



Photo-oxidation: Major sink of oxygen in the ocean surface layer



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ABSTRACT

Evidence is presented that the oxygen demand associated with photochemical processes in the surface layer of oceans and seas worldwide is of the same order of magnitude as the amount of oxygen released by photosynthesis of the world's marine phytoplankton. Both estimates are of necessity quite rough and therefore the agreement between oxygen loss and production, earlier found only locally in the Atlantic Ocean and the North Sea, came as a surprise. The heavy photochemical oxygen demand of the world's oceans must be explored further in oxygen budget studies by biogeochemical modelling in which special attention is paid to regional and temporal differences in the vertical stratification regime at the surface. Indeed, stratification is the *conditio sine qua non* for photochemical processes that are driven by ultraviolet radiation. Oxygen cannot be expected to be released from the sea to the atmosphere in the permanently stratified open ocean when year-round the oxygen loss associated with photochemistry is so high. In the upper layer of sea and ocean regions of the temperate zone vertical stratification is only pronounced during spring, summer and early autumn, so photochemical oxygen demand there is restricted to those months. We argue that the constancy of the oxygen concentration observed at the surface of the oceans in the tropics and subtropics (80% of Earth's marine regions) is the consequence of the balance between three processes that influence oxygen dissolved in seawater: loss due to photochemical processes and to the activity of microheterotrophs on the one hand, photosynthetic oxygen production by phytoplankton on the other.

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1. Introduction: aquatic-marine versus terrestrial primary productivity

One fundamental aspect of aquatic primary production is hardly ever mentioned in recent publications in the field of marine chemistry: the oxygen that is produced during photosynthesis of microalgae (to be more precise: by cyanobacteria) was 3 billion years ago the *conditio sine qua non* for the development of life on Earth thanks to its release to the atmosphere. Nowadays, oxygen supersaturation at the surface of coastal seas during microalgal blooms (up to 140%, e.g., Gieskes and Kraay, 1977) no doubt still contributes to high atmospheric levels – but only quite locally. In contrast, in open ocean regions the oxygen concentration in the upper mixed layer is very constant (Tijssen, 1979; Gieskes and Kraay, 1982) and oversaturation is hardly ever recorded. The opposite (constant undersaturation) is true for many lakes, especially the humus-rich ones, where low saturation values are the rule rather than the exception (Miles, 1979). In the present essay the background of these contrasting situations is illustrated by focusing attention on an aspect of the oxygen cycle in the ocean that has until now largely been overlooked: the oxygen loss that is associated with photochemical

processes at the surface of seas and oceans. We argue here that this loss factor is so massive and therewith important that it should no longer be ignored in studies of world-wide oxygen cycling and in considerations of the world's oxygen budget.

2. Oxygen cycling in the ocean: sources and sinks

In recent reviews of the world's aquatic oxygen dynamics and its biogeochemical consequences (Blough, 2001; Testa and Kemp, 2011; Haeder et al., 2014) the molecular diffusion at the water–air interface is correctly described as the mechanism responsible for the exchange of oxygen to the atmosphere. In these reviews the concentration of oxygen in the water is basically considered to be determined at the level of photosynthesis on the one hand, and the counteracting process of respiration by heterotrophs and the abiotic process of air–water exchange on the other. Chemical redox reactions (see Larson and Hufnal, 1980) are apparently of minor importance in determining oxygen concentrations in the water phase except locally, in shallow coastal environments. Photo-reduction processes, e.g., of iron–organic matter complexes in shallow humic coastal waters, may result in low dissolved oxygen concentrations (Miles, 1979).

In the reviews just mentioned the importance of photo-oxidative processes (Zepp et al, 1977; Zafriou et al., 1985; Moran and Zepp,

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1997; Zika, 1981) in the ocean's oxygen budget, noticed by Gieskes and Kraay (1982) and (Obermosterer and Herndl, 2000) in open-ocean tropical waters and soon thereafter observed by Laane et al. (1985) in the northern North Sea, was unfortunately not treated at all. In 1980 S.B. Tijssen, former supervisor of marine chemistry student Hein de Baar, had presented a new Winkler procedure with photometric endpoint titration (Tijssen, 1979) that increased the accuracy of oxygen concentration measurements greatly. A comparison of primary productivity levels in the open subtropical Atlantic Ocean derived from diurnal variations in oxygen concentration measured with this high-precision method (Tijssen, 1979) with data obtained with a quite new approach to the C-14 method (Gieskes et al., 1979: measurements in very large bottles to avoid bottle effects on the enclosed plankton) resulted in estimates of phytoplankton productivity during the hours of daylight that were 10 times higher than thought previously.

In spite of the high levels of photosynthetic oxygen production that were registered, net production over a day–night cycle was practically zero in the region of study, i.e., the subtropical Atlantic Ocean from the African coast westward (Tijssen, 1979). This constancy in oxygen concentration in the euphotic zone, even during the hours of daylight, was at the time ascribed to the balancing effect of high heterotrophic activity by micro-organisms (bacteria, protozoa, and the nanophytoplanktonic primary producers themselves) that clearly counteracted the surprisingly high gross primary productivity of these open-ocean waters (Postma and Rommets, 1979); gas exchange at the air–water interface was taken to be minor, and not variable over a diurnal cycle. The contribution of photochemical reactions to the extensive loss of oxygen was not taken into consideration, although it was already well-known at the time that photoreactive matter sensitising the photochemical generation of singlet oxygen is not only present near shores and in shallow seas but also in the open ocean; singlet oxygen is the highly reactive species that may oxidise a wide variety of organic and inorganic molecules. Its production can be rapid in seawater, as already pointed out by Zepp et al. (1977); all of the photo-reactive matter present in seas and oceans can be affected, including algal pigments, excretory products of organisms and other dissolved organic matter such as humic substances, also called “Gilvin” and “yellow substance” (Zafriou et al., 1985; Zika, 1981).

