

Report as of FY2009 for 2006MT89B: "Carbon cycling and the temporal variability in the concentration and stable carbon isotope composition of dissolved inorganic and organic carbon in streams"

Publications

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Report Follows

Temporal Variability in the Concentration and Stable Carbon Isotope Composition of Dissolved Inorganic and Organic Carbon in Two Montana, USA Rivers

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Abstract Here we report diel (24 h) and seasonal differences in the concentration and stable carbon isotope composition of dissolved inorganic (DIC) and organic carbon (DOC) in the Clark Fork (CFR) and Big Hole (BHR) Rivers of southwestern Montana, USA. In the CFR, DIC concentration decreased during the daytime and increased at night while DOC showed an inverse temporal relationship; increasing in the daytime most likely due to release of organic photosynthates and decreasing overnight due to heterotrophic consumption. The stable isotope composition of DIC ($\delta^{13}\text{C}$ -DIC) became enriched during the day and depleted over night and the $\delta^{13}\text{C}$ -DOC displayed the inverse temporal pattern. Additionally, the night time molar rate of decrease in the concentration of DOC was up to two orders of magnitude smaller than the rate of increase in the concentration of DIC indicating that oxidation of DOC was responsible for only a small part of the increase in inorganic carbon. In the BHR, in two successive years (late summer 2006 & 2007), the DIC displayed little diel concentration change, however, the $\delta^{13}\text{C}$ -DIC did show a more typical diel pattern characteristic of the influences of photosynthesis and respiration indicating that the isotopic composition of DIC can change while the concentration stays relatively constant. During 2006, a sharp night time increase in DOC was measured; opposite to the result observed in the CFR and may be related to the night time increase in flow and pH also observed in that year. This night time increase in DOC, flow, and pH was not observed 1 year later at approximately the same time of year. An in-stream mesocosm chamber used during 2006 showed that the night time increase in pH and DOC did not occur in water that was isolated from upstream or hyporheic contributions. This result suggests that a “pulse” of high DOC and pH water was advected to the sampling site in the BHR in 2006 and a model is proposed to explain this temporal pattern.

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1 Introduction

Investigations over the past 20 years have shown that diel (24 h) changes in the concentration of chemical species in flowing systems are reproducible processes that play an integral role in the health and water quality of river systems. Healthy rivers can exhibit large diel pH, dissolved O₂ (DO), and CO₂ cycles that are largely driven by aquatic plants and microbes which alternately consume or produce CO₂ depending on whether photosynthesis or respiration is the dominant process (Odum 1956; Pogue and Anderson 1994; Nagorski et al. 2003; Parker et al. 2005, 2007a). These short term variations are driven by the daily photoperiod, which influences: aquatic photoautotrophs; instream temperature cycles; changes in dissolved gas gradients between air and water; and affect either directly or indirectly concentration changes in metals and metalloids (e.g., Nimick et al. 2003, 2005; Jones et al. 2004; Gammons et al. 2005; Parker et al. 2007a, b and references therein). While researchers investigating the mechanisms influencing diel processes have provided great insight into the “driving forces” behind these daily changes, there is still much that is not well understood. By gaining deeper insight into the underlying mechanisms controlling diel concentration changes of important dissolved and particulate species we will be able to develop a better fundamental understanding of how streams function. This knowledge will help scientists, resource managers and others make better predictions on how streams will respond to shifting conditions caused by climate change, changing agricultural practices, restoration activities, nutrient fluxes and development.

Previous work has demonstrated that there is a significant and reproducible diel cycle in the stable isotope composition of dissolved inorganic carbon ($\delta^{13}\text{C-DIC}$) in both the Clark Fork River (CFR) and Big Hole River (BHR) in Montana, USA as well as a substantial cycle in the ^{18}O composition of dissolved molecular oxygen ($\delta^{18}\text{O-DO}$) in the BHR and other streams (Parker et al. 2005, 2007a, 2009). These daily changes in the isotope composition of the DIC and DO are caused by the combined effects of photosynthesis and respiration of aquatic plants and microbes as well as gas-exchange and groundwater influx. Additionally, $\delta^{13}\text{C-DIC}$ has been used as a tracer of the origins and sources of carbon in watersheds (e.g., Gaiero et al. 2005), but these data must be used carefully since substantial diel changes in $\delta^{13}\text{C-DIC}$ can occur (up to 4.5‰, Parker et al. 2009).

Dissolved organic carbon (DOC) represents a significant pool of reduced carbon in most aquatic ecosystems that is readily available to heterotrophic microorganisms as an energy source (McKnight et al. 1997; Volk et al. 1997). It has also been suggested that the DOC pool may be the largest source of carbon for microbial activity (Kaplan and Bott 1982; Hobbie 1992). Additionally, it has been shown that different size classes of DOC molecules exist and that the distribution can change over a diel period (Amon and Benner 1996; Zeigler and Fogel 2003). Depending on the size and composition of the DOC some classes of molecules may be more refractory than others and consequently consumed at different rates (Thurman 1985; Zeigler and Fogel 2003).

The types and concentration of the DOC can have a significant influence on the chemical composition of surface waters such as the bioavailability of metal ions and the absorption of

light in the visible and UV ranges (McKnight et al. 1997). Much of the literature examining DOC in rivers has concentrated on sources of organic carbon and its fate and transport to downstream areas (e.g., Thurman 1985; Olivie-Lanquet et al. 2001; Bianchi et al. 2004, 2007; Hood et al. 2005; Dalzell et al. 2007). Several researchers have shown that diel changes in DOC concentration occur in streams and can be attributed to daily changes in the level of productivity of algal communities (e.g., Manny and Wetzel 1973; Kaplan and Bott 1982; Harrison et al. 2005; Spencer et al. 2007). However, there is little literature that reports investigations of temporal changes in DOC and the ^{13}C -composition of DOC ($\delta^{13}\text{C}$ -DOC) simultaneously on a diel scale in surface waters (Zeigler and Fogel 2003). Since community respiration is using the DOC as a carbon source and other aquatic species are producing organic molecules as a consequence of their daily productivity, it is reasonable to expect changes in the isotopic composition of the DOC as it is influenced by the daily changes in the rates of metabolic activity (Barth and Veizer 1999; Zeigler and Fogel 2003; Zeigler and Brisco 2004).

DOC can include water soluble forms of amino acids, carbohydrates, organic acids, alcohols as well as fulvic and humic acids (Thurman 1985). Sources of DOC in streams can include decomposition of detrital organic matter, importation of organics from external (allochthonous) sources and in-stream production by aquatic plants and microbes (autochthonous). Microbes using DOC as a carbon source will produce CO_2 from respiration with a carbon isotope signature characteristic of the organic carbon substrate (Clark and Fritz 1997). In temperate regions, plant organic matter, that serves as the carbon source for microbial respiration has a $\delta^{13}\text{C}$ of -20 to -30% (Clark and Fritz 1997). In contrast, atmospheric CO_2 has $\delta^{13}\text{C}$ of -7 to -8.5% (NOAA 2008) and consequently DIC produced by gas exchange will be isotopically enriched compared to that produced by respiration.

A significant portion of DOC in natural waters falls in the category of natural organic matter (NOM), and most of the NOM fits into the operationally defined subcategories of fulvic acids (FA) and humic acids (HA; Thurman 1985; Macalady 1998). The fulvic and humic acids as well as other organic acids are well known for their ability to complex metal ions in solution (Saar and Weber 1982; Clapp et al. 1998). It is known that the fulvic and humic acids can contribute to daily variations in surface water iron concentrations by affecting Fe redox cycling through changes in the photoreactivity of Fe in the aqueous system (Voelker et al. 1997; Hrnecir and McKnight 1998).

In this study, we investigated diel changes in the concentration of DOC and DIC in two different rivers systems (CFR and BHR). These rivers are geographically close but exhibited approximately inverse diel patterns in the concentration of DOC during the late summer of 2006. An in-stream mesocosm chamber was used in the BHR during 2006 to compare diel cycles and levels of DOC and DIC that were isolated from the flowing water column or hyporheic water exchanges. A follow-up study was conducted in the BHR 1 year later to assess the reproducibility of the diel DOC pattern observed the previous year. Additionally, in order to identify possible sources of DOC in the BHR a series of seeps (streamside springs) and shallow sediment water was sampled during the follow-up work in 2007. The rates of DOC consumption and DIC production in the CFR were compared in order to determine what portion of the inorganic carbon being produced resulted from the oxidation of DOC. The $\delta^{13}\text{C}$ -DOC was examined in the CFR as well as the $\delta^{13}\text{C}$ -DIC in the CFR and BHR. These isotope results are used here in conjunction with the seep and chamber data to investigate the relationship of the diel changes in DOC and DIC to the processes influencing these changes. Models are presented to help interpret the

diel behavior of DOC in the CFR and the differences in the diel behavior of DOC observed in the BHR between 2006 and 2007.

