Sources and Decomposition of Dissolved Organic Matter in Desert Streams

by

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ABSTRACT

Dissolved organic matter (DOM) is an important part of aquatic foodwebs because it contains carbon, nitrogen, and other biological elements required by heterotrophic organisms. It has many sources that determine its molecular composition, nutrient content, and biological lability and in turn, influence whether it is retained and processed in the stream reach or exported downstream. I examined the composition of DOM from vascular wetland plants, filamentous algae, and riparian tree leaf litter in Sonoran Desert streams and its decomposition by stream microbes. I used a combination of field observations, *in-situ* experiments, and a manipulative laboratory incubation to test (1) how dominant primary producers influence DOM chemical composition and ecosystem metabolism at the reach scale and (2) how DOM composition and nitrogen (N) content control microbial decomposition and stream uptake of DOM. I found that differences in streamwater DOM composition between two distinct reaches of Sycamore Creek did not affect *in-situ* stream respiration and gross primary production rates. Stream sediment microbial respiration rates did not differ significantly when incubated in the laboratory with DOM from wetland plants, algae, and leaf litter, thus all sources were similarly labile. However, whole-stream uptake of DOM increased from leaf to algal to wetland plant leachate. Desert streams have the potential to process DOM from leaf, wetland, and algal sources, though algal and wetland DOM, due to their more labile composition, can be more readily retained and mineralized.

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GENERAL INTRODUCTION

Through runoff, groundwater interactions, and infiltration, streams integrate aquatic and terrestrial ecosystems. They receive nutrients, carbon, and contaminants from the landscape that are then transformed, stored, or exported downstream. Inland waters such as streams also play an important role in the global carbon cycle. Each year streams and rivers process nearly 2 petagrams (Pg) of terrestrial carbon (Battin et al. 2008). Headwater streams are key to these cycling processes because they comprise much of the world's total stream length. These small streams receive significant amounts of dissolved organic carbon (DOC) and mineralize it via microbial respiration and photo-oxidation (Marx et al. 2017; Cole et al. 2007).

DOC is chemically bound with other elements in molecules of dissolved organic matter (DOM). DOM has many sources; large fractions come from leaching of organic materials such as soils and plants on land, and it is also derived from in-stream organisms like algae, bacteria, and wetland plants by exudation and decomposition. As a result of these different sources, DOM molecular composition is extremely variable. Molecules that make up the DOM pool can range from simple, nitrogen-rich proteins to highly structural lignin compounds. The types of molecules represented in the DOM pool depends on its sources and degree of decomposition and has implications for stream processes such as microbial respiration.

DOM is an critical energy source to stream microbes because it contains carbon (C) and other essential elements like nitrogen and phosphorus (Jones 1995; Sobczak and Findlay 2002; Battin et al. 2003; Wiegner et al. 2005). It is the main substrate supporting stream respiration; however, bulk DOC concentration is not an accurate predictor of respiration rates because of its highly variable composition. Some DOM is more easily broken down by microbes than others depending on its source and

molecular composition. This lability determines whether the organic C is respired to the atmosphere, incorporated into microbial biomass, or exported downstream. Terrestrial DOM is believed to be less biologically available than stream-derived DOM, but little work has been done to directly identify differences in DOM lability and reactivity among the two classifications of sources.

Arid and semi-arid Arizona streams provide a unique opportunity to focus on the differences between the decomposition of stream-derived and terrestrial DOM. Sporadic storm events and low overall yearly rainfall result in prolonged periods where streams receive little to no DOM inputs from the surrounding landscape. Instead, much of the DOM fueling stream processes like respiration comes from in-stream primary producers. Projected changes in rainfall timing and intensity as a result of climate change will likely impact stream DOM pools, shifting DOM molecular composition and nutrient composition in unknown ways that will affect its ultimate fate within aquatic ecosystems.

The overarching research question of this thesis is: how does DOM source influence its molecular composition and microbial decomposition? I investigated the molecular composition, decomposition, and retention dynamics of DOM from three common sources (i.e., algae, wetland plants, and leaf litter) in two desert streams. I used bulk DOC concentration, optical properties of DOM, and modeled metabolism rates from diel variation in dissolved O_2 concentration to assess linkages between DOM composition and bacterial mineralization. I isolated DOM from wetland plants, algae, and leaf litter and measured its chemical and optical properties. I directly measured bacterial decomposition of the three sources in laboratory incubations using respiration rates and DOM loss as metrics of decomposability. To further examine the influence of DOM source and its properties on stream uptake, I conducted a field experiment

introducing leaf, algae, and wetland plant leachates to a study reach and measured its uptake kinetics.

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SOURCES AND LABILITY OF DISSOLVED ORGANIC MATTER IN A SONORAN DESERT STREAM

1.1 Abstract

Despite many studies investigating dissolved organic matter (DOM) processing in headwater streams, there has been little focus on DOM from in-stream sources and its microbial decomposition. Desert streams, due to low annual rainfall and low terrestrial primary production, receive fewer DOM inputs from the landscape than mesic streams and instead may receive the majority of DOM from in-stream producers. Thus, desert streams provide a unique opportunity to investigate the composition and reactivity of in-stream produced DOM. During summer 2017, I compared carbon composition and ecosystem metabolism rates between two stream reaches that differed in their dominant primary producer; one reach was dominated by vascular wetland plants and, in contrast, the other was dominated by benthic algae. Indices derived from excitation-emission matrices (EEMs) indicated that DOM composition differed for the two reaches; the wetland reach exhibited more aromatic, terrestrial DOM than the algae reach. Despite differences in DOM composition, rates of ecosystem respiration and production were similar for the two reaches. To further investigate DOM sources and their microbial decomposition, I conducted laboratory incubations of stream sediments with DOM derived from the leaching of wetland plants, algae, and leaf litter. Though DOM composition differed among the three leachates, initial respiration rates and long-term lability were similar across treatments. Initial DOC concentration was

the most important driver of long-term DOM lability with high DOC resulting in the highest lability. Together these findings provide little evidence that DOM molecular composition drives ecosystem metabolism and microbial respiration rates, and instead suggest stream microbes are able to use DOM from the three sources approximately equally.

1.2 Introduction

Headwater streams are hotspots for carbon (C) processing and can contribute a substantial portion of the total carbon dioxide (CO_2) returned to the atmosphere by rivers and streams via microbial mineralization (Marx et al. 2017). Dissolved organic matter (DOM) dominates the organic carbon pool in aquatic systems and, in addition to many other functions, is the main substrate for heterotrophic respiration (Kaplan and Cory 2016). DOM has many sources and is broadly classified as either allochthonous or autochthonous. Allochthonous DOM can come from the leaching of terrestrial materials such as soil organic matter, leaf litter, and woody debris. Autochthonous DOM is produced within the stream and can come from the exudate and detritus of algae, aquatic plants, and bacteria.

DOM is a catch-all term that describes a large pool of organic molecules. These molecules can consist of many different soluble compounds that have varying chemical functional groups (Nelson and Coble 2008). The source of DOM determines its chemical composition (Mutschlecner et al. 2017; Catalán et al. 2013; Hansen et al. 2016). DOM from terrestrial sources is generally more aromatic and has low nutrient content (McKnight et al. 2001; McArthur and Richardson 2002), whereas DOM from in-stream sources often shows the opposite characteristics (Hansen et al. 2016). Despite this

trend, vascular wetland plants growing in the stream can also contribute complex aromatic compounds (i.e., lignin) to the DOM pool (Catalán et al. 2013; Williams et al. 2010).

DOM molecules differ in their reactivity and ecological significance (Jaffé, Cawley, and Yamashita 2014; Berggren and Giorgio 2015). Low molecular weight and nitrogen (N)-rich DOM (i.e., protein-derived compounds) is prone to uptake and microbial consumption, whereas large or aromatic C compounds may require a high-energy investment by microbes to break down and can thus be more refractory to decomposition (Bernhardt and McDowell 2008; Cory and Kaplan 2012; Fasching et al. 2016). However, to what extent DOM molecular composition controls its lability is not clear. Aromatic C compounds may still be labile (Warrner et al. 2009). Humic DOM has historically been classified as refractory to microbial decomposition, but more recent studies suggest it may support a significant proportion of heterotrophic respiration (Cory and Kaplan 2012).

DOM composition is tightly linked to rates of gross primary production (GPP) and ecosystem respiration (ER) in streams. Growth of in-stream producers such as algae and wetland plants not only controls rates of GPP, but also provides DOM to the stream. High GPP can drive shifts in the DOM pool towards a higher proportion of lower molecular weight compounds if terrestrial inputs are relatively low (Halbedel, Büttner, and Weitere 2013). This shift in DOM composition towards more labile DOM can stimulate stream microbes, supporting higher rates of ER (Wiegner et al. 2005). In addition, GPP and ER can be directly linked because ER includes both heterotrophic and autotrophic respiration, thus more production results in more respiration (Hall 2016) .

Streams are generally heterotrophic (GPP<ER), meaning they are sinks for rather

than sources of organic matter. However, in desert regions the extremely high rates of stream GPP, along with low terrestrial GPP and few opportunities for terrestrial DOM input, result in occasional or even prolonged periods of positive net ecosystem production (NEP; GPP>ER) (Mulholland et al. 2001; Hall 2016). The contribution of internally produced DOM due to high rates of GPP in arid and semi-arid streams can be significant; however, little work has been done to determine the molecular composition and microbial decomposition of this DOM. This knowledge gap is likely because terrestrial DOM is the dominant source in organic matter budgets in most studied streams (Thurman 1985). In addition, few studies have addressed the differences in decomposition of in-stream versus terrestrial DOM. Because DOM produced in the stream is often more protein-like, less aromatic, and has higher nutrient content than terrestrial DOM, it has potential to contribute disproportionately to heterotrophic respiration (Berggren and Giorgio 2015; Jones 1995).

