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BRIEF COMMUNICATION

On oxygen production by photosynthesis: A viewpoint

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Abstract

In this brief communication we provide an estimate of the part of the incident solar energy used for oxygen evolution as well as the time, in years, needed for the generation of the present amount of molecular oxygen in the biosphere by photosynthesis on land and in the ocean. We find this to be ≈3,000 yr. We also find that the ocean produces 22% more oxygen than the land surface.

Additional key words: Govindjee; net primary production; oceanic oxygen production; solar radiation; terrestrial oxygen production.

Astronomical and atmospheric factors

For basics of oxygenic photosynthesis on land and in the oceans, see Rabinowitch and Govindjee (1969), Falkowski and Raven (2007), and Blankenship (2014). The amount of solar radiation reaching the Earth's atmosphere varies by about 6.9% over the year due to the ellipticity of the Earth's orbit around the sun. There are also small (~0.2%) longer-term variations due to the 22-yr cycle and other cycles of the Sun. We shall adopt a value of 1,360.8 W m^{-2} for the so-called solar "constant", or more correctly, the solar irradiance, at the average Earth distance (Kopp and Lean 2011, Zagoni 2016). This is a value for the solar minimum. The value at solar maximum is ~0.2% higher (Fröhlich 2000). A solar constant of 1,360.8 W m^{-2} means that the Earth surface, averaged over 24 h and latitude, receives 340.2 W m^{-2}, as the cross-sectional area of a sphere is 1/4 of its surface area.

When the solar radiation reaches the atmosphere, part of it is reflected or scattered back from the atmosphere and clouds back to space. With, on the average, 60% of the Earth surface being covered by clouds, we estimate this to be ~75.1 W m^{-2} for the whole Earth surface. A further 79.8 W m^{-2} is absorbed by the atmosphere and clouds (Zagoni 2016), which leaves us with 185.3 W m^{-2} reaching the ground, of which 25.1 W m^{-2} is reflected back from the ground.

We know that not light of all wavelengths reaching the ground or the sea level can be used for oxygenic photosynthesis. PAR is defined as radiation from 400 nm to 700 nm. The ratio between PAR and total radiation depends on the spectrum of the radiation, and that in turn depends on how much air (air mass) the radiation has passed through, and this is a function of the solar zenith angle. Escobedo *et al*. (2011) tabulated literature values of the average ratio daily for 16 places having latitudes from 15°S to 52°N, and the mean ± standard deviation of these being 0.467 ± 0.028. Spectra presented by Mecherikunnel and Richmond (1980) indicate that the ratio decreases with solar elevation, so it is possible that the average would have been somewhat lower than 0.467 if higher latitudes had been included. Since only a small fraction of total net primary production takes place at these high latitudes (Field *et al*. 1998) we will disregard this and use the value of 0.467 in the following discussion.

Using the fraction of 0.467 (for PAR/total radiation), and multiplying it by the total amount of solar radiation (*see* above), we arrive at an average irradiance, available for oxygenic photosynthesis, of 0.467 × 185.3 W m^{-2} = 86.53 W m^{-2}. After multiplying it by the surface area of the Earth (510,100,000 km^2 = 5.101 × 10^{14} m^2) and the number of seconds in a year (31,556,926 = 3.1556926 × 10^7), we obtain the energy available to be: 1.39 × 10^{24} J for photosynthesis per year.

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Abbreviations: NPP – net primary production.
Acknowledgements: In celebration of our good friend Govindjee's 85th birthday on October 24, 2017. In our view, Govindjee is the unique symbol and banner of PHOTOSYNTHESIS of our days. His infectious enthusiasm, and service to the photosynthesis community is unmatched. And, his research and teaching contributions have surpassed most of the grand masters of our time.

Quantification of global photosynthesis

NPP (net primary production) is the amount of photosynthetically fixed carbon available to the primary consumers, *i.e.*, at the first heterotrophic level in an ecosystem or the whole biosphere and also the difference between autotrophic photosynthesis and respiration (Field *et al*. 1998). Field *et al*. (1998) calculated the total NPP on the planet to be 48.5 Pg(C) yr^{-1} for land, but for the oceans, 56.4 Pg(C) yr^{-1} [1 Pg(C) = 1 petagram of carbon = 10^{15} g(C)].

