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Temporal dynamics of dissolved organic matter (DOM) in mountain lakes: the role of catchment characteristics

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ABSTRACT

Climate change is affecting mountain ecosystems by increasing vegetation coverage and altering meteorological conditions. These changes are likely to impact the timing and magnitude of dissolved organic matter (DOM) inputs to lakes from the surrounding catchment. We examined temporal dynamics of DOM using *in situ* optical sensors that measured DOM fluorescence (fDOM) through the ice-free season in five lakes with differing catchment characteristics. We also measured changes in lake level and compiled daily meteorological data from nearby weather stations. At a seasonal timescale, fDOM dynamics occurred in two phases. fDOM declined in the first phase, which lasted until late July/mid-August, and corresponded to a decline in lake level following spring snowmelt. This decline was more pronounced in lakes with more vegetated catchments. At a shorter timescale, fDOM increased following precipitation events with a 0-1 day lag. Rates of fDOM increase per cm change in lake level were greater in lakes with vegetated catchments. As climate change increases vegetation coverage, DOM will likely become more dynamic at daily and seasonal timescales and impact water transparency and productivity of mountain lakes.

Keywords: alpine, lakes, dissolved organic matter, glacier, vegetation coverage

INTRODUCTION

Dissolved organic matter (DOM) is a complex of substances that play a critical role in structuring lake ecosystems (Williamson et al. 1999, Solomon et al. 2015). Both autochthonous and allochthonous DOM serve as important energy and carbon sources for aquatic food webs (Pace et al 2004, Karlsson et al. 2012). The composition and amount of DOM in a lake can also affect nutrient availability, pH and bioavailability of heavy metals and organic contaminants (Landrum et al. 1987, Miskimmin et al. 1992). Chromophoric DOM (CDOM), a subset of DOM derived primarily from allochthonous sources, can have additional effects on primary production and thermal structure by regulating water transparency (Strock et al. 2017). Because absorption of solar radiation decreases as wavelength increases, CDOM is particularly important in controlling ultraviolet radiation transparency and exposure (Morris et al. 1995).

Inputs of DOM vary among lakes depending on the type and amount of terrestrial vegetation in the catchment (Canham et al. 2004, Winn et al 2009). Because DOM sources are connected to lakes through surface and groundwater inflows, loading also varies temporally due to meteorological conditions that affect hydrologic inputs. For example, rainfall events can generate short-term pulses of DOM to lakes (Raymond and Saiers 2010, Sadro and Melack 2012, Lambert et al. 2014). Similarly, spring snowmelt can deliver large quantities of allochthonous DOM in temperate and high latitude systems (Hood et al. 2003, Cai et al. 2008, Tiwari et al. 2018). Conversely, drought conditions decrease DOM loading as hydrologic inputs are reduced (Schindler et al. 1997, Strock et al. 2016). Due to variation in meteorological conditions, DOM concentrations in lakes can be highly dynamic at short-term, seasonal, and interannual time scales (Sobczak and Raymond 2015).

Much of our understanding of DOM dynamics in lakes is based on low elevation temperate systems. In mountain lakes, terrestrial DOM inputs are typically low due to limited vegetation coverage and low net primary production in lake catchments (Sadro et al. 2012, Rose et al. 2015). In addition, spring snowmelt often dominates the hydrologic cycle and serves as an important vector of terrestrial DOM inputs which can affect ecosystem metabolism (Sadro et al. 2011a, b, Jepson et al. 2019). However, mountain landscapes are being affected by climate change (Holsinger et al. 2019). Treelines are advancing upslope in many mountainous regions, (Danby and Hik 2007, Harsch et al. 2009) and in the Canadian Rockies, Trant et al. (2020) documented widespread advances in treeline, increases in tree density, and changes in tree growth form from krummholtz to erect trees over the past 100 years. Similarly, Davis et al. (2020) found an upslope treeline advance in the Canadian Rockies of between 0.2 and 2.0 m/year, although the rate of advance depends on region and tree species. In addition to treeline advance, the productivity of existing vegetation in alpine regions is expected to increase due to longer growing seasons (Baptist and Choler 2008, Gao et al. 2016, Davis et al. 2020). At the same time, patterns of summer and winter precipitation are changing, with many regions experiencing an earlier transition from snow to rain (Klos et al. 2014), increases in frequency and intensity of summer droughts (Schindler and Donohue 2006), and the potential for decreased snow accumulation in winter (Lapp et al. 2005). The rapid loss of glaciers is also altering the timing and magnitude of summer hydrologic inputs to mountain lakes (Milner et al. 2017). All of these changes have the potential to modify the timing and magnitude of DOM inputs to mountain lakes from the surrounding catchment.