2 Field Sites

2.1 CFR Site

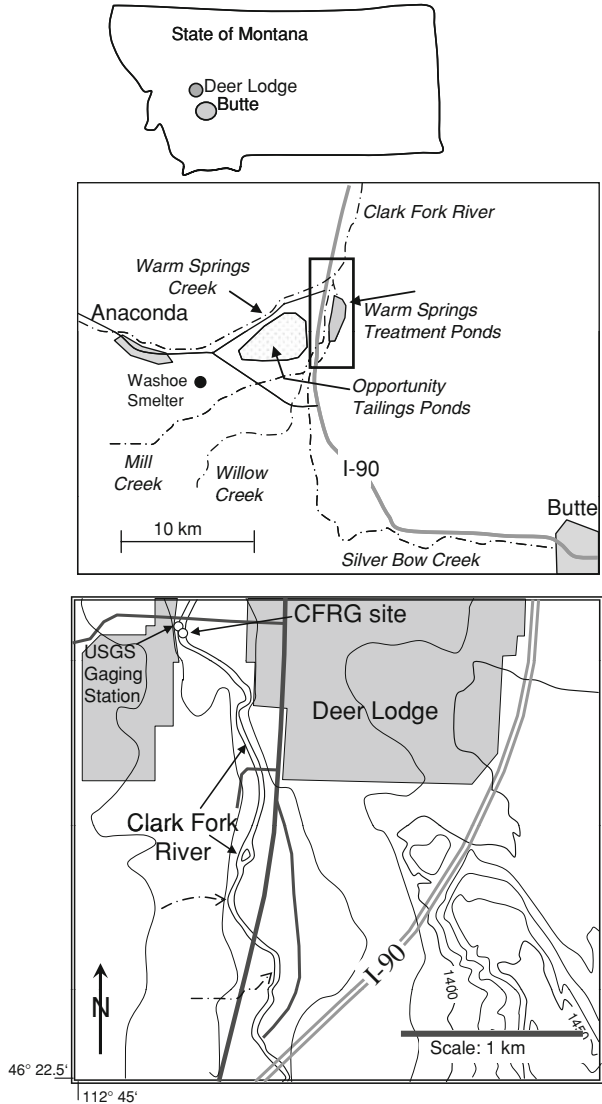
The field site on the Clark Fork River ($46^{\circ}23'51''\text{N}$; $112^{\circ}44'33''\text{W}$; sampling site CFRG) was within the city limits of Deer Lodge, MT and directly across from the USGS gaging station (Fig. 1, USGS Gage #12324200, 1,372 m elevation). Streamflow measurements were taken from the USGS gaging station which records every 15 min. The Clark Fork here is a second order stream with a discharge of roughly $0.6\text{--}60\text{ m}^3\text{ s}^{-1}$ depending on the time of year. The river in the study reach has moderate alkalinity ($\sim 3,200\text{--}3,700\text{ }\mu\text{eq l}^{-1}$; Parker et al. 2007a) and a pH range of about 8.0–9.0 during the summer months. Aquatic plants are dominated by *Cladophora* and diatom algae (Watson 1989). The mining and smelting centers of Butte and Anaconda are situated at the headwaters of the upper Clark Fork River along Silver Bow and Warm Springs Creeks, respectively (Fig. 1) such that the floodplain and streambed of the upper Clark Fork River contain highly elevated quantities of metals and metalloids (e.g., Fe, Cu, Zn, Pb, Cd, As) deposited as the result of mining, milling, and smelting activities (Moore and Luoma 1990). Currently, most of the heavy metal load in Silver Bow Creek is removed by a lime treatment facility at Warm Springs (Fig. 1). However, elevated concentrations of dissolved arsenic have been measured in the water exiting the treatment ponds ($>40\text{ }\mu\text{g L}^{-1}$) during summer base-flow periods (Duff 2001; Gammons et al. 2007). Diel changes in the concentration of metals and arsenic in the upper CFR have been previously characterized (Brick and Moore 1996; Parker et al. 2007a; Gammons et al. 2007).

2.2 BHR Site

The field site near the Mudd Creek Bridge on the Big Hole River ($45^{\circ}48'28''\text{N}$, $113^{\circ}18'51''\text{W}$; sampling site BHRG) was about 50 m upstream from the USGS gaging station (Fig. 2; USGS Gage #6024540, 1795 m). Annual flows range from 5 to $140\text{ m}^3\text{ s}^{-1}$ depending on time of year. Flow data for this site was obtained from the USGS gaging station which records discharge every 15 min. The BHR is a headwater tributary to the Missouri River and is a free-flowing river draining a sparsely-populated, high elevation basin ($\sim 1,900\text{ m}$ above sea level) of approximately $7,200\text{ km}^2$ in extent. This river is relatively pristine and there is little historical impact from mining or industrial sources. The principal activities in the basin are agriculture and recreation.

Previous work (Gammons et al. 2001; Ridenour 2002; Wenz 2003; Parker et al. 2005) has summarized the general geochemical characteristics of the Big Hole River. Overall, the Big Hole River at Mudd Creek Bridge can be classified as a Na–Ca–bicarbonate water, with alkaline pH and low to moderate alkalinity ($1,500\text{--}1,800\text{ }\mu\text{eq L}^{-1}$). The lower alkalinity of the BHR versus the CFR described above results in lower buffering capacity of the BHR stream water that often leads to larger ranges in and higher absolute values of pH during summer low flow periods.

Fig. 1 Location map of the upper Clark Fork River showing Butte, MT; Anaconda, MT; Warm Springs Ponds, Opportunity Ponds and the CFRG sampling site on the Clark Fork River near Deer Lodge, Montana, USA



3 Methods

3.1 Field Methods

3.1.1 Clark Fork River

Diel sample collection on the CFR began on 27 July 2006 at 11:15 and continued until 13:15 on 28th of July. All times are reported as local time (MDT, GMT−0600).

In situ temperature, pH, specific conductivity (SC), dissolved oxygen (DO) concentration and percent O₂ saturation were measured at each sampling time with a Hydrolab MS-5 datasonde (Luminescent DO probe) or an In Situ Troll 9000 (Clark DO probe) as

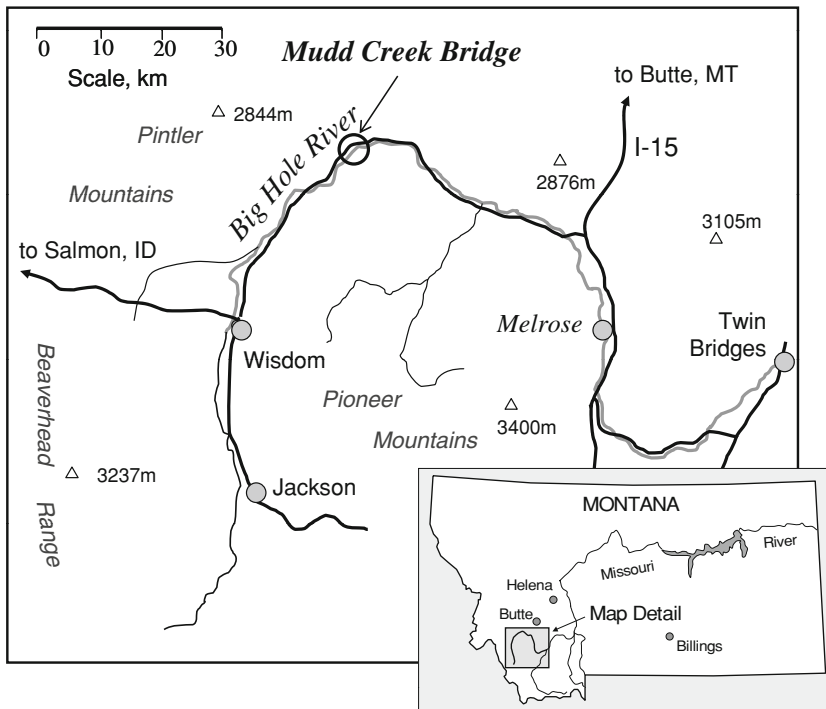


Fig. 2 Site map showing the Mudd Creek Bridge sampling area of the Big Hole River located in southwestern Montana, USA

well as a hand-held meter (WTW 340i). The instruments were calibrated according to the manufacturer's specifications.

Several samples were collected for laboratory analysis of DO using the Winkler method (Wetzel and Likens 1991). Unfiltered water was collected in 500 mL glass bottles with no head space and stored on ice until analysis in the laboratory within 48 h. The results of these analyses were compared to the DO measurements using hand and in situ instruments (shown in results).

