Dam tailwaters compound the effects of reservoirs on the longitudinal transport of organic carbon in an arid river

A.J. Ulseth[1,2,3] and R.O. Hall, Jr.[2]

[1]{Program in Ecology, University of Wyoming, Laramie, Wyoming, USA}

[2]{Department of Zoology and Physiology, University of Wyoming, Laramie, Wyoming, USA}

[3]{now at: École Polytechniqe Fédérale de Lausanne, Lausanne, Switzerland}

Correspondence to: A.J. Ulseth (amber.ulseth@gmail.com)

Abstract

Reservoirs on rivers can disrupt organic carbon (OC) transport and transformation, but less is known how river reaches directly below dams contribute to OC processing. We compared how reservoirs and their associated tailwaters affected OC quantity and quality by calculating particulate (P) OC and dissolved (D) OC fluxes, and measuring composition and bioavailability of DOC. We sampled the Yampa River near Maybell, Colorado, USA and the Green River above and below Fontenelle and Flaming Gorge reservoirs, and their respective tailwaters from early snowmelt to base flow hydrological conditions. In unregulated reaches (Yampa River, Green River above Fontenelle reservoir), DOC and POC concentrations increased with snowmelt discharge. POC and DOC concentrations also increased with stream discharge below Fontenelle reservoir, but there was no relationship between DOC and stream flow below Flaming Gorge reservoir. The annual load of POC was 3-fold lower below Fontenelle Reservoir and nearly 7-fold lower below Flaming Gorge reservoir, compared to their respective upstream sampling sites. DOC exported to downstream reaches from both reservoirs was less bioavailable, as measured

with bioassays, than DOC upriver of the reservoirs. Lastly, tailwater reaches below the reservoirs generated OC, exporting potentially 1.6-2.2 g C m^{-2} d^{-1} of OC to downstream ecosystems. Therefore, the effect of impounding rivers on C fluxes is greater than the impact of the reservoirs alone given the additive effect of tailwater reaches below dams, which may produce and export comparable amounts of likely autochthonous carbon to downstream reaches.

1 Introduction

Unregulated streams and rivers compose a continuous ecosystem where a gradient of physical processes drive biological processes from headwaters to the river deltas (Vannote et al. 1980). Along this continuum, rivers receive terrestrial organic carbon (OC) and export it to the ocean (Cole et al. 2007). The amount of OC that enters the oceans, however, is only a fraction of the estimated input from the terrestrial landscape (Aufdenkampe et al. 2011). A larger fraction of OC entering rivers and streams is believed to be stored and mineralized to CO_2 within these ecosystems (Cole et al. 2007; Battin et al. 2009; Aufdenkampe et al. 2011).

Flow regulation by damming has converted most rivers into a series of lotic and lentic reaches (Ward and Stanford 1983; Benke 1990), affecting OC cycling and transport (Ward and Stanford 1983; Miller 2012; Stackpoole et al. 2014). Reservoirs on rivers may trap particulate OC (POC) (Friedl and Wuest 2002; Downing et al. 2008; Tranvik et al. 2009), and transform and produce dissolved OC (DOC) (Mash et al. 2004; Knoll et al. 2013). Increased water residence time (Vörösmarty et al. 1997; Sabo et al. 2010) allows for OC to be respired, incorporated into microbial production, or buried while production of autochthonous or microbial DOC increases (Mash et al. 2004; Knoll et al. 2013). This autochthonous DOC can be more bioavailable than terrestrial sources (del Giorgio and Davis 2003); therefore increasing autochthonous production within these ecosystems potentially increases the bioavailability of DOC, although there is little understanding of the bioavailability of DOC exported downstream of reservoirs. Compositional changes of DOC may or may not occur as well. For instance, DOC composition did not change from upstream to downstream of reservoirs in boreal-forested rivers in northern Ontario where catchment characteristics had a stronger influence compared to the presence of impoundments (Nadon et al. 2014). Therefore coupling DOC bioavailability and composition is needed to understand the transformative processes reservoirs can have on DOC and ultimately riverine C-cycling. In regards to DOC concentration, various studies have found that reservoirs may increase (Parks and Baker 1997), decrease (Miller 2012; Knoll et al. 2013), or not alter DOC concentrations to downstream ecosystems (Parks and Baker 1997; Nadon et al. 2014). Prior work has shown DOC fluxes increased longitudinally in the upper basin of the Colorado River, but then decreased with the presence of large reservoirs in the lower basin (Miller 2012; Stackpoole et al. 2014). Conversely DOC fluxes increased in the lower Missouri River despite the presence of large reservoirs (Stackpoole et al. 2014). These studies have given insight into longitudinal OC fluxes in light of flow regulation by dams, but an understanding of fluxes in combination with bioavailability and composition of DOC is less understood.

Tailwater reaches can be found directly downstream of all dams (Ward and Stanford 1983); yet, coupled reservoir and tailwater OC fluxes are unclear within the context of riverine OC budgets. Within the scope of this research, we define tailwater reaches as the stream reach directly downstream of dams, which have no tributary input. These tailwater ecosystems physically and biologically differ from their upstream or pre-dam counterparts (Ward and Stanford 1983), which may affect DOC and POC dynamics. In these tailwater reaches, sediment transport is lower and bed sediment is more stable than upstream of the reservoir (Schmidt and

Wilcock 2008). These highly altered physical processes result in increased primary production in tailwaters relative to the unaltered or pre-dam river (Davis et al. 2011). Such high production can increase transported POC and DOC (Webster et al. 1979; Perry and Perry 1991; Lieberman and Burke 1993; Benenati et al. 2001). Tailwater POC may consist of sloughed algae from production within the river reach (Webster et al. 1979; Perry and Perry 1991). Algae in tailwaters may increase DOC concentration via exudation (Baines and Pace 1991; Bertilsson and Jones 2003). For example, autochthonous DOC flux was correlated with gross primary production in the tailwater of Glen Canyon Dam on the Colorado River and may equate to 7-91% of gross primary production in the tailwater (Ulseth 2012). Tailwater ecosystems produce algal OC, which is exported (Perry and Perry 1991; Lieberman and Burke 1993), transformed, buried, or consumed. This source of autochthonous, likely more labile C (del Giorgio and Davis 2003), may result in increased bioavailability of DOC, which could impact riverine C cycling, but the extent of bioavailability variability in relation to dams and their tailwaters is unknown.

We studied a series of reaches on the Green and Yampa Rivers located in the upper basin of the Colorado River, USA to quantify the role of hydrological regulation on OC quantity and quality. Within this objective, we asked the following questions: 1. How do OC concentration, fluxes, and DOC composition and bioavailability vary temporally in hydrologically regulated reaches compared to free-flowing rivers? 2. How does the bioavailability and composition of DOC vary longitudinally in a river altered by reservoir-tailwater ecosystems? We addressed these questions by quantifying POC and DOC concentration and DOC composition and bioavailability in regulated and unregulated river reaches in the upper Colorado River basin. We sampled from the onset of snowmelt, where we expected transport processes to dominate, and during base flow river conditions where we expected within ecosystem production to drive OC quality and transport.

2 Methods

2.1 Study site

The Colorado River basin is heavily regulated (Nilsson et al. 2005), making it an opportune river basin to study DOC dynamics in impounded rivers. We selected sampling sites to capture OC processes of non-regulated reaches, above and below reservoirs, and also to capture tailwater OC dynamics. In total, we selected seven sites on the Green and Yampa Rivers located in the upper basin of the Colorado River (Fig. 1). Two sites served as unregulated reaches: the Green River above Fontenelle reservoir near La Barge, Wyoming (Fig. 1, A) and the Yampa River near Maybell, Colorado (Fig. 1, G). To capture potential longitudinal changes in OC transport and DOC composition and quality, we continued our sampling downstream starting above Fontenelle reservoir. Fontenelle reservoir had a mean water capacity of 0.26 km^3 and a mean water residence time of 0.13 yr for 2011 (Table A1). We sampled below Fontenelle dam at two locations: directly below the dam (Fig. 1, B) and another site 39.6 km downriver to measure the OC dynamics in the tailwater (referred to as Fontenelle tailwater, Fig. 1, C). Further downstream, we sampled above Flaming Gorge reservoir (Fig. 1, D). During 2011, Flaming Gorge reservoir had a mean volume of 4.08 km^3 and a mean residence time of 1.61 yr (Table A1). We sampled at two locations below Flaming Gorge dam, immediately below the dam (Fig. 1. E) and 25.7 km further downriver to capture tailwater effects on OC dynamics (referred to as Flaming Gorge tailwater, Fig. 1., F). Our sampling sites were located at US Geological Survey gaging stations, except for tailwater sites. For tailwater sites we assumed no change in discharge over these short distances from the dams.

We sampled from the onset of snowmelt to base flow in one year to compare processes during runoff and base flow in these snowmelt driven rivers. We sampled at the beginning of snowmelt in late April 2011 and continued into October of 2011 every 2 – 7 weeks for a total of 8 sampling periods. In 2011, the Yampa and Green Rivers had high-sustained flows into late July (Fig. 2). All sampling sites were accessible by car, and collection of samples took place over a two-day period for each round of sampling.

2.2 Sample Collection

We collected samples to quantify DOC concentration, composition, and bioavailability as well as particulates for POC. We used acid-washed polyethylene Cubitainers to collect water from each sampling site. We immediately placed the collected water on ice, and filtered within 8 hours of collection. We used a pre-rinsed Supor capsule filter (0.2-μm capsule filter; Pall SUPOR AcroPak 200) to filter approximately 4 L of water from each site for the bioassay experiments described below. From the remaining water, we collected samples for absorbance spectroscopy measurements and DOC concentration. The water samples were filtered into acid-washed, pre-combusted 40 mL amber glass vials. Four replicates were immediately acidified with 400 μL of 2N HCl for later DOC analysis, and four other replicates were used for spectral measurements. All DOC samples were kept cold and dark until analyses. We analyzed DOC samples on a Shimadzu TOC 5000A in Laramie, Wyoming. Individual samples were run a minimum of three times to estimate analytical precision. The coefficient of variation for replicate runs of the same sample was < 2%.