The aim of this study was to investigate (1) the effect of dominant primary producers on stream DOM composition and ecosystem metabolism (GPP and ER), and (2) the response of stream microbes to DOM from distinct sources. I conducted an observational field study comparing modeled rates of stream metabolism, DOC bulk concentration, and DOM optical properties between two reaches of a Sonoran Desert stream that differed in their dominant primary producer. I incubated stream sediment microbes with DOM from algae, a wetland plant, and leaf litter. I directly measured DOM lability using sediment respiration rates. I measured DOM loss and compositional changes over the incubation period. I predicted that (1) an algae-dominated reach would exhibit more labile DOM signatures than a wetland reach, and that this difference would result in higher ecosystem respiration rates, and (2)

stream microbes would rapidly metabolize and mineralize greater amounts of DOM from in-stream sources as opposed to a terrestrial source.

1.3 Methods

1.3.1 Site Description and Field Data Collection

This study was conducted within a 200-meter reach of the main stem of Sycamore Creek in Maricopa County, Arizona, U.S.A. Sycamore Creek is a spatially and temporally intermittent stream that drains a mountainous watershed with an area of 505 km^2. It is a tributary of the Verde River located northeast of the Phoenix metropolitan area. I chose two longitudinally connected reaches of Sycamore Creek; an open reach with riparian trees restricted to the high-flow stream margin and dominated by benthic algae (the gravel reach) and a shaded reach just downstream with riparian trees and dominated by wetland plants (the wetland reach). Light availability differs between the two reaches, with the gravel reach experiencing higher daily maximums of photosynthetically active radiation than the wetland reach.

To capture daily fluctuations in DOM composition and DOC concentration, one water sample was collected each hour for 24 hours from both reaches of Sycamore Creek in June and July 2017. Water samples were collected automatically using an automated sampler (Teledyne ISCO 6700, Lincoln, NE) outfitted with acid-washed, high-density polyethylene plastic bottles. The gravel reach was sampled on 29 and 30 June to cover a span of 24 hours. The wetland reach was sampled on 2 and 3 July. High and low temperatures and daylength did not differ between sampling days. Samples were retrieved within 24 hours of collection, transported to the laboratory at

ambient temperature, filtered to 0.7 µm (Whatman GF/F filters), and frozen until analysis.

1.3.2 O_2 Measurement and Metabolism Modeling

GPP and ER were determined using a single-station, open system diel method (Odum 1956). Dissolved O_2, temperature, and depth were measured at 15-minute intervals in both reaches using water probes (Eureka Manta 2, Austin, TX) over the course of a week. Photosynthetically active radiation (PAR) was measured at 15-minute intervals over the same period using a PAR Sensor (Onset model S-LIA-M003, Bourne, MA) and data logger (HOBO Micro Station, Bourne, MA). Light data were collected at each site in the riparian area near the water probes. In situ ecosystem metabolism rates were modeled in R (R Core Team 2017) using the 'streamMetabolizer' package developed by the United States Geological Survey (Appling et al. 2018). A maximum likelihood model was used to calculate GPP, ER, and a gas exchange coefficient that resulted in agreement between measured and modeled O_2 concentration.

1.3.3 Laboratory Incubations

Senescent and living *Schoenoplectus americanus* (wetland sedge), Zygnetmatales (filamentous algae), and *Populus fremonti* (cottonwood) leaves were collected from the study site and transported back to the lab. Wetland plant material and leaves were clipped into 2.5-cm pieces and leached in deionized water for 24 hours, then filtered through 0.7 µm filters (Whatman GF/F) that were pre-combusted (550°C for two hours). Algae were leached in acid-washed Erlenmeyer flasks in the sun for 24 hours

to stimulate primary production and exudation of organic compounds, then filtered through pre-combusted 0.7 µm GF/F filters. Leachates were frozen until use.

Sediment was collected from each reach of interest at Sycamore Creek by scraping off the top 2 cm to avoid sampling benthic algae, then inserting a clear plastic tube 8 cm down to a total depth of 10 cm. Cores were transported back to the lab at ambient temperature and stored at 10°C overnight. A composite sediment sample was created by mixing sediment from both reaches in equal proportions. Approximately 80 grams wet mass of sediment were added to each respiration chamber (16 chambers total). Chambers were 15-cm long clear plastic tubes (4.4 cm diameter) sealed on both ends with rubber stoppers. Leachates were diluted to a target concentration of 10 mg C L^{-1} (about 7 mg C L^{-1} above ambient stream concentration) and added to respiration chambers. All laboratory measurements of dissolved O_2 were made using optical dissolved oxygen probe (YSI ProPlus ODO/CT, Yellow Springs, OH). Respiration rates were calculated as the change in total dissolved O_2 concentration over a 1-hour period and normalized to the mass of dry sediment in each column. To account for differences in background metabolic rates among columns, I first measured respiration rates in each chamber with filtered streamwater from Sycamore Creek. Streamwater was then carefully siphoned off the sediment and replaced with diluted leachates or more streamwater (control) and respiration was measured again. Streamwater was used as a control to estimate ambient sediment respiration and DOM loss. Preliminary experiments showed that deionized water as a control resulted in bacterial death and DOM release. Respiration measurements were performed over two days. Following respiration measurements, sediment columns were left in the dark at 25°C. After 24 days, overlying water from each column was collected and DOC concentration and optical properties were measured. To account for DOM contribution from sediments,

optical properties and bulk DOC at the start of the experiment were obtained by mixing treatment leachate or streamwater (control) with sediment in equal proportions to incubation columns. The slurry was filtered for analysis and used to describe the starting conditions of the experiment.

1.3.4 Chemical and Optical Analysis

Bulk DOC and total dissolved nitrogen (TDN) were analyzed for filtered and acidified water samples by combustion analysis using a Shimadzu TOC-V analyzer. C:N ratios were calculated by taking the ratio of molar DOC to molar TDN. Organic matter composition was characterized by absorbance spectroscopy using a Shimadzu UV-mini 1240 with a 20W halogen lamp. Absorbance was collected over a range of 190-1100 nm with a 1-nm step size. Organic matter composition was characterized by fluorescence spectroscopy using excitation-emission matrices (EEMs) measured using a Horiba Job Yvon Fluoromax-4 spectrofluorometer with a 150W xenon lamp. Excitation wavelengths ranged from 240-450 nm with a 10-nm step size, and emission wavelengths range from 300-500 nm with a 2-nm step size. EEMs were blank-corrected and Raman-normalized. Four indices were calculated from the EEMs. The fluorescence index (FI) describes whether the organic matter is microbial or terrestrial in origin and is calculated as the emission intensity at 470 nm divided by the emission intensity at 520 nm obtained at an excitation of 370 nm (McKnight et al. 2001). The humification index (HIX) is inversely related to the hydrogen:carbon (H:C) ratio, such that higher HIX corresponds to lower H:C, and thus more aromatic carbon. HIX is calculated as the area under the emission spectra at 435-480 nm divided by the sum of the peak area between 300-345 nm at excitation of 254 nm (Zsolnay et al. 1999). Freshness (β:α)

is calculated as the emission intensity at 380 nm divided by the maximum emission intensity between 420-436 nm at an excitation of 310 nm (Parlanti et al. 2000). It is an indicator of how recently the organic matter was produced; higher values indicate more recently produced DOM. Specific UV absorbance (SUVA) is calculated as the absorbance at a wavelength of 254 nm normalized by bulk DOC concentration of the sample and is a proxy for DOM aromaticity (Weishaar et al. 2003). Thus, higher values of FI and freshness and lower values of HIX and SUVA would be associated with simpler, and presumably more labile, DOM.

1.3.5 Statistical Analysis

I assessed differences in optical properties, bulk DOC concentration, and rates of ecosystem metabolism between the two reaches of Sycamore Creek using two-tailed t-tests and assumed significance for values of $p<0.05$. Data were first inspected for normality and equal variance before tests were performed. A Welch's t-test was used for groups that were normal but did not meet the assumption of equal variance. A Mann-Whitney U test was used to assess differences in freshness between the two reaches because data could not be transformed to meet the assumptions.

To assess the impact of leachate additions on sediment microcosm respiration rates, I used a two-way analysis of variance (ANOVA) with treatment and time as fixed effects and day that respiration rates were measured as a random effect. Data were normally distributed and treatment groups exhibited equal variance. To understand changes in carbon composition in treatment microcosms over the incubation period, I used paired t-tests and assumed significance for values of $p<0.05$. Data were inspected for normality and equal variance and transformed if needed before tests were

performed. A Welch's t-test was used for groups that were normal but didn't not meet the assumption of equal variance. I used multiple linear regressions to explore the factors with the greatest influence on per cent DOC loss in the microcosms. Per cent DOC loss was log-transformed to meet assumptions of normality. I included DOM optical properties (FI, HIX, Freshness, and SUVA), initial DOC concentration, and mass of dry sediment in each sediment chamber as variables. One outlier was removed from the dataset because it fell outside 1.5 times the inner quartile range. To make parameter estimates interpretable, predictor variables were scaled by subtracting the mean and dividing by the standard deviation. I used backward and forward step-wise variable selection, as well as R-squared and AIC values to choose the best fit model. All statistical analyses were performed in R (R Core Team 2017).