Water was sampled from the main stem of the river in a well mixed, rapidly flowing reach approximately 0.5 m deep, 3 m from shore and at a depth approximately half way between surface and bottom. Filtration was done using a peristaltic pump and disposable 142 mm diameter 0.1 μm cellulose-ester filter membranes (for further details see Gammons et al. 2005). Samples (filtered) for DOC analysis were collected in 250 mL amber bottles that had been acid washed (5% HNO_3), triple rinsed with deionized water and oven dried (100°C). Filtered samples for ^{13}C -isotope analysis of dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) were collected in 125 or 250 mL acid-washed, oven dried, glass bottles with no head-space and the DIC was precipitated in the laboratory as SrCO_3 after Usdowski et al. (1979).

A detector was used to measure photosynthetically active radiation (PAR) flux values (400–700 nm, $\mu\text{E m}^{-2} \text{s}^{-1}$) which were based on the manufacturer's calibration of the sensor. The PAR went to zero at 21:00 h in the evening and rose above zero at 06:30 in the morning. This *dark* period (zero PAR) is represented by the shaded region on all diel graphs.

All samples collected in the field were stored on ice, in sealed plastic bags and returned to the laboratory immediately following the field work.

3.1.2 Big Hole River

Two separate diel samplings occurred on the BHR approximately 1 year apart: 8 to 9 August 2006 and 31 July to 1 Aug 2007. Sampling was performed similar to that described in the previous section on the Clark Fork site. Alkalinity was measured in the field using a Hach titrator and standardized H_2SO_4 . Samples from seeps above the main sampling site were collected with a clean 60 mL syringe that was triple rinsed with sample water and then filtered using 0.2 μm PES syringe filters into glass bottles. Sediment pore water was collected at two locations near the sampling site with a 60 mL syringe that was inserted approximately 12 cm into the shallow sediments in the middle of the river. The syringe plunger was very slowly withdrawn to minimize water from being pulled around the barrel of the syringe from the above river; taking 2–3 min to fill the 60 mL volume. This water was filtered using 0.2 μm PES filters into glass bottles.

An isolation chamber was used during the 2006 sampling that was made from a 10 cm inside diameter clear acrylic plastic cylinder 22 cm long. One end was sealed and the other end was removable (both clear acrylic). Each end had a tubing connector fastened to a drilled and threaded hole in the center. Prior to the start of the diel sampling, the chamber was filled approximately half-full with cobbles ranging from 2 to 10 cm in diameter collected from the sampling site that were covered with attached periphyton and biofilms. The chamber lid was sealed with silicone vacuum grease and held in place with an elastic strap. Clear plastic tubing was used to connect the chamber to a peristaltic pump mounted on a tethered platform in the river, then to a low volume flow chamber on a datasonde and back to the chamber. The chamber and datasonde were placed on the river bottom at a depth of ~ 0.5 m. At the beginning of the sampling period, the chamber was flushed with river water, filled and purged to remove most of the trapped air. The chamber water was sampled every 2 h as described previously for DOC and DIC; then flushed and refilled with fresh river water. The datasonde connected to the chamber recorded pH, temperature, DO, and SC every 30 min throughout the diel period.

3.2 Analytical Methods

A pre-concentration step for samples for $\delta^{13}\text{C}$ -DOC analysis was performed by evaporating 250 mL of filtered river water to near-dryness at 50°C and resuspending in 4 mL of 1% H_3PO_4 .

The SrCO_3 precipitates (described above) for $\delta^{13}\text{C}$ -DIC and the DOC concentrates for $\delta^{13}\text{C}$ -DOC were analyzed using a Eurovector elemental analyzer interfaced to a Micromass Isoprime stable isotope ratio mass spectrometer after Harris et al. (1997) and Gandhi et al. (2004), respectively. Replicate analyses (three per sample set) indicated an average relative standard deviation (RSD) of 0.95‰ for $\delta^{13}\text{C}$ -DOC and 0.55‰ for $\delta^{13}\text{C}$ -DIC.

All analyses for total carbon (TC) and DOC were performed at Montana Tech using an Ionics (Model 1505) Total Carbon Analyzer (combustion method). All samples for TC analysis used filtered, unacidified water. Samples for DOC analysis used filtered water that was acidified to 1% (v/v) with concentrated H_3PO_4 and sparged for 5 min with N_2 . These samples were then sparged in the instrument for an additional 3 min with CO_2 -free air and analyzed. Standards were prepared from a stock solution of $1,000 \text{ mg l}^{-1}$ potassium hydrogen phthalate (KHP) prior to each analysis. All glassware used for carbon analyses

was acid-washed and oven dried prior to use (100°C). DIC was determined by subtracting DOC concentration from TC. Replicate analyses indicated an RSD of 5% for DOC and DIC.

3.3 Modeling

The partial pressure of dissolved (wet) CO₂ ($p\text{CO}_2$, μatm) was calculated for the CFR and BHR with the modeling program CO₂SYS (Lewis and Wallace 1998) using the temperature, pH and either the total alkalinity or DIC to determine the carbon speciation.

4 Results and Discussion

4.1 Clark Fork River

4.1.1 Field Results

Temperature, flow, pH, and specific conductivity from the diel sampling on the CFR in 2006 are shown in Fig. 3. A diel pH change of approximately 0.6 units (range 7.8–8.4) was observed which is attributed to daytime net consumption of CO₂ by aquatic photosynthesis and night time production of CO₂ by community respiration. The temperature reached a daytime maximum of 24.6°C and night time minimum of 16.5°C. A diel change in flow of approximately 13% was observed most likely due to evapo-transpiration in the streamside riparian zones (Bond et al. 2002). The dissolved oxygen reached a daytime high of 158% of saturation (385 $\mu\text{mol L}^{-1}$) and a night time low of 65% (164 $\mu\text{mol L}^{-1}$). DO concentrations ($n = 3$) determined by Winkler titration were in good agreement with instrument readings (Fig. 3c). The $p\text{CO}_2$ was above atmospheric partial pressure ($\sim 252 \mu\text{atm}$) during the whole diel period; decreasing during the day and increasing at night (Fig. 3c).

4.1.2 DOC and DIC

DOC showed a 1.8-fold diel change in concentration from a minimum of 124 to a maximum of 231 $\mu\text{mol C L}^{-1}$ (Fig. 4a). At the same time the average concentration of DIC was ~ 52 -times higher than that of the DOC. The DIC showed a ~ 5 -fold diel change in concentration from a minimum of 3.4 to a maximum of 17.0 mmol C L^{-1} (Fig. 4a). The diel change in DOC is most likely produced by release of soluble organic carbon compounds (i.e., amino acids, sugars, organic acids) by photosynthetic organisms during the daytime (Kaplan and Bott 1982; Vymazal 1994 and references therein) followed by consumption of those soluble organics by heterotrophic microbes during the night. The gradual increase in DOC after about 23:00 suggests a net accumulation due heterotrophic processing of larger insoluble organics from sediments or particulates (Zeigler and Fogel 2003). The DIC concentration decreased during the daytime due to removal of CO₂ by photosynthesis and increased at night due to community respiration.

The molar ratio of DIC/DOC reached a minimum of 16 at $\sim 17:00$ and a maximum of 104 at $\sim 06:00$ the following morning (Fig. 4b). This large increase in DIC relative to DOC at night suggests that oxidation of DOC contributed only a small part of the increase in DIC and that the majority of DIC was produced from other sources (e.g., aerobic or anaerobic respiration of microbes within the sediment bed; or groundwater influx). The



Fig. 3 Temperature and pH (a), specific conductivity (SC) and flow (b), dissolved oxygen (% saturation and $\mu\text{mol L}^{-1}$) and $p\text{CO}_2$ (c) at the Clark Fork River sampling site in Deer Lodge, MT. The cross marks (+) indicate Winkler DO measurements (see methods) performed to verify O_2 concentrations from instruments. Shaded bars in all diel graphs represent night time as determined by PAR signal of zero

rates of change in the concentration of DIC and DOC between sampling times can be compared to better understand how these two parameters were changing relative to each other (Fig. 4c). For example, at 19:15 the $\Delta\text{DOC}/\Delta t$ is about $-4.8 \mu\text{mol C L}^{-1} \text{h}^{-1}$ while the $\Delta\text{DIC}/\Delta t$ is approximately $1530 \mu\text{mol C L}^{-1} \text{h}^{-1}$; the concentration of DIC is increasing ~ 316 times faster than the concentration of DOC is decreasing. This also suggests that the majority of the increase seen in DIC was from sources other than the oxidation of the measured DOC.