2.3 DOC Composition

We used spectrophotometric absorbance to evaluate DOC chemical composition. We used a scanning spectrophotometer to measure the absorbance of DOC from 200 to 600 nm on a Beckman DU spectrophotometer. We scanned the DOC samples using a 5-cm quartz cuvette and used deionized water as the blank. To characterize the structure of DOC, we used the absorbance measured at 254 nm, normalized by the DOC concentration to calculate specific ultraviolet absorption, otherwise referred to as $SUVA_{254}$ ($L\ mg\ C^{-1}\ m^{-1}$). $SUVA_{254}$ indicates the aromaticity of the C compounds and is positively correlated with double C bonds and molecular weight, with higher values indicating more aromaticity of the DOC compounds (Chin et al. 1994; Weishaar et al. 2003). Additionally, we calculated the spectral slope ratio (S_R). S_R is the ratio of the spectral slopes ($S_{275-295}$:$S_{350-400}$) at wavelength regions of 275-295 and 350-400 (Helms et al. 2008). S_R is inversely correlated with DOC molecular weight and has been shown to shift in response to DOC photo alteration (Helms et al. 2008). By using $SUVA_{254}$ and S_R we expected higher $SUVA_{254}$ values and lower S_R values for more aromatic, higher molecular weight DOC, and lower $SUVA_{254}$, higher S_R for less aromatic and lower molecular weight DOC.

2.4 Bioassay experiments to estimate bioavailability of DOC

Bioassay experiments, where we measured the decline in DOC over time, represent the potential bioavailability of DOC to the microbial assemblage (del Giorgio and Davis 2003). For each bioassay experiment, we added 1 L of 0.2-μm filtered river water to an acid-washed, pre-combusted glass jar. Then, we inoculated the filtered river water with 10 mL of 0.7-μm filtered water (pre-combusted glass fiber filter; Whatman GF/F, similar pore size to Bano et al. 1997). We chose 0.7-μm filtered water as inoculum to exclude any large particulates, but include bacteria that would likely not pass through the 0.2-μm filters. We inoculated deionized water with 10 mL of 0.7-μm filtered water as a control. We ran the bioassays in triplicate, with one control per site and date. We incubated all bioassay experiments in the dark throughout the experiment. We collected DOC samples from the bioassay jars every few days for 28 days and then preserved and analyzed as described above. The decline in DOC concentration over time was fit to a 1st order exponential decay model (Guillemette and del Giorgio 2011) such that,

$$lnDOC_{total} = lnDOC_{initial} - kt \tag{1}$$

where $lnDOC_{total}$ is the natural log transformed total DOC concentration (mg L^{-1}), $lnDOC_{initial}$ is the natural log transformed initial concentration of DOC (mg L^{-1}), k is the decay rate (d^{-1}) and t is incubation time (d). We used the *lm* function (linear model) in R (R Development Core Team, 2012) to solve for k by regressing the natural log of DOC concentration by day.

2.5 Particulate organic carbon

We filtered 0.2 – 5 L of river water, depending on the site and amount of sample visibly retained on the filter, through pre-combusted glass fiber filters to estimate POC (pre-combusted glass fiber filter; Whatman GF/F). Triplicate samples were dried at 60°C, weighed for dry mass, and combusted at 500°C. Following combustion, we re-wetted the filters to account for potential clay dehydration, re-dried, and weighed again. The ash free dry mass (AFDM, mg L^{-1}) of the particulate samples was calculated as the difference in the dry mass (mg) and combusted mass (mg) divided by the volume filtered (L). To estimate POC, we assumed that 45% of the AFDM was OC (Whittaker and Likens 1973).

2.6 Statistical Analyses

To address longitudinal changes on OC transport, we compared the mean POC and DOC concentrations, $SUVA_{254}$, S_R, and bioavailability as k (d^{-1}) at each site along the Green River with the closest upstream site. We used a paired t-test to evaluate if the mean OC concentrations, spectral data, and bioavailability statistically differed between sites in relation to upstream or downstream of Fontenelle or Flaming Gorge reservoirs and their respective tailwaters (Dalgaard 2008). We used R (R Development Core Team, 2012) to conduct all statistical analyses.

2.7 Fluxes of DOC and POC

We calculated the daily fluxes and annual loads of DOC and POC for each sampling site. Daily fluxes of DOC and POC were calculated as:

$$Flux_d = Q_d \times [OC]_d \tag{2}$$

where $Flux_d$ was the daily DOC or POC flux (g d^{-1}), Q_d (m^3 d^{-1}) was the mean discharge of day *d*, and $[OC]_d$ was the mean concentration (g m^{-3}) of either DOC or POC for day *d*. We developed a rating curve for each sampling site relating *[OC]* to *Q* using our 8 sampling points to estimate $[OC]_d$ for the 2011 calendar year where

$$ln[OC] = \beta_0 + \beta_1 lnQ + \beta_2 lnQ^2 \tag{3}$$

[OC] is POC or DOC concentration, $ß_0$, $ß_1$, and $ß_2$ are the model coefficients and *Q* is discharge (m^3 s^{-1}) (similar to Stackpoole et al. 2014). Equation (3) was parameterized for each sampling site (using *lm* function in R, R Development Core Team, 2012) to predict daily POC and DOC concentrations based on daily Q, except for sites located below Flaming Gorge dam and its respective tailwater where there was no statistical relationship between DOC concentration and *Q* (Table 1). For these sites, we used the mean of measured DOC concentrations for $[OC]_d$. All linear models met the assumption of linear regression and given post-analyses diagnostics (Dalgaard 2008), the models were appropriate given the data. We used linear regression (*lm* function in R, R Development Core Team, 2012) to compare predicted $Flux_d$ to observed $Flux_d$

to further quantify beyond model fit if Eq. (3) was appropriate for predicting $[OC]_d$ based on Q for the subsequent $Flux_d$ calculations. The estimated $Flux_d$ from predicting daily $[OC]_d$ from Eq. (3) (and using the mean DOC concentrations for sites located below Flaming Gorge dam) was similar to the $Flux_d$ estimates from measured $[OC]_d$ (Table 2), and therefore we were confident in extrapolating daily $Flux_d$ from predicted $[OC]_d$ and Q_d for the calendar year of 2011. These daily fluxes were then summed to estimate the 2011 annual loads for DOC and POC for each sampling site. Furthermore, we estimated the potential variation of these annual loads for 2011. We used the 95% confidence interval of the predicted $[OC]_d$ from Eq. 3 to re-parameterize the equation in order to predict the 95% confidence interval for daily DOC and POC concentrations for each site. These predicted lower and upper bound $[OC]_d$ were then summed as described above to estimate the 2011 annual loads for both DOC and POC for each site. As for the sampling site below Flaming Gorge dam and its respective tailwater site, we used the lower and upper bound of the 95% confidence interval of the measured mean DOC concentration, as there was no linear relationship with DOC concentration and Q at these sites.

3 Results

3.1 Organic carbon concentrations and transport

Longitudinal OC concentrations, and the subsequent OC load for 2011 fluctuated in the presence of reservoir-tailwater ecosystems along the Green River (Table 3). POC concentrations were lower below both Fontenelle and Flaming Gorge dams compared to upstream of the reservoirs (Fig 2). POC concentrations averaged 1.2 mg L^{-1} above Fontenelle reservoir compared to 0.4 mg L^{-1} below the dam (paired t-test, p=0.002). Lower concentrations of POC directly below Fontenelle dam translated to an annual POC load, although highly variable both above and below the reservoir, that was on average nearly 3-fold lower compared to upstream of the reservoir (Table 3). POC concentrations (Fig. 2) and subsequent OC loads (Table 3) above Fontenelle reservoir also had the most temporal variability, similar to the Yampa River, compared to the other sampling sites along the Green River. POC concentrations above Flaming Gorge reservoir averaged 1.4 mg L^{-1} compared to directly below Flaming Gorge dam, which averaged 0.2 mg L^{-1} (paired t-test, $p<0.0001$). The annual POC load for 2011 was reduced nearly 7-fold on average directly below Flaming Gorge dam compared to upstream of the reservoir (Table 3).

Although POC loads were lower directly below both dams compared to above, POC concentrations increased within their tailwaters (Fig. 2). POC concentrations rebounded 2-fold at the Fontenelle tailwater site relative to directly below the dam (paired t-test, $p<0.0001$) and averaged 0.9 mg L^{-1}. Higher POC concentrations resulted in an annual POC load that was nearly 3-fold greater at the Fontenelle tailwater site compared to directly below the dam, although the annual load estimate was highly variable (Table 3). POC concentrations averaged 0.6 mg L^{-1} at the Flaming Gorge tailwater site, which equated to a 3-fold increase in concentration (paired t-tests, $p<0.0001$) and an annual POC load for 2011 nearly 4-fold greater relative to directly below the dam (Table 3).

Variation in DOC concentrations and the annual load of DOC along the Green River was less pronounced than that for POC. Mean DOC concentrations did not vary above and below either reservoir during 2011 (paired t-test, $p>0.1$ for both reservoirs). However, snowmelt DOC concentrations above both reservoirs were greater than DOC concentrations directly below their respective dams, and vice versa during base flow conditions. Similar to the Yampa River, DOC concentrations peaked prior to peak discharge above Fontenelle reservoir, but peaked with discharge below the reservoir (Fig. 2). Although mean DOC concentrations did not differ, higher discharge below Flaming Gorge dam compared to upstream of the reservoir equated to, potentially a 1400 Mg yr^{-1} increase in DOC annual load below the dam compared to above the reservoir (Table 3).

