

## Response to Referees

### Sources and fate of nitrate in groundwater at agricultural operations overlying glacial sediments” by Sarah A. Bourke et al.

#### Referee #1

**1. General comments** It is interesting to assess the sources and fate of agriculturally derived  $\text{NO}_3\text{-N}$  by the concentration of  $\text{NO}_3\text{-N}$  and  $\text{Cl}^-$ . The idea of using  $f_d$  and  $f_m$  to quantify the impact of denitrification and dispersion are good. The tables and figures were displayed clearly and easy to understand.

*Thanks for taking the time to review, we are pleased that you saw value in the manuscript.*

**2. Specific comments** However, some specific scientific questions should be answered in this manuscript. Although the error in  $f_m$  introduced by neglecting  $\text{Cl}_b$  was discussed by authors, however, the error range may be underestimated. The largest error (calculated as 23% by authors) may be double as the  $\text{Cl}_b$  (assumed as 10 mg/L by authors)  $\text{Cl}_i$  increased to 20 mg/L. The suggestion to improve this part in manuscript is to use an equation related to the ratio of  $\text{Cl}_b / \text{Cl}_i$ . I would also suggest to share the Excel sheet or program used by this manuscript. (page 6, line 35 to line 38).

*Our thanks to the reviewer for drawing our attention to this section of the manuscript. We propose to update this discussion of the error introduced by neglecting background concentrations in response to this comment and Referee 2's comment about background  $\text{NO}_3$ .*

*The assumption that background concentrations can be neglected is a very useful simplifying assumption and is consistent with our understanding of the sites investigated. As such, we prefer to retain it in the final manuscript. Rather than altering the mathematical treatment, we suggest including a new figure (Figure 9) demonstrating the influence of background concentrations on the calculated  $f_m$ .*

*In lieu of an excel spreadsheet we propose adding a new table to Supplementary Material outlining values of each of terms in the mixing model calculation for each sample. The only thing this Table doesn't include is the solver code in Excel, which is rudimentary.*

#### Proposed change

*Delete text p12 L35-37: if we assume a  $\text{Cl}_b$  of 10 mg L<sup>-1</sup> and a  $\text{Cl}_i$  of 100 mg L<sup>-1</sup>, the error in  $f_m$  introduced by neglecting  $\text{Cl}_b$  is 9%; if  $\text{Cl}_b$  is 20 mg L<sup>-1</sup>, the error is 23%.*

*Replace with text: The error introduced by neglecting background concentrations was assessed by comparing  $f_m$  calculated with and without background concentrations included, using the full range of values in this study (Fig. 9). Neglecting background concentrations results in overestimation of  $f_m$  (i.e. underestimation of the amount of attenuation mixing) with the largest errors when measured concentrations are close to background concentrations. For  $\text{Cl}$  the maximum difference of 0.13 is in the mid-range of  $f_m$  values. For  $\text{NO}_3\text{-N}$ , the difference is consistently  $< 0.1$  with the largest errors at the lowest values of  $f_m$ .*