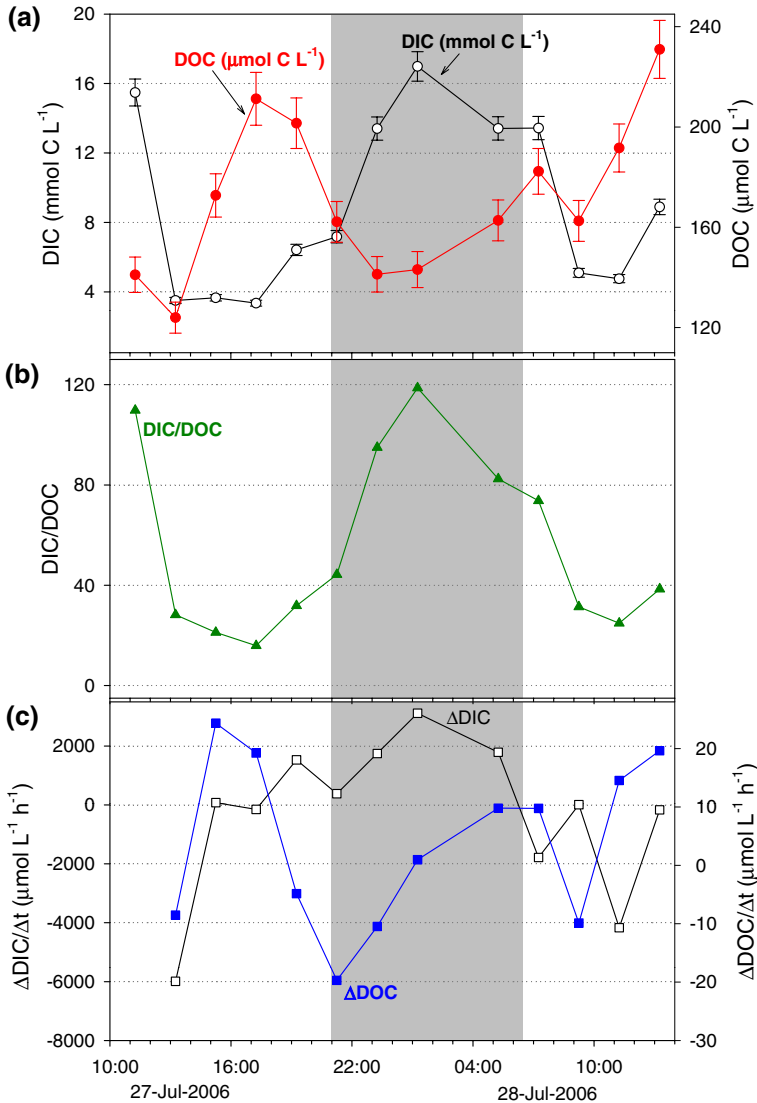


Fig. 4 DOC ($\mu\text{mol C L}^{-1}$) and DIC (mmol C L^{-1}) at CFRG during diel sampling in 2006 (a); molar ratio of DIC to DOC at CFRG (b) and the rate of change in DIC ($\text{mmol C L}^{-1} \text{h}^{-1}$) and DOC ($\mu\text{mol C L}^{-1} \text{h}^{-1}$) (c). Error bars represent 5% RSD based on replicate determinations

4.1.3 $\delta^{13}\text{C}$ -DOC and $\delta^{13}\text{C}$ -DIC

The isotopic composition of DOC ($\delta^{13}\text{C}$ -DOC) and DIC ($\delta^{13}\text{C}$ -DIC) also showed changes over the sampling period (Fig. 5). Diel changes in $\delta^{13}\text{C}$ -DIC have been observed previously in the CFR and BHR (Parker et al. 2005, 2007a). Photosynthesis removes CO_2 during the day with a reported isotopic depletion of about -29% (Falkowski and Raven 1997); such that the residual DIC becomes isotopically enriched. Gas-exchange with atmospheric

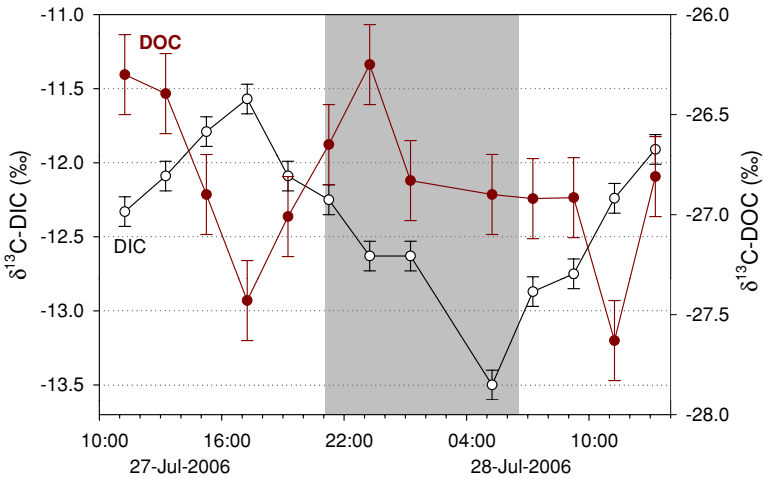


Fig. 5 $\delta^{13}\text{C-DOC}$ and $\delta^{13}\text{C-DIC}$ values measured during diel sampling in the CFR. Error bars represent a RSD of 0.95% for $\delta^{13}\text{C-DOC}$ and 0.55% for $\delta^{13}\text{C-DIC}$

CO_2 ($\delta^{13}\text{C} = -7$ to -8.5‰) will tend to elevate the $\delta^{13}\text{C-DIC}$ which had an average value over the diel period of -12.4‰ . However, as reported in Sect. 4.1.1 the $p\text{CO}_2$ was above atmospheric levels during the diel period such that the net flux of CO_2 would have been from the water to the atmosphere for the 24-h period. Diffusional fractionation associated with CO_2 outgassing should have caused the $\delta^{13}\text{C-DIC}$ to become isotopically heavier but the opposite was observed, with the $\delta^{13}\text{C-DIC}$ becoming increasingly depleted over night. This is consistent with community respiration being the dominant process which was influencing the $\delta^{13}\text{C-DIC}$.

The $\delta^{13}\text{C-DOC}$ showed the inverse isotopic diel trend to that of the DIC. The concentration of DOC increased during the day (Fig. 4a) due to soluble organics that were “leaking” from photosynthetic organisms and since photosynthesis discriminates against ^{13}C it follows that the DOC produced during this time will be isotopically depleted. Zeigler and Fogel (2003) suggested that the daytime decrease in $\delta^{13}\text{C-DOC}$ observed in a tidal wetland was due to the exudation of carbohydrates produced by phytoplankton and macrophytes. As photosynthesis decreased in the late afternoon ($\sim 17:00$), community respiration consumed this pool of soluble (isotopically light) organics, discriminating against the heavier isotope (kinetically) such that the remaining DOC pool becomes isotopically enriched (concentration decreasing, Fig. 4a). It is also possible that these “leaking”, isotopically light photosynthates such as carbohydrates are more readily bioavailable and are used first for respiration (Zeigler and Fogel 2003). After $\sim 23:00$ the isotopic composition of the pool stabilizes at approximately -26.9‰ . The $\delta^{13}\text{C}$ of the local aquatic and streamside vegetation was not measured during this study, but temperate region C_3 plants should have an isotope composition in the range of -20 to -30‰ (Clark and Fritz 1997). Consequently, this $\delta^{13}\text{C-DOC}$ plateau from 01:00 to 09:00 may reflect the DOC being produced by microbial degradation of detritus with an isotope signature typical of temperate region vegetation. This is consistent with the increase in DOC concentration after 23:00 (discussed above) being due to heterotrophic degradation of organic detritus accumulated within the sediment bed.

During the night as community respiration consumes the isotopically light DOC and insoluble organic matter in the sediments, it produces light CO_2 which causes the $\delta^{13}\text{C}$ -DIC to continue dropping until photosynthesis reverses the trend starting about 06:30 (Parker et al. 2009).

