

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

J. B. Heffernan et al.

james.heffernan@duke.edu

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Summary of reviews

We wish to thank all of the reviewers, including Pete McMahon, Samuel Panno and K.C. Hackley, and the two anonymous reviewers for their thorough and helpful comments on our manuscript. All four reviews seem to be positive about the manuscript, particularly the novel scale and scope of our measurements, the approaches used to estimate groundwater denitrification, and the implications for water quality management. Our revisions will therefore focus on the suggested improvements in context, presentation, and interpretation of our methods and results, which we believe will substantially improve the paper.

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Responses to general comments

Pete McMahon identifies three areas in need of clarification. The first of these concerns relates to the potential effects of mixing of water with different age (and thus chemistry) on estimates of denitrification and its relation to isotopic composition. We are aware of Green's 2010 work on mixing, and agree that further discussion of these effects is warranted. Since the effects of mixing on dissolved gases would be linear, we believe that the bias associated with estimates of excess N₂ at each spring are likely to be minimal. However, both the O₂ thresholds that support denitrification and isotopic changes resulting from NO₃ pool depletion are non-linear and thus potentially subject to mixing effects. Since we lack data for both contributing end-members and their relative contributions, quantitative analysis of mixing effects are not possible. In terms of qualitative assessment, the sharpness of the threshold in the observed O₂-N₂-den relationship in our study (Fig. 4), and the strong relationship between denitrification progression and isotope values suggest that mixing effects are unlikely to qualitatively influence our results. To the extent that they do, the effects would be to increase the apparent O₂ threshold that supports denitrification, and to reduce the slope of the relationship between denitrification progression and $\delta^{15}\text{N}$ -NO₃. The latter would result in a reduction in the apparent $\delta^{15}\text{N}$ -NO₃ of initial NO₃ pools, so the results presented in Fig. 9 would be underestimates of the differences between observed and initial isotope values. We intend to revise the manuscript to acknowledge these qualitative patterns, but will not be able to quantify their magnitude.

The second area identified by Pete McMahon concerns age dating. ³H/³He dates were obtained from the same sources that provided Ne data (ca. 30 springs), because noble gas data are used to assess contamination, but Dr. McMahon is correct to note that the source of these data is not made clear in the manuscript. We will revise the methods section to make clear the origin and scope of these data.

The third area identified by Dr. McMahon is the derivation of fractionation coefficients, and their subsequent use to estimate original source isotopic composition. The frac-

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tionation factors were derived from the slope of empirical relationships between the natural log of the residual nitrate pool and $\delta^{15}\text{N}$ - NO_3 (Fig. 8). However, the estimation of these slopes is not explicitly reported in the methods, and their values not directly reported in the text. We will revise the manuscript to correct both oversights.

S. Panno and K.C. Hackley raise several issues of ambiguity in the manuscript. The first of these is the lack of end-member measurements in our study. Studies of N sources in north Florida have relied on the measurements of Heaton (1986), whose summary values are $<6\%$ for synthetic sources, $>9\%$ for animal-derived sources, and Kendall (1998). Since 1) we do not perform quantitative end-member mixing analysis, 2) because the precise value of those sources may vary somewhat across our broad study region (and in time), and 3) because the thresholds we use to separate synthetic, animal-derived, and mixed N sources are those used by regional decision-makers, we believe that the values used in our analysis are most appropriate. However, we will revise the manuscript to clarify the basis for our values and those of the studies on which we rely.

A second issue raised by Panno and Hackley relates to the availability of dissolved organic carbon in the UFA and its potential role as an electron donor fueling denitrification. They point out the negative relationship, reported by Duarte et al. (2010), between discharge and DOC concentration in Floridan Aquifer springs. We wish to clarify that we do not intend to discount the potential role of organic matter in UFA denitrification. Rather, our intent is to highlight the influence of relatively low DOC concentrations on earlier assumptions that denitrification in the UFA was negligible, and to make readers aware of the emerging literature suggesting the importance of alternative electron donors in other aquifer denitrification studies. We also note that the DOC concentrations observed in small springs are still relatively low (typically $<1 \text{ mg L}^{-1}$), and that many of the springs in our study are relatively large (already noted on pg. 10270 ln. 5). We intend to revise the manuscript to clarify these points, and particularly to reduce the confidence with which we attribute denitrification to alternative electron donors rather

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than dissolved organic matter.

Panno and Hackley also request that raw data from this study be provided to readers. We intend to present all data (including measurements and derived estimates from earlier studies) in appendices organized by data type (i.e. O_2 and isotopes only vs. those with dissolved gas data), spring and date of measurement. We hope that other researchers will be able to take advantage of this resource; we will work with the associate editor to ensure online publication of the data.