It is obvious that NPP must vary from year to year, depending on ENSO [the southern (El Niño/La Niña)] climatic oscillation and other factors. Huston *et al*. (2009) found the ocean NPP to vary from a value of 59.90 to 62.60 Pg(C) yr^{-1}, while Behrenfeld *et al*. (2001) calculated NPP to be in the range of 54–59 Pg(C) yr^{-1} for the oceans and 57–58 Pg(C) yr^{-1} for the land.

In this paper, we will use the average values from Behrenfeld *et al*. (2001) of 57.5 Pg(C) yr^{-1} for the land and 56.5 Pg(C) yr^{-1} for the oceans; this gives a total of 114 Pg(C) yr^{-1}. For simplicity, we shall assume that this comes in the form of a dilute sucrose solution. To convert this to solid sucrose requires the use of 16.3 kJ mol^{-1} energy (Miller and de Pablo 2000); further, burning of sucrose will yield 5,644.6 kJ mol^{-1} (Domalski 1972). This amounts to a net energy release of 5,628.3 kJ mol^{-1} or 5,628.3/12/12 kJ g^{-1}(C) = 3.91×10^4 J g^{-1}(C), since there are 12 carbon atoms in a molecule of glucose and carbon has an atomic mass of ≈12. In other words, this means a capture of $3.91 \times 10^4 \times 114 \times 10^{15}$ J yr^{-1} which equals 4.46×10^{21} J yr^{-1} for the primary production (Behrenfeld *et al*. 2001).

Based on the above, we deduce that the energy efficiency of the biosphere's photosynthesis is: energy captured in primary production per year divided by energy available for photosynthesis per year = 4.46 $10^{21}/(1.39 \times 10^{24})$ = 3.21×10^{-3}, or 0.32%. Note that this is based on PAR reaching the ground, vegetation, and ocean surface; however, the efficiency based on the total amount of solar radiation intercepted by the Earth is (using the values from above for extraterrestrial irradiance, seconds per year, and surface of the Earth) $4.46 \times 10^{21}/(340.2 \times 3.1556926 \times 10^7 \times 5.101 \times 10^{14})$ = 0.00081 = 0.081%. This is close to the value (≈0.1%) that one of us (Borisov 1979) had estimated before the current data were available.

Factors limiting photosynthesis

The energetic efficiency of photosynthesis (0.32%) as presented above may seem very low. We discuss below the reasons for this low value.

There is a thermodynamic limit for this efficiency. Several values are available, but they have different bases. Taking into account just the primary reactions of photosynthesis, Knox (1969) obtained an efficiency of about 70% for the conversion of sunlight into free energy available for photosynthesis. However, Albarrán-Zavala and Angulo-Brown (2007) calculated the maximum efficiency of 27.3% for oxygenic photosynthesis, which included the Calvin-Benson cycle for CO_2 fixation.

We know that all light that strikes the photosynthetic organism is not absorbed, and even some, which is absorbed, is in pigments (*e.g*., anthocyanins or some carotenoids) that do not channel energy to photosynthesis. In particular, many organisms possess yellow pigments absorbing some of the blue-violet light that is not involved in photosynthesis (*e.g*., McCree 1972, Paradiso *et al*. 2011).

To a greater extent than any of the above, unfavorable environmental factors limit NPP. Terrestrial NPP is limited by low concentration of CO_2 in the environment, and by temperature, drought or nutrient deficiency in many places on our Earth. Fig. 1*A* shows the relative importance of limiting water, light, and temperature. Fig. 1*B* shows the resulting distribution of annual terrestrial net primary production.

Even with sufficient water and nutrients, and optimal temperature, light might be so strong that not all of it can be used. Sometimes plants must dissipate excess energy, as heat, to avoid damage (Demmig-Adams *et al*. 2014).

Since the world oceans have more than twice the area of the land on our planet, and the total NPP expressed in terms of carbon is almost the same for both (Field *et al*. 1998; *see* also Brown *et al*. 2014), we can immediately see that the productivity per area unit is much less for the oceans. As we see from Fig. 1*C*, much of the oceanic productivity is concentrated in the coastal areas, nourished by runoff and wind-blown dust from land, and by upwelling deep-sea water in some areas. At the surface, temperature and light are more limiting than the nutrients only at the highest latitudes.