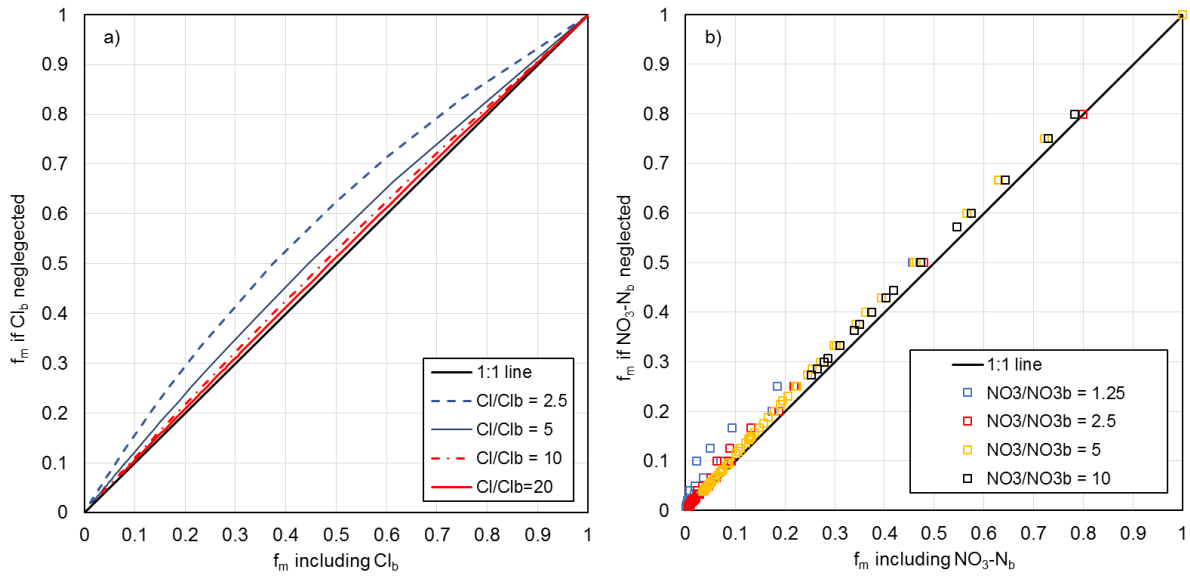


Figure 9 Effect of neglecting background concentrations in the mixing model on calculated  $f_m$  over the range of values in this study.

Insert new Table S10 in Supplementary Material:

Table S10 Constraining values and results of mixing model calculations

Sample ID	Cl	NO <sub>3</sub> -N	$f_d$ (mean ± stdev)	NO <sub>3</sub> -N <sub>i</sub> /Cl <sub>i</sub> (mean ± stdev)	Cl <sub>i</sub> (mg L <sup>-1</sup> )		NO <sub>3</sub> -N <sub>i</sub> (mg L <sup>-1</sup> )		$f_m$	
	(mg L <sup>-1</sup> )	(mg L <sup>-1</sup> )			min	max	min	max	min	max
<b>CFO1</b>										
DMW11	436.1	17.1	0.17 ± 0.07	0.23 ± 0.10	436	667	98	150	0.65	1
DMW12	78.0	2.6	0.23 ± 0.10	0.14 ± 0.06	78	1047	11	150	0.07	1
DMW13	56.7	23.7	0.56 ± 0.22	0.75 ± 0.29	57	189	42	141	0.30	1
DP10-2	74.5	11.8	0.52 ± 0.22	0.30 ± 0.13	74	277	23	84	0.27	1
DP11-12b	95.7	0.6	0.15 ± 0.08	0.04 ± 0.02	96	1300	4.2	90	0.07	1
DC15-22_10m	73.0	11.0	0.47 ± 0.21	0.32 ± 0.14	73	289	23	93	0.25	1
DP11-13_4.3m	28.5	7.0	0.30 ± 0.15	0.82 ± 0.41	29	184	23	150	0.15	1
DP11-13_5.2m	25.0	7.8	0.34 ± 0.13	0.91 ± 0.35	25	160	23	146	0.16	1
DP11-13_7m	72.3	12.0	0.27 ± 0.13	0.62 ± 0.30	72	244	45	150	0.30	1
DP11-13_7.9m	70.8	9.1	0.17 ± 0.09	0.76 ± 0.40	71	199	54	150	0.36	1
DP11-13_8.8m	81.7	11.0	0.32 ± 0.15	0.89 ± 0.42	82	323	39	150	0.25	1
<b>CFO4</b>										
BC4	163.1	35.1	0.37 ± 0.13	0.58 ± 0.20	163	258	95	150	0.63	1
BMW2	595.6	16.5	0.13 ± 0.06	0.21 ± 0.10	596	707	127	150	0.84	1
BMW5	131.2	12.9	0.34 ± 0.16	0.29 ± 0.14	131	520	38	150	0.25	1
BMW6	156.0	0.4	0.01 ± 0.01	0.26 ± 0.26	156	1300	0.4	150	0.12	1
BMW7	134.7	11.6	0.21 ± 0.11	0.41 ± 0.22	135	365	55	150	0.37	1

**3. Technical corrections** There are several technical corrections should be done before it can be published.

1)I notice that, the last paragraph of “introduction” belongs to “experimental site description” of “methodology”. (page 3, line 7 to line 20).

