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The fate of photons absorbed by phytoplankton in the global ocean

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Solar radiation absorbed by marine phytoplankton can follow three possible paths. By simultaneously measuring the quantum yields of photochemistry and chlorophyll fluorescence *in situ,* we calculate that, on average, ~60% of absorbed photons are converted to heat, while only 35% are directed toward photochemical water splitting and the rest are re-emitted as fluorescence. The spatial pattern of fluorescence yields and lifetimes strongly suggests that photochemical energy conversion is physiologically limited by nutrients. Comparison of in situ fluorescence lifetimes with satellite retrievals of solar induced fluorescence yields suggest that the mean values of the latter are generally representative of the photophysiological state of phytoplankton, however the signal to noise ratio is unacceptably low in extremely oligotrophic regions, which comprise 30% of the open ocean

For several decades, chlorophyll concentrations based on remotely sensed variations in ocean color have been used to derive global phytoplankton productivity (*1*, *2*). Primary productivity models implicitly include physiological processes, but their explicit representation has, thus far, been elusive (*3*, *4*). Variable chlorophyll fluorescence is the most sensitive, non-destructive signal detectable in the upper ocean that reflects instantaneous phytoplankton photophysiology (*5*–*7*). Over the past two decades, many hundreds of thousands of discrete in situ measurements of variable fluorescence have been made using ship-based active fluorometers. These instruments, primarily designed to quantify the quantum yield of photochemistry (F_v/F_m) in photosystem II (PSII), the reaction center responsible for splitting water, have been used to follow phytoplankton photophysiology in response to iron fertilization (*8*), across eddies (*9*, *10*) along meridional transects (*11*), and many other phenomena (*12*, *13*). Although active variable fluorescence measurements have become almost routine, by themselves, they do not allow closure on the fate of light absorbed by phytoplankton. Here, we report the fraction of sunlight absorbed by phytoplankton that actually is used to form chemical bonds in the global ocean. Further, we compare the spatial distributions of photochemical energy conversion to the pattern inferred from space-based retrievals of solar induced fluorescence yields

The biophysical basis of fluorescence measurements derives from the three possible fates of solar energy absorbed by any photosynthetic organism (*14*). Absorbed photons can (1) generate photochemical reactions leading to production of organic matter (with the rate k_p), (2) be dissipated as heat (k_t), or (3) be emitted back to the environment as fluorescence (k_f) (*15*). In a dark-adapted state or under low irradiance (when k_t is constant), the quantum yield of chlorophyll fluorescence, ϕ_f (= $k_f/(k_p+k_t+k_f)$), is inversely related to the quantum yield of photochemistry in PSII, ϕ_p = $k_p/(k_p+k_t+k_f)$ = F_v/F_m.

Substitution and rearrangement leads to:

$$\phi_f = \phi_{fm} (1 - F_v/F_m) \quad (1)$$

where ϕ_{fm} (= $k_f/(k_t+k_f)$) is the maximum fluorescence yield obtained when photochemistry is nil (e.g., at saturating background light).

This biophysical model predicts an inverse linear relationship between the quantum yield of photochemistry and that of chlorophyll fluorescence. However, by the early 1980's it was realized that exposure to high continuous irradiance can lead to a suite of thermal dissipative mechanisms, collectively called non-photochemical quenching (NPQ) (*16*). These reactions markedly decrease the quantum yield of fluorescence at high background light. Hence, the relationship between chlorophyll fluorescence and photochemistry, described in Eq. 1, becomes highly non-linear as NPQ phenomena play an increasingly larger role in energy dissipation.

Calculating the budget of absorbed solar radiation requires measurements of the quantum yields of at least two pathways, for example, photochemistry and fluorescence. Although the development and use of variable fluorescence techniques over the past two decades has provided unprec-

edented information about photochemical conversion in phytoplankton in situ, these instruments are unable to measure the absolute quantum yields of fluorescence. To overcome this basic limitation, we constructed an extremely sensitive sea-going instrument that measures chlorophyll fluorescence lifetimes in the picosecond time domain (*17*). The fluorescence lifetime can be quantitatively related to the absolute quantum yield of fluorescence (*18*):

$$\phi_f = \tau / \tau_n \quad (2)$$

where τ_n is the intrinsic (or natural) lifetime constant for chlorophyll *a* molecules (*17*). Thus, the longer the lifetime, the higher the quantum yield of fluorescence.

