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Assessment of diel chemical and isotopic techniques to investigate biogeochemical cycles in the upper Klamath River, Oregon, USA

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ABSTRACT

The upper Klamath River experiences a cyanobacterial algal bloom and poor water quality during the summer. Diel chemical and isotopic techniques have been employed in order to investigate the rates of biogeochemical processes.

Four diel measurements of field parameters (temperature, pH, dissolved oxygen concentrations, and alkalinity) and stable isotope compositions (dissolved oxygen–$\delta^{18}O$ and dissolved inorganic carbon–$\delta^{13}C$) have been performed between June 2007 and August 2008. Significant diel variations of pH, dissolved oxygen (DO) concentration, and DO–$\delta^{18}O$ were observed, due to varying rates of primary productivity vs. respiration vs. gas exchange with air. Diel cycles are generally similar to those previously observed in river systems, although there are also differences compared to previous studies. In large part, these different diel signatures are the result of the low turbulence of the upper Klamath River. Observed changes in the diel signatures vs. sampling date reflect the evolution of the status of the algal bloom over the course of the summer.

Results indicate the potential utility of applying diel chemical and stable isotope techniques to investigate the rates of biogeochemical cycles in slow-moving rivers, lakes, and reservoirs, but also illustrate the increased complexity of stable isotope dynamics in these low-turbulence systems compared to well-mixed aquatic systems.

1. Introduction

Dissolved O_2 (DO) is a crucial biogeochemical component in aquatic communities, and is therefore a primary indicator of ecosystem health. Dissolved O_2 concentrations are controlled by varying rates of gas exchange between the atmosphere and the dissolved phase vs. primary production by photosynthesis vs. consumption by respiration, driven by a variety of environmental conditions (e.g. light, temperature, nutrient availability, and substrate availability). Dissolved O_2 may also be added to the system by groundwater accrual. Dissolved inorganic carbon (DIC) concentrations are also affected by gas exchange, photosynthesis (which will consume CO_2), and respiration (which will produce CO_2), but are further affected by processes such as carbonate mineral precipitation/dissolution, and in cases where there is a groundwater input to the aquatic system, groundwater accrual of DIC is very likely. These processes also have an effect upon pH, due to either the addition or removal of CO_2, which will respectively decrease or increase the pH.

These processes also affect the isotopic compositions of DO and DIC. Photosynthesis by aquatic plants produces DO that has the same isotopic composition as the water (Guy et al., 1993; Telmer and Veizer, 2000), and as most natural waters are isotopically lighter than O_2 in air, photosynthetic production of O_2 will lower the isotopic composition of DO. In contrast, photosynthesis preferentially consumes isotopically light DIC (Falkowski and Raven, 1997), which shifts the isotopic composition of residual DIC to an isotopically heavier composition. Community respiration preferentially consumes isotopically light DO (Kroopnick, 1975; Guy et al., 1993) and shifts the isotopic composition of residual DO to isotopically heavier values, and in the case of C3 plants, will produce isotopically light CO_2 ($\delta^{13}C = -20$ to -30‰: Clark and Fritz, 1997) which shifts the isotopic composition of DIC to isotopically lighter values. Gas exchange between air and the dissolved gaseous phase will shift DO and DIC towards equilibrium concentrations and isotopic compositions with air–O_2 and air–CO_2, respectively. For DO, there is a small isotopic fractionation of +0.7‰ during dissolution of air–O_2 that is relatively independent of temperature (Benson and Krause, 1980), and as air–O_2 has a constant global average of 23.5‰ (Kroopnick and Craig, 1972), DO in equilibrium with air is expected to have an isotopic composition of 24.2‰. For DIC in waters with alkaline pH, equilibrium with air–CO_2 is somewhat dependent on temperature and pH, but should produce DIC with $\delta^{13}C = -1$ to 3‰, (Clark and Fritz, 1997). In the case of any groundwater accrual of DO or DIC, groundwater-DIC is expected to be isotopically light vs. river-DIC and groundwater-DO is expected to be isotopically heavy vs. river-DO due to the effect of respiration

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processes in the subsurface (although groundwater DO-δ^{18}O values as light as 12‰ have been observed: Wassenaar and Hendry, 2007).