Mean DOC concentrations increased from directly below both dams through their tailwater reaches, resulting in approximately 200-244 Mg yr^{-1} of DOC. The DOC concentration directly below Fontenelle dam averaged 3.4 mg L^{-1} compared to the tailwater sampling site, which averaged 3.5 mg L^{-1} (paired t-test, p=0.018). The error associated with the annual load estimates was high, but this concentration increase in DOC equated to potentially a 200 Mg increase in the annual DOC load within the 39.6 km reach (Table 3). DOC concentration averaged 3.7 mg L^{-1} at the Flaming Gorge tailwater sampling site compared to 3.6 mg L^{-1} directly below Flaming Gorge dam (paired t-test; p<0.0001). Similar to the Fontenelle tailwater, although the annual load estimates were highly variable, the increase in DOC concentration between the two sampling sites equated to an annual load of 244 Mg of DOC within the 25.7 km Flaming Gorge tailwater reach (Table 3).

3.2 DOC bioavailability and composition

DOC bioavailability, as measured by the decay rate k (d^{-1}) of DOC, was lower directly downstream of both reservoirs than the bioavailability of the DOC upstream (Fig. 3, Table B1). Mean bioavailability above Fontenelle reservoir was 0.0036 d^{-1} compared to 0.0024 d^{-1} directly below the dam (paired t-test, p=0.0005). Average DOC bioavailability was 2-fold greater above (0.0030 d^{-1}) Flaming Gorge reservoir compared to directly below the dam (0.0014 d^{-1}, paired t-test, p=0.0002). Some seasonal variation in bioavailability was measured where k (d^{-1}) was higher during onset of snowmelt, but decreased and remained relatively constant through the remaining snowmelt and base flow conditions (Table B1).

Bioavailability was greater at the tailwater sites relative to sampling sites directly below their respective dams (Fig. 3, Table B1). Bioavailability of DOC significantly increased from directly below Fontenelle dam to the tailwater site downstream (0.0024 to 0.0030 d^{-1}; paired t-test, p=0.04). Although k (d^{-1}) increased from directly below Flaming Gorge reservoir to the tailwater site downstream, this difference was not statistically significant (0.0014 to 0.0018 d^{-1}; paired t-test, p=0.09).

The most pronounced changes in DOC composition, as measured by S_R and $SUVA_{254}$, were between the sampling sites upstream of Flaming Gorge reservoir and directly downstream of the dam. S_R increased, and $SUVA_{254}$ decreased from above Flaming Gorge reservoir to directly below its dam (Fig. 4). DOC composition directly below Flaming Gorge dam reflected less aromatic and smaller molecular weight DOC compared to more aromatic and larger molecular weight DOC above the reservoir (t-test, $SUVA_{254}$: $p<0.0001$, S_R: $p<0.0001$). In comparison, $SUVA_{254}$ and S_R remained relatively unchanged above and below Fontenelle reservoir, although composition shifted at each site during the transition from snowmelt to base flow (Fig. 4).

DOC composition, based on $SUVA_{254}$ and S_R, varied little through the tailwater reaches. $SUVA_{254}$ decreased from directly below Fontenelle reservoir to the Fontenelle tailwater site, indicating less aromatic DOC (mean difference = 0.04 L mg C^{-1} m^{-1}, paired t-test, $p<0.0001$), but there was no statistically significant difference in S_R between these sites (paired t-tests, p=0.1). Flaming Gorge tailwater reach had no effect on $SUVA_{254}$ or S_R ($SUVA_{254}$: paired t-test, p=0.27, $S_{R:}$ paired t-tests, p=0.08).

4 Discussion

Impoundments on rivers may disrupt longitudinal OC transport (Ward and Stanford 1983; Miller 2012; Stackpoole et al. 2014); however, the combination of reservoir-tailwater ecosystems on OC dynamics is less understood than the impact of reservoirs alone. By measuring OC concentrations and DOC composition and bioavailability, we found that longitudinal OC dynamics fluctuated in the presence of reservoir-tailwater ecosystems. POC concentrations and DOC bioavailability were reduced below both reservoirs compared to upstream reaches and OC was produced within the tailwaters. We will discuss how these combined effects of reservoirs and corresponding tailwater river reaches likely increased the impact on OC cycling compared to the presence of impoundments alone by magnifying the transformation of both POC and DOC.

4.1 Temporal OC dynamics

Hydrological seasonality drove variation in POC and DOC concentrations in the upper Green and Yampa Rivers (Fig. 2). The hydrological flushing hypothesis posits that terrestrial carbon within the watershed accrues during low flows and is flushed into streams and rivers during the initial infiltration of melt water during the onset of snowmelt (Hornberger et al. 1994; Boyer et al. 1997). Therefore, our findings of peak OC concentrations preceding peak discharge were not surprising above Fontenelle reservoir and at the Yampa River sampling site. This pattern indicates the terrestrial supply of DOC is exhausted, resulting in hysteresis between DOC concentration and stream discharge (Hornberger et al. 1994; Finlay et al. 2006; Ågren et al. 2008). In comparison, peak concentrations of OC coincided with peak discharge below Fontenelle reservoir, which was likely driven by a combination of factors including dam operations and longer residence time of water in the reservoir relative to the river. For instance, a similar finding of peak OC concentration with peak discharge was found below natural Alpine lakes in Idaho, USA, which was attributed to residence time of the lake (Goodman et al. 2011).

Riverine DOC sources, and therefore bioavailability and composition, can be seasonally dependent. The initial flushing of terrestrial OC from a watershed during early snowmelt can be more bioavailable than base flow DOC because shallow sub-surface runoff from the catchment can export stored terrestrial OC into aquatic ecosystems (Michaelson et al. 1998; Pacific et al. 2010; Pellerin et al. 2011). In contrast, DOC composition in semi-arid and arid rivers reflected autochthonous DOC during base flow conditions as opposed to high flows, due to the contribution of algal and microbial exudates from increased primary production (Westerhoff and Anning 2000). High-sustained flows during spring and summer 2011 in the Yampa and Green Rivers (Fig. 2) likely decreased the onset and magnitude of primary production (Uehlinger 2000), which could account for our findings of stable, as opposed to increasing, DOC bioavailability after peak snowmelt. Furthermore, increased $SUVA_{254}$ and S_R indicated that base flow DOC likely comprised more aromatic, but smaller molecular weight carbon molecules than snowmelt DOC, likely due to microbial or photo-transformation of DOC (Helms et al. 2008; Kraus et al. 2011; Miller 2012) as opposed to production of labile DOC (Weishaar et al. 2003; Goodman et al. 2011). Transformation of DOC, rather than production of labile DOC from algal-exudation supports our DOC bioavailability findings.

4.2 Longitudinal OC dynamics

Not only total water storage, but also reservoir size may alter DOC dynamics and longitudinal transport. The annual DOC loads (Mg yr^{-1}) above Fontenelle reservoir and directly below the dam were similar (Table 3). In comparison, there was greater difference in DOC annual load from upstream to downstream of Flaming Gorge reservoir, where the DOC annual load increased downstream of the reservoir in comparison to upstream of the reservoir. These annual DOC loads for the Green River were similar to the upper Colorado River with comparable drainage areas (Fig. 5, Miller 2012; Stackpoole et al. 2014); yet, the increase in DOC annual load with drainage area was greater in the upper Colorado River (drainage area < 50,000 km^2) compared to the Green River (Fig. 5). The upper Colorado River had approximately 4.6 km^3 of reservoir storage dispersed among 464 dams within the upper reaches (drainage area < 46300 km^2) (Miller 2012). Similarly, the Green River directly downstream of Flaming Gorge dam has a drainage area of 39083 km^2 and in 2011 the mean reservoir storage was approximately 4.3 km^3 (Table A1), but most of the storage was within Flaming Gorge reservoir. The difference in the relationship of DOC fluxes with watershed area between the upper Colorado River and Green River suggest reservoir scheme (i.e. many small versus a few large reservoirs) may drive a decrease in OC loads in this semi-arid watershed.

Residence time likely drove, at least in part, the longitudinal DOC concentration and flux patterns we observed in relation to the reservoirs, although we do not have the appropriate data to adequately budget OC for either of the reservoirs. Increased residence time due to impounding a river reduces water velocity, which allows POC to settle and allows more time for the production and transformation of DOC (Mash et al. 2004; Kraus et al. 2011; Knoll et al. 2013). Although not man-made reservoirs, residence time explained a similar shift in DOC concentration and timing of peak discharge above and below natural Alpine lakes in snowmelt-dominated catchments in Idaho, USA (Goodman et al. 2011). The timing of reservoir filling and dam operations resulted in an arid reservoir in Arizona, USA (Westerhoff and Anning 2000) and two temperate reservoirs located in Ohio, USA (Knoll et al. 2013) to fluctuate between net source and net sink of DOC to downstream reaches. Also, seasonal shifts in reservoir primary production drove a reservoir in California, USA to shift between a DOC source and sink (Kraus et al. 2011). A combination of residence time and autochthonous production within reservoirs may lead to production (Parks and Baker 1997; Kraus et al. 2011) or loss of DOC (Kraus et al. 2011; Miller et al. 2012; Knoll et al. 2013) to downstream ecosystems, likely driven by magnitude of hydrological variation such as high versus low flow years (Knoll et al. 2013).