1.4 Results

1.4.1 DOM content, DOM composition, and Metabolism in Two Reaches of Sycamore Creek

During the diel sampling there was no difference in DOC concentration or SUVA between sites. DOM composition based on FI, HIX, and freshness differed between the gravel and wetland reaches of Sycamore Creek ($p<0.05$, Table 1). FI values for both sites indicate a mixture of microbial and terrestrial sources of DOM, with the wetland reach exhibiting a more pronounced terrestrial influence. HIX was higher in the wetland reach than the gravel reach, indicating a higher degree of humic, aromatic organic matter in the wetland reach. Freshness was higher in the gravel reach, indicating more recently produced organic matter. SUVA was higher at the

wetland reach indicating more aromatic C, though it was not significantly different than the gravel reach.

Modeled rates of ecosystem metabolism were similar for the two reaches over the course of a week (Figure 1); the gravel site had a mean GPP of 1.00±0.04 g O_2 m^{-2} d^{-1} and mean ER of -2.3±0.09 g O_2 m^{-2} d^{-1} while the wetland site had a mean GPP of 0.91±0.05g O_2 m^{-2} d^{-1} and mean ER of -2.22±0.02 g O_2 m^{-2} d^{-1}. The open gravel reach exhibited higher GPP on 5 of the 6 measured days and higher ER on 4 of the 6 measured days.

1.4.2 Laboratory Incubations

1.4.2.1 Respiration Rates

Initial respiration rates of sediment chambers incubated with streamwater were comparable among columns with mean respiration rate of 2.94±0.25 μg O_2 g^{-1} h^{-1} ($p>0.05$, Figure 3). After streamwater was siphoned off and additional streamwater or treatment leachate was added, respiration rates changed variably (Figure 3). Respiration in the algae and wetland treatments increased by a factor of 1.04 and 1.08, respectively ($p>0.05$). Respiration in the leaf leachate treatment decreased by a factor of 0.95 ($p>0.05$). Respiration in the control treatment decreased by a factor of 1.33 ($p<0.05$). Results from a two-way ANOVA indicated neither treatment nor time had a significant effect on sediment chamber respiration rates.

1.4.2.2 DOM loss and optical properties

Treatment leachates differed in their initial optical properties, as shown by EEMs (Figure 2). Both wetland and leaf leachate exhibited protein-like and humic-like peaks (Fellman, Hood, and Spencer 2010). Algae leachate and control water exhibited humic-like peaks indicative of aromatic, high molecular weight DOM. Optical indices provided further information on leachate properties. Freshness was highest in the control and lowest in the leaf leachate, with algal and wetland leachates falling in between (Table 2). The HIX values indicated a higher degree of humification in control and algae treatments, compared to low humification in wetland and leaf treatments. The FI was comparable among treatments and indicated a mixture of both microbial (i.e., algal) and terrestrial DOM. Initial mean SUVA among treatments ranged from 0.57-2.33 L mg^{-1} m^{-1}, and increased from algae to leaf to control to wetland treatments, indicating low aromaticity in the algae treatment and high aromaticity in the wetland treatment.

After 24 days of incubation, DOM composition looked similar across treatments (Figure 2). All treatments shifted from their variable initial composition with the appearance of protein-like peaks and a loss of humic-like peaks (Fellman, Hood, and Spencer 2010). Freshness increased significantly in all treatments. The HIX changed variably depending on the treatment. Both treatments that had high initial HIX (i.e., control and algae) experienced a decrease over the incubation period ($p<0.05$), whereas treatments that had relatively low initial HIX (i.e., wetland and leaf) experienced an increase.

FI changed significantly in all treatments except algae, though the margins of change were small (<4%). FI decreased in the control and wetland treatments,

indicating a decrease in the microbial DOM or an increase in terrestrially derived DOM. FI increased in the algae and leaf treatment, indicating an increase in the proportion of DOM from microbial sources or a decrease in the proportion of DOM from terrestrial sources.

SUVA increased in all treatments, indicating a shift to a more aromatic C pool over the course of incubation (Table 3). This increase in SUVA was statistically significant only in the algae treatment.

The coefficients of variation (CV) of optical properties before incubation were 3.33 for FI, 80.65 for HIX, 13.28 for freshness, and 108.20 for SUVA. Post-incubation CV'-s were 1.11 for FI, 49.32 for HIX, 17.42 for freshness, and 45.85 for SUVA. CV decreased during incubation for all optical properties except Freshness.

DOM loss over the incubation was assessed using DOC concentration. There was no difference in percent change in DOC among treatments ($p>0.05$, Table 3). To assess what other variables might drive DOC loss other than treatment, I performed a multiple linear regression and found that the primary driver of DOC loss in the incubation chambers was DOC concentration in the initial treatment water ($p<0.05$, Figure 4). Initial DOC concentration had a negative relationship with log per cent DOC loss and explained 60.0% of the variation in log percent DOC loss over the course of the experiment. The other predictor variables were not included in the final model because they did not contribute to a better fit, based on AICc and R-squared values.

Initial C:N increased from wetland to control to leaf to algae treatments (Table 3). C:N declined in all treatments over the incubation period, but the change was only significant in the algae treatment ($p<0.05$).

1.5 Discussion

1.5.1 Field Observations

I examined how primary producers can influence DOM composition and ecosystem metabolism rates in a field study of a desert stream. The two study reaches in Sycamore Creek differed in dominant primary producer and DOM composition. DOM in the wetland plant-dominated reach was more terrestrially derived, more humic, less fresh, and higher molecular weight than DOM in the algae-dominated gravel reach. Wetland plants, although sources of autochthonous DOM, have been shown to contribute to the aromatic, humic-like components of DOM due to their high lignin content (Catalan 2013, Simon 2002). Algae are expected to contribute to labile DOM signatures in freshwater systems (McKnight et al. 2001), and algal exudate is often used as a proxy for labile carbon (Hotchkiss et al. 2014; Jones 1995). The optical properties of DOM in the gravel reach support these previous findings; DOM in the reach had lower HIX, higher Freshness, and higher FI than DOM in the wetland reach.

In this study, modeled ecosystem metabolism metrics did not differ significantly between reaches, indicating no tight linkage between DOM composition and primary production and bacterial mineralization in the stream. Previous studies have demonstrated a link between organic matter composition and ecosystem metabolism, though with contradicting findings. Fuß et al. (2017) found humic, aromatic carbon was associated with higher ER. Other studies have reported correlations of optical properties describing fresh, microbial carbon such as FI and Freshness with higher ecosystem metabolism rates (Halbedel, Büttner, and Weitere 2013; Masese et al. 2017). There are a few reasons we would not necessarily expect to see differences in our modeled

ecosystem metabolism rates even though there were clear, significant differences in DOM composition.

DOM in the gravel and wetland reaches was perhaps not different enough to greatly influence ER. Slight differences in DOM composition between the two reaches may not result in quantifiable differences in bacterial mineralization. Hansen et al. (2016) found that DOM was similarly labile across five different sources that different greatly in their optical properties, suggesting that DOM source may not be a strong predictor of its lability. Another explanation for the lack of relationship between metabolism and DOM is local adaptations of bacteria to DOM sources. Koetsier III, McArthur, and Leff (1997) found that DOM lability was dependent on both its source and the bacterial community, with highest lability occurring when bacterial communities received DOM common to their location. Thus, even though our study reaches differed in carbon composition, bacteria in each reach could be adapted to processing DOM from the dominant source. This homogenization of stream DOM lability between reaches could explain the similar rates of GPP and ER between reaches in Sycamore Creek.

Finally, other important controls on ER such as temperature, nutrients, and GPP may have had a stronger influence than DOM composition on rates of ecosystem respiration. Metabolism was measured in midsummer near the time of high sunlight and peak biomass, thus GPP is expected to be high (Bernot et al. 2010). High GPP is often correlated with high rates of ER, indicating high an overwhelming contribution of autotrophic respiration to ER (Griffiths et al. 2013; Beaulieu et al. 2013) In addition, high mean daily temperatures could drive similar rates of ER between the two reaches (Mulholland et al. 2001).

1.5.2 Laboratory Experiment

To investigate how isolated sources of DOM may influence bacterial mineralization, I performed laboratory incubations using sediment chambers and leachates. There was no strong effect of leachate on treatment on respiration rates (Figure 3). The addition of wetland plant and algae leachates increased respiration rates in microcosms, though not significantly, indicating that those sources could potentially provide labile DOM to the system that could be rapidly metabolized. The addition of leaf leachate lowered chamber respiration rate, indicating an inability of the DOM to stimulate respiration on a short timescale. Though the control was inoculated with filtered streamwater (and thus, a fresh DOM source) at the same time that other microcosms received leachate treatments, respiration rate declined. Similar rates of respiration among treatments could be a result of the methods and timescale used to measure respiration. Previous studies have demonstrated multiple timescales of DOM turnover. Labile DOM can be metabolized in a matter of minutes, while more recalcitrant DOM can be metabolized on timescales of days to even years (Cory and Kaplan 2012; Jones 1995; Kaplan and Cory 2016; Caraco et al. 2010). The timing of my respiration measurements may not have captured differences in mineralization. Jones (1995) measured differences in respiration treatments on a timescale of four hours, while Mann et al. (2014) found differences after a 5-day incubation. Berggren and Giorgio (2015) demonstrated that measurements on even smaller timescales than hours could tease apart differences in bacterial respiration among DOM sources. Instantaneous measurements of changes in O_2 could give a more accurate representation of initial respiration rates and capture the immediate mineralization of DOM.