4.2 Big Hole River

4.2.1 Field and Isolation Chamber Results

Diel samplings were conducted on the BHR in two successive years during late summer, low flow conditions (2006 and 2007) within 8 days of the same date each year (Fig. 6). The hydrographs for a 6–7-day period bracketing the sampling for the 2 years show that the average flow in 2007 was about 1.7-times higher than in 2006 during the sampling period and that different temporal flow patterns were present in the 2 years (Fig. 7). The flow during the diel sampling period in 2006 showed a ~ 2.7 -fold minimum to maximum increase and exhibited a sharp decrease during the late afternoon ($\sim 17:00$) followed by a gradual increase with a maximum at about 01:00–03:00 (Fig. 6b). The flow in 2007 showed a ~ 1.3 -fold minimum to maximum increase during the sampling period with a gradual decrease throughout the afternoon reaching a minimum about 21:00 through 02:00 followed by a gradual increase through the following morning (Fig. 6e). The 2007 pattern is more typical of one expected to be produced by evapo-transpiration from productive

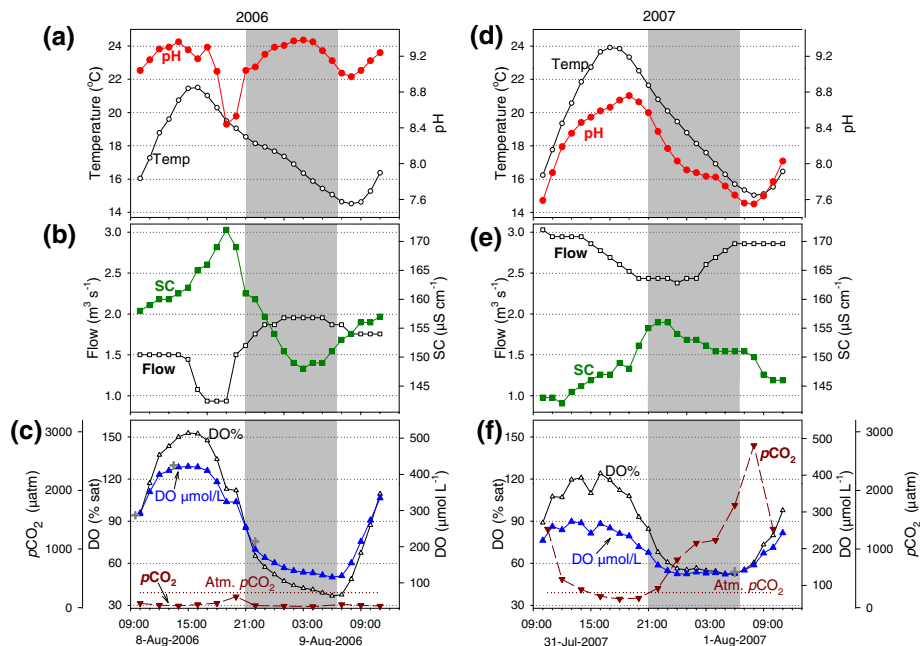


Fig. 6 Temperature and pH (a; 2006) and (d; 2007); flow and specific conductivity (SC) (b; 2006) and (e; 2007); and dissolved oxygen (% saturation and $\mu\text{mol L}^{-1}$) (c; 2006) and (f; 2007) for the BHR. The cross marks (+) indicate Winkler DO measurements (see methods) performed to verify O_2 concentrations from instruments

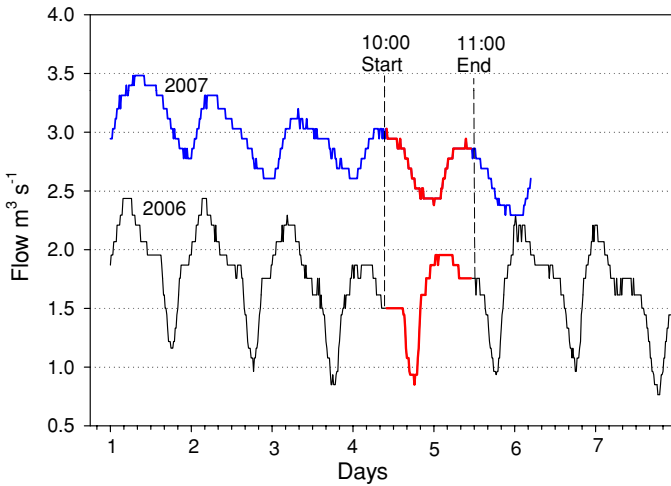


Fig. 7 Hydrographs (USGS gage data) for the BHR site for a 6–7 day period around the field work in 2006 and 2007. *Red lines* show the sampling period in both years and *dashed lines* show the approximate starting (10:00) and ending (11:00) times for sampling

upstream riparian zones (Bond et al. 2002) while the pattern observed in 2006 is not well understood (discussed below).

The pH variation observed in 2006 is very unusual with a sharp pH drop in late afternoon ($\sim 17:00$), at approximately the same time that the flow dropped (Fig. 6a). This was followed by a gradual increase in pH with a maximum at $\sim 03:00$; approximately the same time that the flow peaked in 2006. The late afternoon decrease in flow in 2006 described above was also accompanied by a sharp increase in specific conductivity (SC) at the same time ($\sim 18:00$, Fig. 6b). The SC dropped after this time with a minimum at $\sim 03:00$, the same time that the flow reached a maximum. The behavior of DO in 2006 was “normal” with the exception of a small shoulder at approximately 19:00 which corresponds to the sharp flow decrease in the late afternoon (Fig. 6c). In contrast to the CFR described above, the $p\text{CO}_2$ in the BHR in 2006 was below atmospheric levels ($\sim 252 \mu\text{atm}$) for the 24-h sampling period (Fig. 6c) which is due to the high pH (avg. 9.1) and high productivity as shown by the large diel change in O_2 concentration (37–152% sat.) during this base flow period. The late afternoon drop in pH described above ($\sim 17:00$) was mirrored by a small increase in $p\text{CO}_2$ followed by a night time decrease as the pH began to rise. This is an unusual $p\text{CO}_2$ pattern since it usually increases over night due to community respiration and decreasing pH, as observed in the CFR (Fig. 3c).

In 2007, the changes in flow, SC, and pH were more typical of “normal” stream behavior (Fig. 6d, e). The diel change in DO was not as large in 2007 as in 2006 and was possibly modulated by the larger flow (Fig. 6f). Maximum stream temperature was higher in 2007 than 2006 which also decreased O_2 solubility. The $p\text{CO}_2$ during 2007 was above atmospheric levels except for a brief period in the afternoon ($\sim 16:00$ – $20:00$) and showed a more “typical” pattern (Fig. 6f). The higher $p\text{CO}_2$ levels are in part due to the lower pH values in 2007 (avg. 8.1) versus 2006 (avg. 9.1).

An isolation chamber with stream water plus cobbles and attached periphyton was used during the 2006 sampling (Fig. 8a). This allowed a comparison of temperature, pH, and DO between the river and water in the chamber which was isolated from chemical species

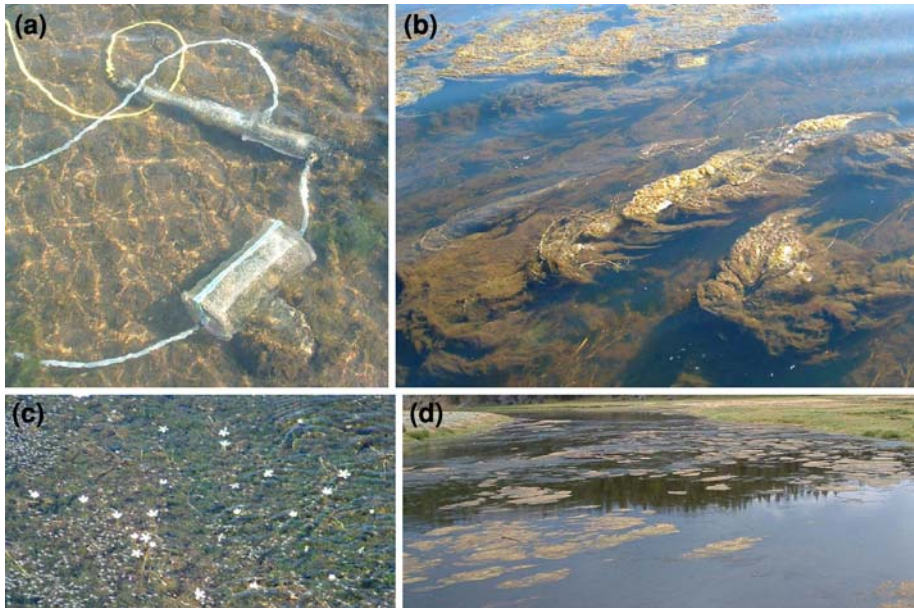


Fig. 8 Pictures of the isolation chamber (a), streaming algal mats (b), area of *Ranunculus aquatilis* (river buttercups, c) and river with algal mats near sampling area (d) in the BHR

transported to the sampling site from upstream or from hyporheic discharge (Fig. 9). Consequently, the observed changes in chemistry of the chamber water were dominated by interactions with the enclosed benthic materials. Temperature and DO both in the chamber and in the river were similar through the diel period although at night the DO in the chamber did reach a minimum of about $31 \mu\text{mol L}^{-1}$ versus $115 \mu\text{mol L}^{-1}$ in the river (Fig. 9a, c). This night time difference in DO was most likely due to the absence of gas exchange with the atmosphere in the chamber. The pH in the chamber did not show the same unusual pattern displayed in the river (Fig. 9b). Since the chamber was refilled with river water every 2 h, it does show evidence of a subdued version of the decrease in pH seen in the river at $\sim 19:00\text{--}20:00$. The pH in the water isolated in the chamber showed a 0.13 unit change in pH versus 0.86 units in the river in the time period from 17:00 to 19:00. Since the pH profile in the chamber was similar to the more typical pattern found in river systems (i.e., CFR Fig. 3a) and that it was refilled with river water every 2 h emphasizes the temporal period over which the pH modification can occur. The $p\text{CO}_2$ in the chamber (Fig. 9c), similar to pH, showed a more typical diel behavior and did not show the small increase around 19:00 as was seen in the river. The potential causes of these differences in the diel pH and $p\text{CO}_2$ patterns in 2006 between the river and the chamber will be discussed in the next section.