Combined concentration (DO and DIC) and stable isotope (DO-δ^{18}O and DIC-δ^{13}C) analyses can provide quantitative values for primary productivity, respiration, and gas exchange, and have recently been employed and modeled for a number of rivers (e.g. Parker et al., 2005, 2007; Tobias et al., 2007; Venkiteswaran et al., 2007; Waldron et al., 2007; Venkiteswaran et al., 2008; Parker et al., 2009-this issue). The combined concentration-stable isotope approach has an advantage over other techniques, such as incubations and substrate tests, as it measures the rates of productivity, respiration, and gas exchange for the whole community, and because the concentration-stable isotope approach can measure absolute rates of productivity, respiration, and gas exchange, as compared to the productivity:respiration ratio that can be obtained by diel DO concentration curve analysis (e.g. Odum, 1956). Gas exchange rates can be measured directly, e.g. tracer techniques such as application of SF_6 (e.g. Tobias et al., 2009), or can be calculated using a number of parameters such as wind speed (e.g. Crusius and Wanninkhof, 2003; Ro and Hunt, 2006). However, as pointed out by Ro et al. (2007), many empirical equations exist in the literature for predicting gas exchange rates, but these equations can predict different gas exchange rates and it can be difficult to select an equation appropriate for the particular field conditions under consideration.

The studies on rivers to date illustrate that the combined concentration-stable isotope approach can generate fundamental, detailed, and quantitative information concerning the rates of biogeochemical processes, and hence provide an assessment of the current environmental status, and ultimately, how this status may change over time as conditions may change. However, many of these studies do not consider carbon systematics in addition to oxygen systematics, and the majority of these studies have investigated relatively fast-moving, turbulent and shallow rivers, which are well-mixed. In contrast, lakes, reservoirs, and slow-moving rivers are less turbulent, and vertical stratification may take place. A number of lake studies have employed DO–δ^{18}O analyses as a technique to investigate the rates of photosynthesis and primary production (e.g. Russ et al., 2004; Ostrom et al., 2005; Wang et al., 2008), but diel DO-δ^{18}O and DIC-δ^{13}C studies of lakes and reservoirs are relatively rare in the literature, such as the FLUDEX medium C reservoir, Ontario (DO only, 0.8 m depth: Venkiteswaran et al., 2007) and the Sulejów reservoir, Poland (DO and DIC, average depth 3.3 m: Trojanowska et al., 2008).

The upper Klamath River, Oregon, is characterized by "very poor" water quality status during the summer, with adverse environmental conditions for fish and other aquatic organisms, notably with regard to ammonia, dissolved oxygen, pH and chlorophyll *a* (Mrazik, 2007; Oregon Department of Environmental Quality, 2007). The poor water quality in the summer is associated with the proliferation of the cyanobacterial alga *Aphanizomenon flos aquae* (AFA), which is also present as an annual bloom in Upper Klamath Lake (e.g. Wood et al., 2006). An improved understanding of water quality, and the in-stream processes that help control water quality, is needed in order to facilitate management of the system and to provide appropriate restoration and remediation strategies. In particular, characterization and quantification of the effect of the large summer-time population of AFA upon water quality is necessary. Since 2007, the U.S. Geological Survey, Watercourse Engineering Inc., and the U.S. Bureau of Reclamation have been studying the upper Klamath River, between the Link River Dam (just below Upper Klamath Lake) and Keno Dam (Fig. 1), in order to construct a water quality and hydrodynamic model that includes the most important in-stream water quality processes, and which will be used to assess the utility of proposed management alternatives (Sullivan et al., 2008).