Changes in DOM composition over the course of the incubation provide evidence

that some compounds are selectively removed by microbial mineralization while others are left behind, resulting in some homogenization of the DOM pool. Overall, significant changes in DOM properties indicate a shift towards more humic, aromatic DOM. The coefficient of variations for all optical properties except freshness decreased during the experiment, suggesting a loss of variation in the DOM pool. Previous studies have found similar shifts in DOM optical properties after incubation with aquatic microbes to a more complex DOM pool. Hur, Lee, and Shin (2011) found that SUVA increased in both algal and leaf leachate treatments after incubation. Hansen et al. (2016) similarly found that SUVA and HIX, both measurements of humic, aromatic carbon, increased during incubation regardless of the DOM source. Despite these expected changes towards more humic and aromatic DOM, freshness changed unexpectedly in all treatments. Because increasing freshness indicates the production of new organic material, we would expect it to decrease following microbial processing during incubation; however, freshness increased in all treatments. Hansen et al. (2016) observed a similar phenomenon when they incubated wetland, soil, and algal leachates over time. Freshness increased within the first 10 days, then decreased over the next 100 days. Thus, the length of this experiment could explain why freshness increased over time and perhaps would have followed a different trend over time if the experiment was prolonged.

The algae treatment exhibited unexpectedly low FI and high HIX compared to the other leachates. Catalán et al. (2013) similarly found that autochthonous DOM sources had higher SUVA and lower FI than allochthonous DOM. Unexpected autochthonous optical indices could be a result of an overwhelming sediment signal, since leachates were mixed with sediments in proportions similar to what was used in the incubation to assess initial conditions.

DOC used in the experiment was highly labile, regardless of source. All treatments exhibited substantial average per cent loss of DOC over the incubation period (53.01±17.67 per cent). The two samples that exhibited an increase in DOC over the length of the experiment (Figure 4) started with abnormally low DOC concentrations, which could have caused bacterial senescence and release of DOC (Brookshire et al. 2005).

Lability of DOM, assessed as the per cent of DOC lost, in sediment incubations was primarily dependent on initial DOC concentration (Figure 4), rather than DOM optical properties. Mutschlecner et al. (2018) similarly found DOC concentration controlled DOM lability. High overall DOC loss during the experiment coupled with no effect of optical properties on DOC loss implies desert stream bacteria have the ability to mineralize DOM from leaf, wetland, and algal sources similarly.

1.6 Conclusion

This study has attempted to tease apart the relative influence of both in-stream and terrestrial sources of DOM on bacterial decomposition in streams. *In-situ* respiration rates measured on a daily scale do not exhibit dependence on DOM source and composition. There are many factors controlling in-stream metabolic processes that likely overwhelmed the influence of DOM composition.

In 24-day incubations of stream sediments with DOM from algae, wetland plants, and leaf litter, DOM lability was predominantly controlled by initial DOC concentration, not optical properties, suggesting that DOM is similarly labile across sources regardless of DOM molecular composition.

Overall, DOM molecular composition was not a driver of bacterial decomposition.

Both in-stream and terrestrial sources of DOM have the potential to provide C, energy, and other necessary elements to stream microbes.

Small, headwater streams have a profound influence on water quality as they process and deliver nutrients, contaminants, and water to downstream ecosystems (Alexander et al. 2007). Results from this study show that a desert stream can similarly process DOM from in-stream and terrestrial sources, removing it from the system and directly influencing what is exported downstream. In addition, streamwater DOM does not directly influence ecosystem metabolism.

Table 1: Optical and chemical properties of streamwater from diel sampling of Sycamore Creek

Summary table of optical properties from streamwater collected during a diel sampling of an algae-dominated reach (gravel) and a wetland plant-dominated reach (wetland). Included is the fluorescence index (FI), humification index (HIX), freshness index (β:α), specific ultraviolet absorbance (SUVA, L mg^{-1} m^{-1}), and DOC (mg L^{-1}). Statistics are reported as means ($\pm$ 1 SE). Properties with an asterisk indicate a significant difference between reaches ($p<0.05$).

Site	FI*	HIX*	Freshness (β : α)*	SUVA (L mg^{-1} m^{-1})	DOC (mg L^{-1})
Gravel	1.53 ($\pm$0.003)	12.23 ($\pm$0.20)	0.65 ($\pm$0.002)	3.64 ($\pm$0.30)	3.49 ($\pm$0.50)
Wetland	1.49 ($\pm$0.003)	14.5 ($\pm$0.20)	0.63 ($\pm$0.0007)	3.72 ($\pm$0.30)	4.07 ($\pm$0.80)

Table 2: Changes in fluorescent properties of DOM during incubation experiments

Change in fluorescent indices over a 24-day incubation with stream sediments, shown as initial and final values (± 1 SE) and percent change. Percent change values with an asterisk indicate significant change over time ($p<0.05$).

	FI			HIX			Freshness ($\beta : \alpha$)		
Treatment	Initial	Final	% change	Initial	Final	% change	Initial	Final	% change
Control	1.48 ±(0.01)	1.44 ±(0.01)	-3.18*	7.65 ±(0.50)	2.84 ±(0.90)	-62.86*	0.66 ±(0.01)	1.02 ±(0.09)	54.71*
Algae	1.39 ±(0.02)	1.42 ±(0.005)	2.41	8.70 ±(0.09)	3.22 ±(0.05)	-62.92*	0.61 ±(0.02)	0.92 ±(0.07)	50.31*
Wetland	1.49 ±(0.003)	1.43 ±(0.008)	-3.59*	1.25 ±(0.06)	3.22 ±(0.9)	157.60	0.53±(0.001)	0.97 ±(0.10)	81.28*
Leaf	1.41 ±(0.005)	1.42 ±(0.008)	0.78*	1.03 ±(0.06)	2.60 ±(0.90)	151.60	0.47 ±(0.01)	1.02±(0.01)	112.36*

Table 3: Changes in SUVA, DOC, and C:N during incubation experiments

Changes in specific ultraviolet absorbance (SUVA, L mg^{-1} m^{-1}), DOC (mg L^{-1}), and molar C:N in sediment columns over a 24-day incubation, shown as initial and final values (± 1 SE) and percent change. Percent change values with an asterisk indicate significant change over time ($p<0.05$).

	SUVA (L mg^{-1} m^{-1})			DOC (mg L^{-1})			C:N		
Treatment	Initial	Final	% change	Initial	Final	% change	Initial	Final	% change
Control	1.815±(1.08)	2.275 ±(0.98)	25.34	45.35 ±(25.16)	30.79 ±(21.37)	-32.07	194.16 ±27.56	63.35±47.23	-36.65
Algae	0.567 ±(0.44)	3.072 ±(0.40)	441.41*	106.96 ±(54.6)	6.56 ±(1.06)	-93.87	465.44±58.66	17.40±3.46	-82.60*
Wetland	2.33 ±(0.75)	3.16 ±(0.64)	35.58	30.37 ±(25.58)	9.18 ±(3.57)	-69.77	105.75±61.54	15.16±5.51	-84.85
Leaf	0.77 ±(0.33)	2.63 ±(0.67)	240.0	64.45 ±(34.65)	10.01 ±(1.83)	-84.47	276.22±134.30	18.94±3.34	-81.06

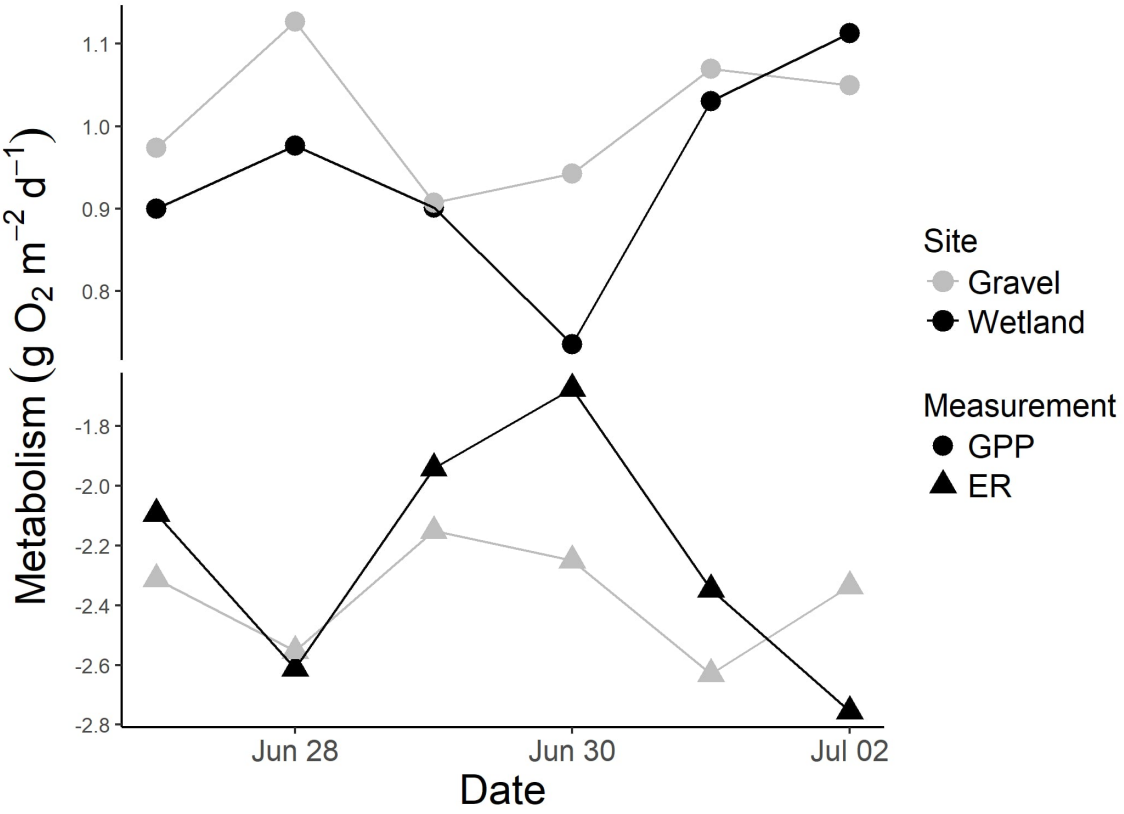


Figure 1: Ecosystem metabolism rates in a gravel and a wetland reach of a desert stream.