DOC composition differed from upstream to downstream of both Fontenelle and Flaming Gorge reservoirs. All $SUVA_{254}$ values were < 3 L mg C^{-1} m^{-1}, which indicates that DOC across our sampling sites was of low aromatic content (Weishaar et al. 2003), similar to values found in the Colorado River (Miller 2012). Despite this low range of values, DOC composition below Flaming Gorge dam was less aromatic (as indicated by $SUVA_{254}$) and reflected lower molecular weight OC (as indicated by S_R) compared to DOC composition upstream (Fig. 3). These small, but statistically significant, changes could be due to photodegradation (Brooks et al. 2007; Kraus et al. 2012; Cory et al. 2014) coupled with autochthonous production of DOC (Chin et al. 1994; Nguyen et al. 2002). A similar decreasing $SUVA_{254}$ pattern from upstream to downstream of reservoirs was reported below Lake Powell and Lake Mead in the lower Colorado River basin (Miller 2012). In addition, DOC bioavailability was reduced below Flaming Gorge dam compared to upstream of the reservoir (Fig. 3). This pattern along with our absorbance data indicates that DOC exported from Flaming Gorge reservoir was likely a combination of transformed and microbially produced DOC. In comparison, DOC composition did not vary above and below Fontenelle reservoir based on $SUVA_{254}$ and S_R metrics. But, similar to Flaming Gorge reservoir, bioavailability of DOC was significantly lower below Fontenelle dam compared to above the reservoir (Fig. 3). Reduced bioavailability below the dam indicates that even with no observed spectral changes (i.e., $SUVA_{254}$ and S_R) above and below Fontenelle reservoir, DOC processing or transformation occurred within this reservoir ecosystem, but to a lesser extent than the larger Flaming Gorge reservoir.

POC concentrations were 10-fold lower downstream of Fontenelle and Flaming Gorge dams when compared to upstream of both reservoirs (Fig. 2), and subsequently resulted in a reduction POC flux and annual load for Flaming Gorge reservoir and a marginal reduction for Fontenelle reservoir (Table 3). This pattern is well established for large impoundments on rivers; impoundments allow for the settling of POC (Friedl and Wüest 2002; Downing et al. 2008; Tranvik et al. 2009). We did not measure within reservoir OC fate, but the fate of buried POC in reservoirs was likely a combination of preservation (Downing et al. 2008), mineralization to CO_2 (St. Louis et al. 2000; Knoll et al. 2013), and transformation to DOC (Meyer et al. 1998).

4.3 Tailwater organic carbon transport

Despite the low POC concentration emanating from Fontenelle and Flaming Gorge dams, POC concentrations increased to 40-74% of concentrations measured upstream of the reservoirs within the short tailwater reaches. There were no perennial tributaries in either tailwater; therefore the POC fluxes from the tailwater reaches were likely of autochthonous origin. Primary production likely drove this flux of POC from both tailwater reaches (Table 3). Tailwaters have high primary production (Webster et al. 1979; Davis et al. 2011) where algae and particulates are sloughed during discharge releases from the dam (Perry and Perry 1991). The annual POC load from Fontenelle reservoir tailwater was similar to the annual POC load into the reservoir, indicating that an equivalent amount of the POC load reduced from above to below the reservoir was generated within the 39.6-km tailwater. Similarly, the Flaming Gorge tailwater generated about half the amount of POC that entered the reservoir (Table 3). Recognizing the high variability of our annual load estimates, we compared the potential POC load to potential primary production within the reach. We estimated POC area-specific fluxes from the tailwaters by dividing the difference in POC annual load (g yr^{-1}) by reach area (m^2) and 365 (d^{-1}). The POC daily flux from Fontenelle tailwater was potentially 1.9 g C m^{-2} d^{-1} and from Flaming Gorge tailwater 1.3 g C m^{-2} d^{-1}. Although we did not measure primary production in Flaming Gorge tailwater, primary production in Fontenelle tailwater can be has high as 8.1 g C m^{-2} d^{-1} (Hall et al. in revision). Also, these POC area-specific flux estimates were within the upper 50th percentile of gross primary production measurements from 72 streams showing that primary production can support this high OC flux (Bernot et al. 2010). The POC flux likely consisted of current primary production and organic matter from primary production accrued throughout the year. Low discharge releases from Fontenelle and Flaming Gorge dams during the winter months combined, with the increased flows released from the dam during the onset of our sampling (Fig. 2), likely flushed the organic matter that had accrued within the tailwaters throughout the year (Parks and Baker 1997; Brooks et al. 2007).

Fontenelle and Flaming Gorge tailwaters were likely a source of autochthonously produced DOC. Similar to POC annual loads, we recognize the high variability of the DOC annual loads, but also compared the potential daily flux of DOC to plausible primary production fluxes. The daily estimated flux of DOC from the tailwaters were 4 to 6-fold lower than POC fluxes, 0.3 g C m^{-2} d^{-1} for both Fontenelle and Flaming Gorge tailwaters. Autochthonous DOC fluxes were similar from the tailwater segment directly below Lake Powell on the Colorado River (0.3 – 2.1 g C m^{-2} d^{-1}) and these fluxes were positively correlated with gross primary production (Ulseth 2012). In addition, autochthonous DOC fluxes in the Grand Canyon reach of the Colorado River ranged from 0.09 – 0.39 g C m^{-2} d^{-1} (Ulseth 2012). Although estimated DOC fluxes were lower than POC fluxes, they were within the lower 50th percentile of primary production rates across 72 streams in North America (Bernot et al. 2010) indicating that authochthonous derived DOC flux, similar to POC flux, was potentially a substantial proportion of primary production (Hotchkiss and Hall 2014) from these tailwater ecosystems. The DOC flux from tailwater algae had a minimal effect on total DOC composition, given our absorbance data. However, bioavailability was higher at the Fontenelle tailwater compared to directly below the dam, suggesting freshly produced, labile DOC. Increased total DOC bioavailability from the tailwater likely produced an export of labile DOC, potentially subsidizing the microbial food web in the downstream reaches.

The net effect of dams on the reduction of OC (POC + DOC) transport was essentially low (~6-14%, $(Annual\ Load_{in} - Annual\ Load_{out})/Annual\ Load_{in} \times 100$, Table 3) given the high error associated with our flux estimates and in comparison to the changes in POC annual load alone (66 – 85%) and likely POC and DOC composition. This finding affects how impoundments are viewed from an OC cycling perspective. We potentially underestimated the effect of impounding rivers on OC fluxes in the upper basin of the Colorado River because total concentration based fluxes do not represent transformation processes in river-reservoir-tailwater ecosystems. The Fontenelle and Flaming Gorge tailwater ecosystems contributed to the effect of reservoirs on OC transport in the Green River by increasing the export of likely autochthonous OC downriver. Therefore, the reservoirs regulated OC transport by reducing POC and altering the composition and bioavailability of DOC. We suggest that the effect of impounding rivers on C cycling is larger than the reservoirs alone because of the additive impacts of tailwater reaches, which produce and then export a comparable amount of autochthonous OC than what is likely stored behind dams. However, accurately quantifying annual fluxes of OC can be difficult, as illustrated by the potential variability of our annual load estimates (Table 3). To assess the effects in terms of regional carbon budgets, we need to consider not only reservoirs in regards to their capacity to transform terrestrial OC (Knoll et al. 2013), but also the additive effects of their tailwater ecosystems.

Author contribution

A.J.U and R.O.H designed the sampling plan. A.J.U. carried out all sampling and sample and data analyses. A.J.U. and R.O.H. prepared the manuscript.

Acknowledgements

This research was funded in part by the George S. Menkens Memorial Scholarship from the Zoology and Physiology Department at University of Wyoming to A.J. Ulseth and by a cooperative agreement 05WRAG0055 from the U.S. Geological Survey to R.O. Hall, E.J. Rosi-Marshall, and C. Baxter. Thank you to Harold Bergman, Indy Burke, Ted Kennedy, Bryan Shuman, and Jakob Schelker for insightful comments on the manuscript. We thank Eriek Hansen for GIS assistance.

References

Ågren, A., Buffam, I, Berggren, M., Bishop, K., Jansson, M. and Laudon, H.: Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer, J. Geophys. Res. 113, G03031, DOI:10.1020/2007JG00674, 2008.

Aufdenkampe, A.K., Mayorga, E., P.A. Raymond, P.A., Melack, J.M., Doney, A.C., Alin, S.R., Aalto R.E., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9, 53-60, 2011.

Baines, S.B., and Pace, M.L.: The production of dissolved organic matter by phytoplankton and its importance to bacteria: Patterns across marine and freshwater systems, Limnol. Oceanog., 36,1078-1090, 1991.

Bano, N., Moran, M.A., and Hodson, R.E.: Bacterial utilization of dissolved humic substances from a freshwater swamp, Aquat. Microb. Ecol., 12, 233-238.

Battin, T.J., Luyssaert, S., Kaplan, L.A., Aufdenkampe, A.K., Richter, A., and Tranvik, L.J.: The boundless carbon cycle, Nat. Geosci., 2, 598-600, 2009.

Benke, A.C.: A perspective on America's vanishing streams, J. N. Am. Benthol. Soc., 9, 77-88, 1990.

Benenati, E.P., Shannon, J.P., Hagan, J.S., and Blinn, D.W.: Drifting fine particulate organic matter below Glen Canyon Dam in the Colorado River, Arizona. J. Freshwater Ecol., 16, 235-248, 2001.

Bernot, M.J., Sobota, D.J., Hall, R.O., Mulholland, P.J., Dodds, W.K., Webster, J.R., Tank, J.L., Ashkenas, L.R., Cooper, L.W., Dahm, C.N., Gregory, S.V., Grimm, N.B., Hamilton, S.K., Johnson, S.L., McDowell, W.H., Meyer, J.L., Peterson, B., Poole, G.C., Valett, H.M., Arango, C., Beaulieu, J.J., Burgin, A.J., Crenshaw, C., Helton, A.M., Johnson, L., Merriam, J., J., Niederlehner, B.R., O'Brien, J.M., Potter, J.D., Sheibley, R.W., Thomas, S.M., and Wilson, K.: Inter-regional comparison of land-use effects on stream metabolism, Freshwater Biol., 55, 1874-1890, 2010.

Bertilsson, S. and Jones Jr., J.B.: Supply of dissolved organic matter to aquatic ecosystems: autochthonous sources, Aquatic ecosystems: Interactivity of dissolved organic matter, SEG Findlay and Sinsabaugh, R.L., Academic Press, San Diego, California, USA, pp. 3-25, 2003.

