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Interactive comment on "Quantification of multiple simultaneously occurring nitrogen flows in the euphotic ocean" *by* Min Nina Xu et al.

Anonymous Referee #2

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Title: Quantification of multiple simultaneously occurring nitrogen flows in the euphotic ocean Author(s): M. N. Xu, Y. Wu, L. W. Zheng, Z. Zheng, H. Zhao, E. A. Laws, and S.-J. Kao MS No.: bg-2016-298 MS Type: Research article Min Nina Xu and co-workers present an original experimental design to quantify multiple nitrogen transformation processes (rates of ammonium, nitrite and nitrate uptake, ammonia oxidation; nitrite oxidation; nitrite excretion; DON release; and potentially remineralization) by adding a single 15N-labelled ammonium substrate into a single incubation system. No inhibitors were used and special attention was given to minimize the alteration of the system by adding a limited amount of tracer. Examples of field measurements are presented and different calculation methods are discussed. The article is written in a clear and understandable manner and fits well with the scope of Biogeosciences (BG). The study is worthy of publication but the authors need to address a number of comments to improve their manuscript (ms).

I have a concern about the method used to solve the rate law equations. Here the mass balance differential equations for determining the N-transformation rates are not integrated, neither analytically or numerically. This is rather unusual and in opposition with standard methods acclaimed for the treatment of chemical reaction kinetics. Such an approach, using rates instead of the generated profile of concentrations versus time, presents serious drawbacks, namely regarding the uncertainty on the estimated parameters (rates or rate constants). Unfortunately this point is not addressed in the ms. The authors should therefore convince the reader that their method is at least as good as conventional integration methods in terms of accuracy and precision, and this requires an uncertainty assessment (see specific comments)

The authors are not the first to propose a mass balance approach to derive multiple N-transformation rates. As far as I know, such an approach was used and discussed at least in three previous publications. 1. Elskens et al., Global Biogeochemical Cycles, vol. 19, gb4028, doi:10.1029/2004gb002332, GBC-2005 2. De Brauwere et al. Chemometrics and Intelligent Laboratory Systems 76, 163– 173, CILS-2005 3. Pfister et al., Biogeosciences, 13, 3519–3531, BGS-2016. In the GBC approach, the rate law equations are analytically integrated while in the BGS, the differential equations are solved numerically using an ODE function. Currently the use of the ODE function for solving ordinary differential equations is easy to implement (see https://cran.r-project.org/web/packages/deSolve/deSolve.pdf) and the generated profile of concentrations versus time can be fitted using least squares methods (see GBC, CILS and BGS papers). It would be appropriate to address these points in the introduction, and throughout the discussion, the authors should argue why their simplified approach can be an asset when compared to the aforementioned papers.

Also I'm not convinced that adding a single 15N-labelled ammonium tracer into the incubation system allows an accurate determination of the ammonium, nitrite and nitrate uptake rates. According to me the kinetic reactions corresponding to the matrix expressions (Eqns 16-17) with the labelling of a single ammonium substrate is under-identified. Under this condition, the 15N-labelling of PN proceeds via the uptake of ammonium and/or via nitrification and the subsequent uptakes of nitrite and nitrate. These processes are thus not independent, and may result in a multimodal optimization problem, i.e., multiple solutions providing similar responses. The authors should address this point, especially because little information is available in the ms regarding the method used to solve Eqns. (16-17).

Specific comments Line 47 –p3: What is meant by the inventory method? Line 100 – p6: The term validation is not appropriate since the Stella model is based on the reaction kinetics outlined in Fig.1, and thereby submitted to the same underlying hypotheses than Eqns (16-17). At best we can say that the matrix solutions are consistent with a model run generating concentration versus time curves through back calculation. Lines 280/281/397/399/417. Please pay attention to the number of significant decimals when reporting data (e.g. 22.3 ± 4.3 μM or 5376.4 nM). Line 348/354: How did the authors define ‘undetectable’ or ‘below detection limit’ in their ms? Line 420 – p23: In Fig.4 a nonlinear behavior for the concentration versus time doesn’t demonstrate that the rate laws follow first order. Line 438 – p23: What is meant by ‘this positive offset was compensated for by organic nitrogen utilization’. Line 518 – p27: I guess it is rather an ‘accurate measurement of. . .’ Line 544 – p 29: ‘The uncertainty estimate for this isotope matrix method is not a simple statistical question’. Yet the authors have the means to do so. If they build rate profiles from their concentration measurements, and optimize values for Fi or ki (Eqns 16- 17) using a least squares method, they will get access to the uncertainty on these parameters via the variance-covariance matrix.

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