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Biogeosciences Discussions

Interactive comment on "Nitrate retention and removal in Mediterranean streams with contrasting land uses: a ^{15}N tracer study" *by* D. von Schiller et al.

D. von Schiller et al.

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We thank the referee for providing helpful comments and suggestions that we think have clearly improved the manuscript. The referee8217;s comments are repeated here and our responses are inserted after each comment.

1. Reaeration estimates

Reaeration rates of O2, N2, and N2O have not been measured in this study via gas tracer additions or night-time oxygen regressions, but been modelled using one of numerous empirical models available (e.g., see models reviewed by Genereux and Hemond 1992). According to my experience, reaeration rates obtained from different models can differ substantially and there is no way of knowing whether the model chosen by the authors delivers realistic results; particularly as the authors do not present any of the obtained reaeration coefficients. This is a crucial point for this study, because uncertainty in ecosystem metabolism (especially R) has been demonstrated to critically depend on the magnitude and precision of the reaeration coefficient (McCutchan et al. 1998). Likewise, uncertainty in denitrification rate should be strongly influenced by the magnitude and precision of the reaeration coefficient. Thus, I suggest that the authors attempt to estimate reaeration using the night-time oxygen regression method (Young and Huryn 1996). At least for the agricultural stream which exhibited sufficient GPP this should be possible. Alternatively, all conclusions related to ecosystem metabolism and denitrification should be toned down.

Answer: When we designed the experiments, our idea was to calculate the reaeration coefficient using different methods (i.e., gas tracer injections, night-time regression and empirical models) in order to obtain more realistic and comparable results. Unfortunately, the gas tracer (i.e., butane) injections did not work well due to analytical problems. In addition, when we analyzed the DO diel curves, it was not possible to calculate the reaeration coefficient using the night-time regression method probably due to insufficient GPP in the study streams. The empirical model we finally chose to calculate the reaeration coefficient was the surface renewal model (Owens, 1974) because it is one of the most widely used and respected empirical models (see Bott, 2006). In addition, comparisons between the night-time regression method and Owen8217;s method with data from previous studies in these streams gave reasonably similar reaeration coefficients. We agree with the referee that uncertainty in metabolism and denitrification strongly depends on the reaeration estimation. We have added some lines on this aspect and a citation (Genereux and Hemond, 1992) in the discussion section of the revised manuscript. The obtained reaeration rates (k2) for both N2 and N2O were already shown in Fig. 2 of the manuscript together with the denitrification estimation results. In the revised version we have included the reaeration rates for oxygen in Table 1.

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2. Metabolism estimates

Errors in the calibration of DO electrodes can result in substantial error of R in streams with high surface reaeration, such as the studied streams (McCutchan et al. 1998). Thus, the authors should add a few lines as to how and when the DO electrode was calibrated. As Clarke electrodes are subjected to drift due to biofilm development on the membrane and electrolyte consumption, it would be interesting to know whether the electrode was corrected for drift. Moreover, a graph on diel DO metabolism - such as fig. 2 in Mulholland et al. 2001 or fig. 4 in Gücker et al. 2008 - would be helpful. Finally, the respiration rate presented for the agricultural stream (table 1) is amongst the highest reported in the literature, but there appears to be no organic matter source or environmental condition (tables 1 and 2) explaining this huge difference in R between the agricultural stream and both other streams.

Answer: The WTW (Weilheim, Germany) DO electrodes were calibrated according to the manufacturers8217; instructions. We have added a sentence on this in the Methods section. We did not correct the DO electrode measurements for drift for two reasons: i) the direct analysis of the DO data showed no evidence of drift, and ii) drift due to biofilm development on the electrode was rather unimportant in our experiment because the electrodes were in the water for only one day and we did not observe any biofilm growth or leaf accumulation on the probe. Because the main scope of our work was N cycling (metabolism parameters were mainly used as environmental descriptors), we think that a graph on diel metabolism would confuse the reader and unnecessarily lengthen the manuscript. Finally, we were also surprised by the high respiration value in the agricultural stream. The fact that the stream was drying out during the period of study (it dried out completely about two weeks after the end of the 15N addition) could partially explain the obtained result. At conditions of low flow and slow water velocity the contribution of respiration in the hyporheic zone may have been enhanced. Unfortunately, our data do not allow us to test this hypothesis. We

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also would like to note that previous studies have found higher stream respiration rates than ours. For instance, a recent review by Battin et al. (2008, Nature Geoscience) with data from 62 streams found a range in respiration from 0.78 to 21.7 g C m-2 d-1 (i.e., 2.08 to 57.9 g O2 m-2 d-1 assuming a respiratory quotient of 1). In another recent study, Izaguirre et al. (2008, JNABS) found a respiration range from 6.3 to 42.6 g O2 m-2 d-1 in polluted streams from Northern Spain.