*We agree that Lines 8-15 on p3 are a description of the sites and these can be moved to the top of methods as a site description subsection.*

#### **Proposed change**

*Final paragraph of Introduction becomes:*

*In this study, we present the application of this approach at two confined feeding operations (CFOs) in Alberta, Canada, with differing lithologies and durations of operation. Concentrations of  $Cl^-$  and nitrogen species (N-species) and the stable isotopes of  $NO_3^-$  were measured in groundwater samples collected from monitoring wells and continuous soil cores, as well as manure filtrate at both sites. These data were interpreted to (1) assess the extent of agriculturally derived  $NO_3^-$  in groundwater, (2) identify sources and initial concentrations of  $NO_3^-$  at the point of entry to the groundwater system, and (3) assess the dominant attenuation mechanisms controlling subsurface  $NO_3^-$  distributions at these sites.*

*A new sub-section added to Methods as follows, and numbering of subsequent sections of Methods updated accordingly:*

#### ***2.1 Experimental site description***

*The first study area (CFO1), located 25 km northeast of Lethbridge, Alberta, was established in 1928 and had approximately 150 head of dairy cattle at the time of the study (Fig. 1). An associated earthen manure storage (EMS) facility for storing liquid dairy manure was constructed in the 1960s. A 2000-head beef feedlot, established in the 1960s, was also present at CFO1. The second study area (CFO4), located approximately 30 km north of Red Deer, Alberta and 300 km north of CFO1, was constructed in 1995 (including an EMS) and had 350 head of dairy cattle at the time of the study. To the best of our knowledge, fertilizers have not been applied at either of these sites, and infiltration of manure waste is assumed to be the cause of elevated  $NO_3^-$  concentrations in the local groundwater.*

2)This manuscript didn't mention what is the sampling depth for the “water table wells” in the “methodology” section. To my understanding, there were little difference between groundwater monitor well and groundwater sampling well. Normally, the groundwater sampling well take water samples in a specific range of depths.

*The screen intervals of all wells are presented in Table 1 (cited p3 L25) along with a description of monitoring wells in 2.1.1. Table 1 reports total well depth and screen length along with the statement in the caption that all screens are at the bottom of the well – which allows the reader to easily determine screen depth for each well.*

*The distinction between water table wells and piezometers is about the screen length and potential for the screen interval to include part of the unsaturated zone. For a water table well the screen interval is ~4 m and is screened so that water levels will be within the screen interval throughout seasonal or annual water table fluctuations. Piezometers are screened at discrete depths within the*

aquifer and in this study screen lengths were usually 0.5 m. The full length of these piezometers remains within the saturated zone at all times. This distinction is relatively standard within the North American hydrogeology community.

We provide this information for the benefit of readers, but once defining these terms simply refer to both as monitoring wells through-out the manuscript. We feel that this approach provides a good balance between providing detailed information if the reader desires it without unnecessarily complicating the text.

**Suggest no change made**

3)Sampling frequency. I'm not sure if the sample frequency of the chloride and N species were high enough to draw the conclusion, since the sample sizes was less than 30 and standard deviation seems not low.