The fourth major issue raised by Panno and Hackley, also raised by anonymous reviewer #1, relates to the effective boundaries of our study system. Both reviews correctly point out that denitrification could occur in soil horizons and other surficial environments or in overlying geologic strata, and resulting excess N_2 subsequently advected into the UFA. Our approach would be unable to distinguish this N_2 from that produced by denitrification within the UFA. For several reasons, we believe that the vast majority of the excess N_2 is derived from denitrification within the Floridan Aquifer. The first reason is that much of the water entering the UFA does so through sinkholes and other karst features in which contact with surface soils and other OM-rich environments is likely to be minimal. Second, the inflow of surface-derived excess N_2 would require that the denitrification occur after the last contact of infiltrating water with the atmosphere. Finally, the strong relationship between denitrification progression and $\delta^{15}\text{N}$ - NO_3 suggests that most of the denitrification is occurring subsequent to the last contact of infiltrating water with the atmosphere. If substantial portions of our excess N_2 were derived from surface soils, it is likely that at least some of that denitrification would occur prior to last atmospheric contact, which would result in retention of the isotopic but not nitrogen gas signal, disrupting the observed relationship. Nonetheless, we intend to revise the methods section (specifically, section 2.4) of the manuscript to reflect the ambiguity of the upstream boundary of our study system, and acknowledge that some unknown proportion of denitrification may be occurring prior to entry of water into the UFA per se.

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The other primary concern of anonymous reviewer #1 relates to the clarity of the presentation of methods. In response to reviewer #1's questions:

1) FAVA provides a quantitative assessment of aquifer vulnerability to pollution based on hydrogeologic features and geochemical and hydrogeologic proxies. Based on these variables, areas are assigned to categories of less vulnerable, vulnerable, and most vulnerable. The less vulnerable category is essentially absent in our study region, so we used the area of the 'most vulnerable category within each springshed to predict excess air entrainment. We will revise to manuscript to clarify these points.

2) For springs samples that included both Ne and Ar data, recharge temperature and excess air are calculated from noble gas concentrations, most proximately based by simultaneously solving Eqs. 1 and 2. Fig. 2 is intended to convey the dependence of these derived estimates on the concentrations of Ne and Ar, but we do not have an estimate of those physical parameters independent of noble gas concentrations. We propose to revise our manuscript to clarify the points above, and will present methods for calculation of noble gas equilibrium concentrations prior (Eqs 3-5) before presenting the methods for estimating physical parameters (Eqs. 1-2). We hope that this will clarify the derivation of these estimates.

3) The difference between N₂ den and [NO₃]R is that the former is an absolute measure of the accumulation of N₂ gas (and thus denitrification), while [NO₃]R is a measure of that magnitude relative to the original nitrate pool. Areal estimates of the rate of denitrification (mass/area/time) are based on N₂-den, but calculation of [NO₃]R is necessary for determination of isotopic effects of denitrification since fractionation is essentially a dilution process. Since N₂ den is used in calculations of [NO₃]R (p. 10260 ln14; Eq. 9), these measures are not independent, but they are not simply inverses of one another (principally because initial NO₃ concentrations vary spatially), and provide distinct information. Moreover, some of our estimates of [NO₃]R (specifically for the time series for the Ichetucknee springs) are not based on N₂-den, but rather differences in NO₃ concentrations among springs with different O₂ concentrations within

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that river system.

6+4) The Ichetucknee headspring is simply the upstream-most of the 6 large springs that feed the Ichetucknee River, rather than a direct water source for the remaining springs. Reviewer 1 questions whether, in calculating [NO₃]R from NO₃ concentrations in the Ichetucknee River springs, we are assuming the thing we are trying to prove. We answer that by pointing out that 1) we have direct measurements of denitrification in the Ichetucknee Spring showing that N₂den is low relative to that observed in other springs, 2) that the headspring is high in O₂, and 3) that the headspring has low $\delta^{15}\text{N}$ -NO₃. In contrast, other springs of the Ichetucknee River (particularly Mill Pond, Devil's Eye, and Mission Springs) have low O₂, higher N₂-den and $\delta^{15}\text{N}$ -NO₃. Moreover, comparison of estimates of [NO₃]R from N₂den suggest a reasonable correspondence with estimates based strictly on nitrate concentrations. Finally, we believe the end results of these analyses, namely the strong relationship between NO₃ concentration and $\delta^{15}\text{N}$ -NO₃, and its close correspondence to the pattern observed for springs with dissolved gas data, provide additional, strong validation of our inference that variation in both NO₃ concentrations and isotopic composition in the Ichetucknee springs are driven by denitrification. If our assumptions were invalid (i.e., if NO₃ concentrations were driven by loading, but $\delta^{15}\text{N}$ -NO₃ driven by variation in sources), it would be extraordinarily unlikely that the data from the Ichetucknee springs would follow the observed pattern and match as well with our other observations.

5) Where possible, we will revise the figure axis labels to more clearly describe the relevant variables.

Anonymous reviewer #1 raises several additional concerns:

1) Direct measurements of water collected from the UFA via groundwater wells makes clear that the aquifer itself is comparably enriched. We will add a statement to this effect (and relevant citations) to the revised manuscript.