Daily rates of gross primary production (GPP) and ecosystem respiration (ER) in the an algae-dominated reach (gravel) and a wetland plant-dominated reach (wetland) of a desert stream from 27 June - 2 July.

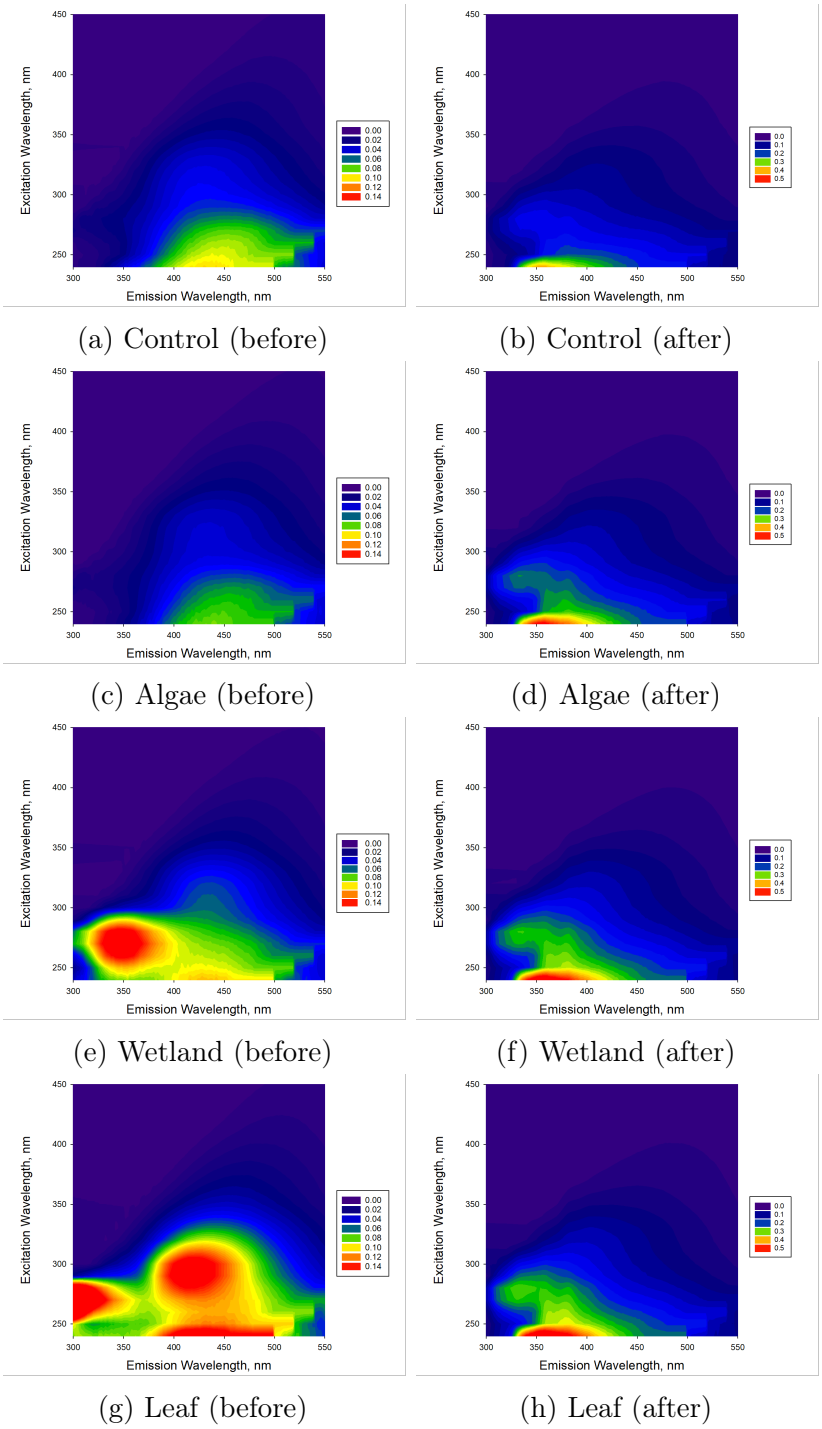


Figure 2: Representative EEMs before and after 24-day incubation with sediments

Representative excitation-emission matrices (EEMs) from leachates and control water used in the incubation experiment. EEMs from before incubation are in the left column and EEMs after 24 days of incubation with sediments are in the right column. Control, algae, wetland plant, and leaf leachates are shown.

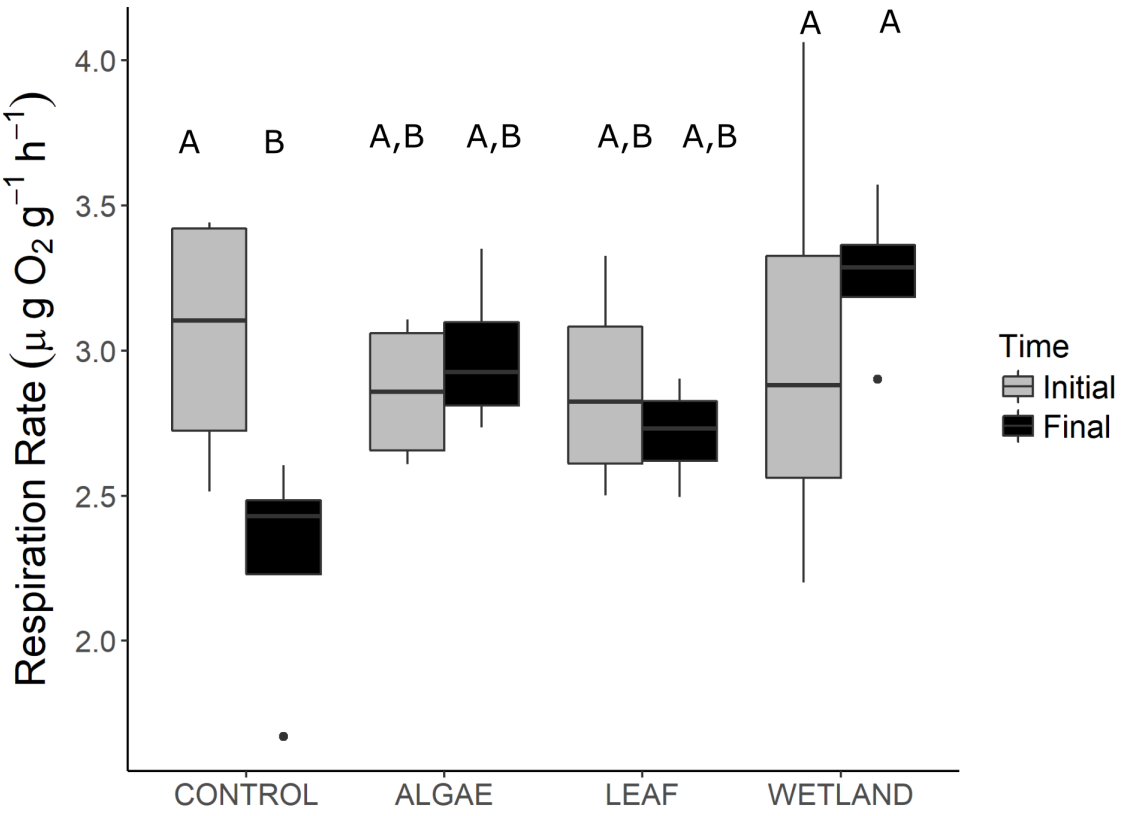


Figure 3: Boxplots of respiration rates in sediment chambers before and after leachate addition.

Initial respiration rates (grey bars) were measured in each chamber as the change in O_2 after one hour of incubation using filtered streamwater. Streamwater was siphoned off and replaced with each treatment leachate or control streamwater and final respiration rates were measured again (black bars). Each treatment was replicated four times. Black points indicate outlier respiration rates. Letters indicate siginificant differences between groups based on Tukey's honestly significant difference test.