As a first step towards better understanding the impacts of these changing environmental conditions on mountain lake ecosystems, we examined DOM dynamics in a set of five headwater lakes in the Canadian Rocky Mountains that differed in catchment characteristics. Specifically, lakes varied in vegetation coverage, presence of glaciers, and location above or below treeline. Together, these lakes represented a chronosequence of glacial loss and vegetation advance that is predicted to occur in the coming century. In each lake, we deployed *in situ* optical sensors that measured DOM fluorescence (fDOM), a commonly-used surrogate measure of terrestrial CDOM concentration (Pellerin et al. 2012), through the ice-free seasons of 2018 and 2019. Daily mean values were then evaluated for seasonal changes and for responses to meteorological conditions. Our objective was to compare lakes at daily, seasonal and interannual time scales in order to gain insight into the potential implications of changes in catchment characteristics and meteorological conditions on DOM dynamics.

METHODS

Study Sites

The five lakes included in this study were located in the central Rocky Mountain ecosystem in Banff and Yoho National Parks, Canada. Physical characteristics of each lake are summarized in Table 1. Zigadenus and Opabin were fed by small pocket glaciers that covered 13.2 and 4.7% of the catchment, respectively. These lake catchments also had relatively low (<5%) vegetation coverage. Catchments of the other three lakes lacked glaciers and varied in catchment vegetation coverage from 23% for Redoubt to 39% for Ptarmigan and 83% for Smith. Smith Lake was in the montane ecoregion and vegetation

coverage was dominated by coniferous forest of lodgepole pine (*Pinus contorta*) and Engelmann spruce (*Picea engelmannii*). The other four lakes were in the alpine ecoregion where vegetation coverage is primarily wildflowers and grasses with isolated stands of alpine larch (*Larix lyallii*). Areas not covered by glaciers or vegetation in our study lake catchments consisted of exposed bedrock, talus slopes, and moraines. Smith, Ptarmigan, Redoubt, and Zigadenus were all fed by spring freshets and permanent surface inflows, but inflow to Opabin was primarily groundwater fed with only a small seasonal surface inflow. Outflow from Opabin was also via groundwater, whereas Smith, Ptarmigan, Redoubt, and Zigadenus had surface outlets.

Meteorological and Hydrological Measurements

Meteorological conditions can be highly variable across small spatial scales in mountainous regions. Therefore, we obtained daily measurements of precipitation and air temperature from the closest meteorological stations to each study lake (Table 1). These stations were within 5 km of the four higher elevation lakes. The meteorological station for the lowest lake (Smith) was 27 km away but in the same valley (Bow River). For all lakes but Opabin, stations were operated by Alberta Environment and Parks or Environment and Climate Change Canada. These data are publicly available data at <https://agriculture.alberta.ca/acis/>. For Opabin Lake, we used data collected by the Lake O'Hara Alpine Hydrological Observatory (He and Hayashi 2019). For all stations, raw precipitation data were used without corrections for wind-induced undercatch of solid precipitation.

