

Interactive comment on “Inter-annual variability of dissolved inorganic nitrogen in the Biobío River, Central Chile: an analysis base on a decadal database along with 1-D reactive transport modeling” by M. Yévenes et al.

Anonymous Referee #2

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Comments on the manuscript by Yevenes et al. “Inter-annual variability of dissolved inorganic nitrogen in the Biobio River . . .”

This paper presents monitoring data on water quality determinands and discharge from several stations in the Biobio river in Chile over an eight year period. An attempt is made to interpret the monitoring data using a 1D model of in-stream mineral nitrogen behaviour (nitrification and denitrification). The basic idea is scientifically sound but I have some significant reservations about the quality of the work presented in the paper

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as submitted. I suggest that the paper is not ready for full publication in HESS at this time, although it may be that with some additional work, the data and ideas it contains could make an interesting publication.

My main issues are as follows:

As it is, the paper is relatively parochial – I don't think that there is enough of a generic "take-home message" for publication in an international peer-reviewed journal at this stage. Whilst there may be a case for publishing the results on the basis of a paucity of data in Chile, this is in itself a relatively weak justification.

It is good that the monitoring data have been integrated with modelling to give mechanistically plausible interpretations. However, the model employed (off-the-shelf code in 'R') is relatively simplistic and only considers nitrification and denitrification. Insufficient details are given to understand whether reactions are assumed to be temperature dependent and to account for other processes such as uptake by plants and ammonification.

The manuscript lacks polish. There are a number of mistakes and uncertainties which undermine the quality of the overall submission. See below for details but an example can be found in Equation 1 where it is stated that the product of ML-1 and $\mu\text{mol L}^{-1}$ will be tonnes d⁻¹. Overall the discussion is somewhat superficial.

Specific comments and technical issues

Title should read "An analysis based on..." Abstract – It is not clear whether the authors are talking about spatial or temporal patterns of DIN here or both. Similarly statements made about annual average dissolved oxygen concentrations are unclear – Are the authors talking about a decrease from headwaters to mouth? What is the relationship with water temperature? Abstract – what do the authors mean by production and consumption. What does internal production mean? In-stream or in catchment? Clarity required. P707 L8 are we talking about Chile here or for the world in general. I

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am not sure that there is conclusive evidence that rainfall intensity and duration have decreased globally. With global warming we should expect the opposite. L16 If riverine denitrification and plant uptake are low then river could also simply act as passive conduits for nitrate from land to sea. L17 nutrient regeneration – not clear what this means. P708 L2 Re 50% “retention” in estuaries: Is this a general statement for all climatic zones and all estuary types? What is meant by retained? If denitrification is the major process this is a loss rather than a retention. P709 I agree that long term studies are important but there are only 8 years of quality data which is marginal in terms of identifying general trends and relationships. See Howden et al. (2011) and Burt et al. (2010): Burt T.P., Howden, N.J.K., Worrall F. and Whelan M.J. (2010) Long-term monitoring of river water nitrate: how much data do we need? Journal of Environmental Monitoring 12, 71 - 79 Howden N.J.K., Burt T.P. Worrall F. and Whelan M.J. (2011) Monitoring fluvial water chemistry for trend detection: hydrological variability masks trends in datasets covering fewer than 12 years Journal of Environmental Monitoring 13 (3), 514 - 521 P709 Statement that land use activities have “increased” is awkward. P709 L26 Presumably the catchment not the river covers 3% of Chile? P710 L4 I guess precipitation is spatially variable. This is a large catchment. No information is given about where this average rainfall was measured or what the raingauge distributions is, or the fraction of precipitation falling as snow. What is the influence of snow melt or glacier melt on the hydrology of the catchment? P710 Ralco and Pangué dams. No information is given about the location of these features. They are not shown in Figure 1. P711 L1 Sampling was “carried out seasonally”. This is far too vague. How many samples were collected at each station and when? It is not easy to see the sub-basins marked on the map. P711 L10 “molecular spectrophotometer”. Vague. Specific details needed of methods employed. Presumably these were standard colorimetric methods. Please give references. P712 Equation 1 will yield units of mol d⁻¹ not tonnes d⁻¹. This is sloppy. Are the calculations of load correct? P712 L12 not clear what NO₃-NO₃-NO₃ means. Equation 2. Several terms not defined. Model used appears to be off the shelf so novelty is limited. The model is quite simplistic (some processes omitted) and the

