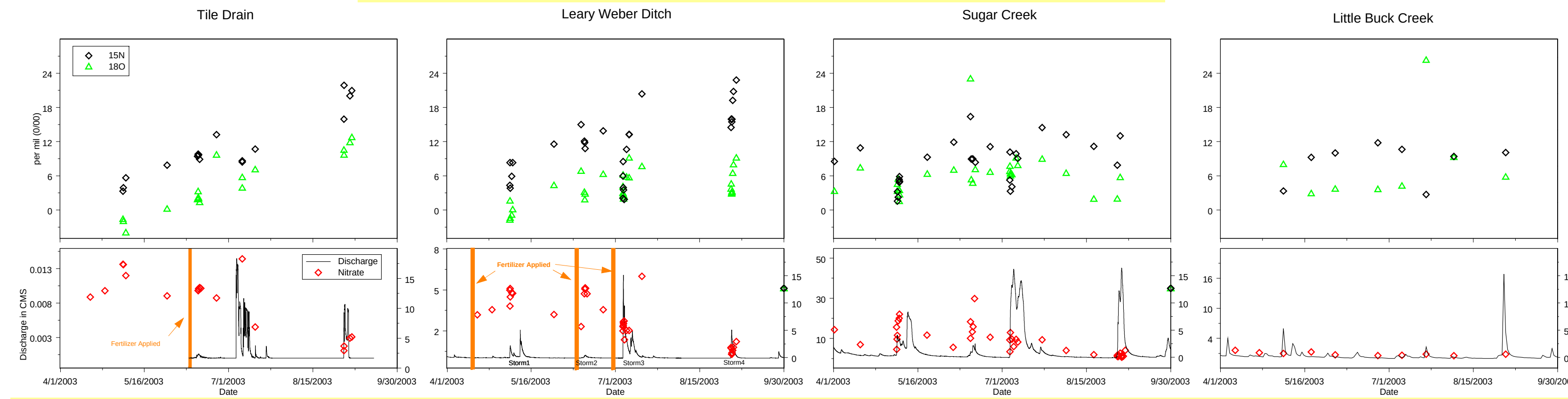

Fig 2. Stable isotope values at nested agricultural sites (Tile & LWD) become heavier with time as [NO3] decline. As [NO3] decline (plant uptake and possible denitrification), isotopic values shift from light "fertilizer" in early spring storms to heavier NO3 left after plants take up light NO3 and possible denitrification. Sept. storms may also bring atmospheric NO3 enriched in $\delta^{18}O$ ● These patterns were not seen at Sugar, a much larger site 246 km^2, probably because the fingerprint is "lost" due to mixing. ● [NO3] at the urban site were low and the isotopic values more constant.

Nitrate Concentrations and δ15N and δ18O Values in Leary Weber Ditch

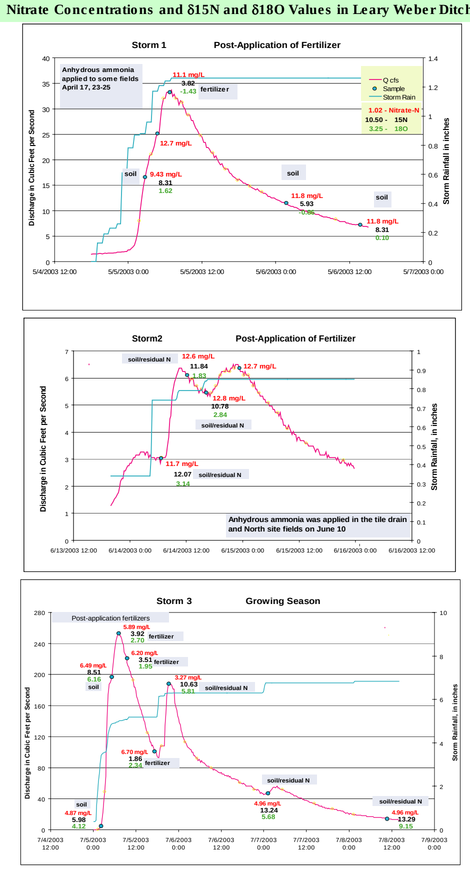

Fig. 3. NO3 concentrations, discharge, and isotopic values for three storms at LWD.

Storm 1

The storm hydrographs show changes in nitrogen sources over the growing season and during the course of a storm. During storm 1 after application of anhydrous ammonia, soil NO3 was carried by the rising limb. As soil NO3 was "flushed" down into the tiles and into the Ditch, it was replaced by fertilizer. By the end of storm 1, the isotopic signature returned to soil nitrate.

Storm 2

Storm 2 in mid-June was small, without an overland flow component. All isotope samples had soil/residual NO3 signatures.

Storm 3

Storm 3 in early July was the biggest of the year and had a double rise in the hydrograph. The isotopic signatures on the first rise started at soil NO3 but switched towards fertilizer as discharge peak ed and fell. The isotopic signature changed dramatically for the second peak in Storm 3 and looked like a mix of soil.

