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Interactive comment on “Denitrification and inference of nitrogen sources in the karstic Floridan Aquifer” by J. B. Heffernan et al.

Anonymous Referee #1

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This study quantifies denitrification in a generally confined groundwater aquifer (the Upper Floridan Aquifer) that underlies the large, mixed land-use landscape of northern Florida. It estimates the role of denitrification in NO₃ removal, and in $\delta^{15}\text{N}$ isotope fractionation. This is an important study for both management purposes and for basic biogeoscience; aquifer denitrification may play an important role in mitigating eutrophication of northern Florida’s rich and diverse array of freshwater and marine habitats, and denitrification (and its role in regional N budgets) at very large spatial extents remains poorly constrained. The authors do an excellent job of framing their study, writing an introduction that clearly lays out the issue from the standpoint of management and basic biogeoscience knowledge gaps.

Their methods are innovative (i) in the new empirical data they collect (e.g., MIMS),

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(ii) in resourceful use of existing data, and (iii) in the creative but appropriate use of computed variables that defy direct measurement. Their methods section, however, was quite difficult to follow. My primary recommendation is that they rewrite it and perhaps ask a co-author who is less directly familiar with the study's data analyses and computation of derived variables to read it for clarity from the standpoint of the prospective audience. I make this recommendation for the authors' benefit, thinking that they might have better audience retention with a more straightforward methods section. I'm no specialist in aquifer denitrification or the use of conservative trace gases, but am quite well versed in nitrogen biogeochemistry generally, yet I found the connections between how the data were computed and what they meant or how they were used in hypothesis testing to be opaque. Here are some of my areas of confusion.

-1) The third paragraph of section 2.3. Is FAVA a single number, from which the authors extracted multiple hydrogeo variables? It's hard from the writing to determine when they are simply describing FAVA (e.g., what variables are input into it), and when they are talking about the variables they obtained for their own analysis. For example, "point observations of aquifer properties. . ." Are these point observations used in this study? Or are the authors generally describing how FAVA is computed?

-2) Where is Trec estimated? Sec. 2.4 starts with saying that Ne and Ar concentration were used to determine Trec. I see in Fig 2 that Ne and Ar are used as predictors of Trec in regression, but I don't see where the Trec data come from. The methods don't have an equation or model for Trec.

-3) Why both [N₂]den and [NO₃]R as estimates or proxies of denitrification? It seems that, broadly speaking, one is just the inverse of the other. Beyond this, do they tell us something different, yet complementary? Do they pertain to different subsets of the overall suite of sample sites/times owing to differential variability in the data used to compute them?

-4) First full paragraph on pg 10261. It seems like the authors are assuming ("denitrifi-

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cation rates in the Ich. Headspring are negligible) the very thing ([NO₃]R) that they are trying to estimate.

-5) Many figure axis labels are the authors' computed variables. This doesn't give the reader an intuitive feel for what the figure is supposed to convey. Use real words to ecological or biogeochemical meaning in axis titles.

-6) What's the Ichetucknee Headspring? A common recharge point for all water eventually discharging into the six Ich springs?

To help alleviate some of these confusions, I would recommend that addition of one or more tables that plainly lay out (1) data sources, (2) variables (direct and computed) and what they mean ecologically, and (3) statistical analyses and how each is used either to test a hypothesis or compute a variable. If this would make the paper too long, maybe the isotopic fractionation component could be split off as another paper.

Aside from these areas of confusion, I have the following substantive concerns.

-1) First full paragraph, pg 10253. To what extent might increases in stream NO₃ concentrations reflect direct runoff (surface or surficial aquifer) into springs, and thus might not be a Floridan aquifer issue?

-2) Are previously published N₂ data comparable to those collected by the authors via MIMS? To what extent can these various data sources really be aggregated?