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effects of tributaries neglected (p713 L4). The effects of DO concentrations on nitrification appear to have been taken into account but not on denitrification (p713 equation2 R1 and R2) – why not? P712 Regeneration – not clear what is meant here. P713 L1-2 More details needed. Nitrification and denitrification rates are mentioned but presumably these will be concentration dependent? No details are given of the type of kinetics employed. First order kinetics? In that case do the authors refer to rate constants here? P713 L11 40km reach. This is confusing as it is stated earlier that the study considers 80km. Which is it? P715 It is stated (L1) that the dominant form of DIN is nitrate but this is not always the case at all stations and in all seasons. P715 L 23. It is stated that concentrations vary with land use but these data are not shown. Ideally some sort of statistical analysis should be performed to formally test this hypothesis. Otherwise it is rather speculative. It is interesting and disappointing that the authors do not give any idea of the population of the catchment (people and animals) and the relative contribution of sewage effluent to flows and nutrient loads. P715 Expressing concentrations in $\mu\text{mol/L}$ is fine most of the time but is unhelpful when you talk about DO and BOD which are more commonly expressed in mg/L To convert you need to make an assumption of the molar mass – However, are we considering the molar mass of O or O_2 ? P716 It is remarkable that BOD is higher in winter than in summer which suggests that it is not coming from sewage. P716 L21 water volumes – Do the authors mean discharge here? Solid lines in Fig 6 show summer concentrations of all determinands, not just nitrate. P717 L12-L15 Unclear paragraph which does not convey any insight into process dynamics. P717 L21 three times higher. Compared to what? Again, too vague. There is a large body of literature which shows that leaching occurs predominantly during wet periods. Refs required. P718 L4. How is chemical weathering related to nitrate leaching or even NH_4^+ fluxes? This suggests a poor overall understanding of the N cycle. P718 L28 during high precipitation. ... Hydrological connectivity will be related to soil moisture content combined with precipitation. The reason why dry soils are buffered hydrologically from surface waters is because unsaturated hydraulic conductivity is low and the air-filled pore space is high. Again, lacks detail. P719 L 14 extreme values of

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what? Nitrate? P719 ONI index needs definition. P720 The discussion about correlations between the fluxes of DIN and ENSO are interesting but can the authors be sure that these correlations are generally applicable? Is there enough data? Can the data be supplemented with data from other Chilean catchments? P720 The “flushing effect” discussed is all quite superficial and vague. This needs to be given more attention in terms of the relationships which exist with precipitation and soil moisture deficits and in terms of process dynamics (sources and sinks of N in the soil). P720 L21 + The discussion of in-stream process dynamics is rather speculative, given that the model does not consider uptake by plants and algae and ammonification of organic N. I am not convinced that the model is capable of representing process dynamics in this river because the measured data are fairly sparse. In terms of the total annual flux, it would be helpful if the authors could convert the 159 Mmol y⁻¹ value into kg/y and kg/ha/y. In the conclusions it is suggested that land use is an important control over water chemistry of the river but I am not sure that the evidence has been presented in the paper to support this conclusion robustly. The authors also state that the study supports the case for continuing with high frequency data collection on water quality. However, I am still unclear as to what sampling frequency was actually employed in this study. Have I missed something? Figures and Tables Table 1 Several aspects unclear. Affluent? Urban (No.)? Kraft pulp mills? Table 2. Looks like ranges for water quality variables are given but this is not clearly stated in the caption. What do the errors represent? SD, SEM, CIs? This is sloppy. Fig 1. It is not clear where the catchment boundary is here. Are the provincial borders relevant to the study? Fig. 2. This is very unclear. Why show scales in b and c up to 3000? Why not express Q as runoff (mm/y)? Does the top graph show daily rainfall? Monthly? What are the units? Where were these data measured? Where is the gauging station? If the average flow is approx. 1000 m³/s this works out at a mean annual runoff of 1300 mm/y which is approx. the same magnitude as the precipitation figures given. What is going on here? Fig. 5 Caption Is DBO BOD? Fig 6 What is the x axis here? Km? From where? Not clear which measured data refer to the summer and which refer to the winter.

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