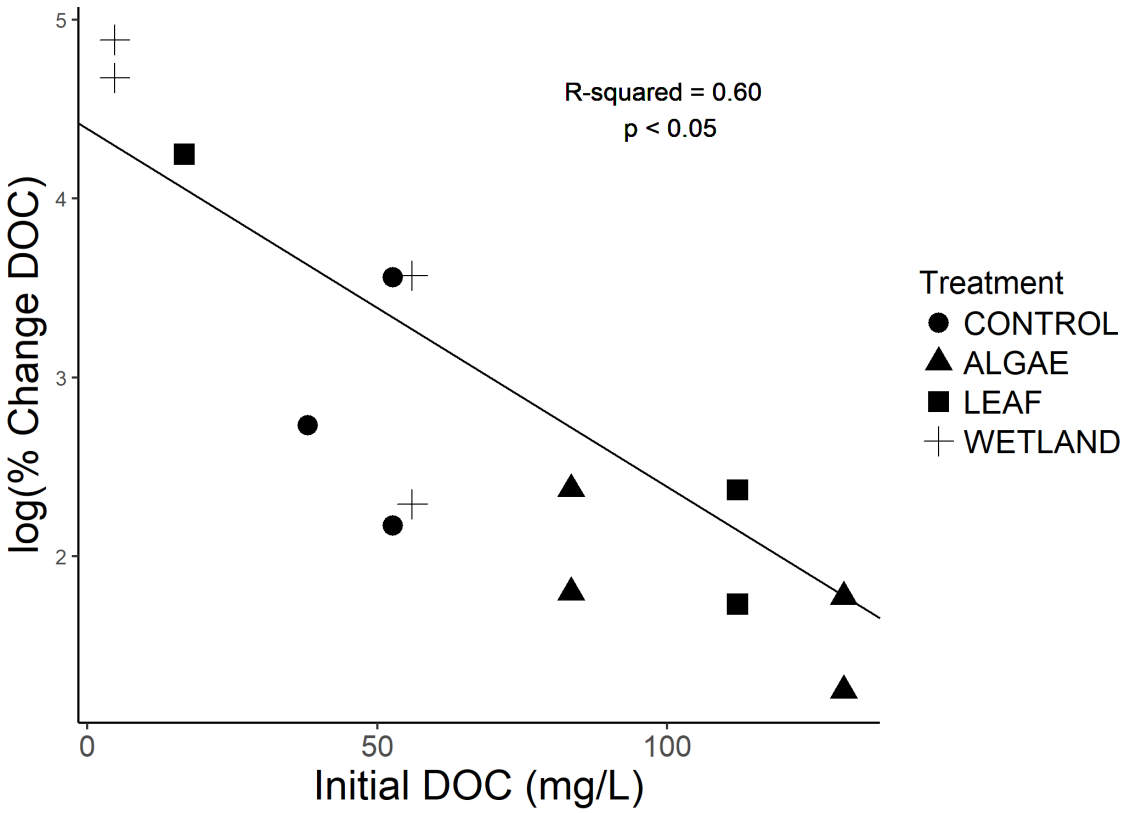


Figure 4: Log-transformed percent change in DOC as a function of initial dissolved C:N in sediment microcosms.

Log-transformed percent change in DOC (mg L^{-1}) after 24 days of incubations as a function of initial DOC (mg L^{-1}). Each point represents one chamber, and the shape of the point indicates the treatment. One leaf leachate-treated chamber was lost during incubation and is not shown here. One algae-treated chamber was a statistical outlier and is not shown. Initial DOC concentration, as opposed to DOM optical properties, explained 60.0% of the variance in the log of the percent change in DOC ($p<0.05$).

Chapter 2

UPTAKE OF DOM IN RYE CREEK: A (WATERSHED) TEA PARTY

2.1 Abstract

Small streams have the ability to retain and process large amounts of organic matter and in doing so, can regulate downstream water quality and the global carbon cycle. Dissolved organic matter (DOM) is the dominant form of organic matter in streams and is the main substrate for heterotrophic respiration. Both DOM structural composition and nutrient content can influence the retention of DOM in streams. To investigate the control of DOM composition and nutrient content on DOM retention, I performed pulse releases of leachates from three sources: wetland plants, riparian tree leaf litter, and filamentous algae. I measured leachate carbon (C) content, nitrogen (N) content, and optical properties. Leachates were released into the stream and their uptake kinetics were measured. Leachates varied in carbon composition and nitrogen content. Overall, wetland leachate was less aromatic and more protein-like than algae and leaf leachate. Algae leachate was more humic than leaf and wetland leachate, but was intermediate in freshness and aromaticity. Molar C:N increased from algae to wetland to leaf leachate. Leaf leachate had the slowest uptake velocity, whereas wetland plant leachate had the fastest. These results suggest that both leachate N content and DOM composition affect uptake; N stimulates DOM uptake, while complex, aromatic compounds reduce uptake.

2.2 Introduction

Headwater streams make up more than 95 percent of total number of streams globally and thus, have the potential to retain and process large amounts of carbon. Dissolved organic matter (DOM), nicknamed 'watershed tea' (Kaplan and Cory 2016), is a key energy source to stream heterotrophs because it contains dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and other elements essential to biological activity. Streamwater DOM has many sources and thus, is a complex mixture of organic molecules and elements that vary in their biological availability (Battin et al. 2008; Nelson and Coble 2008; Sobczak and Findlay 2002). DOM has many fates and ecological roles; once reaching the stream it may be mineralized by bacteria, retained through physical processes, transported further downstream, or lost through abiotic processes such as flocculation, adsorption to sediments, and photo-oxidation (Findlay and Sobczak 1996; Fasching and Battin 2012).

Both DOM molecular structure and nutrient content can influence its fate within stream ecosystems (Mutschlecner et al. 2017; Fellman et al. 2009). Structurally complex DOM requires a high-energy investment by microbes to break down (Mann et al. 2014). Labile compounds can be more easily decomposed; monomeric carbohydrates and low molecular weight compounds in DOM are more readily removed than complex ones (Bernhardt and McDowell 2008). Stream microbes can be nutrient limited, which shifts resource allocation from carbon mineralization to nutrient acquisition and can slow the rate at which DOM is decomposed. Both nitrogen (N)-containing DOM and DOM with high phosphorus (P) content have been shown to increase DOM decomposition in streams (Bernhardt and McDowell 2008; Fellman et al. 2009; Mutschlecner et al. 2017). In addition to relieving nutrient limitation, N and P can

also contribute to abiotic DOM retention; both N (as ammonium) and P have been shown to adsorb to sediments via ionic bonding, increasing overall stream DOM retention (Triska et al. 1994). Substantial amounts of aromatic, terrestrial DOM can be abiotically adsorbed to sediments (Kothawala et al. 2012). Teasing apart the relative influence of DOM composition and nutrient content on its stream retention is difficult because they are often linked; N-rich DOM such as proteins are often low molecular weight and less aromatic than non-N-rich compounds (Hur, Lee, and Shin 2011).

DOM composition and nutrient content are controlled by DOM source (Cory and Kaplan 2012; McKnight et al. 2001). Thus, DOM from various sources should be differentially retained. DOM can be transported to streams from the surrounding terrestrial environment from sources such as soils and leaf litter, but it is also produced in the stream from algal, bacterial, and wetland plant exudate and detritus. Terrestrial DOM is traditionally classified as less microbial, more complex, and less nutrient rich than DOM produced in the stream (Torremorell et al. 2015; Fellows et al. 2006; McKnight et al. 2001). Internally produced DOM can support high respiration rates and high long-term carbon losses compared to external DOM, presumably due to its overwhelmingly low molecular weight, N-rich, and less aromatic composition (Jones, Fisher, and Grimm 1995; Berggren and Giorgio 2015; Griffiths et al. 2013; Hur, Lee, and Shin 2011). Most studies of DOM uptake in streams have focused on external sources (Fellman, Hood, and Spencer 2010; Bernhardt and McDowell 2008; Mutschlecner et al. 2017; Wiegner et al. 2005), likely because they dominate the DOM pool in most studied streams (Thurman 1985). Little attention has been paid to the differential stream retention of external versus internal DOM, even though these types of DOM vary greatly in their composition and nutrient content.

Stream-produced DOM may dominate the DOM pool in arid and semi-arid Arizona streams. Low annual rainfall provides few opportunities for the leaching and transport of terrestrial materials to the stream, whereas abundant sunlight stimulates high rates of primary production within the stream. Thus, in-stream DOM, because of its abundance and labile composition, has the potential to contribute disproportionately to heterotrophic stream processes (Kaplan and Cory 2016). There are currently no estimates of whole-stream DOM uptake in desert streams. Arizona streams may exhibit very different relationships of DOM composition and nutrient content with uptake compared with streams elsewhere because the ability of streams to decompose DOM is closely associated with their unique microbial communities (Koetsier III, McArthur, and Leff 1997). Furthermore, very few studies have tested whole-stream uptake using DOM from in-stream sources, instead focusing on only terrestrial sources.

To address this knowledge gap, I assessed how DOM composition and N content control DOM whole-stream uptake. I performed pulsed releases of leachates from three different sources in a small, intermittent, headwater stream in Arizona. I hypothesized that both DOM composition and nitrogen (N) content, controlled by the DOM source, would drive rates of whole-stream uptake. I predicted that leachates from two in-stream sources (wetland plants and algae) would exhibit more labile DOM signatures and be taken up faster than leachate from a terrestrial source (riparian tree leaf litter).

2.3 Methods

2.3.1 Site Description and Field Data Collection

Rye Creek is a small, spatially and temporally intermittent stream draining 316 km^2 in Tonto National Forest, Arizona (34.1 °N , -111.35 °W). It is an upstream tributary to a drinking water reservoir (Theodore Roosevelt Lake) on the Salt River at an elevation of 954 m above sea level. Surrounding vegetation is high-desert oak and juniper forest. The dominant riparian tree species are *Populus fremonti* (cottonwood) and *Platanus wrightii* (sycamore).

I performed pulse releases of three leachates in a 90-meter reach in June 2018, when respiration was expected to be high due to high daily mean temperatures and high DOM contributions from active primary producers. Gross primary production (GPP) and ecosystem respiration (ER) were determined using a single-station, open-system, diel method (Odum 1956). Dissolved O_2 was measured at 15-minute intervals using a dissolved oxygen sensor(PME miniDOT, Fairborn, OH). *In-situ* ecosystem metabolism rates were modeled in R (R Core Team 2017) using the package 'streamMetabolizer' developed by the United States Geological Survey (Appling et al. 2018). I modeled light as photosynthetically active radiation within the package using Rye Creek's location and typical maximum light values seen in Arizona streams. A maximum likelihood model was used to calculate GPP, ER, and a gas exchange coefficient for optimal agreement between measured and modeled O_2 concentration.