4.2.2 DOC and DIC

A 4.6-fold minimum to maximum diel change in DOC in the BHR was observed in 2006 while no regular diel change in DOC concentration was observed in 2007 (Fig. 10a, b). The night time peak in DOC concentration in 2006 occurred at $\sim 01:00$, which coincides

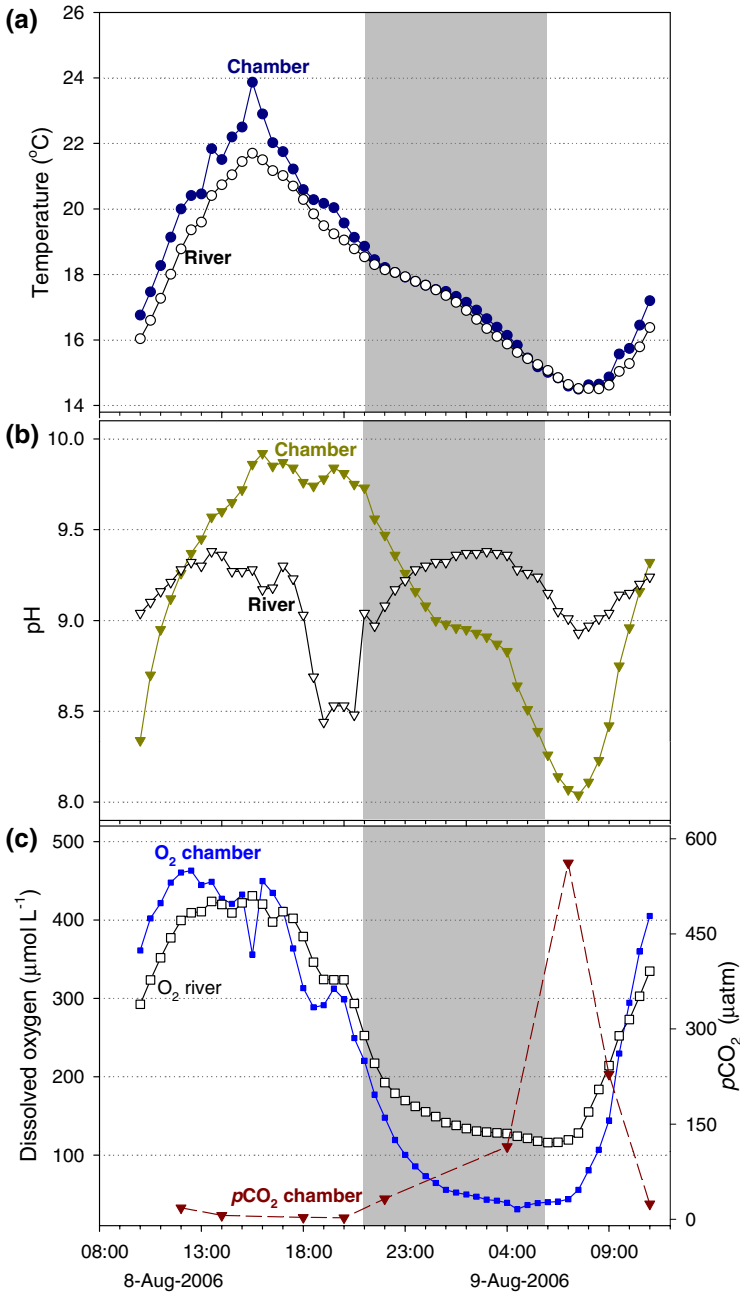


Fig. 9 Temperature (a), pH (b) and dissolved oxygen (% saturation and $\mu\text{mol L}^{-1}$) (c) for the isolation chamber and BHR during the 2006 sampling

approximately with the timing of the maximum values reached by both flow and pH (Fig. 6a, b). At the same time, the concentration of DIC both in 2006 and 2007 did not change significantly over the diel period. The load of DOC (concentration \times flow) in 2006

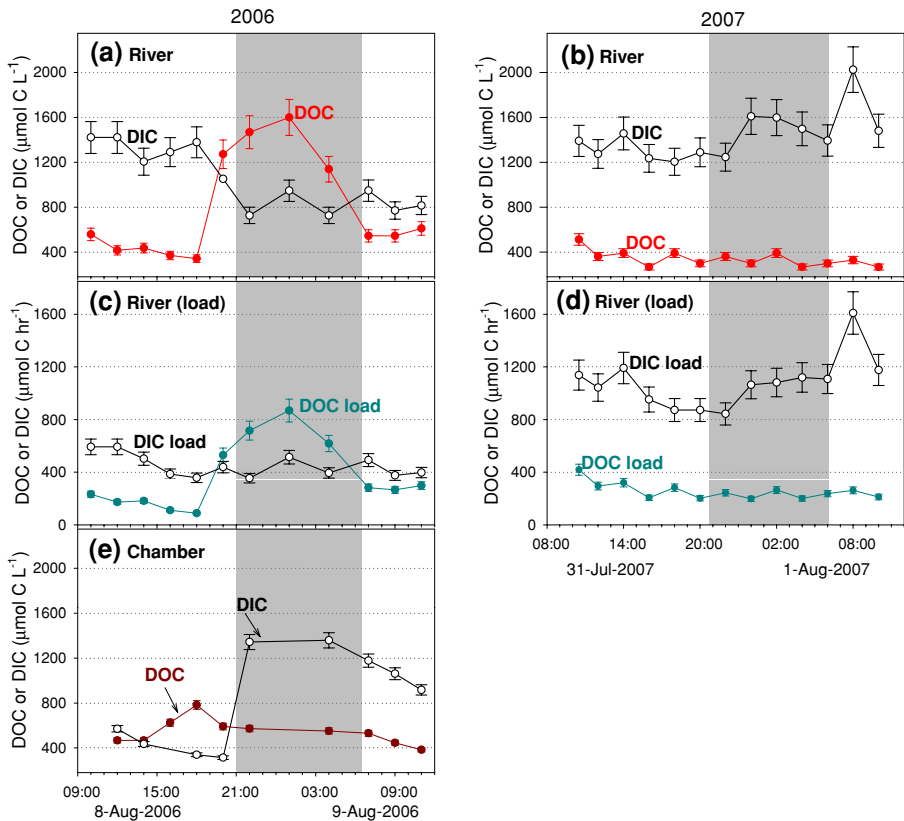


Fig. 10 Concentrations DIC and DOC in the BHR in 2006 (a) and 2007 (b); load of DOC and DIC in the BHR in 2006 (c) and 2007 (d); and DOC and DIC in the isolation chamber during 2006 (e). Error bars represent 5% RSD based on replicate determinations

shows the same night time increase with a maximum at $\sim 01:00$ when the flow peaked while there was no change in load of DOC over the diel period in 2007 (Fig. 10c, d). This indicates that the diel change in concentration in 2006 (Fig. 10a) was not an artifact of the change in flow (Fig. 6b) since the load of DOC increased simultaneously. Although the average load of DIC in 2007 was about 2.4 times higher than in 2006 there was no apparent regular diel pattern in either year (Fig. 10c, d).

