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Hydrology and Earth System Sciences
Discussions

Interactive comment on "High-frequency NO_3^- isotope (δ^{15}N, δ^{18}O) patterns in groundwater recharge reveal that short-term land use and climatic changes influence nitrate contamination trends" *by* Martin Suchy et al.

Anonymous Referee #2

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General comments:

Nitrate contamination in groundwater is a widespread problem often associated with industrial agriculture. Many attempts to address excessive nitrate concentrations in groundwater by landuse management changes have yielded only sluggish or negligible success, indicating that our knowledge about sources and processes affecting nitrate in groundwater and the associated transit times are still rather incomplete.

The manuscript by Suchy et al. makes a highly valuable contribution to close this knowl-

edge gap by providing excellent new insights into sources and processes affecting nitrate concentrations in young groundwater in the transboundary Abbotsford-Sumas aquifer. The determination of 700 nitrate isotope compositions for age-controlled groundwater (< 5 years old) collected between summer 2008 and spring 2013 yielded novel insights about sources of groundwater nitrate in a study area where the predominant nitrogen inputs have recently shifted somewhat from manure towards synthetic fertilizers. In addition, the authors were able to determine the effects of local crop rotations and disturbances due to their spatially and temporally intensive sampling strategy. Since nitrate contamination in this aquifer has previously been reported by Wassenaar (2005) and Wassenaar et al. (2006), the authors were also able to report on subtle shits of nitrate sources on decadal time scales. These new findings make a highly valuable contribution to enhancing the understanding of sources, processes, and timelines of nitrate contamination of groundwater and hence will be of high interest to the readership of Hydrology and Earth System Sciences.

The current draft manuscript contains several moderate and numerous minor deficiencies that should be addressed prior to acceptance of this manuscript, including the following:

- In the introduction, the authors outline the differences in ïĄď15N values between synthetic fertilizers and manure-derived nitrate and also elaborate on the oxygen isotope ratios on synthetic nitrate-containing fertilizers. What is missing is a short description of oxygen isotope ratios of nitrate expected from nitrification of organic N, urea, and ammonium-sulfate in dependence of the ïĄď18O value of local water in the unsaturated and saturated zones. It is important to add this information to the introduction to provide the readership with a full background on the usefulness of isotopic tracers for distinguishing sources and processes affecting nitrate in the study area.

- Due to the importance of landuse changes and the trends away from manure additions towards synthetic fertilizers, is appears highly desirable to describe the changes in agricultural practices at the study site in a bit more detail in this manuscript.

-The authors have made an excellent effort to constrain their sampling of the aquifer to wells that access aerobic groundwater of average age of less than 5 years to link the detected trends to recent agricultural activities. While this argumentation holds most likely true for the water-saturated portion of the study area, it is important to realize that a similar reasoning is not entirely valid for the unsaturated zone including the soils. In the water-unsaturated and soil zones, “subsurface biogeochemical processes” are certainly ongoing with N immobilization and re-mineralization potentially delaying N transfers for years or decades (see for instance Sebilo et al. (2013): Long-term fate of nitrate fertilizer in agricultural soils; PNAS 110(45): 18185-18189), although the manuscript text on line 134 seems to suggest the opposite. Throughout the manuscript, the authors should make it more clear that their approach provides only very limited insights into N cycling and its transit times in the soil and water-unsaturated zones.

- In Figure 2a and associated text on lines 216-224, the authors assign the nitrate isotope data to three nitrate sources. Nitrate in irrigation water (ïĄď15N of +9 ‰ and manure (ïĄď15N of +8 ‰ are the sources with the highest ïĄď15N values, but Figure 2a shows numerous samples with ïĄď15N values between 10 and 17 ‰Å short explanation for these elevated ïĄď15N values is desirable at this point in the manuscript.

- Line 241: The mean ïĄď15N value of +5.0 ‰ is not very close to that of synthetic fertilizers (ïĄď15N near 0 ‰. Is it possible that intensive N cycling in the soil with associated N isotope effects causes a shift to higher ïĄď15N values in the seepage water nitrate? If this is a requirement to explain the data patterns, this should be acknowledged in the text of this manuscript.

- In my view, the evidence for climatic impacts on trends in the chemical and isotopic composition of groundwater nitrate presented in this manuscript is very weak (e.g. lines 323-325) and is mainly based on references to data presented elsewhere rather than in this manuscript. I am not convinced that a few years on increased precipitation (2008-2011) justify mentioning “climatic changes” in the title of this manuscript especially since no climate data are presented.

- Table 1 lists another nitrate source, namely nitrate-containing irrigation water with a ïĄď15N of +9 ‰ evidently derived from manure-applications. Throughout the text, this nitrate source receives very little attention. Is it not relevant?

In addition there are a number of minor deficiencies that include the following more specific comments:

- Line 47-50: It should be made clear that atmospheric nitrate inputs are not leached into the groundwater conservatively, but usually undergo intensive recycling via immobilization and ammonification + nitrification in the unsaturated zone prior to reaching the groundwater zone.

- In line 58, the authors state that manure-derived nitrate has ïĄď15N typically >10‰ but subsequently report on line 61 that the ïĄď15N of poultry manure in the study area is closer to 8 ‰Ẇhat explains the discrepancy? Is the former range mainly for cattle manure?

- In lines 101-107 the aquifer is well described, but one essential piece of information, the depth of the water table below ground surface is not clearly revealed. The authors should add this information in a more transparent fashion;

- To support the statement that the aquifer is largely under aerobic conditions it would be beneficial to add dissolved oxygen concentrations to the manuscript (for instance in table 4).