Deserts are areas of very low NPP, but they are important for providing nutrients to other areas. For example, wind-blown dust from the Sahara desert fertilizes not only the Atlantic ocean, but is even an important nutrient component for the Amazonian rainforest (Yu *et al*. 2015).

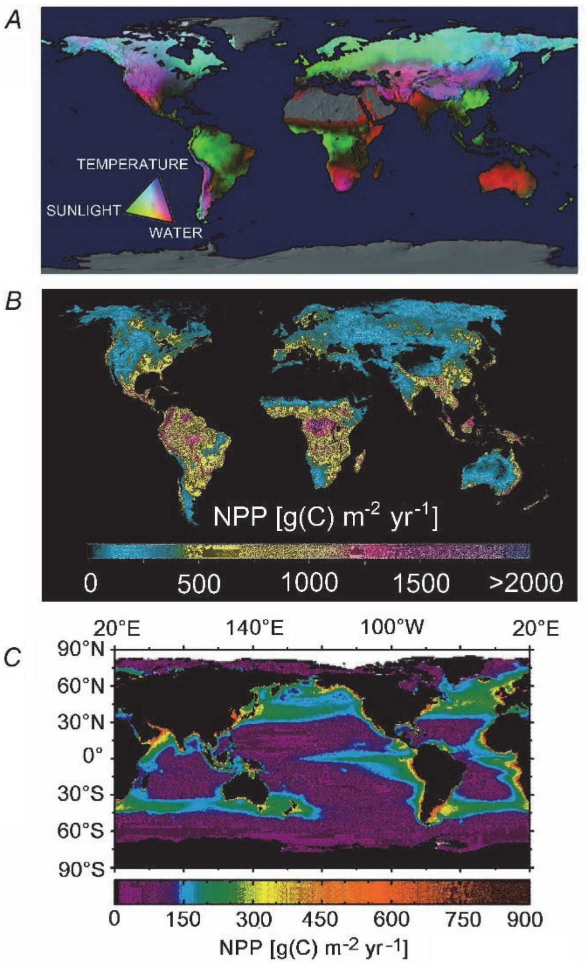

Fig. 1. *A*: Relative importance of light, temperature, and water in limiting terrestrial net primary production in various land areas in our world. Modified from Running and Zhao (2015) (also see Zhao *et al*. 2011), based on data in Nemani *et al*. (2003); *B*: Distribution of annual terrestrial net primary production. Modified from Running *et al*. (2004); *C*: Distribution of annual oceanic net primary production. Modified from Brown *et al*. (2014).

Production of molecular oxygen, O_2

As mentioned above, Behrenfeld *et al*. (2001) had calculated an NPP on land of 57.5 Pg(C) yr^{-1}, and in the oceans of 56.5 Pg(C) yr^{-1}. To convert this to oxygen production we consider the formula:

CO_2 + H_2O + light ==> nO_2 + plant (or algal or cyanobacterial) ”matter” (1)

which in text books is written as (CH_2O), letting n to be 1. However, plant matter does not have the composition exactly corresponding to (CH_2O). For land vegetation (plants) the difference is not that great, and a more realistic estimate for n is 1.05 (Keeling 1988a,b). The composition of cyanobacteria and algae differs considerably from that of terrestrial plants, and according to Keeling *et al*. (1993), the average oceanic value for n is 1.30 (*see* Eq. 1).

We now ask: How much time does it take for the oxygenic photoautotrophs to produce the amount of O_2 currently present in the atmosphere and oceans? According to Keeling *et al*. (1993), the atmosphere contains 37,000 Pmol or 1.18×10^{21} g(O_2), whereas Budyko *et al*. (1987) give this value to be 37,500 Pmol or 1.20×10^{21} g. However, Long *et al*. (2016) point out that the amount dissolved in the oceans is much lower – about 237 Pmol of dissolved O_2 or 3.8×10^{18} g. However, we shall use the value 1.19×10^{21} g for the whole biosphere.

Thus, taking the molecular mass of C (12) and O_2 (32) into account, we can calculate the mass of oxygen produced per year as: $(1.05 \times 57.5 + 1.3 \times 56.5) \times 32/12$ Pg = $= (60.4 + 73.5) \times 2.67$ Pg = 357 Pg = 3.57×10^{17} g.