*The Cl and NO<sub>3</sub> concentrations were measured at monthly to quarterly sampling intervals over a period of approximately 5 years and adequately capture temporal variation (see Figures 3 and 5). However, the isotope data are effectively a snapshot in time and do not capture temporal variation. This is already noted in the text (p12 L40-P13 L2).*

*A sample size of 30 (note that Cl and NO<sub>3</sub> data set is larger than this) is not unusually small for a study of nitrate in groundwater using isotopes. A brief survey of published papers yields: n= 16 (Mengis et al., 2001), n=29 (Mariotti et al., 1988), n = 24 (Durka et al., 1994).*

*It isn't entirely clear which conclusion(s) the reviewer thinks are not supported by the data. We acknowledge the limitations of the individual data sets, which is why the conclusions were drawn from a synthesised analysis of multiple lines of evidence that included the spatial and temporal distribution of NO<sub>3</sub> in groundwater and sources, the isotopic composition of that NO<sub>3</sub> and the mixing model results.*

*We believe that the conclusion that denitrification is proceeding in the groundwater system and that denitrification reduces NO<sub>3</sub> concentrations substantially at the farm-scale is strongly supported by the data. The attribution of sources has more uncertainty in it, but nonetheless, we feel that the spatial distribution of NO<sub>3</sub> as well as the mixing ratio analysis supports the conclusion that earthen manure storages are not the largest source of agricultural nitrate in groundwater at these sites.*

**Suggest no change**

4)Text clarity. Section 3.1 and 3.2 mentioned several "water table wells" labeled as DMW11, DMW14, etc. However, it's not easy for reader to look for those wells from figure 1 (the site description map)

*It's not clear exactly what the issue is here. DMW11 is clearly visible at the top of Figure 1, DMW14 is clearly visible on the RHS of the inset (area covered delineated by blue rectangle as stated in caption), which is included specifically so that these closely spaced wells can be identified. If further guidance can be provided we have no problem making adjustments so that it is easier for the reader to understand. Perhaps just having the Figure 1 imbedded in the text rather than at the end of the manuscript will help?*

**Suggest no change made**

## Referee #2

This paper presents a study of using isotope (N15 and O18) to study the nitrate mixing and transport. Denitrification of nitrate was considered in this study. The authors argued that their study used isotope in a quantitative way, different from the qualitative way of previous study. This however seems an overstatement to me, because they only used the isotope data to calculate the mixing ratios and denitrification coefficients. This is not very quantitative.

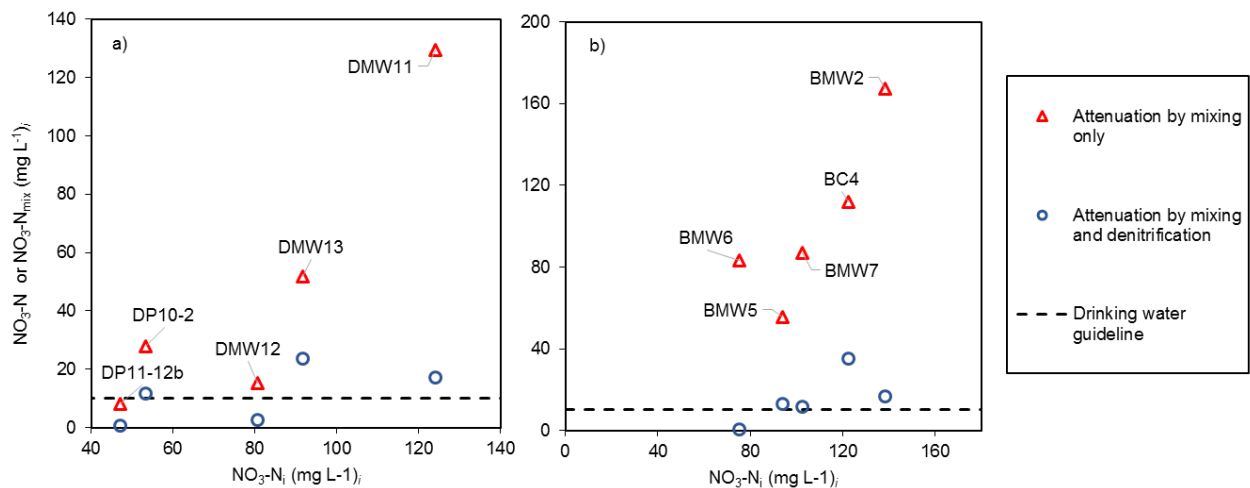
*In the Introduction, we state that this paper uses nitrate isotopes to identify denitrification and quantify the fraction of nitrate that has been denitrified. This is in contrast to other published papers, which use nitrate isotopes to identify denitrification, but do not use the isotope fractionation to quantitatively estimate the fraction of  $\text{NO}_3$  that has been lost through denitrification. We believe this is a clear distinction and our results are correctly described as quantitative.*