Between 2008 and 2014, we obtained >150,000 discrete chlorophyll fluorescence lifetime measurements from the Pacific, Atlantic, Arctic, and Southern Oceans. These measurements comprise the map of quantum yields of chlorophyll fluorescence from phytoplankton in the upper ocean (Fig. 1). The night-time in situ lifetimes ranged from 0.5 to 2.7 ns with a mean of 1.13 ± 0.33 ns (Fig. 2). This naturally dark-adapted condition corresponds to a state when all functional reaction centers are open and NPQ is absent. These values span the entire range of published lifetimes of in vivo chlorophyll fluorescence obtained from cultured phytoplankton (*17*) and reflect extraordinary variability in phytoplankton physiology in the global ocean. The general pattern of the fluorescence lifetimes in the central gyres of the global ocean is rather featureless although phytoplankton growth is subject to both macro- and micronutrient limitation (*14*). The shortest fluorescence lifetimes (<1ns) were observed along continental margins, in the Antarctic convergence, Subtropical Atlantic and Pacific oceans. These lifetime distributions support the hypothesis that phytoplankton in the central gyres are acclimated to broad scale and persistent nutrient limitation (*11*, *12*). In contrast the longest fluorescence lifetimes were observed in high-nutrient-low-chlorophyll (HNLC) regions of the equatorial Pacific Ocean and the Southern Ocean where primary production is limited by the paucity of iron (*19*), a micronutrient that is critical for the function of photosystem II (*20*, *21*). The exceptionally high values of fluorescence lifetimes in these areas of the global ocean are consistent with extremely low F_v/F_m values and indicative of a large fraction of non-functional PSII reaction centers and energetically uncoupled antenna pigment-protein complexes (*21–23*).

There is a strong diel cycle in fluorescence lifetimes; in general, lifetimes were longer at night than during daytime, in spite of a marked reduction in the quantum yields of photochemistry under strong sunlight (Fig. 2). The >5 fold variability in dark-adapted fluorescence lifetimes in situ far exceeds that predicted by Eq. 1. However, this dynamic range is greatly attenuated in high light, when NPQ processes are activated. For example, exceptionally long lifetimes (>2 ns) measured in a dark-adapted state in HNLC regions decrease by more than two-fold in high light, whereas relatively short lifetimes (~ 1 ns) in low-nutrient-low-chlorophyll (LNLC) regions decrease by only 30% under the same conditions (Fig. 2A). Regardless of the molecular mechanisms responsible for NPQ, the net result for high light conditions is increased thermal dissipation of absorbed light in PSII leading to both reductions in photochemical energy conversion efficiency and in the range of variability of the quantum yields of fluorescence.

With the launch of the Moderate Resolution Imaging Spectroradiometer (MODIS) and MEdium Resolution Imaging Spectrometer (MERIS) satellites, which possess the capability of remotely detecting solar induced chlorophyll fluorescence signals from the global ocean, it became theoretically possible to calculate the quantum yield of chlorophyll fluorescence from space (*24–26*). However, the theoretical basis for estimating the relationship between chlorophyll fluorescence and photochemistry was developed before there was an understanding of NPQ (*24*). We therefore examined how the measured in situ fluorescence lifetimes are related to satellite-derived estimates of the quantum yield of chlorophyll *a* fluorescence.

Statistical analyses (effective sample size >20,000) by both Pearson's linear correlation coefficient and two non-parametric Kendall's tau and Spearman's rho coefficients revealed a weak linear correlation ($p<0.01$) between these satellite derived solar induced fluorescence yields and the ship based measurements (Table S1). Satellite-based estimates of the quantum yield are derived from observations of the surface ocean close to local noon (*27*). Hence, the remotely sensed estimates inevitably are obtained at very high irradiances and are strongly influenced by NPQ, a phenomenon that is extremely difficult to quantify in global biophysical models. NPQ is not only critically dependent on pigment composition within the light harvesting antennae (which, in turn, is affected by phytoplankton community composition), but also on upper ocean turbulence as it affects the light field experienced by the community (*28*), as well as nutrient stress (*19*). Despite these complications, qualitative comparison of satellite-derived maps of quantum yields of chlorophyll fluorescence (Fig. 3) reveals basic trends that often, but not always correspond to in situ lifetime measurements. For example, in the Southern Ocean (an HNLC region), satellite-derived quantum yields are high and correlate with long lifetimes. In this iron limited region of the world oceans, there is a well-documented reduction in photosynthetic energy conversion efficiency as a result of impairment of PSII reaction centers and potential energetic uncoupling of the antenna pigment-protein complexes (*7*, *22*). In the low nutrient, low chlorophyll regions of the central oceanic gyres of the North and South Pacific and the