One possible explanation for this significant late afternoon/night time increase in DOC in 2006 and not in 2007 may be linked to the unusual flow pattern observed in 2006. After the late afternoon decrease in flow in 2006 ($\sim 17:00$; Fig. 6b), the following increase may have included a groundwater influx from bank-storage and/or benthic sediments. This water may have carried additional concentrations of DOC from decaying organic matter producing the DOC increase observed in the river. In order to better address the DOC concentration and pH of bank storage/sediment pore waters during the 2007 sampling, water was collected from seeps (small springs) along the river bank as well as pore water withdrawn from the shallow stream bottom sediments. The seeps were on both sides of the river between 300 and 800 m upstream from the sampling site. The seeps all had higher

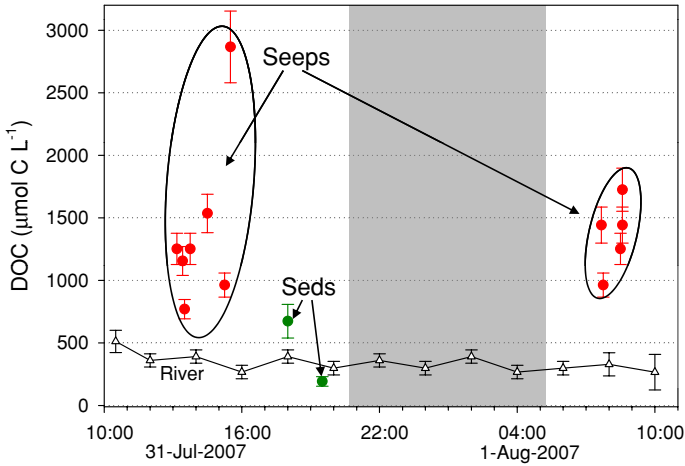


Fig. 11 Concentration of DOC ($\mu\text{mol C L}^{-1}$) in seeps (red), shallow sediments (green) and the BHR (open triangles) during the 2007 sampling site

DOC concentrations and lower pH values than the river water at the sampling site (Fig. 11; Table 1). The average DOC concentration of the seeps was $1,385 \mu\text{mol C L}^{-1}$ while the average DOC in the river over the diel period was $341 \mu\text{mol C L}^{-1}$. The DOC concentration of the shallow sediment water sampled was similar to that of the river (Fig. 11), which is characteristic of shallow, short range hyporheic flow paths (Poole et al. 2008). The average pH of the seep waters was 6.8 while the average pH of the river during the 2007 diel sampling was 8.1 (9.1 in 2006). This suggests that if the night time increase in DOC in 2006 was due to a significant influx of bank storage water, then the pH should have decreased simultaneously; not increased. This is not to suggest that streamside/groundwater contributions of DOC and other solutes did not occur but that those contributions were relatively constant while the large night time increase in DOC was produced by a separate process.

Another hypothesis that has been considered to explain the large diel changes in flow that have been observed periodically during late summer in the BHR has been the presence of large stretches of algae and macrophytes (*Ranunculus aquatilis* and other species) that float to the surface during the day while they are actively photosynthesizing, effectively forming an “in-stream” dam (see Fig. 8b–d). At night these photosynthetic organisms sink toward the bottom allowing the trapped water to flow down the river as a wave. This model is consistent with stream flow observations in this reach of the river during a similar flow regime in 2005 when the river stage (water level) increased and the flow decreased (C. Gammons personal communication). This might explain the decrease in flow in the late afternoon during 2006 followed by an increase in water at night from upstream as the in-stream damming action ceased. This pulse of water that was retarded by the plants and algae during the day may have been higher in pH due to photosynthetic removal of CO_2 and contain higher amounts of DOC due to leakage of organic photosynthates as discussed above in Sect. 4.1.2.

This model that conceptualizes a “wave” of water moving down the river can be further analyzed by looking at the SC of the water over the diel period. The average diel SC of the river was significantly lower in 2006 ($157 \mu\text{S cm}^{-1} \pm 6.7$; $n = 51$) than that of the seeps

Table 1 Concentrations of DOC from seeps and sediments from the Big Hole River sampled during 2007

Site	<i>T</i> (°C)	pH	SC	DO % sat	DO $\mu\text{mol/L}$	DOC $\mu\text{mol C/L}$	Location
Seep 1a	20.8	6.76	130	75.2	165	1,252	N 45°48.429'; W 113°19.147'
Seep 1b	NA	NA	NA	NA	NA	1,442	N 45°48.429'; W 113°19.147'
Seep 2a	25.2	6.88	129	105.2	206	1,155	N 45°48.433'; W 113°19.164'
Seep 2b	NA	NA	NA	NA	NA	963	N 45°48.433'; W 113°19.164'
Seep 3	19.5	6.23	157	52.0	117	770	N 45°48.433'; W 113°19.174'
Seep 4	23.0	7.12	157	135.5	288	1,252	N 45°48.436'; W 113°19.195'
Seep 5a	20.1	6.91	622	0.9	2.0	1,536	N 45°48.708'; W 113°19.564'
Seep 5b	11.7	7.05	608	43.9	119	1,252	N 45°48.708'; W 113°19.564'
Seep 6	23.4	6.91	167	104.7	214	964	N 45°48.439'; W 113°19.196'
Seep 7	15.6	6.23	124	123.4	278	2,867	N 45°48.439'; W 113°19.203'
Seep 8	11.4	6.83	582	25.0	68	1,442	N 45°48.712'; W 113° 19.579'
Seep 9	10.1	7.40	617	58.8	165	1,725	N 45°48.707'; W 113°19.567'
Sed 1	NA	NA	NA	NA	NA	674	N 45°48.450'; W 113°18.750'
Sed 2	NA	NA	NA	NA	NA	193	N 45°48.450'; W 113°18.750'

All seeps are between 300 and 800 m upstream from BHR sampling site

T temperature; pH in standard units; *SC* specific conductivity ($\mu\text{S/cm}$); *NA* not available

sampled in 2007 (avg. $329 \mu\text{S cm}^{-1}$; range: 124–622). Additionally, the effect of the higher *SC* of the seeps on the river *SC* was investigated with a synoptic survey through the sampling area in 2007. This survey showed consistently higher conductivity water near the stream banks (avg. $157 \pm 4.6 \mu\text{S cm}^{-1}$, $n = 8$) than in the middle of the channel (avg. $147 \pm 3.9 \mu\text{S cm}^{-1}$, $n = 49$) which shows that additions of water from streamside areas were entering the river. Assuming that the chemistry of the seep/groundwater was similar in the 2 years, the increase in *SC* of the river observed in 2006 (Fig. 6b) during the late afternoon when the flow decreased is consistent with a lower volume of river water (lower *SC*) relative to groundwater (higher *SC*). This was then followed by a decrease in *SC* as the flow increased in the first part of the night ($\sim 21:00$ – $01:00$; Fig. 6b) possibly related to an increase in the volume of river water being advected into the sampling area relative to the groundwater contributions.

In further support of this model, the *DOC* concentration and *pH* in the isolation chamber did not display the same night time increase observed in the river in 2006 (Fig. 10e). This difference in *DOC* and *pH* behavior between the chamber and the river is consistent with the model described above suggesting that a “slug” of water migrated downstream that was higher in *pH*; passing the BHR sampling site between 17:00 and 01:00. If the increase in *DOC* and *pH* was produced by aquatic vegetation in the direct area of the sampling site, it should have been observed at some level in the chamber as well as in the river. Additionally, the *DIC* concentration in the chamber showed a pattern that is more “typical” of productive systems with the *DIC* decreasing during the day, while photosynthesis is the dominant metabolic process, resulting in a net removal of CO_2 ; followed by increasing CO_2 at night as community respiration returns it to the water column (Fig. 10e). This was the same pattern observed for the *DIC* concentration in the CFR (Fig. 4a).

Another possible cause of the large and reproducible abnormal flow cycle observed in 2006 could have been a significant daily change in irrigation withdrawals upstream from

the sampling site. The hydrologist for the Montana Department of Natural Resources and Conservation indicated: (1) that there was no one irrigation structure that could remove that amount of water upstream from our site; (2) that the irrigators generally don't turn their ditches on and off, especially on a regular schedule; and (3) most irrigators were not withdrawing water at that time of year due to low flows (M. Roberts personal communication). Consequently it seems unlikely that there was any anthropogenic cause of the flow pattern observed in 2006.

These explanations for the abnormal flow, pH, and DOC behavior observed in 2006 are currently the focus of a continued investigation to better understand the hydrology and biogeochemistry of the upper Big Hole River.