*To highlight the quantitative nature of the analysis we propose an additional figure (Figure 8) that shows the reduction in  $\text{NO}_3\text{-N}$  concentrations associated with mixing and denitrification.*

### Proposed change

*Additional text added to Section 3.4 Mechanisms of attenuation and associated figure:*

*The concentration of  $\text{NO}_3\text{-N}$  that would be measured if mixing was the only attenuation mechanism ( $\text{NO}_3\text{-N}_{\text{mix}}$ ) was calculated by dividing the measured concentration by  $f_d$ . Comparison with measured concentrations (which reflect attenuation by both mixing and denitrification) suggests that the sample from 20 m depth (DP11-12b) is the only sample that would be below the drinking water guideline if mixing was the only attenuation mechanism (Fig. 8).*



*Figure 8 Measured concentrations of  $\text{NO}_3\text{-N}$  (blue circles - attenuation by mixing and denitrification) and  $\text{NO}_3\text{-N}/f_d$  (red triangles - attenuation by mixing only) vs mid-range estimate of  $\text{NO}_3\text{-N}_i$ . Dashed line is drinking water guideline (10 mg L<sup>-1</sup> of  $\text{NO}_3\text{-N}$ ).*

I also have a few questions, listed below, related to their calculation of the mixing ratios and denitrification coefficients. The authors used in equation (4) of the two-member mixing method to calculate the nitrate mixing ratio. This does not seem right to me, because there should be more than C1 two nitrate sources, such as the background ambient groundwater, the direct infiltration

from fertilizer, the manure source, and the transformation from ammonium to nitrate. I doubt that the two end-member method is adequate to consider the multiple sources.

*To the best of our knowledge (including interviews with long-time landowners/farmers at the sites, historic air photos) fertilizer (other than manure) has not been applied at the sites. As such, manure is the only source of agricultural nitrate at these study sites, which is stated in the original manuscript (p3 L13-15).*

*The nitrate in groundwater will have originally been ammonium, and  $\text{NH}_3$  dominates N in the EMS at both sites (see Supp material). However, the data demonstrate that  $\text{NH}_3$  is generally a relatively small component of total-N in groundwater (<10%) so that  $\text{NH}_3$  can be neglected in the mixing model, which only considers the N-pool in the groundwater system.*

*At CFO4 ammonium concentrations in the groundwater system are negligible (consistently < 0.23 mg/L. At CFO1, well DMW3 directly adjacent to the EMS has  $\text{NH}_3$  is present at high concentrations in and  $\text{NO}_3$  concentrations were low, but the mixing calculation were not conducted on data from this well. In samples for which the mixing calculation was conducted  $\text{NH}_3$  was <10% of total-N (note that  $\text{NH}_3$  wasn't measured in core from DP11-13 were collected at depths <9 m. Likely  $\text{NH}_3$  concentrations in these samples were inferred from the water table well at this location which was screened to 7 m depth). Also,  $\text{NO}_2$  concentrations in groundwater at CFO1, which would be expected to be elevated in the presence of nitrification (Vogel et al., 1981), was consistently < 0.5 mg/L (see p12 L14-23 and Supplementary material). The one exception is core sample DP22\_6.5m, which will be removed from the mixing calculation results (Tables, Figures and text).*

*As such, we believe that it is reasonable to use a two-end member mixing model for the samples reported at these sites, where the end-members represent manure-based  $\text{NO}_3$  and background (pre-agricultural) concentrations.*

#### **Proposed change**

*Mixing calculation results from core sample DP22\_6.5m will be removed from the mixing calculation results (Tables, Figures and text).*