3. Photochemistry and oxygen loss in the ocean's surface layer: role of stratification

Photo-oxidative reactions in aquatic environments are widely known to be driven mainly by the effect of ultraviolet radiation that can penetrate to much greater depths than was thought: even UV-B can reach to depths of over 25 m in clear ocean water (Smith and Baker, 1979). Interactions of this radiation with the photo-reactive substances just mentioned should lead to a considerable photochemical oxygen demand (Amon and Benner, 1996; Andrews et al., 2000), a process that was documented quantitatively by Obermosterer et al. (2001) during a study in the open subtropical Atlantic Ocean. They reported a demand that could even be in excess of bacterioplankton respiration. Interestingly, the mean values they reported are close to those found 20 years earlier in the open tropical Atlantic by Gieskes and Kraay (1982): between 0.1 and 0.3 μM oxygen per litre per hour, mean of 12 hours daylight; and just as Obermosterer et al. (*loc. cit.*), Gieskes and Kraay (1982) had concluded that consumption of oxygen by heterotrophs, including microzooplankton, was roughly equal to the oxygen loss that could be ascribed to photochemical reactions during the hours of daylight.

In actual fact, the relatively large losses of oxygen in the tropical Atlantic were observed by Gieskes and Kraay (1982) in surface water trapped in large enclosures floating at the surface (plastic bags of 500 l, depth 5 m); oxygen loss was not recorded in the open water around the enclosures, where the oxygen concentration in the upper mixed layer remained stable at 420 μM for days; in the entrapped

water, in contrast, oxygen concentrations reached undersaturation (less than 405 μM within 48 h). The explanation was that replenishment with oxygen from below due to vertical mixing of the euphotic zone was cut off by the plastic of the bags. Activity of heterotrophic microorganisms, including microflagellates, remained the same over a day–night cycle, while microalgae in the enclosures (the nanophytoplankton dominating in the tropics and subtropics) remained active thanks to the abundance in the cells of zeaxanthin, a radiation-protective pigment characteristic of these cyanobacteria (mainly *Synechococcus*); zeaxanthin concentrations were even higher than those of chlorophyll a, both measured by high-performance liquid chromatography (HPLC).

Strong vertical stratification of the surface layer is a phenomenon that is more the rule than the exception nearly everywhere in the ocean (Jurado et al., 2012). Vertical mixing of the euphotic zone, e.g., during strong winds, would mitigate photochemistry-induced oxygen loss in the surface layer because of replenishment from below. The ephemeral nature of vertical stratification is visualised in Figs. 1 and 2. The model that allowed the design of the vertical temperature profiles near Bermuda and in the Oyster Ground region in the North Sea was forced with local meteorological data sets of air temperature, air humidity, wind speed and wind direction, and cloudiness. The meteorological data, measured on a buoy for the Bermuda site, are available on the web (NOAA, 2015). The meteorological data of the Oyster Grounds that we used were obtained from the ECMWF ERA-40 and Operational Reanalysis (European Centre for Medium-Range Weather Forecasts, 2006a,b). The physical model GOTM (General Ocean Turbulence Model) was used for simulation of the profiles presented in Figs. 1 and 2. GOTM is a public domain, one-dimensional Finite Difference hydrodynamical water column model designed initially for testing turbulence closure models (Burchard et al., 1999; www.gotm.net). It solves the one-dimensional vertical partial differential equations for conservation of mass, momentum, salt and heat.

The modelling effort reveals that in subtropical-tropical ocean regions, here the location near Bermuda, the upper part of the water column, in general stratified throughout the year, can become vertically mixed over the course of a day or two, in this case during short-lived events of strong winds (Fig. 1); in northern temperate waters, here the Oyster Grounds in the North Sea, strong winds occur more often, even in summer, with deep mixing as an immediate result (Fig. 2). The diurnal variation in the temperature profile in the upper part of the water column at these two locations indicates how variable temperature stratification can be in seas and oceans, depending as it is on solar heating of the surface layer and, once established, on local winds but also current patterns (the latter not shown here). The vertical temperature profiles (Figs. 1 and 2) illustrate the correlation between stratification and wind force: during periods of low winds stratification develops rapidly due to surface heating. Stratification is maintained as long as the wind speed is below 10 m/s (Beaufort 7 to 8): the most common situation.

4. Quantifying photochemical oxygen demand in the ocean's surface layer, globe-wide

Thus, stratification is the normal situation at the surface of most of the world's tropical and subtropical oceans and seas throughout the year, only disturbed during short periods of strong winds. In the upper layer of sea and ocean regions of the temperate zone vertical stratification is normally pronounced only during spring, summer and early autumn. Since the tropical and subtropical oceans comprise 80% of Earth's marine regions we can extrapolate the photochemically-induced loss of oxygen (a mean of 0.2 μM O_2 per litre per hour calculated by Gieskes and Kraay (1982), Laane et al. (1985) and Obermosterer et al. (2001) in the upper layer of the subtropical and tropical Atlantic Ocean; a higher range in the North Sea up to 2.8 μmol $\text{O}_2 \cdot \text{l}^{-1} \cdot \text{d}^{-1}$) to a globe-

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