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Comment

## ***Interactive comment on “Photochemical production of ammonium in the oligotrophic Cyprus Gyre (Eastern Mediterranean)” by V. Kitidis et al.***

### **Anonymous Referee #3**

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Review of ‘Photochemical production of ammonium in the oligotrophic Cyprus Gyre (Eastern Mediterranean)’ by Kitidis et al.

#### General comments

Kitidis et al. present experimental data of the rate of photo-ammonification of open ocean DON from in-situ incubations of surface seawater collected in the oligotrophic eastern Mediterranean Sea. This study is a welcome addition to the literature on this process in the open ocean, and in nutrient-deficient oceanic provinces in particular. It is carefully thought out and well presented, including the scaling up of their findings. I do not have major concerns with this article, which merits publication. Some points

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need clarification or amendment and are outlined below.

### Specific comments

p.452, line 7: What is C18 extracted DOM? Are such specifics necessary or relevant at this stage of the manuscript?

p. 453, lines 5 - 7: My understanding of the productivity situation in the eastern Mediterranean is that this region is N-limited, i.e. DIN supply does not meet demand by autotrophic organisms, despite photo-ammonification. Unless I am missing something, what further implications can photo-ammonification have in an overall N-limited oceanic region? The word here is contribution to the regional productivity rather than implication for it, as the issue is to quantify the potential role or contribution of DON photo-oxidation to ammonium to primary production in the particular conditions of nutrient limitation. This is ultimately is what the authors do towards the end of the article.

p. 453, line19: What is SF6?

p. 455, lines 5 - 6: I do not think this level of detail (gloves) is necessary.

p. 456, top paragraph: The HCO<sub>3</sub><sup>-</sup> method used determines total dissolved nitrogen (TDN). The DON is then calculated by difference of independently determined DIN (nitrate + nitrite + ammonium) from the TDN. If so, it should be stated clearly at this point, along with the methodology for nitrate determination. If, on the other hand, the DIN was not taken into account owing to its very low concentration (nmol/L) in the region by comparison with the elevated concentration of the TDN (micro-mol/L), hence TDN = DON, this should be stated clearly.

p. 458, lines 7 - 8: This statement is inconclusive. Did DOC and DON co-vary over the investigated depth range?

p. 458, 19 - 23: I do not see how the dark controls can be collectively summarized in a single sentence. They deserve better. They showed less variability in the ammonium concentration than irradiated samples, such that the increase in the ammonium

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concentration in the latter samples is discernible. The dark controls in experiments (b), (c), (f), and (g) were similar to  $t = 0$  within 1 nmol/L, i.e., analytical precision. What is the photo-ammonification rate corrected for then in these cases and how, when there is no discernible slope in the dark controls? The dark controls in experiments (d) and (h) indicated an increase by 2 and 5 nmol/L, respectively, approximately 25% and 50%, respectively, of the increase in the ammonium concentration in the corresponding irradiated samples, while in experiment (e) the dark controls showed a decline by 2 nmol/L, hence the correction of the corresponding ammonification rates.

p. 459, line 3: It looks as though it was duplicate rate determinations. If not, give number of replicate determinations.

p. 459, lines 5 - 6: The way it is written, it reads as though the IREX 1 simply experienced an extended irradiation period. How does this discern photo-consumption from photo-production of ammonium?

p. 459, lines 11 - 12: This is an interesting finding. It would be useful to indicate the parts of the irradiated biosphere this is relevant in the discussion.

p. 459, lines 13 - 14: Please specify if you are referring to irradiance-normalized photo-ammonification rates. The same applies throughout the text. At the end of this sentence, I presume you mean DOC-normalized CDOM.

p. 459, lines 15 - 17 and 19 - 21: How is the presence of phosphate/SF<sub>6</sub> expected to affect photo-ammonification rates?

p. 460, line 10: Please give an indication of the concentration range of DOM in freshwaters. Similarly in line 17, what are the typical concentrations of Fe and ammonium in freshwaters? In the same vein, although a detailed description of the distribution of a host of geochemical properties of the current water mass is presented in section 3.1 (Initial sample properties), information on the ammonium concentration in the oligotrophic Cyprus gyre is absent from the text and from Table 1. It may be obvious from

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the  $t = 0$  of Fig. 2, for example, but should be properly presented in the Results section.

p. 460, bottom paragraph, p. 461 top paragraph: Given that this study is about net photo-production of ammonium and that photo-consumption of ammonium is addressed less rigorously, I find the detail on photo-consumption here distracting from the main point. The point at this stage of the discussion is the systematic photo-ammonification observed in all experiments with Cyprus gyre seawater by comparison with no photo-ammonification or even photo-consumption of ammonium in other studies with waters of different origin and initial properties. Any attempt at dissecting explanations why this is the case is speculative.

p. 461, line 20: what correlated with DOC-normalized CDOM absorbance at 300 nm?

p. 462, top paragraph: To what is surface CDOM compared here? Deeper water samples or other studies, or both?

p. 464, line 12: I suggest that the equivalence of the measured rates with atmospheric N deposition in the area should be included in the abstract.

p.464, line 20: Does bacterial activity include heterotrophic or just autotrophic microbial activity? Perhaps a more exact term is needed here.

p.464, lines 22 - 23: Following the previous statement, photo-production of ammonium will stimulate primary production in the presence of sufficient P.

#### Technical corrections

p. 464, line 5: This is 0.75, not 75.

Table 1: I suggest the same units for the non-normalized rate in brackets and the irradiance-normalized one.

Fig. 2: I had difficulty reading the open symbols on a printout. Also, the scale on the y-axis is different in each graph. Either make all y-axes the same scale or point out that they are different in the caption.

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Interactive comment on Biogeosciences Discuss., 3, 449, 2006.

**BGD**

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