Biogeosciences **Disucssion: Review of Heffernan et al. "Denitrification and inference of nitrogen sources in the karstic Floridan Aquifer"**

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General Comments

Heffernan et al. have conducted a carefully-constructed investigation into the fate of nitrate within the Upper Floridan Aquifer (UFA). The authors present a study that was well thought out and executed, and involved the collection and analysis of an impressive number of water samples from 33 springs discharging from the Floridan Aquifer, as well as the incorporation of published spring data for a total of 113 spring locations. From these data, the authors attempted to measure the degree of denitrification on a regional basis in the UFA by using noble gases to predict excess N_2 concentrations and by using nitrate isotopic signatures to identify the sources and fate of nitrate. Using multiple lines of evidence, they conclude that denitrification is a major factor accounting for the loss of about one third of the estimated nitrate inputs to the UFA.

Specific Comments

The authors discuss the collection and analyses of field parameters, nutrients and isotopic analyses but do not include any data tables or a reference where the newly collected data can be accessed. There also seems to be a lack of nitrate or ammonium concentrations and nitrogen isotope values for end members such as sewage effluent, soil organic matter, fertilizer-nitrogen, precipitation/atmospheric inputs for the study area. The authors do have a short discussion that the geochemistry of the UFA is a mixture of two end members, older anoxic water, low in nitrate, characteristic of deep flowpaths through matrix type porosity with younger oxic, nitrate enriched water characteristic of shallower flowpaths through macro/conduit type porosity (p. 10252, lines 23-26). However, no data are given showing ranges of concentrations or isotopic compositions representative of these groundwater end members. Some references to published data for end member values would be beneficial as would a reference where the newly collected data could be accessed; such information would help future investigators studying similar environments.

The authors' state that UFA groundwater is a mixture of two end-member waters (old and anoxic and young and oxic) as discussed above. However, karst aquifers are usually more complex than a dual-porosity system. The authors should consider the soil zone and the Surficial Aquifer overlying the UFA as possible sites of denitrification especially since many of the springs in this study are located where the UFA is unconfined (based on Figure 2 of Plummer and Sprinkle 2001). Further, sinkhole lakes are possible sources of organics and sites for denitrification prior to entering the UFA. Sinkhole ponds overlying caves of southwestern Illinois' sinkhole plain are constantly discharging into the caves, and the incoming seepage water is typically very low in nitrate (by a factor of 10 or more) and sulfate (by a factor of three or more) relative to cave-stream and spring water (Panno, ISGS, unpublished data). Work by Sacks et al. (1998) suggests that some of the sinkhole lakes in Florida breach the intermediate confining unit thereby allowing leakage of lake water into the UFA. Whereas, recharge water from the Surficial Aquifer feeding sinkhole lakes of Highlands County, Florida have nitrate-N concentrations ranging from <0.02 to 36 mg/L, only 3 out of 10 lakes studied had measureable nitrate (Sacks et al. 1998). However, given the abundance of large sinkhole lakes in northern and central Florida, it is likely that residual nitrate from some nitrate-enriched lake water would be seeping through reduced lake sediments into the UFA. Tihansky and Sacks (1997), observed evidence of denitrification in the shallow upper aquifer zone of lake basins in Polk and Highlands Counties in Central Florida. In addition, there are peat deposits within the Surficial Aquifer at least in the southern part of the study area (Basso and Hood 2005). Katz and Choquette (1991) studied the aqueous geochemistry of the sand and gravel aquifer in northwest Florida and found no significance changes in major ion chemistry with depth and distance within the aquifer, with the exception of sulfate. It is possible that the loss of sulfate in the sand and gravel aquifer is an indication of sulfate reduction in Surficial Aquifer suggesting noteworthy reduction may be occurring in the shallower aquifers overlying the UFA or perhaps the influx of sulfate-depleted water from sinkhole pond seepage. Studies in the sinkhole plain of southwestern Illinois suggest that the shallow hydrogeologic system including the soil are probable sites for denitrification primarily due to oxidation of DOC (Hackley et al., 2007). Overall, the lakes, soil zone, springshed margins, and peat deposits could provide the reducing conditions responsible for some of the denitrification observed in the spring water of the study area, and should be considered as possible sites of denitrification prior to entering the UFA.

The authors indicate that the source of electron donor initiating denitrification in the UFA is unknown because dissolved organic carbon (DOC), typically considered the predominant electron donor for denitrification, is of very low concentration in the UFA springs. However, Duarte et al (2010) indicated that it was primarily the large discharge springs of the UFA that exhibited low DOC (<0.2 mg/L) while many of the smaller discharge springs (<~2.8m^3/S) showed substantially higher amounts of DOC (~0.5 to 0.9 mg/L). Those UFA springs with greater discharge also contained greater nitrate concentrations whereas those springs with lower discharge contained much lower nitrate concentrations (our Figure 1) (Florida Springs Task Force, 2000; Duarte et al., 2010). Additionally, Plummer and Sprinkle (2001), using wells ranging from 34 to 351 feet deep, reported DOC concentrations in the UFA (confined portion in the study area of this review article) ranged from 0.1 to 7.0 mg/L with a median concentration of 2.15 mg/L (n = 26). If DOC concentrations range as high as 0.9 mg/L within some of the springs and possibly higher within the matrix of the UFA, it seems plausible that DOC could be one of the primary sources of electron donors for denitrification observed by Heffernan et al., especially considering that the concentration of nitrate-N in the UFA springs they analyzed ranged from 0.2 to 0.9 mg/L (Fig. 3, p. 10288). Plummer and Sprinkle (2001) also propose sulfate reduction occurs in parts of the UFA via microbial degradation of organic carbon which would suggest that organic carbon would be the most likely electron donor for microbial denitrification in this system. Heffernan et al. suggest that other alternative electron donors such as iron and sulfide could be acting as the primary reducing complexes which are always a possibility. As suggested by the authors, a correlation of iron and sulfate with denitrification should result; however, the authors indicated that exploration of alternative denitrification pathways were beyond the scope of their study (p. 10268, lines 22-29, p. 10269, line 1-2).