Thus, the answer to the question raised above about the time to produce the present amount of molecular oxygen in our biosphere is: $1.19 \times 10^{21}/3.57 \times 10^{17}$ yr ≈ 3,000 yr.

Concluding remarks

Present-day photosynthesis is the result of a long evolution (Björn and Govindjee 2015; Fischer *et al*. 2016). From an early beginning of ultraviolet photochemistry, the first form of "photosynthesis" driven by visible light (still carried out by extant organisms) was probably mediated by bacteriorhodopsin (Skulachev 1994). Light absorbed by this protein gives rise to a pH difference across a membrane that can drive ATP synthesis *via* reversal of ATPase-mediated ATP hydrolysis. Oxygenic photosynthesis mediated by chlorophyll has come a long way from this, and it is to this process that we owe not only the oxygen we breathe, but also a climate that allows human life. The energetic efficiency on a planetary scale, as calculated above (about a third of a percent), may seem low. We hope to have demonstrated in this brief communication that this is not mainly due to biological deficiency, but to properties of our planet that biology cannot control. At present, due to our inability to control our own actions, the concentration of carbon dioxide in the atmosphere and oceans is rising, while the concentration of oxygen is declining (*see, e.g*., Keeling and Garcia 2002, Sirignano *et al*. 2010, Livina *et al*. 2015). We have a responsibility for the future of our planet.

References

Albarrán-Zavala E., Angulo-Brown F.: A simple thermodynamic analysis of photosynthesis. – Entropy **9**: 152-168, 2007.

Behrenfeld M.J., Randerson J.T., McClain C.R. *et al.*: Biospheric primary production during an ENSO transition. – Science **291**: 2594-2597, 2001.

Björn L.O., Govindjee: The evolution of photosynthesis and its environmental impact.– In: Björn L.O. (ed.): Photobiology: The Science of Light and Life. Pp. 207-229. Springer Science+ Business Media, New York 2015.

Blankenship R.E.: Molecular Mechanisms of Photosynthesis, 2nd ed. Pp. 312. Wiley-Blackwell, Hoboken 2014.

Borisov A.Y.: Photosynthesizing organisms: converters of solar energy. – In: Barber J. (ed.): Photosynthesis in Relation to Model Systems. Pp 1-26. Elsevier/North Holland Biomedical Press, Amsterdam–New York–Oxford 1979.

Brown C.W., Uz S.S., Corliss B.H.: Seasonality of oceanic primary production and its interannual variability from 1998 to 2007. – Deep-Sea Res. **190**: 166-175, 2014.

Budyko M.I., Ronov A.B., Yanshin A.L.: History of the Earth's Atmosphere. Pp. 139. Springer Verlag, Heidelberg, 1987.

Demmig-Adams B., Garab G., Adams III W., Govindjee (ed.): Non-Photochemical Quenching and Energy Dissipation In Plants, Algae and Cyanobacteria, Advances in Photosynthesis and Respiration Including Bioenergy and Other Processes, Vol. 40. Pp. 649. Springer, Dordrecht 2014.

Domalski E.S.: Selected values of heats of combustion and heats of formation of organic compounds containing the elements C, H, N, O, P, and S. – J. Phys. Chem. Ref. Data **1**: 221-277, 1972.

Escobedo J.F., Gomes E.N., Oliveira A.P., Soares J.: Ratios of UV, PAR and NIR components to global solar radiation measured at Botucatu site in Brazil. – Renew. Energ. **36**: 169-178, 2011.

Falkowski P., Raven J.: Aquatic Photosynthesis, 2nd ed. Pp. 484. Princton University Press, Princeton 2007.

Field C.B., Behrenfeld M.J., Randerson J.T., Falkowski, P.: Primary production of the biosphere: integrating terrestrial and oceanic components. – Science **281**: 237-240, 1998.

Fischer W.W., Hemp J., Johnson J.E.: Evolution of oxygenic photosynthesis. – Annu. Rev. Earth Planet. Sci. **44**: 647-683, 2016.

Fröhlich C.: Observation of irradiance variations. – Space Sci. Rev. **94**: 15-24, 2000.

Huston M.A., Wolverton S.: The global distribution of net primary production: resolving the paradox. – Ecol. Monogr. **79**: 343-377, 2009.