- In section 2.2, it would be useful to list the depths of water table below ground surface for the 19 selected monitoring wells.

- Lines 146-7: The measurement uncertainties for concentration analyses (e.g. nitrate, chloride) should be provided;

- Section 3.1: throughout this section it would be more correct to speak about nitrate concentrations of groundwater obtained from wells (since wells have no nitrate concentrations);

- Line 178: state by how much the nitrate concentration increased over the 5-year observation period; if you exclude the three wells mentioned on line 184, is there still an increase in nitrate concentrations for the groundwater from the remaining 16 wells?

-Line 215: The end-member with low ïĄď15N values appears to have “intermediate” nitrate concentrations;

- Lines 221-222: The rational why the Bayesian clustering model that suggest 5 groupings results in 4 distinct groups (line 223) is not clear to me.

- Line 236-239: Are these 4 groups shown in any Figures? Also, to which category belong the samples with ïĄď15N values between 10 and 17 ‰

- Line 278: I suspect not the soil N is flushed to the aquifer, but nitrate derived from nitrification of soil N. - Line 288: Can you quantify the extent of this decrease in ïĄď15N over 5 years? How does it compare to the long-term decrease in groundwater nitrate ïĄď15N observed since 1995?

- Line 328: Logic unclear: if 14-N was preferentially volatilized, should the remaining N compound not be enriched in 15-N?

- Line 359: Please quantify the extent of the observed decrease in ïĄď15N values.

The manuscript is written in excellent English, it follows a logical sequence and is hence very well organized, and the objectives are clearly stated. The applied methods are leading-edge and are sufficiently described. Previous literature is exhaustively considered. Figures and tables are of good quality with minor deficiencies listed below. Hence, if the authors are able to address the limitations identified in this review, publication of this manuscript after moderate revisions is recommended.

Additional technical comments:

Line Comment

20 I suspect you did not measure “recharge” directly, but shallow groundwater up to 5

years old; please re-word accordingly;

35 one or two more recent references that are less than 10 years old may be desirable;

43 do you mean “nitrate” isotopes or also other isotopic parameters? If the latter, please mention which other isotopes?

53 are these ïĄď15N values representative for this study site?

56, 71, 77, 110 et al.

62 & following I suspect the numbers in brackets are N-P-K values for synthetic fertilizers, but this may need to be explained to the readership.

65 add a reference to support this statement;

67 it would be advantageous to spell out the fertilizer sources used in the study area;

70 a more detailed explanation on how the oxygen isotope ratios of nitrate derived from nitrification are controlled is needed here;

75 samplings (should likely be plural)

80 add a reference for “winter-biased recharge”;

84 . . . with a focus on “shallow groundwater” from water table wells . . .

86 something seems wrong or duplicated here: ...” isotope nitrate and isotope . . .”; also “processes” should be plural;

100 “unpublished data” should be moved inside the brackets;

105 delete “surface”

119 . . . of nitrate “in groundwater” . . .

121 if possible add average depths for deep wells and average nitrate-N concentrations;

132 not the wells are aerobic, but the groundwater obtained from the wells;

157 in ïĄď18O the “1” appears to be missing;

168 does this refer to “nitrate concentrations”?

193 indicate in which months the first major recharge occurs? Is it late fall?

197 are vadose zone infiltration lag-times similar for all sites?

199 the groundwater is aerobic, not the wells; I did not find a supplementary table;

200 delete “a”

206 what does this limited variability indicate? Longer transit times through the unsaturated zone?

208 throughout this section, the ïĄď15N values are for nitrate in groundwater, not for wells.

210, 213, 214 no need to report data with 2 decimal places given the measurement uncertainty of this parameter;

250 what is meant with “like group 1a values”. ïĄď15N of 6.7 ‰ is not like 5.0 ‰ and even further away from synthetic fertilizer ïĄď15N values of 0 ‰

261 groundwater flow paths are neither shown in Figure 1 nor in 4;

270 . . . influenced “the nitrate contamination level” in these wells;

278 replace “isotopically” with 15N-enriched;

297 could you not have microbial transformations but with negligible isotope fractionation? Almost all transformations in the N cycle are microbially mediated;

305 I could not find the supplementary table;

314 it is not possible to enrich a delta value. Also, do you mean enrichment in 14-N or

15-N?

323 increasing trend for which parameter?

334 Wasenaar et al. (2006)

336 ïĄď18O of nitrate

338 were anaerobic conditions detected based on DO concentrations? If so what were the DO concentration ranges?

342 and Wassenaar et al. (2006)

343 depletion of 15-N in what: in groundwater nitrate? Why 15-N depletion if you previously talked about denitrification?

363-4 this is new information that was not previously provided in the Results & Discussion section.

376 do you men enrichment in 14-N or 15-N of nitrate?

373 do you mean concentrations and isotopic compositions of nitrate?

390 do you mean “groundwater” nitrate?

518 the inset map requires a distance bar (in km);

541 units are missing for ïĄď15N

544 Table 2: why are concentrations listed here as nitrate, when throughout the rest of the manuscript they are given as nitrate-N? Also units are missing.

547 Depletion (rather than depleting)?

550 nitrate concentration unit is wrong: mg/L rather than ‰

Please also note the supplement to this comment:
https://www.hydrol-earth-syst-sci-discuss.net/hess-2018-35/hess-2018-35-RC2-

supplement.pdf

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2018-35, 2018.