North Atlantic, measured fluorescence lifetimes are significantly shorter compared to HNLC regions. Although the mean fluorescence yield based on the satellite retrievals for the oligotrophic open ocean is 0.043 (Fig. 4) and is generally concordant with that measured in situ values, the high estimates of quantum yields obtained from the space-based platform (Fig. 3) are not corroborated by in situ lifetime measurements. Further, the range of estimated quantum yields derived from satellite-based measurements (> six fold) is far larger than that of the in situ lifetimes measured at high irradiances (~ 3-fold). Indeed, the range of the estimated quantum yields of fluorescence in the global ocean (~ 0.02 to 0.15) appears to exceed that of our current biophysical understanding of photochemistry in phytoplankton. What might be the source of this discrepancy?

In the central ocean gyres, where surface chlorophyll concentrations are very low (<0.1 $mg \cdot m^{-3}$), the fluorescence signals propagated to space are extremely weak. As a result, the current algorithms used to calculate quantum yields of fluorescence become increasingly uncertain (Fig. 4 and (*26*, *29*)). The relationship between measured lifetimes and satellite-derived quantum yields diverge. In contrast to the satellite-derived yields which have significant "noise", the in situ lifetime measurements remain extremely precise (within 5%) even at the lowest chlorophyll concentrations found in the upper ocean. Another factor behind this discrepancy is the effect of pigment packaging within a phytoplankton cell (*25*, *30*, *31*), which is most pronounced in larger cells and reduces the observed quantum yields, as compared to their true "molecular" values inferred from lifetime measurements. Similarly, the uncertainties of the current algorithms for remote sensing retrievals of phytoplankton absorption coefficients (*25*) further reduce the accuracy of satellite-based estimates of the quantum yields.

Although quantum yields of chlorophyll fluorescence obtained from current satellite sensors have many inherent inaccuracies, this approach to understanding global photophysiology of phytoplankton should not be abandoned. We suggest that relating the space-based estimates to in situ measurements of chlorophyll fluorescence lifetimes will provide a pathway to understanding photobiological energy utilization and dissipation processes on a global scale. For example, the maximal average photochemical energy conversion efficiency (ϕ_p) at night in the global ocean, obtained simultaneously with our lifetime measurements, is 0.35 ± 0.11 (Fig. S2). Given an average night-time lifetime of 1.13 ns (Fig. 2), we deduce that thermal energy dissipation accounts for ~ 60% of the photosynthetically active quanta absorbed by phytoplankton globally. In contrast, under optimal growth conditions in the laboratory, an average phytoplankton cell utilizes ~ 65% of the absorbed quanta for photochemistry and dissipates <35% as heat. That thermal dissipation of absorbed quanta by phytoplankton in the upper ocean is so high strongly implies that a large fraction of cells have impaired or non-functional PSII reaction centers, and/or uncoupled photosynthetic antenna. We conclude that, while photochemical energy conversion to biomass in the oceans accounts for half of the global carbon fixed per annum, the overall energy conversion efficiency is relatively low and is limited by nutrient supply