4.2.3 Isotope Composition of DIC

The $\delta^{13}\text{C}$ -DIC was determined for both the 2006 and 2007 samplings in the BHR (Fig. 12). The pattern is typical of $\delta^{13}\text{C}$ -DIC reported previously (Parker et al. 2005, 2009) and similar to those observed in 2006 on the CFR (Fig. 5). There was no discernible diel pattern in DIC concentration in the BHR both during 2006 and 2007 and at the same time the minimum to maximum isotope composition change was ~ 3.3 and 2.7% in 2006 and 2007, respectively. Additionally, the $\delta^{13}\text{C}$ -DIC in 2006 did not show any influence of the aberrant pH and flow cycle (Fig. 8a, b) which appears to have been associated with the diel change in DOC (Fig. 9a). Diel changes in $\delta^{13}\text{C}$ -DIC are influenced by isotopically light CO_2 produced by community respiration, consumption of CO_2 by photosynthesis, gas exchange with the atmosphere, influx of groundwater and dissolution of carbonate minerals. Groundwater contributions of DIC do not appear to be significant in controlling the diel changes in $\delta^{13}\text{C}$ -DIC in 2006 and 2007 in the BHR at this site since these changes are not correlated with the flow cycles. The daytime increases in $\delta^{13}\text{C}$ -DIC have been attributed to kinetic fractionation associated with the consumption of CO_2 by photosynthesis. Since the average pH in 2006 was ~ 1 unit higher than in 2007 the $p\text{CO}_2$ was significantly lower in 2006 versus 2007 (Fig. 6e, f). In 2006 the $p\text{CO}_2$ was below atmospheric levels during the whole diel period while in 2007 the $p\text{CO}_2$ dipped below atmospheric levels during a brief period in the afternoon. During this afternoon period in 2007 when the $p\text{CO}_2$ was low, the net flux of CO_2 would have been from the atmosphere to the water which would have raised the $\delta^{13}\text{C}$ -DIC toward an equilibrium value of -1 to $+3\%$. However, the maximum afternoon $\delta^{13}\text{C}$ -DIC in 2006 and 2007 was -11.5% and -10.5% , respectively, indicating that a balance of metabolic processes was most significant in determining the isotopic composition of inorganic carbon. At night the $\delta^{13}\text{C}$ -DIC both in 2006 and in 2007 decreased during the period when respiration was the only metabolic process operating. In 2006 the $p\text{CO}_2$ remained below atmospheric levels during the whole diel period (Fig. 6c) while in 2007 $p\text{CO}_2$ increased well above atmospheric equilibrium over night (Fig. 6f). Gas exchange in 2006 at night should have resulted in a net influx of atmospheric CO_2 which should have caused an increase in $\delta^{13}\text{C}$ -DIC but since the $\delta^{13}\text{C}$ -DIC continued to decrease, community respiration producing light CO_2 must have been the most significant process affecting the isotope values. In 2007 the night time $p\text{CO}_2$ increased well above atmospheric levels which should have resulted in a net efflux of CO_2 from the water to the air. Diffusional fractionation associated with outgassing should have caused the $\delta^{13}\text{C}$ -DIC to increase but it continued to decrease overnight indicating again that community respiration was again the most significant process influencing the $\delta^{13}\text{C}$ -DIC in the absence of photosynthesis. This emphasizes the dynamic nature of the inorganic carbon pool. While the concentration is not changing in a regular manner, the isotopic

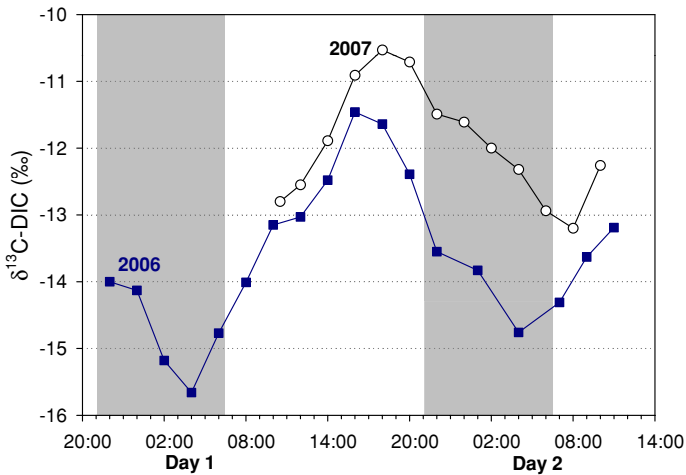


Fig. 12 $\delta^{13}\text{C}$ -DIC at the BHR site during the 2006 (blue squares) and 2007 (open circles) during diel samplings. Error bars represent 3% RSD based on duplicate determinations

composition of the pool was being modified by changing metabolic rates in this highly productive system and this was reflected by the diel pattern of $\delta^{13}\text{C}$ -DIC.

5 Conclusions

Diel concentration cycles in DOC were observed in both the CFR and the BHR in 2006 but very different temporal patterns were observed in these two rivers. No change in DOC concentration was observed at the same location in the BHR approximately 1 year later (2007) suggesting that the presence of diel changes in DOC concentration are dependent on conditions that can change from year-to-year such as different flow regimes (Fig. 6b, e). The average flow in the BHR in 2007 was ~ 1.7 times higher than in 2006 and had a different temporal pattern suggesting that the presence of the observed diel changes in DOC may be linked to circumstances present during extreme low, base flow conditions. During these extreme low flow events the volume of water in the river is low in relation to the mass of attached periphyton which could amplify effects such as instream damming caused by aquatic plants and algae. These hydrologic and biogeochemical dynamics are not well understood and are the subjects of further study.

The DOC cycle in the BHR in 2006 reached a maximum concentration at $\sim 01:00$, which is approximately the time that the flow reached its maximum (Fig. 6b, 7). The pH during the 2006 sampling showed an unusual bi-phasic pattern with a maximum around 14:00 and then again at about 02:00. Between these two maximums there was a steep drop in pH with a minimum at $\sim 17:00$; coincident with the steep drop in flow. Normally pH will reach a minimum in the early morning ($\sim 07:00$ in 2007, Fig. 6d). This pH increase during the night could not have been caused *directly* by photosynthesis removing CO_2 from the water. However, since the flow increased at the same time this pattern is consistent with a mass of water moving into this reach that was chemically modified (higher pH, lower conductivity). Two hypotheses that have been suggested above to explain these data are: (1) increased flow from streamside regions and/or benthic sediments at night as evapo-transpiration decreased;

and (2) the possibility that algae and macrophytes in upstream reaches float up and partially dam the river during the day due to photosynthesis and then sink at night, releasing the water. The second hypothesis has been suggested to explain the large diel changes in flow previously observed in this middle reach of the BHR of up to $2.8 \text{ m}^3 \text{ s}^{-1}$ (100% minimum to maximum) in a period of as little as 2 h (USGS gage data, not shown). These large flow cycles observed in the past have had similar timing and trends to those of the 2006 flow reported in this study.

The first explanation is partially supported by preliminary results of samples collected from a number of seeps along the BHR above the sampling site in 2007. The water from these seeps had DOC concentrations ~ 4 -times higher on the average than the river (Fig. 11). At the same time water extracted from shallow benthic sediments had DOC concentrations similar to that of the river. The pH of the water from the seeps was in general lower than that of the river (avg., 6.8 vs. 8.1; Table 1). Consequently, this makes it seem unlikely that the increase in pH in conjunction with the increase in DOC observed in 2006 was due to a large influx of water from bank storage in streamside areas above the sampling site.

The latter explanation predicts a “slug” of water moving downstream that would be of higher pH due to photosynthetic removal of CO_2 during the day and have a higher concentration of DOC due to leakage of soluble organic photosynthates. It is interesting to note that the $\delta^{13}\text{C}$ -DIC during both 2006 and 2007 had the same pattern and in 2006 appeared to show no influence from the observed flow and pH increase during the night (Fig. 11). This suggests that the biologic processing of inorganic carbon is acting at a time scale resulting in a “normal” $\delta^{13}\text{C}$ -DIC pattern.

In the CFR, the DOC showed an inverse temporal pattern to that observed in the BHR in 2006. The DOC in the CFR reached a maximum concentration at $\sim 16:00$ which is consistent with “leakage” of photosynthates during this active photosynthetic period. The $\delta^{13}\text{C}$ -DOC became isotopically depleted during the afternoon most likely due to incorporation of “light” organics produced by photosynthesis and then became enriched during the night as microbial oxidation of DOC consumed lighter carbon containing compounds at a faster rate. It is also possible that the isotopically heavier DOC is in part a different class of compounds that was more recalcitrant and less readily oxidized than the isotopically lighter, recently synthesized compounds. Additionally, a comparison of the rates of change in the concentration of DOC and DIC indicates that the night time increase in DIC can not be solely attributed to microbial oxidation of DOC.

This study emphasizes the importance of the need for a better understanding of the dynamic nature of diel changes in the concentration of both dissolved inorganic and organic species in rivers. It also underscores the fact that different patterns of DOC concentration can occur seasonally in the same aquatic system. Additionally, it demonstrates a need to better quantify the types of organic compounds included in the DOC pool in relation to both the isotopic composition as well as how readily available these forms are for heterotrophic oxidation. These results also highlight the fact that significant short term temporal changes in DOC can occur and monitoring protocols for DOC need to take diel concentration changes into account. Also, predicting diel concentration patterns based on prior behavior may not always be reliable as shown by the BHR results for 2006 and 2007.

The night time pH maximum observed in the BHR during 2006 that coincided with the large concentration increase of DOC suggests that these two occurrences may have been caused by the same process which is also related to the simultaneous increase in flow. Unfortunately, these “anomalous” flow occurrences don’t happen every year as seen in 2007 but do need to be further investigated when they do happen. This may lead to

significant insight into the function and response of riverine systems to drought/low flow and changing land use conditions.

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