Boyer, E.W., Hornberger, G.M, Bencala, K.E., and McKnight, D.M.: Response characteristics of DOC flushing in an alpine catchment, Hydrol. Processes, 11, 1635-1674, 1997.

Brooks, P.D., Haas, P.A., and Huth, A.K.: Seasonal variability in the concentration and flux of organic matter and inorganic nitrogen in a semiarid catchment, San Pedro River, Arizona. J. Geophys. Res., 112: G03S04, DOI: 10.1029/2006JG00275, 2007.

Chin, Y., Aiken, G., and O'Loughlin, E.: Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances, Environ. Sci. Technol., 28, 1853-1858, 1994.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., and Melack, J.: Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, Ecosystems, 10, 171-184, 2007.

Cory, R.M., Ward, C.P., Crump, B.C., and Kling, G.W.: Sunlight controls water column processing of carbon in arctic fresh waters, Science, 345, 925-928, 2014.

Dalgaard, P. Introductory Statistics with R, 2nd ed. Springer, New York, New York, USA, 2008.

Davis, C.J., Fritsen, C.H., Wirthlin, E.D., and Memmott, J.C.: High rates of primary productivity in a semi-arid tailwater: implications for self-regulated production, River Res. App., 10, 1820-1829, 2011.

del Giorgio P.A., and Davis, J.: Patterns in dissolved organic matter lability and consumption across aquatic ecosystems, Aquatic ecosystems: Interactivity of dissolved organic matter, SEG Findlay and Sinsabaugh, R.L., Academic Press, San Diego, California, USA, 400-424, 2003.

Downing, J.A., Cole, J.J., Middelburg, J.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Prairie, Y.T., and Laube, K.A.: Sediment organic carbon burial in agriculturally eutrophic impoundments over the last century, Global Geochem. Cycles, 22, GB1018, DOI: 10.1029/2006GB002854, 2008.

Finlay, J., Neff, J., Zimov, S., Davydova, A., and Davydov, S.: Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC, Geophys. Res. Lett. 33: L10401, doi: 10.1029/2006GL025754, 2006.

Friedl, G., and Wüest, A.: Disrupting biogeochemical cycles – Consequences of damming, Aquat. Sci., 64, 55-65, 2002.

Goodman, K.J., Baker, M.A., Wurtsbaugh, W.A.: Lakes as buffers of stream dissolved organic matter (DOM) variability: Temporal patterns of DOM characteristics in mountain stream-lake systems, J. Geophys. Res., 116, G00N02, doi:10.1029/2011JG001709, 2011.

Guillemette, F., and P.A. del Giorgio. 2011. Reconstructing the various facets of dissolved organic carbon bioavailability in freshwater ecosystems, Limnol. Oceanogr., 56, 734-748, 2011.

Hall, R. O., Tank, J.L., Baker, M.A., Rosi-Marshall, E.J., and Hotchkiss, E.R.: Metabolism, gas exchange and carbon spiraling in rivers, In revision for submission to Ecosystems.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol. Oceanog., 53, 955-969, 2008.

Hornberger, G.M., Bencala, K.E., and McKnight, D.M.: Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, Biogeochemistry, 25, 147-165, 1994.

Hotchkiss, E.R. and Hall, R.O.: Whole-stream ^{13}C tracer addition reveals distinct fates of newly fixed carbon, Ecology, 96, 403-416, doi: 10.1890/14-0631.1, 2014.

Knoll, L.B., Vanni, M.J., Renwick, W.H., Dittman, E.K., and Gephart, J.A.: Temperate reservoirs are large carbon sinks and small CO_2 sources: Results from high resolution carbon budgets, Global Biogeoch. Cycles, 27, 52-64, doi: 10.1002/gbc.20020, 2013.

Kraus, T.E.C., Bergamaschi, B.A., Hernes, P.J., Doctor, D., Kendall, C., Downing, B.D., and Losee, R.F.: How reservoirs alter drinking water quality: Organic matter sources, sinks, and transformations, Lake Reserv. Manage., 27, 205-219, 2011

Lieberman, D.M., and Burke, T.A.: Particulate organic matter transport in the lower Colorado River, South-Western USA, Regulated Rivers: Research and Management, 8, 323-334, 1993.

Mash, H., Westerhoff, P.K., Baker, L.A., Nieman, R.A., and Nguyn, M.: Dissolved organic matter in Arizona reservoirs: assessment of carbonaceous sources, Org. Geochem., 35, 831-843, 2004.

Meyer, J.L., Wallace, J.B., and Eggert, S.L.: Leaf litter as a source of dissolved organic carbon in streams, Ecosystems, 1, 240-249, 1998.

Michaelson G.J., Ping, C.L., Kling, G.W., and Hobbie, J.E.: The character and bioactivity of dissolved organic matter at thaw and in the spring runoff waters in the arctic tundra north slope, Alaska, J.Geophys. Res., 103, 28939-28946, 1998.

Miller, M.P.: The influence of reservoirs, climate, land use and hydrologic conditions on loads and chemical quality of dissolved organic carbon in the Colorado River, Water Resour. Res., 48, W00M02, doi:10.1029/2012WR012312, 2012.

Nadon, M.J., Metcalfe, R.A., Williams, C.J., Somers, K.M., and Xenopoulos, M.A.: Assessing the effects of dams and waterpower facilities on riverine dissolved organic matter composition, Hydrobiologia, 744, 145-164, DOI 10.1007/s10750-014-2069-0, 2014.

Nilsson, C., Reidy, C.A., Dynesius, M., and Revenga, C.: Fragmentation and flow regulation of the world's large river systems, Science, 308, 405-408, 2005.

Nguyen, M.L., Baker, L.A., and Westerhoff, P.: DOC and DBP precursors in western US watersheds and reservoirs, Journal American Water Works Association, 94, 98-112, 2002.

Pacific, V.J., Jensco, K.G., McGlynn, B.L.: Variable flushing mechanisms and landscape structure control stream DOC export during snowmelt in a set of nested catchments, Biogeochemistry, 99, 193-211, DOI 10.1007/s10533-009-9401-1, 2010.

Parks, S.J., and Baker L.A.: Sources and transport of organic carbon in an Arizona River-Reservoir system, Water Res., 31, 1751-1759, 1997.

Pellerin, B.A., Saraceno, J.F., Shanley, J.B., Sebestyen, S.D., Aiken, G.R., Wollheim, W.M., Bergamaschi, B.A.:Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream, Biogeochemistry, 108, 183-198, DOI 10.1007/s10533-011-9589-8, 2011.

Perry, S. A. and Perry, W.B.: Organic carbon dynamics in two regulated rivers in northwestern Montana, USA, Hydrobiologia, 218, 193-203, 1991.

R Development Core Team.: R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, URL http://www.R-project.org/, 2012.

Sabo, J.L., Sinha, T., Bowling, L.C., Schoups, G.H.W., Wallender, W.W., Campana, M.E., Cherkauer, K.A., Fuller, P.L., Graf, W.L., Hopmans, J.W., Kominoski, J.S., Taylor, C., Trimble, S.W., Webb, R.H., and Wohl, E.E.: Reclaming freshwater sustainability in the Cadillac Desert, Proc. Natl. Acad. Sci., 107, 21263-21269, 2010.

Schmidt, J.C., and Wilcock, P.R.: Metrics for assessing the downstream effects of dams, Water Resour. Res., 44, W04404, doi:10.1029/2006WR005092, 2008.

Stackpoole, S.M., Stets, E.G., and Striegl, R.G.: The impact of climate and reservoirs on longitudinal riverine carbon fluxes from two major watersheds in the Central and Intermontane West, J. Geophys. Res., 119, 848-863, 10.1002/2013JG002496, 2014.

St. Louis, V.L., Kelly, C.A., Duchemin, E., Rudd, J.W.M., and Rosenberg, D.M.: Reservoir surfaces as sources of greenhouse gasses to the atmosphere: A global estimate, BioScience, 50, 766-775, 2000.

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y.,Renwick, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Sobek, S., Tremblay, A., Vanni, M.J., Verschoor, A.M., von Wachenfeldt, E., and Weyhenmeyer, G.A..: Lakes and reservoirs as regulators of carbon cycling and climate, Limnol. Oceanog., 54, 2298-2314, 2009.

Uehlinger, U.: Resistance and resilience of ecosystem metabolism in a flood-prone river system, Freshwater Biol., 45, 319-332, 2000.

Ulseth, A.J.: Sources, fates, and export of organic carbon in the Colorado River Basin, PhD Dissertation, Univ. of Wyoming, Laramie, Wyoming, USA, 2012.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Seell, J.R., and Cushing, C.E.: The river continuum concept, Can. J. Fish. Aq. Sci., 37, 130-137, 1980.

Vörösmarty, C.J., Sharma, K.P., Fekete, B.M., Copeland, A.H., Holden, J., Marble, J., and Lough, J.A.: The storage and aging of continental runoff in large reservoir systems of the world, Ambio, 26, 210-219, 1997.

Ward, J. V. and Stanford, J.A.: The serial discontinuity concept of lotic ecosystems, Dynamics of Lotic Ecosystems, Fontaine, T.D., and Bartell, S.M., Ann Arbor Science, Ann Arbor, Michigan, USA, 29-42, 1983.

Webster, J.R., Benfield, E.F., and Cairns, J.: Model predictions of effects of impoundment of particulate organic matter transport in a river system, The Ecology of Regulated Streams, Ward, J.V., and Stanford, J.A., The Ecology of Regulated Streams, Plenum Press, New York, New York, USA, 339-364, 1979.

Westerhoff, P. and Anning, D.: Concentrations and characteristics of organic carbon in surface water in Arizona: influence of urbanization, J. Hydrol., 236, 202-222, 2000.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., and Mopper, K.: Evaluation of specific ultraviolet absorbance as an indicator of chemical composition and reactivity of dissolved organic carbon, Environ. Sci. Technol., 37, 4702-4708, 2003.