3. Hydrodynamic parameters

This may be a misunderstanding due to the too abbreviated Methods chapter, but with the experimental design described in the Methods (P3312 L21-23 and P3317 L1-6) hydrodynamic parameters can hardly be estimated. The estimation of hydrodynamic parameters from tracer additions using OTIS or any other 1-d transport model requires (1) an injection point about 100 times the mean stream width upstream of the first sampling position in order to allow for full lateral mixing of the tracer, (2) a first sampling position (used as the upstream boundary condition in the inverse modelling procedure)at which full lateral mixing of the tracer has occurred, and (3) at least one downstream sampling position against whose breakthrough curve the model parameters are fitted using least-squares etc.. The injection of the conservative tracer (and the labeled nitrate!) directly into the investigated reach without ensuring lateral mixing and the absence of an upstream boundary condition appears inappropriate.

Answer: The referee is right when he states that the information provided in the methods for the calculation of water transient storage was too abbreviated and led to confusion. To clarify this, we have included more information in the methods (field methods and parameter calculations) of the revised version of the manuscript. Briefly, the solution was released into the stream at a location that was sufficiently upstream to guarantee complete lateral mixing at the first sampling station. The passage of the conservative tracer was recorded both at the first sampling station and at the bottom of the reach. The chloride breakthrough curve at the first sampling station was used

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as the upstream boundary condition. In addition, before applying the OTIS model to the conductivity time-curve data, we calculated the Damkohler number (DaI) to evaluate whether the selected reach length was appropriate (Wagner and Harvey, 1997). Values were between 0.7 and 3.4, which is considered acceptable (Hall et al., 2002; Ensign and Doyle, 2005).

4. Terminology

In my opinion, the definitions of N retention and removal as given and used in the paper (P3308 L5; retention=assimilation, removal=denitrification) are a bit too strict and dogmatic. E.g., N assimilated by benthic compartments is frequently exported to the floodplain during flood events leading to a permanent removal of assimilated N from the stream channel. In my opinion, referring to total nitrate uptake and different uptake processes (e.g., see Mulholland et al. 2004) is more appropriate.

Answer: In our opinion, the use of retention as a surrogate of assimilation and removal as a surrogate of denitrification is appropriate considering the spatial and temporal scale of our study. Moreover, the ways the terms retention and removal are used in this manuscript are well defined at the beginning of the introduction. Both terms are concise and describe the main temporary and permanent pathways that nitrate can undergo during downstream transport, which is of great relevance for the purpose of this manuscript. Export of nitrogen to the floodplain may be important during flood events, but these sporadic events occur mostly in autumn and winter in the study streams. At the time this study was done (summer), the streams were at low base flow and the main processes leading to retention and removal of nitrate were assimilation and denitrification, respectively.

On P3308 L9, L15, and throughout the text the authors refer to a spatial gradient ranging from forested over urban to agricultural using phrases such as the concentration

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of... increased from ... over ... to .... I do not think that this is appropriate with n=1 for each land use category. The authors may want to rephrase this throughout the text to read ... was higher/lower in ... than in .... I am also not convinced that the investigated streams are typical examples of the land use categories they have been assigned to by the authors. E.g., the agricultural stream does not exhibit typical agricultural stressors such as riparian clearcutting, higher water temperature and PAR, and increased SRP concentration and the urban stream has surprisingly low ammonium, SRP, and DOC concentrations. Instead, the difference in altitude between the forested stream and both other streams (about 900 m) and the 7- to 10-fold difference in discharge between the agricultural stream and both other streams appear to be more important differences than land use. I suggest avoiding generalization related to effects of land use in a revised manuscript.