2) Although we are unaware of studies that directly compare GC and MIMS methods

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for measurement of N₂ and Ar, both methods have reasonably high precision. In our data, we found no evidence of bias between historic data and our new observations in springs where both were available.

3) The area of springsheds can be reasonably approximated based on catchment water balance. The delineation of the precise boundaries of these groundwater basins is more challenging given the complexities of karst flowpaths. However, we note that the only calculation that relies on the precise geography of springsheds is the determination of FAVA, a features whose variation occurs at scales much broader than those of individual springsheds. As such, we have little reason to believe that any of our measurements are sensitive to the (admittedly high) uncertainty in delineation of springsheds.

4) This comment is addressed above, but to re-iterate: we acknowledge the possibility that some of the observed N₂ accumulation may reflect denitrification in strata other than the UFA, including surface soils and sinkhole sediments, but argue that strong relationships among O₂, denitrification progression ([NO₃]R), and $\delta^{15}\text{N}$ - NO₃ are most parsimoniously explained by occurrence of denitrification within the Floridan Aquifer, where the correlations among the signals of these processes would be best preserved. Moreover, we are not aware of any evidence that wetland abundance, soil water table levels, etc. are correlated with springs O₂, and so are hesitant to do more than acknowledge the possibility that some denitrification occurs prior to entry into the UFA.

5) We understand and to some extent share reviewer 1's concerns about statistical analysis of statistical metrics; however, we feel that this figure serves the useful role of highlighting that variation within springs follows the same pattern as variation among springs. This is an important, albeit secondary, line of evidence supporting the inference that variation in $\delta^{15}\text{N}$ - NO₃ is driven by denitrification rather than N source. We found it difficult to make this point clearly using only Fig. 4 given the density of data in that figure; thus our decision to include the separate presentation of those within-

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spring relationships in Fig.7, and our preference that this figure remain in the revised manuscript. We will make a final decision about inclusion of this figure in consultation with the associate editor.

6) Our best estimates of denitrification progression are highly correlated ($r^2 = 0.83$) with concurrent $\delta^{15}\text{N}$ - NO₃ measurements, and even our less precise estimates (based on modeled excess air) explain more than 55% of the variation in NO₃ isotopic composition. As such, we are quite comfortable with the stated conclusion that denitrification, rather than source variation, accounts for most of the variation in nitrate isotopic signatures within the UFA. We certainly do not intend to exclude the possibility of fertilizer application as a major input of N; to the contrary, our analysis suggests that inorganic fertilizer is more important than superficially suggested by observed $\delta^{15}\text{N}$ - NO₃ values. We do contend that enriched $\delta^{15}\text{N}$ - NO₃ rarely occurs because of dominance by human- or animal-derived wastes, which we believe our data strongly support. Reviewer 1's request for 'crossed' analysis of denitrification rate and source is unclear, but we are relatively confident in our conclusion that the hypothetical case of animal-derived fertilizers 'crossed' with low denitrification rarely occurs and accounts for very few elevated values of $\delta^{15}\text{N}$ - NO₃ within the aquifer.

7) Since atmospheric deposition accounts for a relatively small fraction of N loading to north Florida landscapes, we do not feel that the comparison of denitrification rates with atmospheric deposition is of sufficient value to warrant adding to the length of the manuscript.

Anonymous reviewer #2 points out the relative to other (more intensively agricultural) landscapes, N enrichment in the Floridan Aquifer is low. We will revise the manuscript to be more explicit about this point, although we also note that N enrichment in the UFA is high enough to have prompted recent imposition of numeric nutrient criteria.

Anonymous reviewer #2 argues that large portions of section 2.5 would more appropriately be presented in the results. We disagree. Section 2.5 does report data, but does

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so in a limited scope and strictly with the goal of supporting our approach for inferring denitrification using NO₃ data in the Ichetucknee springs system. As such, we feel this information is crucial to understanding our approach and is therefore appropriate to include in the methods section.

Finally anonymous reviewer #2 questions the omission of low NO₃ samples from our analysis of fractionation factors. To be clear, springs with low NO₃ were NOT omitted from regional estimates of denitrification or from statistical analysis of its drivers across springs. Low NO₃ springs were only omitted from regressions between the progression of denitrification and springs $\delta^{15}\text{N}$ - NO₃. We omitted these data because the variability in our estimates of denitrification were larger than observed nitrate concentrations, so that these low NO₃ springs were severe outliers in the analysis of fractionation factors. Raw data for these springs will be included in the supplemental materials, and we will revise the manuscript to clarify which analyses these data were omitted from and included in.

In addition to these general comments, Panno, McMahon, and Anonymous reviewer #2 provided a number of more detailed technical comments and corrections. We intend to correct the manuscript in all of these locations as guided by these suggestions. We have attached pdf files of their marked manuscripts as supplements to their comments.

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