Whittaker, R.H. and Likens, G.E.: Carbon in the biota, Carbon and the biosphere, Conf-720510, United States Atomic Energy Commission, Woodwell, G.M, and Pecan, E.V., Springfield, Virginia, USA, 281-302, 1973.

Table 1: A regression model to estimate daily organic carbon concentrations [OC] from mean discharge (Q), $ln[OC] = \beta_0 + \beta_1 ln[Q] + \beta_2 ln[Q]^2$, was fit for each sampling site in order to estimate annual [OC] loads. POC refers to particulate organic carbon and DOC is dissolved organic carbon. β_0, β_1, and β_2 are the model coefficients for each sampling site. P-value and r^2 are selected corresponding model statistics at each site. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

	POC					DOC				
Site	β_0	β_1	β_2	P-value	r^2	β_0	β_1	β_2	P-value	r^2
A.Above Fontenelle reservoir	-22.0	9.8	-1.0	0.02	0.79	-2.8	1.5	-0.1	0.01	0.82
B.Below Fontenelle dam	-14.6	5.5	-0.5	0.05	0.69	2.6	-1.0	0.1	0.00	0.96
C.Fontenelle tailwater	-6.9	2.1	-0.1	0.01	0.82	3.1	-1.2	0.2	0.00	0.94
D.Above Flaming Gorge reservoir	-25.3	10.9	-1.1	0.00	0.90	3.0	-1.1	0.2	0.00	0.95
E.Below Flaming Gorge dam*	-31.5	12.2	-1.2	0.05	0.70	NA	NA	NA	NA	NA
F.Flaming Gorge tailwater*	-41.5	16.3	-1.6	0.00	0.95	NA	NA	NA	NA	NA
G.Yampa River	-9.4	3.9	-0.3	0.00	0.95	-0.8	1.1	-0.1	0.02	0.79

*No statistical relationship between DOC concentration and Q, therefore mean measured DOC concentrations were used to estimate daily fluxes, and to calculate annual DOC load for 2011

Table 2: Select model statistics from linear regression (*lm* in R, R Development Core Team, 2012) models to compare predicted organic carbon fluxes to observed particulate organic carbon (POC) and dissolved organic carbon (DOC) fluxes ($flux_d$, Mg d^{-1}) for each sampling site. Predicted organic carbon fluxes were calculated from estimated daily organic carbon (POC or DOC) concentrations ($[OC]$) and discharge (Q). Linear regression models were used to predict $[OC]$ where $ln[OC] = \beta_0 + \beta_1\, ln[Q] + \beta_2\, ln[Q]^2$, except for sites below Flaming Gorge dam where there was no statistical relationship between DOC and Q. Average measured DOC and discharge were used to estimate daily DOC fluxes for sites below Flaming Gorge dam. Observed OC fluxes were calculated multiplying the mean measured [OC] and corresponding mean daily Q. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

	POC				DOC			
Site	intercept	slope	slope SE	r^2	intercept	slope	slope SE	r^2
A.Above Fontenelle reservoir	2.94	0.59	0.11	0.82	-1.19	1.04	0.04	0.99
B.Below Fontenelle dam	0.04	0.95	0.14	0.89	-0.21	1.01	0.01	1.00
C.Fontenelle tailwater	0.19	0.97	0.07	0.97	-0.28	1.01	0.02	1.00
D.Above Flaming Gorge reservoir	0.41	0.95	0.12	0.92	-0.27	1.01	0.01	1.00
E.Below Flaming Gorge dam	0.07	0.96	0.12	0.92	0.68	0.98	0.04	0.99
F.Flaming Gorge tailwater	0.29	0.96	0.08	0.96	0.41	0.99	0.04	0.99
G.Yampa River	22.69	0.70	0.16	0.76	2.45	0.97	0.06	0.97

Table 3: Daily measured fluxes (*Flux*$_d$, Mg d^{-1}) and annual load (Mg yr^{-1} for 2011) of dissolved organic carbon (DOC) and particulate organic carbon (POC) across sampling sites on the Green and Yampa Rivers. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

	A.Above Fontenelle Reservoir		B.Below Fontenelle dam		C.Fontenelle Tailwater		D.Above Flaming Gorge Reservoir		E.Below Flaming Gorge dam		F.Flaming Gorge Tailwater		G.Yampa River	
Date	DOC	POC	DOC	POC	DOC	POC	DOC	POC	DOC	POC	DOC	POC	DOC	POC
30-Apr-11	5.9	1.0	15.7	1.7	16.3	3.7	16.5	5.6	36.6	1.9	39.0	9.8	64.1	53.5
18-May-11	26.9	23.8	24.6	5.3	24.0	10.8	17.3	15.1	36.6	2.6	41.4	8.6	161.7	231.4
1-Jun-11	28.2	11.2	33.5	5.2	34.6	8.3	34.3	22.1	39.6	2.3	43.4	9.1	174.6	282.2
15-Jun-11	84.5	49.4	65.8	9.7	67.1	18.2	54.9	23.1	74.5	2.6	74.2	16.3	163.6	140.7
30-Jun-11	125.5	14.9	101.3	8.1	103.0	38.8	97.5	33.8	83.4	3.3	81.1	12.9	111.5	86.4
21-Aug-11	5.9	0.9	12.1	0.5	12.3	1.3	11.1	2.3	23.1	0.9	22.8	2.3	8.9	1.3
11-Sep-11	3.6	0.4	7.4	0.6	7.8	1.2	8.6	1.1	23.3	1.0	23.3	1.8	5.0	0.5
16-Oct-11	3.1	0.2	7.7	0.4	8.0	0.7	7.8	0.8	19.0	0.3	18.7	0.7	4.0	0.2
Annual Load*	7604	2092	7641	715	7850	2106	8049	2341	9430**	350	9674**	1316	13717	13189
2.5% CI	4888	663	6890	315	6943	1041	7278	1356	8489	236	9050	1023	11603	7351
97.5% CI	11868	6885	8475	1668	8880	4338	8904	4209	10081	520	10044	1694	16235	23835

*A Regression model to estimate daily organic carbon concentrations [OC] from mean discharge (Q), $\ln([Q]) = \beta_0 + \beta_1 \ln([Q]) + \beta_2 \ln([Q])^2$, was fit for each sampling site in order to estimate annual [OC] loads..

**No significant relationship between [OC] and Q, therefore annual loads were calculated by using the mean measured [OC] to estimate daily fluxes.

Fig. 1: Map of Fontenelle and Flaming Gorge reservoirs located on the Green River in Wyoming and Utah and the Yampa River located in Colorado. The points along the rivers designate the locations from where we collected water from April – October 2011. Two sites located on unregulated river reaches: the Green River above Fontenelle reservoir (A) (USGS gaging station 09209400) and the Yampa River (G) (USGS gaging station 09251000). We also sampled directly below Fontenelle dam (B) (USGS gaging station 09211200) and 39.6 km down river for the Fontenelle tailwater (C). We sampled above Flaming Gorge reservoir (D) (USGS gaging station 09217000) and directly below Flaming Gorge dam (E) (USGS gaging station 09234500) and 25.7 km further downstream for Flaming Gorge tailwater (F).

Fig. 2: Discharge (line, Q m3 s^{-1}) plotted for 2011 along with particulate organic carbon (POC, replicate samples plotted) and dissolved organic carbon (DOC, replicate samples plotted) concentrations from sampling sites located on the Green and Yampa Rivers. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

Fig. 3: Dissolved organic carbon (DOC) bioavailability across all sampling sites as measured by the DOC decay rate per day (k, d^{-1}). The black line represents the median value of k (d^{-1}), the boxes are the upper and lower 25th and 75th percentile, the tails are the maximum and minimum values, and any points are outliers, which exceed 3/2 of the maximum or minimum values. The asterisk (*) designates significant differences (paired t-test, $p<0.05$) in bioavailability between sites. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

Fig. 4: Mean specific ultraviolet absorbance at 254 nm ($SUVA_{254}$, L mg C^{-1} m^{-1}) plotted by the mean slope ratio (S_R) across sampling dates for each site during snowmelt and base flow

conditions. Higher $SUVA_{254}$ and lower S_R indicate greater aromaticity and higher molecular weight DOC compared to lower $SUVA_{254}$ and higher S_R, which indicate lower aromaticity and lower molecular weight of DOC. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

Fig 5: Annual DOC load (Mg yr^{-1}) plotted against drainage area (km^2) from the Green, Yampa, and upper reaches of the Colorado River ($< 50 \times 10^3$ km^2, data from Stackpoole et al. 2014, Miller 2012). Linear regression line was fitted through data from the upper Colorado River where DOC load (Mg yr^{-1}) = $1675.7 + 430.1 \times km^2$, P=0.0001, r^2=0.98)

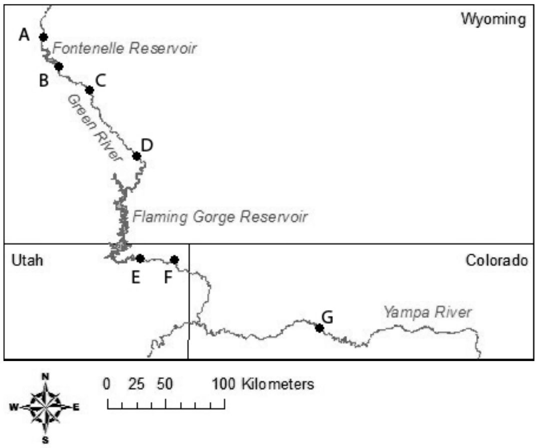
Wyoming
A
Fontenelle Reservoir
B
C
Green River
D
Flaming Gorge Reservoir
Utah
Colorado
E
F
G
Yampa River
N
W
E
S
0 25 50 100 Kilometers