Average stream discharge during the time of the experiments was 2.13±0.81 L s^{-1}. Streamflow was restricted to one main channel with an average width of 2.76 m. Average stream depth was 3.52 cm. Though the stream has abundant canopy cover by

riparian trees, light was high during the experiment with daily maximums reaching up to 2500 μmol m^{-2} s^{-1}. Stream algae included *Chara*, a multicellular green alga, *Nostoc*, and diatoms. Algae covered most of the benthic surface during the experiment, and benthic chlolrophyll *a* concentration was 13.43±6.22 mg m^{-2}. The wetland plants *Typha domingensis* and *Schoenoplectus americanus*) were present in the riparian area.

2.3.2 DOM Uptake Experiments

To investigate the role of DOM composition and N content on stream uptake, I performed pulsed releases of leachates generated from three broadly classified sources into Rye Creek. Leachates were prepared using organic material soaked and macerated in deionized water for 24-36 hours at 10°C at a ratio of 100 g material to 1L water. Organic materials were dried to 60°C prior to leaching. Dried cottonwood and sycamore leaves were crushed into 1-cm pieces by hand and leached together to represent a terrestrial organic matter source. Dried *Typha domingensis* (cattail) was clipped to roughly 2.5-cm pieces and leached as a wetland plant organic matter source. Freshly collected *Cladophora glomerata* (filamentous algae) was dried, crushed by hand, and leached. Leachates were filtered through a sieve to remove any large particles and frozen until use (<5 days).

All leachate releases were performed within 72 hours of each other to minimize any influence of changing discharge on uptake kinetics. Discharge was measured during each injection using NaCl dilution gauging. Three background samples were collected at evenly spaced intervals along the 90-m reach before each injection. I used DOC concentration as a proxy to measure DOM uptake. The leachate solutions were added at the top of the reach (0 m) to raise the concentration of DOC in the

stream by 2 mg $L^{-1}$and chloride by 5 mg L^{-1}. The arrival of the added DOC and NaCl was monitored at a station 90 m downstream from the pulse addition using a water probe (Eureka Manta 2, Austin, TX) equipped with colored dissolved organic matter (CDOM) and specific conductivity sensors. I took 25 samples throughout the breakthrough curve, defined as the change in solute concentration over time as the solute passes by the sampling location. To reduce laboratory costs, I created a standard curve between laboratory-measured DOC concentration and sensor-estimated CDOM concentration. For each leachate release, I chose a subset of water samples to run for DOC concentration that covered the full range of concentrations seen during the experiment and plotted it against the sensor CDOM value observed at the same time the sample was collected. I then used the relationship between DOC and CDOM to calculate DOC concentration throughout the release at the downstream station.

2.3.3 Chemical and Optical Analysis

Bulk DOC and total dissolved nitrogen (TDN) were analyzed for filtered and acidified water samples by combustion analysis using a Shimadzu TOC-V analyzer. C:N ratios were calculated by taking the ratio of molar DOC to molar TDN. Organic matter composition was characterized by absorbance spectroscopy using a Shimadzu UV-mini 1240 with a 20W halogen lamp. Absorbance was collected over a range of 190-1100 nm with a 1-nm step size. Organic matter composition was characterized by fluorescence spectroscopy using excitation-emission matrices (EEMs) measured using a Horiba Job Yvon Fluoromax-4 spectrofluorometer with a 150W xenon lamp. Excitation wavelengths ranged from 240-450 nm with a 10-nm step size, and emission wavelengths range from 300-500 nm with a 2-nm step size. EEMs were blank-corrected

and Raman-normalized. Four indices were calculated from the EEMs. The fluorescence index (FI) describes whether the organic matter is microbial or terrestrial in origin and is calculated as the emission intensity at 470 nm divided by the emission intensity at 520 nm obtained at an excitation of 370 nm (McKnight et al. 2001). The humification index (HIX) is inversely related to the hydrogen:carbon (H:C) ratio, such higher HIX corresponds to lower H:C, and thus more aromatic carbon. HIX is calculated as the area under the emission spectra at 435-480 nm divided by the sum of the peak area between 300-345 nm at excitation of 254 nm (Zsolnay et al. 1999). Freshness (β:α) is calculated as the emission intensity at 380 nm divided by the maximum emission intensity between 420-436 nm at an excitation of 310 nm (Parlanti et al. 2000). It is an indicator of how recently the organic matter was produced; higher values indicate more recently produced DOM. Specific UV absorbance (SUVA) is calculated as the absorbance at a wavelength of 254 nm normalized by bulk DOC concentration of the sample and is a proxy for DOM aromaticity (Weishaar et al. 2003). Thus, higher values of FI and freshness and lower values of HIX and SUVA would be associated with simpler, and presumably more labile, DOM.

2.3.4 DOC Uptake Metrics

Uptake metrics for DOC were calculated as follows.

DOC uptake length (S_w, m) was calculated as k^{-1} using the following equation:

$$lnNx = lnN_o - k_x \tag{2.1}$$

where N_x is the solute concentration at x meters downstream and N_o is the solute concentration at the addition site (0m) (Newbold et al. 1981).

Because uptake length is dependent on stream discharge (Q), I calculated uptake velocity (V_f, mm day^{-1}) for better comparison to other uptake literature .

$$V_f = (Q/w)/S_w \tag{2.2}$$

where w is the mean stream wetted width (Stream Solute Workshop 1990).

The areal rate of DOC uptake (U, mg m^{-2} d^{-1}) is conceptualized as the total amount of DOC that can be taken up in a square meter of stream per day and was calculated as:

$$U = V_f N_b \tag{2.3}$$

where N_b is the background solute concentration in the stream (Stream Solute Workshop 1990).

2.4 Results

The leachates used in the uptake experiments differed in DOM optical properties and C:N (Table 4, Figure 5). EEMs presented in Figure 5 show a protein-like, presumably N-rich signal in all three leachates; however, leachates differ in their aromatic DOM content. EEMs from algae leachate exhibited a humic-like peak, seen by the light blue/green coloration at an excitation of 300 nm and emission of 420 (Fellman, Hood, and Spencer 2010). This peak was not seen in wetland and leaf leachates. Optical indices provided more information on DOM composition of leachates. All leachates exhibited a strong terrestrial influence with FI ranging from 1.09-1.37 (McKnight et al. 2001). Leaf and wetland-derived leachates were both less humic than algae-derived leachate, with HIX values of 0.18 compared to 1.18.

Freshness was highest in wetland leachate, followed by algae and then leaf leachate. SUVA values ranged from 1.60-2.76 and indicated higher aromatic carbon content in leaf and algae leachate than in wetland leachate. Leachates differed in their nutrient composition. C:N ranged from 3.83-88.44, with higher values indicating more carbon relative to nitrogen. Algae-derived leachate had the lowest C:N while leaf leachate had the highest. Wetland-derived leachate had an intermediate C:N of 14.67.

Rates of GPP and ER were similar to another desert stream in summer (Figure 1). Average GPP was 1.14±0.08 g O_2 m^{-2} d^{-1}, while average ER was -2.03±0.09 O_2 m^{-2} d^{-1}. The stream was heterotrophic; ER was higher than GPP on all days of measurement.

DOC was removed from the water column after its release into Rye Creek in all three uptake experiments, with uptake lengths ranging from 158.2–205.1 m. Uptake metrics varied among the three leachates (Table 5). Wetland leachate had the shortest uptake length, fastest uptake velocity, and highest areal uptake rate. Leaf leachate had the longest uptake length, slowest uptake velocity, and lowest areal uptake rate. Algae leachate had intermediate uptake.

2.5 Discussion

2.5.1 DOM properties

Optical properties of leachate DOM differed depending on its source (Table 4, Figure 5). Algae-derived leachate exhibited more aromatic, humic signatures than wetland-derived leachate, contradicting a common assumption that DOM of microbial (algal) origin is less complex than DOM from vascular plants. Wetland plant leachate was more terrestrial than leaf leachate, with the lowest FI of all three leachates,

but was the least aromatic and freshest of all three leachates. Catalán et al. (2013) similarly found unexpected FI and SUVA values, with in-stream sources of DOM having lower FI (more terrestrial) and higher SUVA (more aromatic) than external sources. Unexpected optical index values could be a result of the leaching procedure used in this experiment. During leaching, I macerated organic material which could have shifted optical indices away from what is expected in natural waters, as more complex carbon molecules are released. Maceration was required in order to get leachate DOC concentrations high enough to raise stream DOC by the target 2 mg L^{-1}. In addition, *Cladophora* is highly structural compared to unicellular algae and may contribute humic, aromatic DOM when leached.

2.5.2 DOC Uptake

DOC uptake velocities of all three leachates fall within what is expected of injectate of that type (Mineau et al. 2016). Surprisingly, uptake velocities of leachates in Rye Creek are slower than what has been calculated for soil and leaf litter leachate releases in arctic and boreal streams (Fellman et al. 2009; Mutschlecner et al. 2017)(Table 6). High background DOC in arctic streams may prime stream bacteria for faster uptake (Seybold and McGlynn 2018). Background DOC during the time of our experiments was 0.79 mg C L^{-1}, which is low compared to that of other small streams. In addition, stream benthos organic matter (OM) content was low (1.21% OM). Low DOC uptake velocities in Rye Creek could also be tightly linked to ecosystem respiration. Both ER and GPP were low during the time of this experiment compared to reported stream metabolism rates in arctic streams in summer (Huryn et al. 2017). Lower rates of microbial activity in Rye Creek, and thus lower demand for organic C in

both streamwater and sediment may explain the slower uptake of DOM in Rye Creek compared to other studies.