REFERENCES AND NOTES

1. D. Antoine, J. M. Andre, A. Morel, Oceanic primary production. 2. Estimation at global scale from satellite (coastal zone color scanner) chlorophyll. *Global Biogeochem. Cycles* **10**, 57–69 (1996). doi:10.1029/95GB02832
2. C. B. Field, M. J. Behrenfeld, J. T. Randerson, P. Falkowski, Primary production of the biosphere: Integrating terrestrial and oceanic components. *Science* **281**, 237–240 (1998). Medline doi:10.1126/science.281.5374.237
3. M. J. Behrenfeld, E. Boss, D. A. Siegel, D. M. Shea, Carbon-based ocean productivity and phytoplankton physiology from space. *Global Biogeochem. Cycles* **19**, GB1006 (2005). doi:10.1029/2004GB002299
4. M. J. Behrenfeld, P. G. Falkowski, Photosynthetic rates derived from satellite-based chlorophyll concentration. *Limnol. Oceanogr.* **42**, 1–20 (1997). doi:10.4319/lo.1997.42.1.0001
5. P. G. Falkowski, Z. Kolber, Variations in chlorophyll fluorescence yields in phytoplankton in the world oceans. *Aust. J. Plant Physiol.* **22**, 341–355 (1995). doi:10.1071/PP9950341
6. Z. Kolber, P. G. Falkowski, Use of active fluorescence to estimate phytoplankton photosynthesis *in situ*. *Limnol. Oceanogr.* **38**, 1646–1665 (1993). doi:10.4319/lo.1993.38.8.1646
7. G. H. Krause, E. Weis, Chlorophyll fluorescence and photosynthesis: The basics. *Annu. Rev. Plant Physiol.* **42**, 313–349 (1991). doi:10.1146/annurev.pp.42.060191.001525
8. P. W. Boyd, A. J. Watson, C. S. Law, E. R. Abraham, T. Trull, R. Murdoch, D. C. Bakker, A. R. Bowie, K. O. Buesseler, H. Chang, M. Charette, P. Croot, K. Downing, R. Frew, M. Gall, M. Hadfield, J. Hall, M. Harvey, G. Jameson, J. LaRoche, M. Liddicoat, R. Ling, M. T. Maldonado, R. M. McKay, S. Nodder, S. Pickmere, R. Pridmore, S. Rintoul, K. Safi, P. Sutton, R. Strzepek, K. Tanneberger, S. Turner, A. Waite, J. Zeldis, A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* **407**, 695–702 (2000). Medline doi:10.1038/35037500
9. T. S. Bibby, M. Y. Gorbunov, K. W. Wyman, P. G. Falkowski, Photosynthetic community responses to upwelling in mesoscale eddies in the subtropical North Atlantic and Pacific Oceans. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **55**, 1310–1320 (2008). doi:10.1016/j.dsr2.2008.01.014
10. P. G. Falkowski, D. Ziemann, Z. Kolber, P. K. Bienfang, Role of eddy pumping in enhancing primary production in the ocean. *Nature* **352**, 55–58 (1991). doi:10.1038/352055a0
11. M. J. Behrenfeld, K. Worthington, R. M. Sherrell, F. P. Chavez, P. Strutton, M. McPhaden, D. M. Shea, Controls on tropical Pacific Ocean productivity revealed through nutrient stress diagnostics. *Nature* **442**, 1025–1028 (2006). Medline doi:10.1038/nature05083
12. D. J. Suggett, C. M. Moore, A. E. Hickman, R. J. Geider, Interpretation of fast repetition rate (FRR) fluorescence: Signatures of phytoplankton community structure versus physiological state. *Mar. Ecol. Prog. Ser.* **376**, 1–19 (2009). doi:10.3354/meps07830
13. D. Tchernov, M. Y. Gorbunov, C. de Vargas, S. Narayan Yadav, A. J. Milligan, M. Häggblom, P. G. Falkowski, Membrane lipids of symbiotic algae are diagnostic of sensitivity to thermal bleaching in corals. *Proc. Natl. Acad. Sci. U.S.A.* **101**, 13531–13535 (2004). Medline doi:10.1073/pnas.0402907101
14. P. Falkowski, J. A. Raven, *Aquatic Photosynthesis*. (Princeton Univ., Princeton, NJ, ed. 2, 2007).
15. W. L. Butler, R. J. Strasser, Tripartite model for the photochemical apparatus of green plant photosynthesis. *Proc. Natl. Acad. Sci. U.S.A.* **74**, 3382–3385 (1977). Medline doi:10.1073/pnas.74.8.3382
16. M. Bradbury, N. R. Baker, Analysis of the induction of chlorophyll fluorescence in

