SCIENCE OF THE TOTAL ENVIRONMENT 404 (2008) 236–244

available at www.sciencedirect.com

www.elsevier.com/locate/scitotenv

Stable oxygen isotopic fractionation during photolytic O_2 consumption in stream waters

K.M. Chomicki, S.L. Schiff*

Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, N2L 3G1 Canada

ARTICLE INFO

Available online 6 June 2008

Keywords:
Aquatic systems
Dissolved oxygen isotopes
Fractionation
Oxygen consumption
Photolysis
Respiration
Abiotic reactions

ABSTRACT

Oxygen (O_2) is required for life in higher organisms, however, processes such as respiration, the oxidation of reduced inorganic species, and the photolytic breakdown of dissolved organic matter (DOM) decrease the O_2 concentrations in aquatic systems. Filtered, inoculated, and sterile samples of stream waters from Ontario, Canada, were incubated in natural sunlight to examine the effects of photolysis of DOM, respiration, and abiotic reactions on O_2 consumption and $\delta^{18}O$ of dissolved oxygen ($\delta^{18}O$–O_2). Oxygen consumption rates in the light were up to an order of magnitude greater than in the dark, suggesting light-mediated processes controlled O_2 consumption. Rates of O_2 loss were the same for each treatment (i.e. filtered, inoculated, and sterile) indicating that photolysis was the dominant O_2 consuming process over respiration in these incubations. O_2 consumption rates were different between streams, even when normalized to the change in dissolved organic carbon (DOC), signifying that DOM photolability varied among streams. During DOM breakdown to CO_2, the lighter ^{16}O isotopomer was preferentially consumed. Fractionation factors observed for photolysis, respiration, and abiotic reactions ranged between 0.988 and 0.995, and were similar in both the light and in the dark incubations in all streams. These fractionation factors are not a function of O_2 consumption rates, and are outside the range published for respiration (0.975–0.982). In current models of O_2 and $\delta^{18}O$–O_2, photolysis and respiration are not considered separately and the isotopic fractionation during respiration that is measured in the dark is used in the light. In these incubations, DOM degradation and abiotic reactions are important O_2 consuming and $\delta^{18}O$–O_2 fractionating processes. Current models of O_2 and $\delta^{18}O$–O_2 incorporate photolysis of DOM and other abiotic processes into the respiratory component of O_2 consumption, thereby overestimating respiration and underestimating photosynthesis to respiration ratios. Consequently, photolysis and abiotic reactions should be considered separately, particularly in shallow aquatic systems with high DOC.

1. Introduction

Oxygen is a fundamental requirement for life in higher organisms (Wetzel, 2001). In aquatic systems, O_2 regulates respiratory metabolism, mediates biogeochemical cycles, and is an integral component of water quality. Oxygen concentration is controlled by the balance between various processes including gas exchange with the atmosphere, photosynthesis, respiration, mixing, photolysis, and other redox reactions.

Oxygen mass balances are commonly used to calculate rates of photosynthesis (P) and respiration (R) and thus ecosystem metabolism (Odum, 1956). More recently, $\delta^{18}O$ of dissolved O_2 ($\delta^{18}O$–O_2) has been increasingly used to assess ecosystem metabolism and O_2 dynamics in aquatic systems such as lakes, rivers,

* *Corresponding author*. Tel.: +1 519 888 4567x37284; fax: +1 519 746 7484.
E-mail address: kmchomic@uwaterloo.ca (K.M. Chomicki).

0048-9697/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2008.04.024

and ponds. Quay et al. (1995) demonstrated how O_2 and $\delta^{18}O$–O_2 balances could be used simultaneously to directly constrain the *P*:*R* in aquatic systems under steady state assumptions. Temporal and spatial variability of trophy was assessed by Russ et al. (2004) in a large oligotrophic lake, and Parker et al. (2005) looked at oxygen isotope changes in rivers with up to 13‰ variation in diel cycles. Since many of the studies using $\delta^{18}O$–O_2 are limited by steady state assumptions and do not consider daily oxygen cycles, Venkiteswaran et al. (2007, 2008) developed a dynamic model (PoRGy) to assess metabolic balance. Using diel O_2 and $\delta^{18}O$–O_2 measurements, the rates and ratios of *P*:*R*:*G* (Photosynthesis:Respiration:Gas Exchange) could be assessed.

Oxygen saturation and $\delta^{18}O$–O_2 can be used in conjunction with each other to calculate *P*:*R* and *P*:*R*:*G* ratios. Atmospheric oxygen (23.5‰ vs. SMOW; Kroopnick and Craig, 1972) fractionates in water by 0.7‰ (Benson and Krause, 1984). If gas exchange dominates, O_2 concentrations will be close to saturation, and the $\delta^{18}O$ will remain approximately 24.2‰ (Quay et al., 1993). Aquatic respiration preferentially consumes $^{16}O^{16}O$, decreasing the dissolved O_2 concentration and increasing the $\delta^{18}O$ of the remaining O_2. Fractionation factors for respiration (α_R) in most $\delta^{18}O$–O_2 studies are typically not determined directly but selected from the range of published values for marine and river waters (α_R=0.975–0.982) (Kiddon et al., 1993; Kroopnick, 1975; Quay et al., 1993, 1995). In contrast, during photosynthesis there is no photosynthetic fractionation (α_p=1.000; Guy et al., 1993) and the $\delta^{18}O$–O_2 produced will reflect the $\delta^{18}O$–H_2O. Given that the $\delta^{18}O$–H_2O for most aquatic systems is typically less than 0‰, much less than the $\delta^{18}O$ in air (23.5‰), photosynthetic O_2 added to the aquatic system will lower the $\delta^{18}O$–O_2. Therefore, if photosynthesis is the dominant process (over gas exchange and respiration) O_2 will be supersaturated and the $\delta^{18}O$–O_2 value will decrease.