Fig. 1

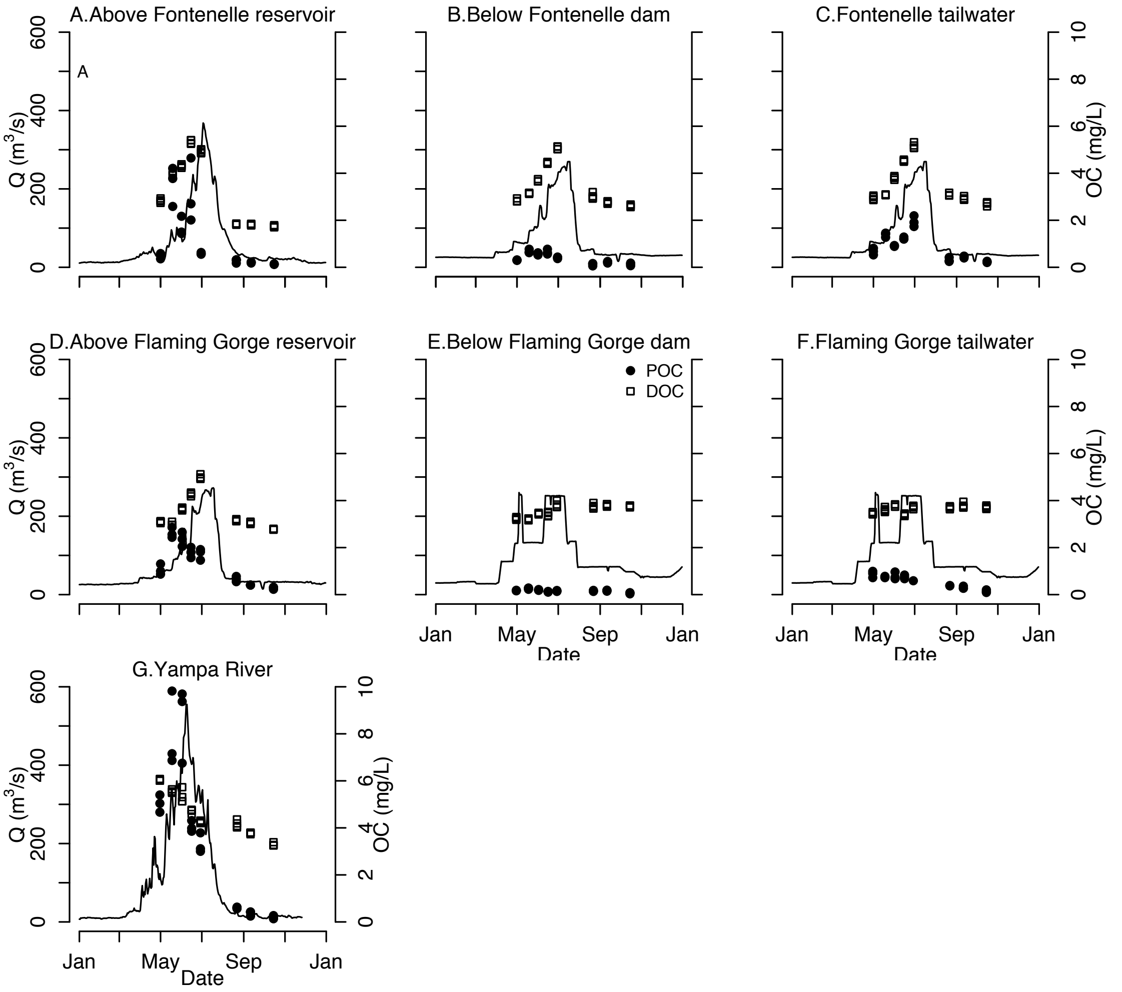
A.Above Fontenelle reservoir
B.Below Fontenelle dam
C.Fontenelle tailwater
D.Above Flaming Gorge reservoir
E.Below Flaming Gorge dam
F.Flaming Gorge tailwater
G.Yampa River
A
● POC
□ DOC
Q (m3/s)
OC (mg/L)
0
200
400
600
0
2
4
6
8
10
Jan
May
Sep
Jan
Date

Fig. 2

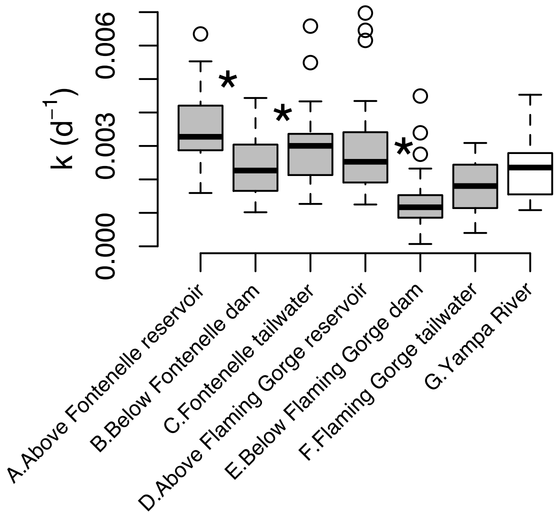
k (d⁻¹)
0.000
0.003
0.006
*
*
*
A.Above Fontenelle reservoir
B.Below Fontenelle dam
C.Fontenelle tailwater
D.Above Flaming Gorge reservoir
E.Below Flaming Gorge dam
F.Flaming Gorge tailwater
G.Yampa River

Fig. 3

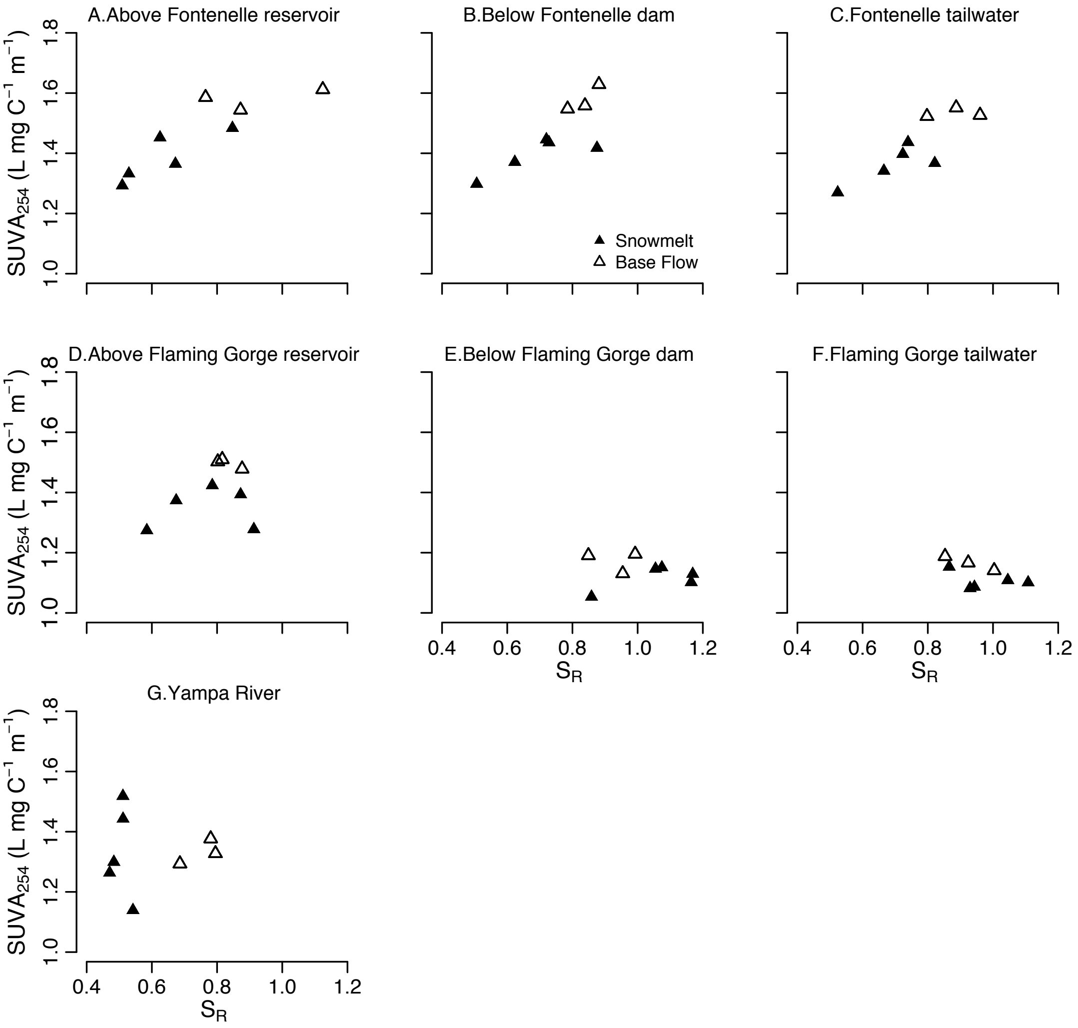
A.Above Fontenelle reservoir
B.Below Fontenelle dam
C.Fontenelle tailwater
D.Above Flaming Gorge reservoir
E.Below Flaming Gorge dam
F.Flaming Gorge tailwater
G.Yampa River
SUVA254 (L mg C−1 m−1)
1.0
1.2
1.4
1.6
1.8
SR
0.4
0.6
0.8
1.0
1.2
▲ Snowmelt
△ Base Flow

Fig. 4

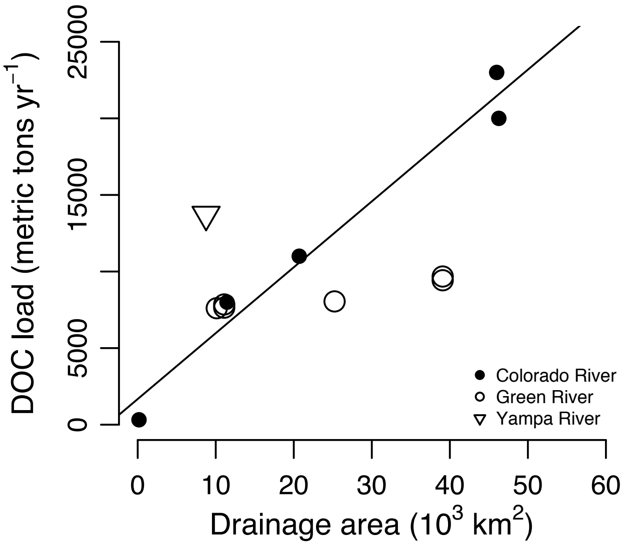
DOC load (metric tons yr^{-1})
0
5000
15000
25000
0
10
20
30
40
50
60
Drainage area (10^3 km^2)
● Colorado River
○ Green River
▽ Yampa River

Fig. 5

Appendix A

Table A1: Fontenelle and Flaming Gorge reservoir volumes and residence time (R_t) for 2011. R_t was calculated by dividing reservoir volume (volume, m^3) by yearly outflow (Q_{out}, m^3 yr^{-1}). Mean residence time was based on mean Q_{out} for 2011, including both base flow and snowmelt. Minimum residence time was based on Q_{out} during snowmelt period of discharge. Maximum residence time was based on base flow Q_{out} only.