leaves and isolated thylakoids - contributions of photochemical and non-photochemical quenching. *Proc. R. Soc. London Ser. B* **220**, 251–264 (1983). doi:10.1098/rspb.1983.0098
17. Information on materials and methods is available on *Science* Online.
18. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Springer Science+Business Media, LLC., New York, ed. 3, 2006).
19. C. M. Moore, M. M. Mills, K. R. Arrigo, I. Berman-Frank, L. Bopp, P. W. Boyd, E. D. Galbraith, R. J. Geider, C. Guieu, S. L. Jaccard, T. D. Jickells, J. La Roche, T. M. Lenton, N. M. Mahowald, E. Marañón, I. Marinov, J. K. Moore, T. Nakatsuka, A. Oschlies, M. A. Saito, T. F. Thingstad, A. Tsuda, O. Ulloa, Processes and patterns of oceanic nutrient limitation. *Nat. Geosci.* **6**, 701–710 (2013). doi:10.1038/ngeo1765
20. J. A. Raven, M. C. W. Evans, R. E. Korb, The role of trace metals in photosynthetic electron transport in O_2-evolving organisms. *Photosynth. Res.* **60**, 111–150 (1999). doi:10.1023/A:1006282714942
21. I. R. Vassiliev, Z. Kolber, K. D. Wyman, D. Mauzerall, V. K. Shukla, P. G. Falkowski, Effects of iron limitation on photosystem II composition and light utilization in *Dunaliella tertiolecta*. *Plant Physiol.* **109**, 963–972 (1995). Medline
22. P. G. Falkowski, R. M. Greene, R. J. Geider, Physiological limitations on phytoplankton productivity in the ocean. *Oceanography (Wash. D.C.)* **5**, 84–91 (1992). doi:10.5670/oceanog.1992.14
23. P. S. Schrader, A. J. Milligan, M. J. Behrenfeld, Surplus photosynthetic antennae complexes underlie diagnostics of iron limitation in a cyanobacterium. *PLOS ONE* **6**, e18753 (2011). Medline doi:10.1371/journal.pone.0018753
24. M. R. Abbott, R. M. Letelier, "Algorithm theoretical basis document: Chlorophyll fluorescence (MODros. Inf. Serv. Product Number 20)" (Ocean Biology Processing Group, NASA's Earth Observing System, 1999).
25. M. J. Behrenfeld, T. K. Westberry, E. S. Boss, R. T. O'Malley, D. A. Siegel, J. D. Wiggert, B. A. Franz, C. R. McClain, G. C. Feldman, S. C. Doney, J. K. Moore, G. Dall'Olmo, A. J. Milligan, I. Lima, N. Mahowald, Satellite-detected fluorescence reveals global physiology of ocean phytoplankton. *Biogeosciences* **6**, 779–794 (2009). doi:10.5194/bg-6-779-2009
26. Y. Huot, B. A. Franz, M. Fradette, Estimating variability in the quantum yield of Sun-induced chlorophyll fluorescence: A global analysis of oceanic waters. *Remote Sens. Environ.* **132**, 238–253 (2013). doi:10.1016/j.rse.2013.01.003
27. A. Savtchenko, D. Ouzounov, S. Ahmad, J. Acker, G. Leptoukh, J. Koziana, D. Nickless, Terra and Aqua MODIS products available from NASA GES DAAC. *Adv. Space Res.* **34**, 710–714 (2004). doi:10.1016/j.asr.2004.03.012
28. A. C. Alderkamp, H. J. W. de Baar, R. J. W. Visser, K. R. Arrigo, Can photoinhibition control phytoplankton abundance in deeply mixed water columns of the Southern Ocean? *Limnol. Oceanogr.* **55**, 1248–1264 (2010). doi:10.4319/lo.2010.55.3.1248
29. T. J. Browning, H. A. Bouman, C. M. Moore, Satellite-detected fluorescence: Decoupling nonphotochemical quenching from iron stress signals in the South Atlantic and Southern Ocean. *Global Biogeochem. Cycles* **28**, 510–524 (2014). doi:10.1002/2013GB004773
30. A. Bricaud, H. Claustre, J. Ras, K. Oubelkheir, Natural variability of phytoplanktonic absorption in oceanic waters: Influence of the size structure of algal populations. *J. Geophys. Res. Oceans* **109**, C11010 (2004). doi:10.1029/2004JC002419
31. A. Morel, A. Bricaud, Theoretical results concerning light absorption in a discrete medium, and application to specific absorption of phytoplankton. *Deep-Sea Res.* **28**, 1375–1393 (1981). doi:10.1016/0198-0149(81)90039-X
32. T. P. Boyer *et al.*, "World Ocean Database 2013" (Silver Spring, MD, U.S., 2013).