Measured values of O_2 concentrations, $\delta^{18}O$–O_2, and gas exchange rates can be used in two mass balance equations to determine *P*:*R* (Quay et al., 1995):

$$\frac{d(O_2)}{dt} = \frac{G}{Z} \times (O_{2s} - O_2) - R + P$$

$$\frac{d(^{18}O_2)}{dt} = \frac{G}{Z} \times \alpha_g \left(O_{2s}\delta^{18}O_a\alpha_s - O_2\delta^{18}O\right) - R\delta^{18}O\alpha_R + P\delta^{18}O_w\alpha_P$$

where O_2 is the dissolved oxygen concentration, *t* is the time, *Z* is the mean depth, *G* is the gas exchange rate, *s* is the O_2 value at atmospheric saturation, *R* is the respiration rate, *P* is the gross production rate, α_g is the gas exchange fractionation factor (0.9972; Knox et al., 1992), $\delta^{18}O_a$ is the ^{18}O:^{16}O atmospheric value, α_s is the equilibrium air–water fractionation factor, α_R is the respiration fractionation factor, $\delta^{18}O_w$ is the ^{18}O:^{16}O isotopic ratio in water, and α_P is the photosynthetic fractionation factor. If there is an accrual of water from surface or groundwater, an additional term can be added. There is no separate term in these equations for the photolytic or abiotic consumption of oxygen and these processes are thus amalgamated within 'R'. Similarly, α_R includes all fractionations associated with O_2 consumption processes, including respiration, and any other abiotic processes and redox reactions.

Previously published studies on $\delta^{18}O$ in aquatic systems only considered respiration, photosynthesis, and gas exchange as processes affecting the isotopic ratio of O_2 (e.g. Quay et al., 1995; Wang and Veizer, 2000; Russ et al., 2004; Parker et al., 2005, Tobias et al., 2007) although some acknowledge O_2 consumption occurs to a lesser extent by chemical oxidation. However, respiration and chemical oxidation are not the only oxygen consuming processes in lacustrine and riverine systems. Northern temperate and boreal lakes are generally net heterotrophic ecosystems, dependent upon decaying or dead organic matter from the terrestrial catchment for sustenance (del Giorgio and Peters, 1994; Algesten et al., 2003). Approximately 50% of the dissolved organic carbon (DOC) entering some oligotrophic lakes in the southern Precambrian Shield is lost to the atmosphere and sedimentation (Dillon and Molot, 1997a). Photolysis is one mechanism that consumes oxygen and that could account for a large DOC loss observed in many boreal lakes with high DOC (Molot and Dillon, 1997).

Dissolved oxygen is an electron acceptor in dissolved organic matter (DOM) photodegradation and, in conjunction with heterotrophs, converts recalcitrant DOM to more labile, carboxylic acids, other smaller organic compounds, and dissolved inorganic carbon (DIC) forms such as CO and CO_2. These smaller organic products can be consumed by and stimulate microbial activity (Miller and Moran, 1997; Tranvik et al., 1999). The breakdown of DOM to CO_2 consumes oxygen and affects the oxygen balance of aquatic ecosystems. It is therefore crucial to understand the photodegradation of DOM, in addition to the other processes controlling oxygen production and consumption, since DOM degradation and O_2 dynamics are linked.

Many studies have looked at DOM photodegradation because of its importance in the carbon cycle (e.g. carbon transport from terrestrial to ocean environments: Miller and Zepp, 1995; supersaturation of CO_2 in lakes: Granéli et al., 1996; and loss of DOM in lake surface layers: Bertilsson and Tranvik, 2000). Other studies have shown that photodegradation of DOM influences water chemistry and transparency (affecting the photic zone depth and the region of photosynthetic activity: Andrews et al., 2000; Anesio and Granéli, 2003), in addition to affecting aquatic organisms (e.g. UV exposure/damage to life and the effects on the food web by altering lability of sustenance sources: Gao and Zepp, 1998). Only a few studies have looked at O_2 consumption in the context of surface water oxygen levels (Amon and Benner, 1996; Miles and Brezonik, 1981), and the relative importance of O_2 consumption during DOM photodegradation due to the combined effects of DOM photodegradation and microbial respiration versus primary production (Lindell and Rai, 1994).

Although photolytic effects on O_2 concentrations have been recognized, changes in $\delta^{18}O$–O_2 during photolytic O_2 consumption have not been investigated. Photolysis could be an important but neglected component in oxygen isotopic models used to determine *P*:*R* ratios in aquatic systems. The goals of this study were to: 1) determine the effects of photolysis, microbial respiration, and other abiotic reactions on $\delta^{18}O$–O_2 in waters from three different forested streams, and 2) determine the $\delta^{18}O$–O_2 fractionation factors associated with photolysis, respiration, and abiotic reactions.

2. Methods

Incubation experiments were performed on typical small inflows from two headwater oligotrophic lakes. Stream water samples were collected from Harp Lake Inflow 4 (H4), Harp