Biogeosciences Discuss., 3, S397–S405, 2006
www.biogeosciences-discuss.net/3/S397/2006/

Biogeosciences Discussions

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

V. Kitidis et al.

Received and published: 22 August 2006

To: Timothy W. Lyons

Re: Manuscript: BGD-2006-0013

Title: Photochemical production of ammonium in the oligotrophic Cyprus Gyre (Eastern Mediterranean)

Authors: V. Kitidis, G. Uher, R.C. Upstill-Goddard, R.F.C. Mantoura, G. Spyres and E.M.S. Woodward

Dear Dr. Lyons,

We would like to thank the reviewers for their positive and constructive comments. The reviewers' comments and suggestions are dealt with individually below. In addition to this response, we would like to submit a revised manuscript which we briefly summarise here. New or expanded text has been added where necessary in order to clarify individual points in the revised manuscript. Figures 1 and 3 have been updated in line with suggestions from reviewers 2 and 3 respectivelly. A new figure has been added (Figure 2) showing the depth distribution of nutrients, DOC, DON, CDOM, Chlorophyll a, temperature and salinity following the reccommendation made by reviewer 1. Following the suggestion made by reviewer 2, a new Table has been added (Table 2) summarising the information given in section 3.1 on differences in mean DOC, DON, CDOM and DOC:DON ratio between near surface (0-30 m) and deeper water (30-1600 m). We believe that the revised manuscript has benefited demonstrably from the open discussion.

We look forward to hearing from you.

Sincerely,

Vassilis Kitidis (on behalf of the authors)

Response to specific comments

Reviewer 1

1. The reviewer found the section on the thermocline/pycnocline of the study area confusing and asked for clarification. We have replaced the words Ď...further, shallow..." with "...secondary, shallow..." in section 2.1 of the manuscript.

2. The reviewer requested that an additional figure be provided showing the depth distribution of nutrients, DOC, DON, CDOM, temperature and salinity for at least one example. Although the hydrography and nutrient biogeochemistry of the study area have been reviewed extensively by Krom et al., 2005 (Deep Sea Research II, 52: 2879-2896), we have provided an additional Figure showing these data (Figure 2 in the revised manuscript).

3. The reviewer pointed out that higher photobleaching rates in freshwaters compared to marine waters were primarily due to higher humic substance levels rather than Fe or NH4+ levels. We agree with the reviewer, but we do not present or discuss CDOM photobleaching rates in this manuscript. In section 4.1 we state that "higher NH4+ photoproduction rates in freshwaters may be attributed to the high DOM levels present in freshwaters, although other environmental variables including pH, iron and initial NH4+ concentration have been implicatedĚ". Nevertheless, the reviewer provided a reference which shows the differences in CDOM levels that are typical between freshwaters and seawater. This reference along with an additional reference (Uher et al., 2001, Geophysical Research Letters 28: 3309-3312) have been included in the revised manuscript to illustrate this point. New text "River CDOM of up to 104 m-1 (e.g. Uher et al., 2001; Kowalczuk et al., 2003), DOC concentrations of 1200 μmol L-1 (e.g. Baker and Spencer, 2004), Fe and NH4+ concentrations of 2.3 μmol L-1 and 2.1 μmol L-1 respectively (e.g. Morris et al., 1978) are typical for freshwaters." has been added to section 4.1 of the revised manuscript.

Reviewer 2

1. The reviewer requested clarification on the apparent contradiction between our statements that a) P-addition did not affect NH4+ photoproduction rates (page 459, lines 15-21) and b) the impact of NH4+ photoproduction on primary production may be controlled by the availability of P (page 464, lines 16-18). We would like to disagree with the reviewer's comment since the two statements in question refer to two fundamentally different issues. The first statement refers to the effect of PO43- addition on NH4+ photoproduction rates while the second statement refers to the fate of photoproduced NH4+ with respect to biological uptake. PO43- had no effect on NH4+ photoproduction, but it would affect the biological uptake of photoproduced NH4+ since primary producers are thought to be P-limited in the study area (Krom, et al., 1991, Limnology and Oceanography, 36(3): 424-432; Krom, et al., 1992, Deep Sea Research, 39(3/4): 467-480; Krom et al., 2004, Limnology and Oceanography 49 (5): 1582-1592; Thingstad, et

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

al., 2005, Science, 309(5737): 1068-1071; Thingstad and Mantoura, 2005, Limnology and Oceanography Methods, 3: 94-100). Therefore, phosphorus limitation might limit the uptake of photoproduced NH_4^+ by phytoplankton. However, should P-limitation be lifted, phytoplankton may utilise available N including photoproduced NH_4^+. This notion is in fact supported by results from onboard microcosm experiments during which NH_4^+ was added to samples with or without PO_4^{3-} (Zohary et al., 2005, Deep Sea Research II, 52: 3024-3040). We have added the following new text to section 4.2 in order to clarify this point: “Although PO_4^{3-} addition had no effect on NH_4^+ photoproduction rates during our study, it would affect the biological uptake of photoproduced NH_4^+ since primary producers are thought to be P-limited in the study area.“.