-3) Despite citing state geology resources in estimates of springshed area, can springshed area really be estimated? I'm not sure it's possible to delimit an area of land surface and state with any certainty that it is the catchment for a given spring. Is there adequate knowledge of Floridan flowpaths to do this? Isn't it possible that water discharging into central Florida springs has been in the aquifer since Georgia?

-4) First full paragraph on pg 10260. The assumption that denitrification is the only sink for NO₃ is essential to how the authors estimate [NO₃]init. I'm not sure that this is a good assumption. The authors point to low/no NH₄ and organic N (DON and PON) in

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spring vent discharge to support that assumption that DNRA and assimilation are negligible NO_3 sinks. This ignores the possibility that no NO_3 in recharging water ($[\text{NO}_3]_{\text{init}}$) is quasi-permanently retained in soil organic matter. Terrestrial N cycling research in the last decade has increasingly shown that soils accumulate N owing to rapid uptake in organic matter, but only slow remineralization. Since recharge points are likely to be organic matter-rich sinkholes (which the authors acknowledge in their discussion), the possibility is all the greater that an alternative sink for NO_3 is retention in sinkhole organic matter. This possibility highlights the importance of declaring where $[\text{NO}_3]_{\text{init}}$ “starts,” just above the land surface, or below the unconstrained surficial sediments at the top of the Floridan aquifer. These considerations are probably better seen as a departure for interesting discussion about this manuscript, and not as a strong critique on the authors’ NO_3 estimates. Likewise, DNRA rates could be really high, and be another NO_3 sink, yet go undetected as NH_4^+ at spring vents since NH_4^+ would bind with the clays in the Hawthorn formation. Again, just where does one begin considering $[\text{NO}_3]_{\text{init}}$ in these geologically diverse strata?

-5) The authors regress $\delta^{15}\text{N}$ vs. dissolved O_2 (DO) for springs with $n \geq 3$ observations, and obtain the correlations (r) and slopes (b) from these regression. Then, they regress r and b against DO for each spring. I’m always a little uneasy with regressing a computed variable (r and b , in this case) against one of the variables used to compute it (albeit r and b come from using discrete dO measurements, and are regressed against mean dO measurements, which of course are computed from the same discrete DO measurements used to obtain r and b). In this case, they find negative b values at low mean DO, and $b \sim 0$ at high mean DO values. This ultimately isn’t any different from figure 4b, showing declining $\delta^{15}\text{N}$ at low DO and flat $\delta^{15}\text{N}$ at high DO. So, I might jettison the analyses in figure 7.

-6) Higher $[\text{NO}_3]$ and lower $\delta^{15}\text{N}$ in springs with high DO is indeed consistent with the hypothesis that denitrification doesn’t happen where DO is high, as the authors argue. I’m not sure it rules out fertilizer application to the landscape as a source for that

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NO₃, however, which the authors seem to suggest, at least indirectly, by stating that denitrification, and not differential source contribution, is the primary driver of isotopic fractionation. It's worth noting that they don't really present an analysis in which denitrification (high vs low) and source contribution (inorganic fertilizer vs. organic sources) are crossed.

-7) Near the beginning of sec. 4.2, when the authors provide a regional estimate of aquifer denitrification of 122 kg km⁻² y⁻¹ (or 1.2 kg ha⁻¹ yr⁻¹), it is worth noting that this is a substantial fraction of wet inorganic N deposition inputs to this region. They should double check, but I think annual wet dep is about 2-4 kg per ha per yr, according to the National Atmospheric Deposition database (available online). They might highlight that aquifer denitrification spares surface waters from perhaps a third to a half of atmospheric dep inputs (albeit direct human N applications to the land surface are another problem).

Overall, this study used innovative methods (MIMS, dual gas tracers) and sophisticated analyses to estimate an important ecological process at a large spatial scale. I would primarily recommend making more clear the connection between how computed variables were derived, and how their analyses were linked to specific hypotheses. Otherwise, I look forward to seeing this work published.

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