Keeling R.F.: Development of an Interferometric Oxygen Analyzer for Precise Measurement of the Atmospheric O_2 Mole Fraction. Pp. 178. – PhD Thesis, Harvard University, Harvard 1988a.

Keeling R.F.: Measuring correlations between atmospheric oxygen and carbon dioxide mole fractions: A preliminary study in urban air. – J. Atm. Chem. **7**: 153-l76, 1988b.

Keeling R.F., Najjar R.P., Bender M.L., Tans P.P.: What atmos pheric oxygen measurements can tell us about the global car bon cycle. – Global Biogeochem. Cy. **7**: 37-67, 1993.

Keeling R.F., Garcia H.E.: The change in oceanic O_2 inventory associated with recent global warming – P. Natl Acad. Sci. USA **99**: 7848-7853, 2002.

Knox R.S.: Thermodynamics and the primary processes of photosynthesis. – Biophys. J. **9**: 1351-1362, 1969.

Kopp G., Lean J.L.: A new, lower value of total solar irradiance: Evidence and climate significance. – Geophys. Res. Lett. **38**: L01706, 2011.

Livina V.N., Vaz Martins T.M., Forbes A.B.: Tipping point analysis of atmospheric oxygen concentration. – Chaos **25**: 036403, 2015.

Long M.C., Deutsch C, Ito T.: Finding forced trends in oceanic oxygen. – Glob. Biogeochem. Cycl. **30**: 381-397, 2015.

McCree K.J.: The action spectrum, absorptance and quantum yield of photosynthesis in crop plants. – Agric. Meteorol. **9**: 191-216, 1972.

Mecherikunnel A.T., Richmond J.C.: Spectral distribution of solar radiation. NASA Report TM 82021. Pp. 86. Goddard Space Flight Center, Greenbelt 1980.

Miller D.P., de Pablo J.J.: Calorimetric solution properties of simple saccharides and their significance for the stabilization of biological structure and function. – J. Phys. Chem. B **104**: 8876-8883, 2000.

Nemani R.R., Keeling C.D., Hashimoto H. *et al*.: Climate-driven increases in global terrestrial net primary production from 1982 to 1999. – Science **300**: 1560-1563, 2003.

Paradiso R., Meinen E,. Snel J.F.H. *et al*.: Spectral dependence of photosynthesis and light absorptance in single leaves and canopy in rose. – Sci. Hortic.-Amsterdam **127**: 548-554, 2011.

Rabinowitch E., Govindjee: Photosynthesis. Pp. 273. John Wiley & Sons, New York 1969.

Running S.W., Zhao M.: User's guide daily GPP and annual NPP (MOD17A2/A3) products NASA Earth Observing System MODIS land algorithm. http://www.academia.edu/4620715/ Users_Guide_GPP_and_NPP_MOD17A2_A3_Products_NA SA_MODIS_Land_Algorithm, 2015.

Running S.W., Nemani R.R., Heinsch F.A. *et al*: A continuous satellite-derived measure of global terrestrial primary production. – BioScience **54**: 547-560, 2004.

Sirignano C., Neubert R.E.M., Rödenbeck C., Meijer H.A.J.: Atmospheric oxygen and carbon dioxide observations from two European coastal stations 2000–2005: continental influence, trend changes and APO climatology. – Atmos. Chem. Phys. **10**: 1599-1615, 2010.

Skulachev V.R.: Bioenergetics: the evolution of molecular mechanisms and the development of bioenergetic concepts. – Anton. Leeuw. **65**: 271-284, 1994.

Yu H., Chin M., Yuan T. *et al*.: The fertilizing role of African dust in the Amazon rainforest: A first multiyear assessment based on data from Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations. – Geophys. Res. Lett. **42**: 1984-1991, 2015.

Zagoni M.: A new diagram of Earth's global energy budget. – Acta Geod. Geophys. **51**: 481-492, 2016.

Zhao M., Running S., Heinsch F.A., Nemani R.: MODIS-derived terrestrial primary production. – In: Ramachandran B., Justice C.O., Abrams J. (ed.): Land Remote Sensing and Global Environmental Change Remote Sensing and Digital Image Processing. Pp. 635-660. Springer, New York 2011.