Review of paper submitted to Biogeosciences Discussions

Title: Abiotic ammonification and gross ammonium photoproduction in the upwelling system off central Chile (36 S)

Authors: A. Rain-Franco, C. Munoz, and C. Fernandez

General Comments

The authors present experimental data on ammonium photoproduction from a coastal region exposed to upwelling conditions. The latter are from two sets of samples, one with phytoplankton exudates and another with natural, filtered samples. These experiments are placed in the context of an annual cycle of field data on surface irradiance and water column light attenuation etc. The biogeochemistry of the region is very interesting and much understudied. Unfortunately, there are two serious problems with the photochemical work. Firstly, the authors poison a subset of samples with mercuric chloride. Mercury is photochemically active (e.g. Ababneh et al., 2006; Pehkonen and Lin, 1998) and can therefore NOT be used to sterilise samples in photochemical studies. Secondly, the authors also "sterilized" their samples by filtering through 0.7 μm GF/F filters. This was clearly not effective as microbial cell counts were similar to what one might expect from unfiltered seawater (cell counts were in the order of 10^5 to 10^7 ml^{-1}). It is likely therefore that in irradiated samples abiotic photoammonification and microbial processes (NH_4^+ regeneration, uptake, nitrification, etc.) co-occurred as the authors point out. However, microbial processes are likely to have been inhibited by light (indeed cell counts in irradiated samples decreased by 50% in Figure 6D). In contrast, microbial processes in the "dark" treatment would not experience light inhibition. This means that the "dark" treatment is not a suitable control for either photochemical or microbial processes. In the future it may be better to use 0.1 μm filters instead. We found that these remove >99% of the microbial community (Kitidis et al., 2011; Kitidis et al., 2006).

Nevertheless, I think the authors have done some good work which may be repackaged in a new manuscript with a different emphasis, outlined below. The authors should be upfront about the limitations of their dark control. The authors should remove all of their mercury-treated-light samples and all the relevant discussion. I suggest they keep the mercury-treated-dark samples as these agree well with the filtered-dark for *C.muelleri* exudates. There is a slight NH_4^+ increase in the filtered-dark compared to the mercury-treated-dark for *T.minuscule* exudates. This would have to be discussed in light of the two main points above. The irradiations of phytoplankton exudates are convincing enough to show photoammonification. The marine DOM irradiations are a lot more difficult to interpret. However, if the authors clearly outline all of the competing and synergistic processes (photochemistry, remineralisation, uptake, nitrification, photo-inhibition…), they may be able to present their results as a net change of NH_4^+, NO_2^-, NO_3^- and cell abundance under irradiation. Please note that NO_2^-, NO_3^- are also photochemically cycled (Kieber et al., 1999; Mack and Bolton, 1999). The authors should not attempt to quantify individual process rates, but rather emphasize the results qualitatively. The question that this paper would then address is "Given all these processes, what is the net effect of UV exposure on these parameters?". Some comparison of the cumulative light dose during irradiation with the respective daily dose in the field would also be required to show that the conclusions are relevant. The field data are nice, but I would like to see a better attempt at explaining why light attenuation was so low in May and only for PAR. Light attenuation throughout the year seems relatively constant with the exception of this period. Furthermore, the fact that this is only for PAR suggests a completely different spectral distribution for light attenuation. Is this a different water mass, advected or upwelled in early May? I am convinced that some of the data are publishable, but not in the present form. My suggestions add up to a major rewrite.

References:

Ababneh, F.A., Scott, S.L., Al-Reasi, H.A., Lean, D.R.S., 2006. Photochemical reduction and reoxidation of aqueous mercuric chloride in the presence of ferrioxalate and air. Science of the Total Environment 367, 831-839.

Kieber, R.J., Li, A., Seaton, P.J., 1999. Production of Nitrite from the Photodegradation of Dissolved Organic Matter in Natural Waters. Environmental Science and Technology 33, 993-998.

Kitidis, V., Tilstone, G., Smyth, T., Torres, R., Law, C.S., 2011. Carbon Monoxide Emission from a Mauritanian Upwelling Filament Marine Chemistry 127, 123-133.

Kitidis, V., Uher, G., Upstill-Goddard, R.C., Mantoura, R.F.C., Spyres, G., Woodward, E.M.S., 2006. Photochemical production of ammonium in the oligotrophic Cyprus Gyre (Eastern Mediterranean). Biogeosciences 3, 439-449.

Mack, J., Bolton, J.R., 1999. Photochemistry of nitrite and nitrate in aqueous solution: a review. Journal of Photochemistry and Photobiology A: Chemistry 128, 1-13.

Pehkonen, S.O., Lin, C.J., 1998. Aqueous photochemistry of mercury with organic acids. Journal of the Air & Waste Management Association 48, 144-150.