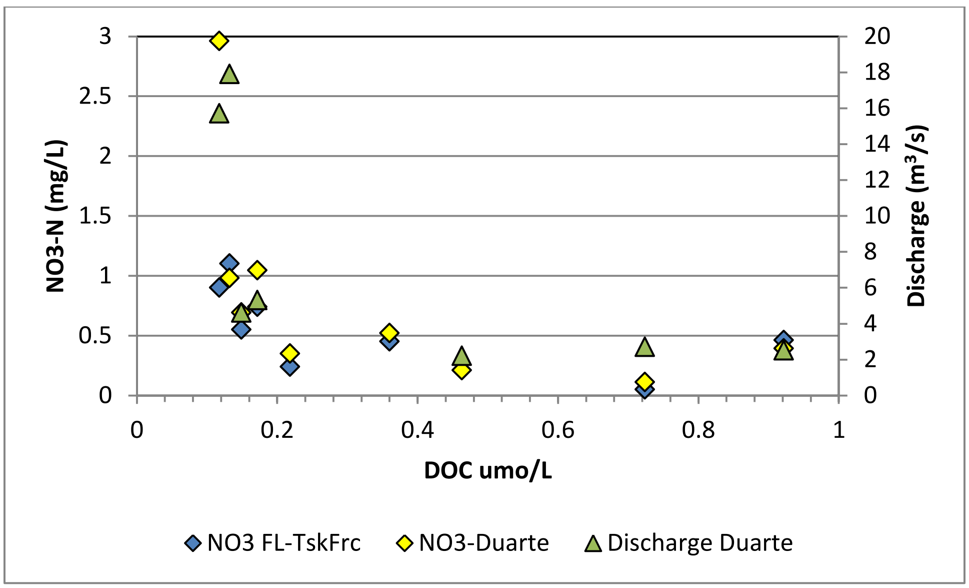

Figure 1. Nitrate concentrations (diamonds) and discharge (triangles) vs dissolved organic carbon (DOC) for springs from UFA (Duarte et al., 2010; Florida Springs Task Force, 2000).

Summary

The authors of this manuscript satisfy their objective in this investigation. However, in the course of their efforts, they did not identify nitrogen-source end members either chemically or isotopically (e.g., agricultural sources, sewage), nor did they characterize their geochemical end member from the UFA (i.e., older groundwater from matrix porosity and deeper flow systems, and younger groundwater from shallow flow paths and conduit flow systems). These easily could be summarized from published literature in a table whose values and used for comparison with their data.

Other sources of residual nitrate should be considered other than the shallow/conduit and deep/matrix flow systems. Specifically, the authors should consider the soil zone, the Surficial Aquifer overlying the UFA, and leakage from sinkhole lakes as possible sites of denitrification.

The argument that DOC within the UFA is too low in concentration to be responsible for denitrification seems too generalized. The authors do not define "low" and should do so. Our examination of the literature suggests that DOC in the UFA is quite variable and potentially adequate to denitrify at least some of the nitrate entering the UFA given its relatively low concentrations. Although the authors indicated that exploration of alternative denitrification pathways were beyong the scope of their study, it would be beneficial for the authors to add more information from references on the ranges of other potential electron donors within the UFA.

The effects of low flow vs. high flow springs on DOC and nitrate concentrations is apparent in published literature (our Figure 1) and should be addressed in more detail.

Technical Corrections

p. 10251, line 15. "counfounded" should be "confounded"

p. 10251, line 15. Another recent paper studying denitrification in karst environments is: Hackley, K. C., S. V. Panno, H.H. Hwang and W. R. Kelly, 2007, Groundwater quality of springs and wells of the sinkhole plain in Southwestern Illinois: Determination of the dominant sources of nitrate. ISGS, Circular 570.

p. 10261, line 27. "reach" should be "each"

p. 10263, line 10. Delete "of"

p. 10268, line 2. Suggest authors include (Tihansky and Sacks, 1997): Tihansky, A. B. and L. A. Sacks, 1997, Evaluation of nitrate sources using nitrogen-isotope techniques in shallow ground water within selected lake basins in the Central Lakes District, Polk and Highlands Counties, Florida. USGS, Water-Resources Investigations Report 97-4207.

p. 10268, line 27. SO4 should be double minus.

p. 10271, line 11. "%" symbol should be "‰".

p. 10272, line 17. Change to "contrast".

p. 10293, Fig. 8 Caption. The graphs labeled “c” and “b” don’t go along with the caption descriptions and should be switched. The graph labeled “c” show $\delta^{15}N$ vs $[NO_3]_R$ for springs that belong to the Ichetucknee River while the graph labeled “b” show the relationship between $\delta^{15}N$ and $\delta^{18}O$.

References

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