We evaluated hydrologic inputs to our study lakes by monitoring changes in lake level. In all lakes but Opabin, we installed PVC stilling wells that housed unvented Levellogger pressure transducers (Solinst, Georgetown ON, Canada) below the water surface. Barologger air pressure transducers (Solinst, Georgetown ON, Canada) were deployed nearby for converting absolute pressure recorded by Levelloggers to water levels. For Opabin Lake, we used measurements collected by a vented pressure transducer (In-Situ Inc., Level Troll, Fort Collins CO, USA) deployed as part of the Lake O'Hara alpine hydrological observatory (He and Hayashi 2019). All measurements were collected at 30-minute intervals and averaged to calculate daily mean lake levels.

Limnological Measurements

We quantified DOM dynamics using *in situ* optical sensors. In each lake, we deployed Cyclops-7F submersible fluorometers (Turner Designs Inc., San Jose CA) with integrated data loggers (Precision Measurement Engineering, Vista CA). These sensors measured the fluorescent component of DOM (fDOM) on exposure to ultraviolet radiation, and expressed concentrations in relative fluorescence units (RFU). Fluorometers were calibrated prior to deployment and suspended 1 m below the surface from a float anchored at or near the deepest part of each lake. Measurements were taken at hourly intervals, starting in late June-early July until late September-early October. This time period corresponds to the ice-free season in the four high elevation lakes. We evaluated raw hourly RFU measurements for extreme values (defined as observations >4.5 times the interquartile range above or below the median for a given day), and removed them prior to calculating daily means. Following Watras et al. (2011), daily mean fDOM values were

corrected for temperature-dependent fluorescence. Because concurrent measurements of daily mean turbidity averaged only 0.67 NTU (maximum=6.3 NTU), we did not correct for turbidity (Downing et al. 2012).

To assess the utility of fDOM as an indicator of DOM dynamics, we compared measurements from *in situ* fluorometers with two direct measures of DOM concentration. Water samples were collected at a depth of 0.5 m from each lake five or six times over the two-year study, for a total of 28 samples. Within 24 hours of collection, samples were filtered through pre-ashed Whatman GF/F filters, wrapped in foil and stored in a refrigerator until shipment. At the end of the sampling season, we shipped samples overnight on ice to an analytical laboratory at Miami University, where DOC and dissolved absorbance (m^{-1}) at 320 nm (a_{320}) were estimated using methods described in Williamson et al. (2014).

Data Analysis

In both years for all five lakes, daily mean DOM fluorescence exhibited high serial autocorrelation (autocorrelations for 1-day lag were all >0.79 , $\bar{X}=0.91$). Therefore, we used nonparametric tests to evaluate seasonal trends in each of the 10 time series. Pettit's tests were used to determine whether a time series had a single break or inflection point (Bates et al. 2012). In cases where a point was detected, Pettit's test also estimated the day at which that break or inflection occurred. We then used Mann-Kendall tests to evaluate monotonic trends in the phases before and after an identified break point (Hu et al. 2019). Sens slope estimates and 95% confidence intervals were calculated for each phase. Slopes of each phase were considered significantly different if confidence intervals did not

overlap. We also estimated Sens slopes for lake levels during the two phases of fDOM dynamics identified by Pettit's tests. All nonparametric time series analyses were conducted using the package TREND (Pohlert 2020) in the R statistical environment (R core team 2018).

In addition to seasonal trends, we also evaluated short-term fDOM dynamics in response to meteorological conditions. For these analyses, fDOM, lake level, and air temperature were all pre-whitened using ARIMA models (1,0,0 or 1,0,1). This operation accounts for the effects of serial autocorrelation and longer-term seasonal trends to facilitate analysis of daily fluctuations in variables (Yue et al. 2002). Data for each lake and year were pre-whitened separately. Precipitation had no autocorrelation and therefore did not need to be pre-whitened. Residuals of ARIMA models reflect deviations from predicted values for a given day based on the overall seasonal trend. We used residuals of these predictions in cross correlation analyses to examine relationships between meteorological drivers (precipitation and air temperature) and lake level, and between lake level and fDOM for time lags ranging from 0 days (i.e., measurements taken the same day) to 7 days (i.e., responses measured 7 days later). These analyses were performed in SPSS version 26 (IBM Corp. 2019).