2. The reviewer requested that data presented in section 3.1 be summarised in a separate table. An additional Table has been provided in the revised manuscript (Table 2).

3. The reviewer expressed his/her preference that NH_4^+ photoproduction rate data presented in Table 2 of the original manuscript, be shown in a bar chart in order to facilitate comparison. However, the variability of NH_4^+ photoproduction rate data presented in Table 2, which span 4 orders of magnitude, are difficult to depict in a bar chart, in particular with regard to variability towards the lower end of observed rates. For example our own data span one order of magnitude, but are still three orders of magnitude lower than the highest rate observed. The data could be presented in a bar chart as log10-transformed rates. However, we prefer presentation in tabular form as in Table 2. As this is mainly a presentation issue, we would like to retain Table 2 (as Table 3 in the revised manuscript) in favor of a bar chart.

4. The reviewer suggested to reposition the inlay in Figure 1 (map showing the study area). We are generally in favor of black & white images where possible in order to facilitate reproduction and have provided a new image on which the study area is centered, in line with the reviewer’s recommendation.

5. The reviewer requested that unnecessary repetition is avoided. In the first example given by the reviewer, a statement from section 3.2 (results) is summarised in section 4.1 as an introduction to relevant discussion. Similarly, background information in section 1 is summarised in section 4.1. These repetitions are minor and in our view make the manuscript more accessible to non-experts. We therefore disagree with the reviewer's comment and would like to retain information summarising each of our findings in the relevant section or paragraph of the discussion in order to accommodate a wider audience.

Reviewer 3

1. The reviewer questioned the necessity of detail with respect to C-18 extracted DOM. C-18 is a resin used in solid phase extraction of hydrophobic organics from aqueous solution. As with all DOM extraction procedures, the process is selective (no more than 60 % of DOC or CDOM is typically retained on the C-18 resin). Therefore, we believe it is useful to state that the results of Kieber et al., 1997, Limnology and Oceanography, 42(6): 1454-1462, were derived from experiments of C-18 extracted DOM, and therefore by implication, considered a specific DOM fraction rather than total DOM.

2. The reviewer requested clarification of the nutrient limitation status of the study region in section 1. Primary production in the region is thought to be P-limited and not N-limited (Krom, et al., 1991, Limnology and Oceanography, 36(3): 424-432; Krom, et al., 1992, Deep Sea Research, 39(3/4): 467-480; Krom et al., 2004, Limnology and Oceanography 49 (5): 1582-1592; Thingstad and Mantoura, 2005, Limnology and Oceanography Methods, 3: 94-100). However, recent studies within the EU CYCLOPS programme have shown that N- and P- co-limitation of phytoplankton may occur in summer (Krom et al., 2005, Deep Sea Research II, 52: 2879-2896; Thingstad, et al., 2005, Science, 309(5737): 1068-1071). This information is given in section 1 of the original manuscript as background. In section 4.2 we estimate the contribution of NH4+ photoproduction to the N-budget of the region. However, as long as P-(co)-limitation prevails this source of N may not contribute significantly to additional primary

BGD

3, S397–S405, 2006

production. This is in fact discussed in section 4.2 of the original manuscript.

3. The reviewer requested a definition of SF6. New text “SF6 (sulphur hexafluoride) is an anthropogenic gas that was used as an inert tracer of physical processes (patch dilution through lateral advection) in this instance.” has been added to section 2.1 in order to clarify the role of SF6. Sulphur Hexafluoride (SF6) is an anthropogenic gas. As it has no natural sources, a very low concentration in the atmosphere and no biological sinks, it has been used as a conservative tracer during similar tracer release experiments. In the case of the EU CYCLOPS programme, it was released with PO43- into a surface mixed layer patch of water. Its detection by GC-ECD is very sensitive, so it was possible to trace the patch even after PO43- had been depleted through biological uptake. Furthermore, since SF6 was diluted in the patch through lateral advection, it was possible to estimate the physical dilution of the patch (after correction for sea-air gas exchange losses of SF6). For further details see Law et al., 2005, Deep Sea Research II, 52: 2911-2927.

4. The reviewer expressed the view that the level of detail (gloves) was not necessary in section 2.2. One of the challenges of working in oligotrophic waters is that analyte concentrations and process rates are very low, often comparable to analytical detection limits of relevant instrumentation. Therefore samples are particularly prone to contamination during handling and storage, potentially leading to erroneous data and conclusions. We believe such detail is necessary in order to demonstrate the scientific rigor and credibility of our study.