Storm 4 (not shown)

By storm 4 early Sept, [NO3] decreased 3-5 fold and there was a consistent signature of heavy NO3, possibly a mixture of atmospheric/residual NO3 not taken up by plants/denitrification. The concentration of NO3 in rain during this time was ~1.1ppm. Similar patterns were also seen at the Tile Drain.

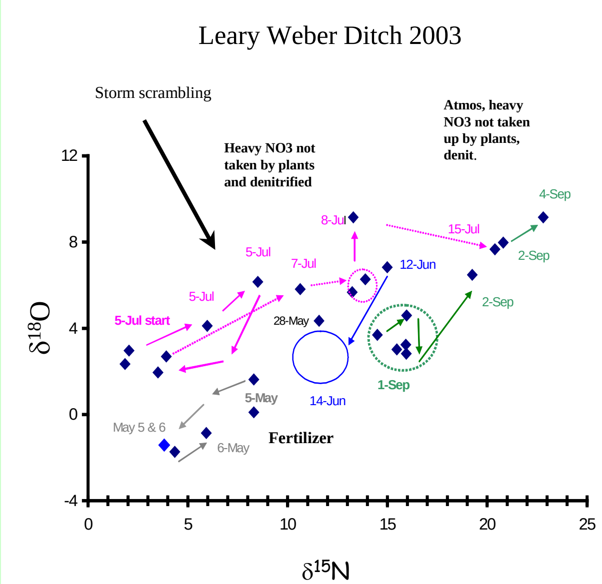

Fig. 4 Isotopic fingerprint becomes heavier with time as NO3 concentrations decline. Over the period of a storm different kinds of NO3 are pulled into LWD. Early May storm brings soil, then fertilizer NO3. End of May storm brings heavy NO3 (plants took light NO3 or denitrification). At the beginning of the big July 4 storm, fertilizer, then more soil /atmospheric NO3 as Q increases. July 15 heavier NO3 (plants took light NO3 or denitrified) June 12 small storm moves denitrified or residual heavy nitrate. Early Sept. some atmos NO3 mixing with remaining heavy NO3 (plants took up light NO3 or denitrification).

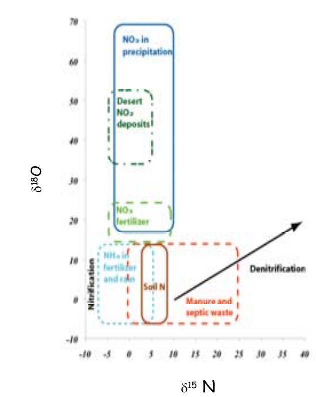

Fig. 5 Cartoon showing relative delta values of different NO_3 sources. In this study small amounts of manure are applied at Sugar Creek only.

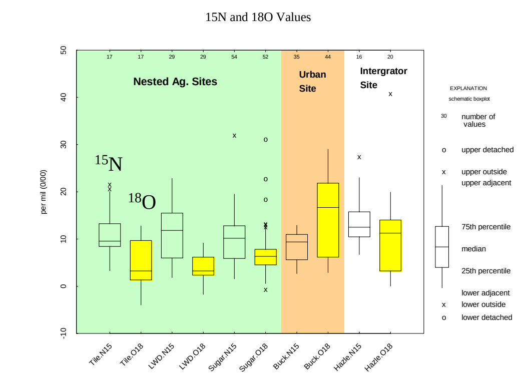

Fig.6 Box Plot of $\delta^{18}O$ and $\delta^{15}N$ of NO_3. The three agricultural sites (Tile, LWD, Sugar), have similar fingerprints, the urban site, L.Buck has heavier $\delta^{18}O$ values (atms) and the integrator site has values that span both ranges.

CONCLUSIONS

Questions we sought to answer

Are there significant differences in isotopic composition between sites with different land use? YES

Are there event related shifts in isotopic values and hence nitrate sources? YES

Is there temporal variability within a site and is this related to agricultural practices, i.e. fertilizer application, peak growing season? YES

Can the isotopic fingerprint be lost as drainage size increases? YES

SUMMARY

The isotopic fingerprint of the urban site was distinguished from agriculturally impacted sites ($\delta^{18}O$ values < 13 ‰; $\delta^{15}N$ up to 22‰) by higher $\delta^{18}O$ values (up to 29‰) & $\delta^{15}N$ that was low and constant (< 15‰). The large integrator site had isotopic values that encompassed both urban and agricultural finger prints:$\delta^{18}O$: 6 to19 ‰; $\delta^{15}N$ 6 to18‰.

At the agriculturally impacted sites, the isotopic signature of NO_3 became progressively heavier from early spring to late summer as NO_3 concentrations declined. Declining NO_3 concentrations are attributed to plant uptake[6] and possible denitrification. High NO_3 concentrations in early spring storms following fertilizer application were accompanied by an isotopic fertilizer fingerprint. Early summer storms were characterized by lower NO_3 concentrations due to plant uptake, possible denitrification, and heavier isotopic values. Late summer storms were characterized by lower nitrate concentrations and higher isotopic values, which are explained by plant uptake, possible denitrification, and atmospheric nitrate.

Changes in the isotopic composition of NO_3 were also seen during individual storms.

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