33. F. I. Kuzminov, M. Y. Gorbunov, Energy dissipation pathways in Photosystem 2 of the diatom, *Phaeodactylum tricornutum*, under high-light conditions. *Photosynth. Res.* (2015). Medline doi:10.1007/s11120-015-0180-3
34. J. Enderlein, R. Erdmann, Fast fitting of multi-exponential decay curves. *Opt. Commun.* **134**, 371–378 (1997). doi:10.1016/S0030-4018(96)00384-7
35. S. S. Brody, E. Rabinowitch, Excitation lifetime of photosynthetic pigments in vitro and in vivo. *Science* **125**, 555 (1957). Medline doi:10.1126/science.125.3247.555
36. G. N. Lewis, M. Kasha, Phosphorescence in fluid media and the reverse process of singlet-triplet absorption. *J. Am. Chem. Soc.* **67**, 994–1003 (1945). doi:10.1021/ja01222a032
37. A. R. Holzwarth, Fluorescence Lifetimes in Photosynthetic Systems. *Photochem. Photobiol.* **43**, 707–725 (1986).
38. F. Morales, N. Moise, R. Quílez, A. Abadía, J. Abadía, I. Moya, Iron deficiency interrupts energy transfer from a disconnected part of the antenna to the rest of Photosystem II. *Photosynth. Res.* **70**, 207–220 (2001). Medline doi:10.1023/A:1017965229788
39. I. Moya, M. Silvestri, O. Vallon, G. Cinque, R. Bassi, Time-resolved fluorescence analysis of the photosystem II antenna proteins in detergent micelles and liposomes. *Biochemistry* **40**, 12552–12561 (2001). Medline doi:10.1021/bi010342x
40. R. Croce, H. van Amerongen, Light-harvesting and structural organization of Photosystem II: From individual complexes to thylakoid membrane. *J. Photochem. Photobiol. B* **104**, 142–153 (2011). Medline doi:10.1016/j.jphotobiol.2011.02.015
41. M. Gorbunov, P. Falkowski, in *Photosynthesis: Fundamental Aspects to Global Perspectives: Proceedings of the 13th International Society of Photosynthesis*, A. van der Est, D. Bruce, Eds. (Alliance Commnuncations Group, Lawrance, KS, 2005), vol. 2, pp. 1029–1031.
42. C. M. Hu, Z. Lee, B. Franz, Chlorophyll a algorithms for oligotrophic oceans: A novel approach based on three-band reflectance difference. *J. Geophys. Res. Oceans* **117**, C01011 (2012). doi:10.1029/2011JC007395
43. A. Bricaud, A. Morel, M. Babin, K. Allali, H. Claustre, Variations of light absorption by suspended particles with chlorophyll a concentration in oceanic (case 1) waters: Analysis and implications for bio-optical models. *J. Geophys. Res. Oceans* **103**, 31033–31044 (1998). doi:10.1029/98JC02712
44. Y. Huot, C. A. Brown, J. J. Cullen, New algorithms for MODIS sun-induced chlorophyll fluorescence and a comparison with present data products. *Limnol. Oceanogr. Methods* **3**, 108–130 (2005). doi:10.4319/lom.2005.3.108
45. A. Morel, Y. Huot, B. Gentili, P. J. Werdell, S. B. Hooker, B. A. Franz, Examining the consistency of products derived from various ocean color sensors in open ocean (Case 1) waters in the perspective of a multi-sensor approach. *Remote Sens. Environ.* **111**, 69–88 (2007). doi:10.1016/j.rse.2007.03.012
46. K. Pearson, Note on regression and inheritance in the case of two parents. *Proc. R. Soc. London* **58**, 240–242 (1895). doi:10.1098/rspl.1895.0041
47. M. G. Kendall, A new measure for rank correlation. *Biometrika* **30**, 81–93 (1938). doi:10.1093/biomet/30.1-2.81
48. C. Spearman, The proof and measurement of association between two things. *Am. J. Psychol.* **15**, 72–101 (1904). doi:10.2307/1412159
49. A. N. Kolmogorov, Sulla determinazione empirica di una legge di distribuzione. *Giornale dell'Istituto Italiano degli Attuari* **4**, 83-91 (1933).
50. N. Smirnov, Table for estimating the goodness of fit of empirical distributions. *Ann. Math. Stat.* **19**, 279–281 (1948). doi:10.1214/aoms/1177730256
51. G. W. Corder, D. I. Foreman, in *Nonparametric Statistics: A Step-by-Step Approach* (Wiley, Hoboken, NJ, 2014), pp. 140–142.
52. H. Abdi, in *Encyclopedia of measurement and statistics*, N. J. Salkind, Ed. (SAGE Publications, Inc., Thousands Oaks, CA, 2007), vol. 2.