5. The reviewer requested clarification of how DON data were derived from TDN measurements. New text has been added to section 2.3 of the revised manuscript: “Since the HTCO method measures total dissolved nitrogen, we subtracted the concentrations of dissolved inorganic nitrogen (NO3-, NO2- and NH4+) to derive DON data. NO3- and NO2- were determined according to Brewer and Riley (1965) and Grasshoff (1983) respectively.”.

BGD

3, S397–S405, 2006

Interactive Comment

EGU

6. The reviewer requested clarification of whether DOC and DON co-varied over the investigated depth-range. DOC and DON did not co-vary as is stated on page 458, line 7 of the original manuscript. The word "would" has been removed from this sentence in order to avoid ambiguity.

7. The reviewer requested further discussion of dark controls in section 3.2, where they are indeed collectively summarised in one sentence, as the reviewer pointed out. However, the purpose of our manuscript is to discuss NH4+ photoproduction rate data. In this context, variations of NH4+ concentrations in dark controls are only of interest in so far as they need to be considered when photoproduction rates are calculated. Corrections for variations in dark controls were already described in detail in section 3.2. We would also like to note that all data including those from dark controls are clearly shown in Figure 3 of the revised manuscript.

8. The reviewer requested that the word "replicate", be replaced by the word "duplicate" on page 459, line 3. This has been corrected.

9. The reviewer requested clarification of photo consumption vs. photoproduction during IREX1. In this experiment, the sample was not subject to an extended irradiation period, but instead was kept in the dark for 2 hours after the end of the irradiation period. We then compared concentrations at the beginning and end of this additional 2 hour period after irradiation. The sentence "During... period" (p. 459, lines 4-6) has been replaced by new text "During IREX 1, an irradiated flask was kept in the dark for 2 hours before NH4+ concentration analysis, following a 2.5 hour irradiation period and then compared to a sample analysed immediately after the end of the 2.5 hour irradiation. This was done in order to examine potential post-irradiation dark uptake of photoproduced NH4+ or continued production of NH4+ in the dark".

10. The reviewer requested that the range of DOM and Fe concentrations in freshwaters be given as well as the range of NH4+ concentrations in the oligotrophic Cyprus Gyre. New text "NH4+ concentration in the surface mixed layer was 30-140 nmol L-1.

The depth distribution of NH4+ showed a pronounced maximum at the base of the seasonal thermocline (˜30 m) and a less pronounced maximum in the vicinity of the primary nitrite maximum (Figure 2)." has been added to section 2.1. New text "River CDOM of up to 104 m-1 (e.g. Uher et al., 2001; Kowalczuk et al., 2003), DOC concentrations of 1200 μmol L-1 (e.g. Baker and Spencer, 2004), Fe and NH4+ concentrations of 2.3 μmol L-1 and 2.1 μmol L-1 respectively (e.g. Morris et al., 1978) are typical for freshwaters." has been added to section 4.1 of the revised manuscript.

11. The reviewer requested that detail on photo-consumption of NH4+ be cut from section 4.1. We disagree with the reviewer on the grounds that our experimentally derived data need to be compared with other datasets from similar experiments whether or not they indicate production or consumption of NH4+. A significant number of studies have observed net NH4+ consumption during such experiment and we would therefore not do our work justice by omitting this comparison. However, we agree with the reviewer that our discussion of possible causes for the observed differences remain speculative. In the original manuscript we therefore stated that "the contrast... presumably reflected...".

12. The reviewer pointed out an omission from the text. The text "of NH4+ photoproduction rates" has been added in the revised manuscript.

13. The reviewer pointed out an omission from the text. The text "(compared to deeper water in our study)" has been added in the revised manuscript.

14. The reviewer suggested that the equivalence of annual rate data with atmospheric N deposition in the area be included in the abstract. The text "Ěand in the same order of magnitude as atmospheric N deposition..." has been added in the abstract of the revised manuscript.

15. The reviewer requested clarification on bacterial activity determined during onboard microcosm experiments. Bacterial activity was measured as 14C-leucine incorporation during incubations under "subdued (laboratory) light". They would therefore

represent largely heterotrophic bacterial activity, but autotrophic bacterial activity cannot be excluded. Readers are referred to Zohary et al., 2005, Deep Sea Research II, 52: 3024-3040, for further details.

16. The reviewer pointed out an omission from the text. The text "Ĕin the presence of sufficient P" has been added in the revised manuscript.

17. The reviewer identified a technical correction in the text. "75" has been changed to "0.75" in the revised manuscript.

18. The reviewer suggested the same units for the non-normalised and irradiance-normalised rates presented in Table 1. The units of concentration for non normalised rates have been changed to x 103 pmol L-1 in the revised manuscript.

19. The reviewer requested that Figure 2 be reworked. The empty circles have been converted to grey filled circles. We prefer not to rescale the y-axis for panels a-h of this Figure (Figure 3 in the revised manuscript) in order to best show differences between irradiated samples and their respective dark controls for each experiment. However, we have specified in the Figure legend that the scales on the y-axes differ.

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