*Additional text p7 L11:*

*This mixing calculation was only conducted on samples for which  $\text{NO}_3$  dominated total-N ( $\text{NH}_3\text{-N}$  <10% of  $\text{NO}_3\text{-N}$ ) so that nitrification of  $\text{NH}_3$  could be neglected.*

*Additional text p12 L37:*

*In this study we applied a two-end member mixing model and assumed that background concentrations can be neglected. Although applicable at these sites, this approach may not be valid at other sites if additional sources of  $\text{NO}_3$  in groundwater (e.g. fertilizer or nitrification) are significant, or if  $\text{NO}_3$  concentrations in groundwater are naturally elevated (Hendry et al., 1984).*

To account for the denitrification, the authors used a denitrification coefficient in equation (4). While this is conceptually OK, it does not consider that denitrification is a kinetic process (zeroth-order or first order). In other words, the denitrification coefficient used in the paper cannot reflect the kinetics of denitrification.

*In this study we assume that fractionation of  $\text{NO}_3$  in groundwater during denitrification follows a Rayleigh distillation process, as described in Section 2.3.1. This approach has been used in numerous*

previously published studies of denitrification in groundwater (Böttcher et al., 1990; Otero et al., 2009; Xue et al., 2009).

The kinetics of the reaction and rates of denitrification are likely to be reflected in the epsilon value (Kendall and Aravena, 2000). In this study we determined a global epsilon of -10 based on data across both sites. In the model, epsilon values were allowed to vary in accordance with a normal distribution (mean = -10, stdev = -2.5), which will reflect a range of possible reaction rates.

#### **Proposed change**

Additional references at p5 L19 citing previous studies that used a Rayleigh distillation approach to assess denitrification in groundwater: (Böttcher et al., 1990; Otero et al., 2009; Xue et al., 2009).

As to denitrification, it is unclear to what extent denitrification occurs in the aquifer. The plots in Figure 2 do not support the conclusion on denitrification, because the slopes shown in Figure 2(a) are not 0.5. For well CFO4, the slope of 0.42 is close to 0.5, and the data listed in Table 2 and the well locations shown in Figure 1 indeed support the conclusion of denitrification. But what about well CFO1?

We assume that the reviewer takes issue with the slope of the isotopic enrichment trend at CFO1 (0.72) as being not close enough to the general trend of 0.5 reported in some studies (Durka et al., 1994). However the value of 0.72 is not unreasonable given the range of values reported for denitrification of groundwater in the published literature of 0.47 – 0.66 (Singleton et al., 2007), 0.67 (Mengis et al., 1999), 0.77 (Fukada et al., 2003). This will be clarified in the revised text.

#### **Proposed change**

Update text p5 L13-14: Nitrate in groundwater that has undergone denitrification is commonly reported as being identified by enrichment of  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  with a slope of about 0.5 on a cross-plot (Clark and Fritz, 1997). However, published studies of denitrification in groundwater report slopes of up to 0.77 (Mengis et al., 1999, Singleton et al., 2007, Fukada et al., 2003).

The authors said somewhere in the manuscript that the initial nitrate concentration can be neglected. I do not think that it is a reasonable assumption for agricultural areas.

Presumably the reviewer is suggesting that there can be an historical legacy of nitrate in agricultural areas. This is true, and we consider “background” as not having been influenced by agricultural activity (whether this is recent or historical). This assumption that  $\text{NO}_{3b}$  can be neglected underpins the simplification of the mathematics and is valid for these agricultural areas. This approach would not be suitable at sites with naturally elevated nitrate concentrations in groundwater.

#### **Proposed Change**

A new figure (Figure 8) will be added to the revised manuscript and a discussion of the effect of neglecting background concentrations updated – see response to Referee 1.

Additional text as previously proposed p12 L37:

In this study we applied a two-end member mixing model and assumed that background concentrations can be neglected. Although applicable at these sites, this approach may not be valid

*at other sites if additional sources of NO<sub>3</sub> in groundwater (e.g. fertilizer or nitrification) are significant, or if NO<sub>3</sub> concentrations in groundwater are naturally elevated (Hendry et al., 1984).*

## **References**

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