Reservoir	Mean volume* (min, max) km^3	Mean R_t (min, max) yr^{-1}
Fontenelle	0.26 (0.12, 0.40)	0.13 (0.06, 0.30)
Flaming Gorge	4.08 (3.79, 4.43)	1.61 (0.86, 2.81)

*Volume data and Q_{out} for Fontenelle and Flaming Gorge reservoirs for 2011 were accessed from the Bureau of Reclamation Upper Colorado River Region Water Operations (http://www.usbr.gov/uc/crsp/GetSiteInfo).

Appendix B

Table B1: Mean decay rates (*k*, d^{-1}) and mean percentage (%) loss of DOC over 28-day bioassay experiment. Mean percentage loss was calculated by dividing the difference in DOC concentration (mg L^{-1}) from day 0 to day 28 by the initial DOC concentration at day 0 and then multiplying by 100. 95% confidence intervals were calculated for *k* d^{-1} and % loss of DOC from 3 replicate bioassay experiments for each site and each date. Letters A-G prior to the site names correspond to sites A-G in Fig. 1.

Site	Date	Mean *k* (d^{-1}) (95% CI)	Mean % Loss DOC (28 d^{-1}) (95% CI)
A.Above Fontenelle reservoir	30-Apr-11	0.0056 (0.0051, 0.0063)	14.4 (12.7, 15.4)
A.Above Fontenelle reservoir	18-May-11	0.0024 (0.0017, 0.0029)	7.3 (4.5, 9.6)
A.Above Fontenelle reservoir	1-Jun-11	0.0029 (0.0023, 0.0037)	8.5 (6.8, 11.0)
A.Above Fontenelle reservoir	15-Jun-11	0.0036 (0.0031, 0.0042)	10.4 (7.8, 13.3)
A.Above Fontenelle reservoir	30-Jun-11	0.0031 (0.0029, 0.0032)	7.7 (7.2, 8.0)
A.Above Fontenelle reservoir	21-Aug-11	0.0044 (0.0040, 0.0050)	10.9 (10.4, 11.4)
A.Above Fontenelle reservoir	11-Sep-11	0.0025 (0.0020, 0.0029)	7.5 (5.8, 9.0)
A.Above Fontenelle reservoir	16-Oct-11	0.0043 (0.0037, 0.0050)	11.4 (9.3, 14.6)
B.Below Fontenelle dam	30-Apr-11	0.0036 (0.0032, 0.0040)	10.7 (9.7, 11.6)
B.Below Fontenelle dam	18-May-11	0.0038 (0.0034, 0.0043)	7.4 (7.3, 7.7)
B.Below Fontenelle dam	1-Jun-11	0.0021 (0.0016, 0.0027)	5.5 (3.8, 7.2)
B.Below Fontenelle dam	15-Jun-11	0.0020 (0.0014, 0.0024)	5.6 (4.1, 6.5)
B.Below Fontenelle dam	30-Jun-11	0.0020 (0.0017, 0.0023)	5.4 (4.4, 6.1)
B.Below Fontenelle dam	21-Aug-11	0.0019 (0.0014, 0.0023)	5.0 (4.7, 5.4)
B.Below Fontenelle dam	11-Sep-11	0.0020 (0.0013, 0.0028)	5.6 (3.2 7.9)
BBelow Fontenelle dam	16-Oct-11	0.0016 (0.0011, 0.0021)	4.8 (2.3, 6.9)
C.Fontenelle tailwater	30-Apr-11	0.0055 (0.0044, 0.0065)	16.6 (13.4, 19.5)
C.Fontenelle tailwater	18-May-11	0.0024 (0.0017, 0.0032)	5.6 (4.6, 7.0)
C.Fontenelle tailwater	1-Jun-11	0.0030 (0.0026, 0.0034)	9.0 (7.8, 11.0)
C.Fontenelle tailwater	15-Jun-11	0.0032 (0.0030, 0.0034)	9.2 (8.5, 9.6)
C.Fontenelle tailwater	30-Jun-11	0.0025 (0.0016, 0.0031)	6.4 (3.5, 8.2)
C.Fontenelle tailwater	21-Aug-11	0.0025 (0.0023, 0.0026)	4.4 (3.7, 5.1)
C.Fontenelle tailwater	11-Sep-11	0.0022 (0.0013, 0.0035)	6.2 (2.4, 10.6)
C.Fontenelle tailwater	16-Oct-11	0.0023 (0.0018, 0.0032)	6.1 (3.1, 9.1)
D.Above Flaming Gorge reservoir	30-Apr-11	0.0065 (0.0062, 0.0069)	17.4 (15.9, 18.9)
D.Above Flaming Gorge reservoir	18-May-11	0.0038 (0.0035, 0.0043)	10.9 (9.9, 11.7)
D.Above Flaming Gorge reservoir	1-Jun-11	0.0021 (0.0018, 0.0024)	5.0 (4.0, 5.7)

D.Above Flaming Gorge reservoir	15-Jun-11	0.0022 (0.0019, 0.0026)	5.2 (4.4, 5.8)
D.Above Flaming Gorge reservoir	30-Jun-11	0.0025 (0.0021, 0.0029)	7.9 (6.3, 8.8)
D.Above Flaming Gorge reservoir	21-Aug-11	0.0014 (0.0013, 0.0016)	2.7 (1.4, 3.7)
D.Above Flaming Gorge reservoir	11-Sep-11	0.0021 (0.0016, 0.0024)	4.8 (1.8, 7.2)
D.Above Flaming Gorge reservoir	16-Oct-11	0.0032 (0.0031, 0.0033)	7.9 (6.4, 8.9)
E.Below Flaming Gorge dam	30-Apr-11	0.0010 (0.0002, 0.0015)	4.8 (1.8, 6.7)
E.Below Flaming Gorge dam	18-May-11	0.0009 (0.0007, 0.0011)	3.3 (2.8, 4.0)
E.Below Flaming Gorge dam	1-Jun-11	0.0011 (0.0008, 0.0014)	4.2 (2.5, 5.6)
E.Below Flaming Gorge dam	15-Jun-11	0.0008 (0.0005, 0.0010)	2.8 (1.4, 4.4)
E.Below Flaming Gorge dam	30-Jun-11	0.0028 (0.0014, 0.0043)	10.3 (5.2, 14.6)
E.Below Flaming Gorge dam	21-Aug-11	0.0026 (0.0021, 0.0033)	8.6 (7.9, 9.0)
E.Below Flaming Gorge dam	11-Sep-11	0.0011 (0.0009, 0.0014)	4.3 (3.0, 5.6)
E.Below Flaming Gorge dam	16-Oct-11	0.0011 (0.0009, 0.0013)	2.1 (1.2, 2.9)
F.Flaming Gorge tailwater	30-Apr-11	0.0019 (0.0012, 0.0029)	8.4 (6.5, 11.4)
F.Flaming Gorge tailwater	18-May-11	0.0025 (0.0020, 0.0030)	8.3 (7.2, 9.9)
F.Flaming Gorge tailwater	1-Jun-11	0.0021 (0.0017, 0.0023)	6.6, 9.1)
F.Flaming Gorge tailwater	15-Jun-11	0.0005 (0.0004, 0.0006)	2.1 (1.6, 2.6)
F.Flaming Gorge tailwater	30-Jun-11	0.0026 (0.0023, 0.0029)	8.5 (7.0, 10.2)
F.Flaming Gorge tailwater	21-Aug-11	0.0019 (0.0012, 0.0026)	4.5 (0.5, 8.0)
F.Flaming Gorge tailwater	11-Sep-11	0.0015 (0.0009, 0.0023)	2.5 (0.3, 4.6)
F.Flaming Gorge tailwater	16-Oct-11	0.0014 (0.0012, 0.0016)	3.0 (2.4, 4.0)
G.Yampa River	30-Apr-11	0.0043 (0.0042, 0.0045)	11.7 (11.5, 11.9)
G.Yampa River	18-May-11	0.0015 (0.0012, 0.0020)	2.8 (2.2, 3.5)
G.Yampa River	1-Jun-11	0.0013 (0.001, 0.0015)	3.5 (2.5, 4.6)
G.Yampa River	15-Jun-11	0.0017 (0.0011, 0.0023)	4.3 (1.9, 6.0)
G.Yampa River	30-Jun-11	0.0022 (0.0017, 0.0025)	6.2 (5.7, 6.8)
G.Yampa River	21-Aug-11	0.0035 (0.0021, 0.0044)	10.3 (6.9, 13.7)
G.Yampa River	11-Sep-11	0.0024 (0.0020, 0.0029)	7.0 (5.0, 9.2)
G.Yampa River	16-Oct-11	0.0025 (0.0024, 0.0026)	4.9 (3.5, 6.8)