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/cgi/content/full/science.aab2213/DC1
Materials and Methods
Figs. S1 to S4
Table S1
References (*32*–*52*)

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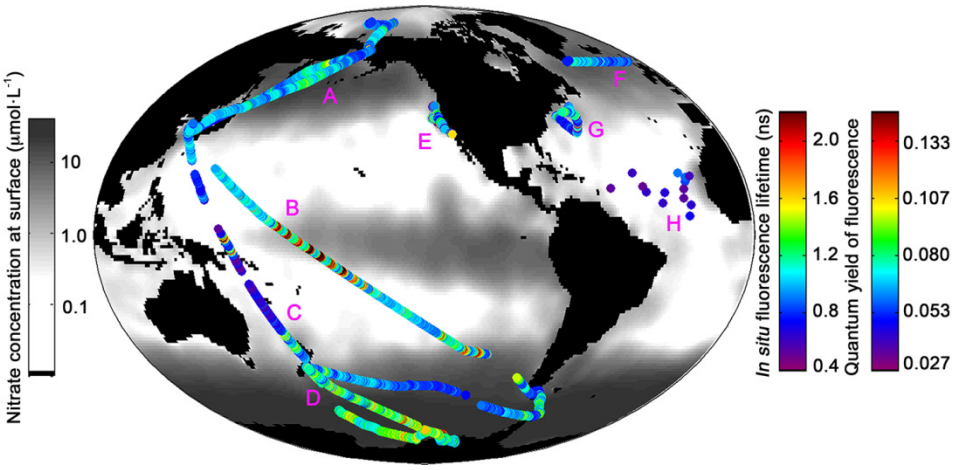
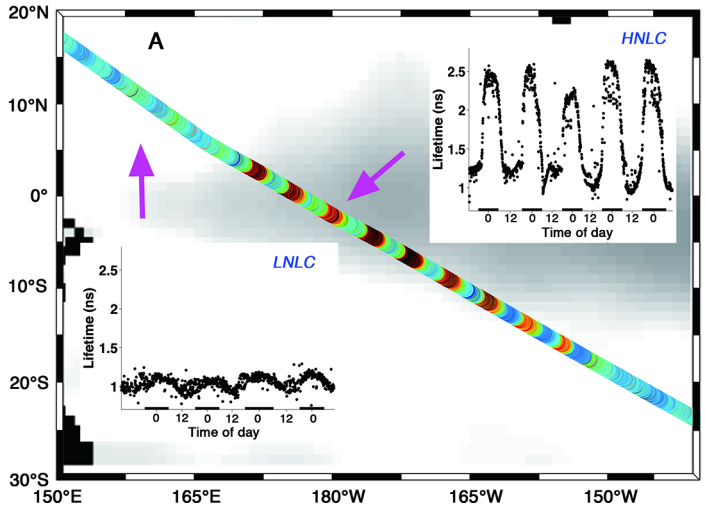


Fig. 1. Global distribution of ship-based measurements of chlorophyll fluorescence lifetimes and the derived quantum yields of fluorescence (Eq. 2) in the upper ocean superimposed on the climatological map of surface nitrate concentrations in the world ocean (*32*). Periods of in situ sampling were (A) July-Aug. 2011; (B) Oct.-Nov. 2011; (C) Oct.-Nov. 2010; (D) Jan. 2012; (E) July 2014; (F) Sept. 2010; (G) May 2014; (H) Aug. 2008.



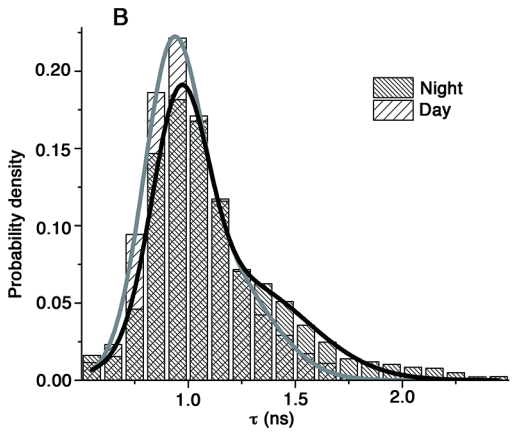


Fig. 2. (A) Representative diel cycles of chlorophyll fluorescence lifetimes in HNLC and LNLC regions of the Pacific Ocean obtained in Oct. 2011. Color bar for lifetimes is the same as in Fig. 1; (B) Histograms of the fractional frequency of lifetime measurements in daytime and at night, respectively. The mean value of nighttime lifetimes is 1.13 ± 0.33 ns and that of daytime lifetimes is 1.02 ± 0.22 ns.