Answer: We agree with the referee: it is not correct to refer to a gradient when there are only three streams. We have removed the term 8220;gradient8221; from the text of the manuscript and we have avoided phrases referring to changes or differences along a gradient. The streams were categorized as forested, urban and agricultural based on the type of land use bordering the study reach. In addition, the streams were chosen to have a relatively well preserved riparian canopy and channel morphology in order to examine differences in nitrate uptake forced by in-stream water chemical (e.g., N availabity) characteristics rather than by the influence of the riparian zone or the hydro-morphology. We have changed 8220;with8221; by 8220;bordered by8221; in the title and other parts of the revised manuscript to clarify this aspect. We have also modified the Study sites section to clarify these aspects. The study streams are typical of the catchment of the river La Tordera. The agricultural and urban streams drain catchments dominated by second growth forest but with agricultural and urban development near the stream. Interestingly, although the streams showed relatively small differences in physical, chemical and biological characteristics, these differences determined great changes in the uptake pathways of nitrate. There are certainly streams with higher nutrient concentrations and riparian clear-cutting in this

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catchment, but we had to limit the number of 15N additions in this study due to budget constraints. In the discussion we already refer to the relevance of the lower discharge in the agricultural stream with respect to the other streams; however, results from all uptake metrics indicate that discharge alone was not responsible for the differences in retention and removal observed among streams.

5. Technical corrections

P3309, L2 Especially biogeochemists have traditionally appreciated reactive transport, whereas rather modellers may have (a long time ago) viewed running waters as inactive conduits. Give references for this statement or consider reformulating.

Answer: This sentence has been removed, according to comments by two of the referees.

P3309, L12-13 This statement refers to ammonium, not nitrate.

Answer: We have changed the previous reference (Webster et al., 2003) to a more general reference (Allan, 1995).

P3311, L5 This appears to be an important argument in your paper (e.g., see title), but what is the ecological/biogeochemical significance of Mediterranean climate for N cycling? You may want to discuss this in greater detail. According to Gasith and Resh 1999, streams in Mediterranean-climate regions are physically, chemically, and biologically shaped by sequential, predictable, seasonal events of flooding and drying over an annual cycle.

Answer: When any type of ecosystem is investigated, it should be placed in a geographical setting. In this case, the study streams were located in the Mediterranean region of NE Spain. The influence of 8220;sequential, predictable and seasonal

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events8221;, which is characteristic of the Mediterranean climate, was not relevant for the present study because the experiments were performed during a short time period. The influence of climate is likely more important in studies which are extended in time and address questions of temporal variability (see for example von Schiller et al., 2008). In the present study, the influence of the Mediterranean setting was rather related to the type of land use found in the catchments drained by the study streams and the hydric stress characteristic of the study period (summer). These two factors were already quite deeply analyzed in parts of the introduction and discussion of the manuscript. Nevertheless, we have added more information on land use in some parts of the revised manuscript.

P3316, L27 Spell CV out.

Answer: We have not found how to spell CV out. To our knowledge that is the way this company is called.

P3324, L4 Replace taken with taking.

Answer: Done

P3324, L6-7 The argumentation that Vf should be used for intersite comparisons, because it corrects for stream size is commonly used, albeit U corrects for stream size in the same way. I personally think both Vf and U should be used for such comparisons, because U is not corrected for C, and thus includes interesting quantitative information on total uptake.

Answer: We used Vf because it has been shown to be the best metric to compare uptake among streams of different size (see Mulholland et al., 2008), and because it is a comprehensive measure of nutrient uptake efficiency. We provided data for U in the

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manuscript, but did not discuss them in the context of other studies because it is out of the scope of this manuscript and would unnecessarily lengthen the text.

P3330, L27 This is a very speculative conclusion, given that it is based on n=1 and that the differences between the agricultural and both other streams were only about 3 mg/L DO. The difference in DO may partially be due to the lower discharge and current velocity of the agricultural stream and differences in reaeration associated with that.

Answer: Following this comment we have changed the sentence to tone it down. However, we must note that the 3 mg/L change in DO concentration represents a change from near 100 percent DO saturation in the forested and the urban stream to about 68 percent DO saturation in the agricultural stream. We have added a sentence on this in the results section of the revised manuscript. Considering that streams are expected to be near saturation, these results indicate high DO consumption in the agricultural stream, which clearly suggests the proposed hypothesis, which may be further tested in future studies.

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