In order to obtain a better understanding of the biogeochemical processes operating in the upper Klamath River, in particular, and low-turbulence aquatic systems, in general, diel sampling events for DO–δ^{18}O and DIC–δ^{13}C were conducted at the Miller Island site, approximately 9 km south-west of Klamath Falls, Oregon (Fig. 1).

2. Methods

Four 24-hour diel sampling events were performed at the Miller Island site (Fig. 1): 26–27 June, 2007 (event #1, sunset–sunrise 19:48–04:33); 28–29 August, 2007 (event #2, sunset–sunrise 18:48–05:29); 24–25 June, 2008 (event #3, sunset–sunrise 19:48–04:33); and 21–22 August, 2008 (event #4, sunset–sunrise 18:58–05:23). All time references are local time (Pacific Daylight Time, −08:00 GMT). During sampling events #1, #2 and #3, the study site was impacted by a dense population of AFA (e.g. Fig. 2). During sampling event #4, AFA was absent from the study site. The weather was clear and sunny for all sampling events, with only sparse and intermittent clouds. The upper Klamath River in the stretch between the Link River Dam and Keno Dam is slow-moving in summer (typical water velocities of 3–9 cm/s), and has a width and maximum depth of 100–400 m and 3–6 m, respectively (Sullivan et al., 2008). Conditions at the Miller Island site are generally representative of this stretch of the upper Klamath River, between the Link River Dam and Keno Dam (Sullivan et al., 2008).

A YSI 600XLM data sonde was continuously deployed mid-channel at a depth of 1 m in the Klamath River at the Miller Island site by the U.S. Bureau of Reclamation, approximately 100 m distant from the Miller Island boat dock, and measured field parameters (temperature, pH, conductivity, and DO) every hour for sampling events #1 and #2. A YSI 600XLM data sonde was deployed at the Miller Island boat dock sampling site at a depth of 0.3 m for sampling events #3 and #4, and measured the same field parameters every 10 min (sampling event #3) or every 5 min (sampling event #4). Data sondes were calibrated following the manufacturer's specifications. Dissolved oxygen concentration measurements were calibrated using a barometric measurement available from the local airport (located approximately 8 km away) at the time of calibration. Values of DO % saturation with air are calculated using measured temperatures, but have not been corrected for any changes in atmospheric pressure over the course of the sampling events.

Water samples were collected approximately every hour from the Miller Island boat dock, at an approximate depth of 0.3 m. Sample collection typically commenced at noon on the first day of field work, and ended at noon on the second day of field work. Unfiltered DO–δ^{18}O samples were collected for all sampling events after the method of Wassenaar and Koehler (1999). A septum-capped, pre-evacuated 125 ml serum bottle containing 50 µl of saturated $HgCl_2$ was immersed to the sampling depth and punctured with a syringe needle to collect the water sample, until filling of the serum bottle was complete, after which the needle was removed while the serum bottle was still immersed. Water grab samples were filtered in the field using a peristaltic pump and 0.45 µm filter, and were collected for water–δ^{18}O, water–δD, alkalinity (sampling events #1, #3 and #4 only), and DIC-δ^{13}C (sampling events #2, #3 and #4 only). Alkalinity and DIC-δ^{13}C samples collected in the field were stored on ice in sealed plastic bags, and returned to the laboratory immediately after completion of field work. Two to four filtered water samples during the four diel sampling events were collected in glass vials with poly-cone vial inserts, and analyzed for water–δ^{18}O and water–δD.

Alkalinity analyses were analyzed by titration following USGS methods (Rounds, 2006). Values of DIC concentrations and CO_2 pressures (PCO_2) were calculated using the geochemical modeling program Visual MINTEQ (Allison et al., 1991), using the measured values for temperature, pH and alkalinity. DO–δ^{18}O samples were analyzed using a headspace equilibration technique, after Wassenaar and Koehler (1999), and DIC–δ^{13}C samples were precipitated as $SrCO_3$ after Usdowski et al. (1979), and analyzed after Harris et al. (1997). Water–δ^{18}O analyses were performed after the CO_2 equilibration