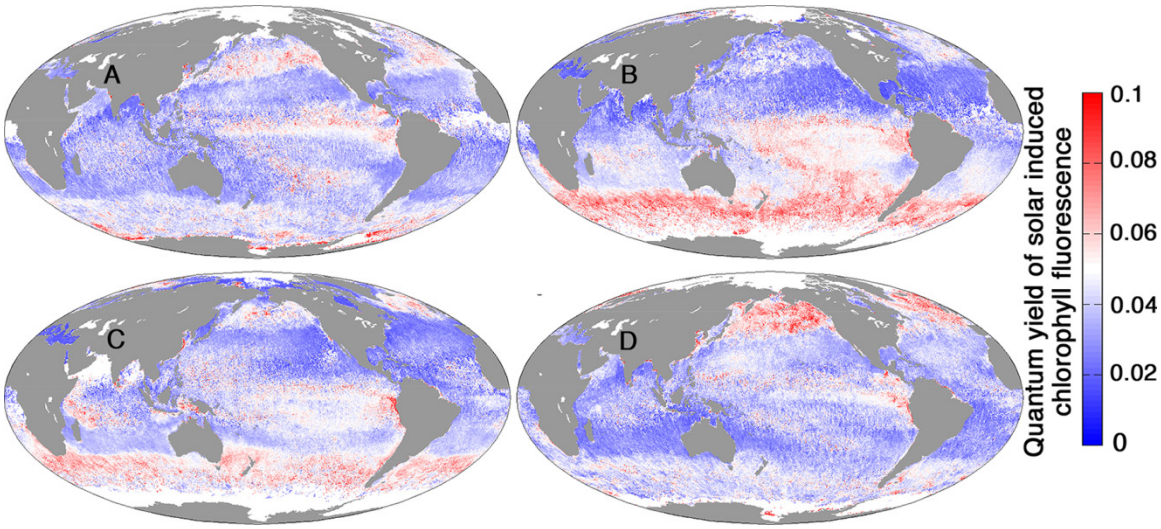


Fig. 3. Global seasonal maps of quantum yields of solar induced chlorophyll fluorescence in the upper ocean. (**A**) boreal winter (21 Dec. 2011 – 20 Mar., 2012); (**B**) boreal spring (21 Mar. - 20 June, 2012); (**C**) boreal summer (21 Sept. – 20 Dec., 2012); (**D**) boreal autumn (21 Sept. – 20 Dec., 2012).

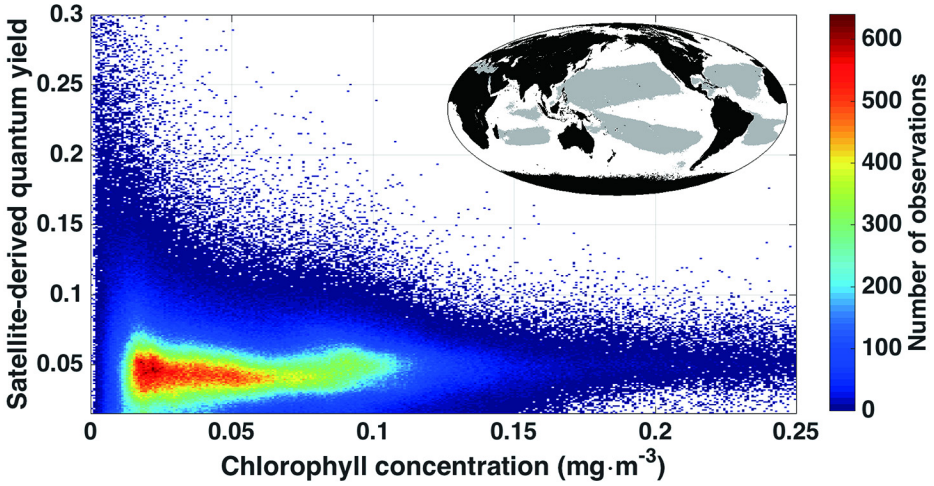


Fig. 4. Variations in MODIS retrievals of the quantum yields of chlorophyll fluorescence (N=5.17 ×10^6) with chlorophyll abundance (*17*). The mean value of these satellite-derived quantum yields is 0.043. The average value of in situ lifetime measurements at noon (between 10 a.m to 2 p.m local time) is 0.99 ± 0.2 ns, which corresponds to the quantum yield of 0.066 ± 0.013. (**Inset**) Global distribution (ten year average) of chlorophyll concentrations in the boreal summer. The grey area indicates oligotrophic regions with chlorophyll concentrations below 0.1 mg·m^{-3}; this area covers ~30% of the global ocean.