DOM retention can occur via multiple processes, including adsorption to stream sediments (Mineau et al. 2016; Sobczak and Findlay 2002). Mutschlecner et al. (2017) found phosphorus (P) content in leachates to be the strongest predictor of whole-stream uptake; however, they posit that it could be due to strong P adsorption to sediments rather than biological uptake. I did not measure leachate P during this study; however, ammonium may also be retained in stream sediments due to adsorption (Triska et al. 1994). However, even though wetland and algae leachates had high N content compared to leaf leachate, abiotic retention was likely not significant. Desert stream sediments have extremely low clay content and do not adsorb ions as readily as clay sediments. In contrast, faster uptake of low-C:N DOM could be biological in nature, as desert streams are often N-limited (Grimm and Fisher 1986). The finding that DOC uptake was correlated with leachate C:N content aligns with other studies that have found nutrient content to be the main driver of uptake as opposed to DOM composition (Mutschlecner et al. 2017; Mineau et al. 2013). Fellman et al. (2009) found no difference in bulk DOC uptake across soil leachates, but saw differential uptake of the protein-like component of DOM, indicating a combination of DOM N content and composition control on stream uptake.

Similarly, this study supports the hypothesis that both DOM composition and N content control stream uptake. Though algae-derived leachate had an extremely low C:N, it exhibited signatures of relatively complex carbon compared to wetland-derived leachate and had a longer uptake length than wetland leachate. Leaf leachate had the longest uptake length and was composed of aromatic, humic organic matter and a high C:N ratio. Wetland leachate exhibited the fastest uptake kinetics and had an

intermediate C:N, but was less aromatic, fresher, and less or as humic as algae and leaf leachates. This study shows strong support for a control of both DOM composition and N content on stream uptake.

2.6 Conclusion

Headwater streams play an important role in regulating the export of DOM, and thus impact water quality downstream (Seybold and McGlynn 2018; Cole et al. 2007). In this study, I found that a small desert stream may be able to more quickly retain and process stream-derived sources of DOM (i.e., wetland and algae leachate) than a terrestrial source (leaf leachate) due to a combination of both more labile DOM properties and higher leachate N content. In addition, streams and other inland water can process large amounts of carbon, contributing to the global carbon cycle. Each year, inland waters store or respire approximately two thirds of the carbon they receive from the terrestrial environment while the remaining third is exported downstream to the ocean (Figure 6). Average removal of DOC from leachate injection experiments was 38.7 per cent, indicating just over a third of the C input to the stream is stored or respired. In comparison to the global carbon cycle, desert streams retain less C and export a larger fraction to downstream systems.

Table 4: Properties of Leachate DOM

Summary table of optical and chemical properties of leachates released into Rye Creek. Included is the fluorescence index (FI), humification index (HIX), freshness index (β:α), specific ultraviolet absorbance (SUVA, L mg^{-1} m^{-1}), and molar C:N. Statistics are reported as means with 1 SE in parentheses.

Leachate	FI	HIX	Freshness (β : α)	SUVA (L mg^{-1} m^{-1})	molar C:N
Algae	1.37 (±5e-04)	1.18 (±0)	0.75 (±5e-04)	2.27 (±0.01)	3.83 (±0.02)
Leaf	1.29 (±0)	0.18 (±0)	0.47 (±0)	2.76 (±0.04)	88.44 (±0.05)
Wetland	1.09 (±0.01)	0.18 (±0.01)	0.90 (±0)	1.60 (±0.03)	14.67 (±0.22)

Table 5: Uptake Metrics for DOM additions of algae, leaf, and wetland plant leachates

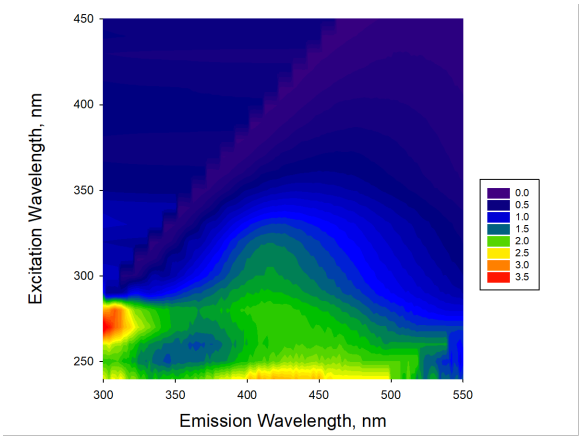
Uptake length (S_w), uptake velocity (V_f), and areal uptake rate (U) for releases of three leachates in Rye Creek.

Leachate	S_w (m)	V_f (mm min^{-1})	U (mg m^{-2} day^{-1})
Algae	181.97	0.238	5.07
Leaf	205.13	0.074	2.55
Wetland	158.20	0.302	6.83

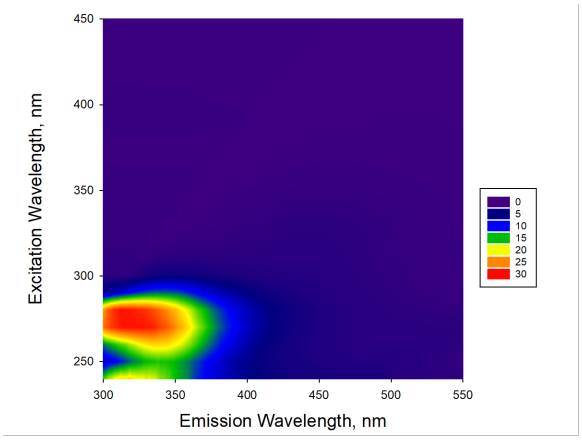
Table 6: DOC uptake metrics from reach-scale leachate additions

DOC uptake metrics obtained in this study, compared to other studies that also performed reach-scale leachate additions. Leachate type, Uptake velocity (V_f), and data source are shown.

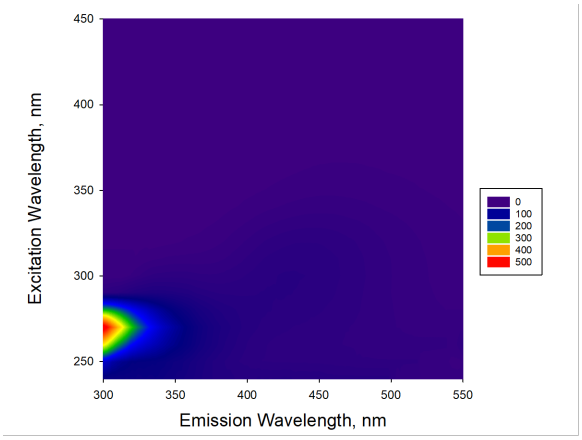
Leachate Added	V_f (mm min^{-1})	Source
Algae	0.238	this study
Leaf	0.074	this study
Wetland	0.302	this study
Leaf	2.83	Mutschlecner et al. (2017)
Leaf	1.13	Bernhardt and McDowell (2008)
Soil	1.26	Fellman et al. (2009)



(a) Algae



(b) Wetland



(c) Leaf

Figure 5: Representative EEMs obtained from leachates

Representative excitation-emission matrices (EEMs) from three leachates released during whole-stream uptake experiments. EEMs from algae, wetland, and leaf leachates are shown.

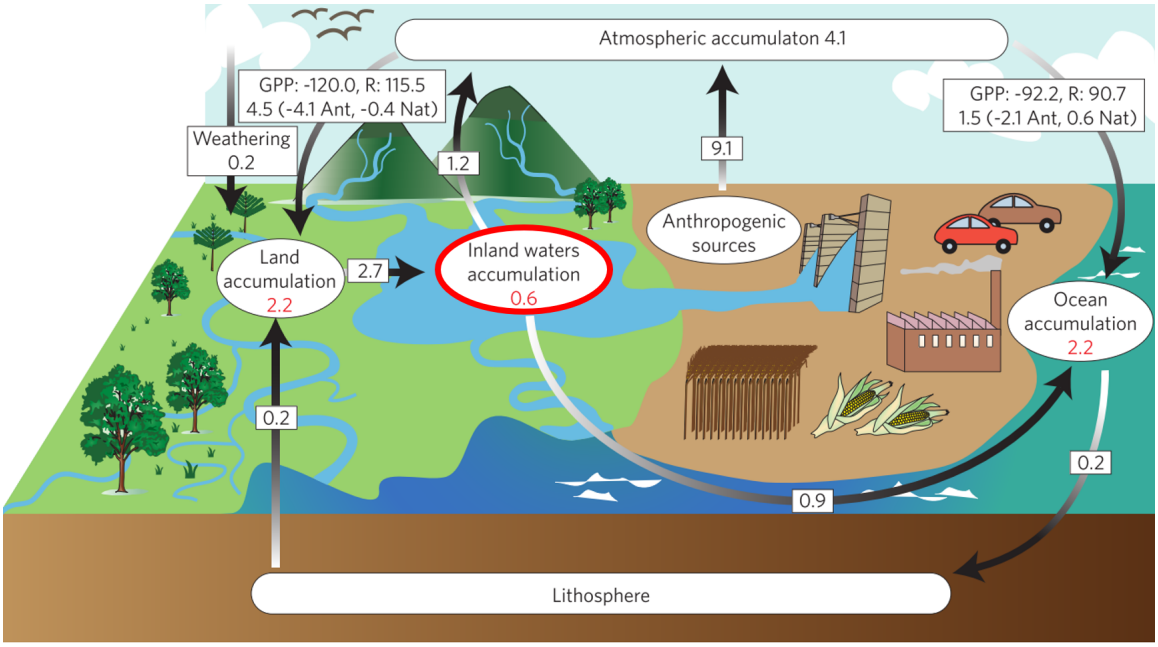


Figure 6: The global carbon cycle (Battin et al. 2009)

The global cycling of carbon with the role of inland waters (rivers, lakes, and streams) highlighted in a red circle. Inland waters receive 2.7 petagrams (Pg) of carbon from land, store 0.6 Pg, return 1.2 Pg to the atmosphere, and export 0.9 Pg to the ocean each year.

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