RESULTS

Meteorological Conditions

The two years of study differed in seasonal patterns of temperature and precipitation. Monthly mean temperatures in the summer (May-August) averaged across the four meteorological stations were 1.3°C higher in 2018 than 2019 (Figure 1a). Total

annual precipitation from 1 October 2017 to 30 September 2018 was similar to 1 October 2018 to 30 September 2019 (683 mm vs. 673 mm). However, winter (October-April) precipitation was higher in 2018, with an average cumulative precipitation of 448 mm (67% of annual total) compared to 303 mm (44% of annual total) in 2019 (Figure 2b). In contrast, summer (May-August) precipitation was lower in 2018 than 2019 (223 vs. 309 mm), particularly in July and August when our sensors were deployed (Figure 2b).

Comparison of fDOM and Direct Measures of DOM

Across the five lakes and two seasons, fDOM fluorescence was strongly related to DOC concentration (Figure 2a: $F_{1,26}=149.0$, $p<0.0001$, $r^2=0.85$). Residuals of this regression were positively correlated with Julian date ($r=0.60$, $n=28$, $p=0.001$). fDOM fluorescence was even more strongly related to a_{320} (Figure 2b: $F_{1,26}=1566.5$, $p<0.0001$, $r^2=0.98$), which is an indicator of CDOM (Williamson et al. 1999). Residuals of this regression were not correlated with Julian date ($r=0.35$, $n=28$, $p=0.068$). Thus, daily measurements of fDOM provided an accurate representation of DOM and particularly CDOM dynamics.

Seasonal fDOM Dynamics

Seasonal patterns of fDOM varied among study lakes and between years (Figure 3). In all 10 time series, we detected a break point that indicated an inflection or other change in the seasonal trend between late July and mid-September (Table 2a). Seasonal break points were earlier in 2019 than 2018 by 25 and 13 days for Redoubt and Opabin, respectively. The opposite pattern was observed for Zigadenus, Ptarmigan, and Smith

where seasonal breakpoints were later in 2019 than 2018 by 11, 13, and 25 days, respectively (Figure 3).

In the first phase (i.e., before the break point), negative Sens slopes indicated that fDOM declined in all lakes in both years except for Redoubt in 2018 where there was no significant fDOM trend (Table 2a). These seasonal declines in fDOM were strongest in Smith and Ptarmigan, which had the highest catchment vegetation coverages (Table 2a, Figure 3d, e). Sens slopes in these lakes were an order of magnitude more negative (-0.086 to -0.015 RFU day⁻¹) than the other three lakes (-0.006 to 0.0002 RFU day⁻¹).

The rate of change in fDOM as estimated by Sens slopes changed significantly between the first and second phase in nine of the ten time series (Table 2a, Figure 3). In Smith Lake, Sens slopes shifted from strongly negative (-0.08 to -0.07 RFU day⁻¹) in the first phase to slightly positive (0.004 to 0.006 RFU day⁻¹) in the second phase in both years, exhibiting the largest magnitude of change in slope that we observed. We observed a similar pattern in Ptarmigan Lake but the initial fDOM decline was more gradual during the first phase (~ -0.02 RFU day⁻¹) and Sens slopes were not significantly different from 0 in the second phase for either year.

For the other three lakes, changes between the first and second phase differed among years (Table 2a, Figure 3). In glacially-fed Zigadenus and Opabin, rates of decline in fDOM in 2018 were slightly stronger in the second phase (-0.003 RFU day⁻¹ in both lakes) than in the first phase (-0.001 RFU day⁻¹ in both lakes). However, the opposite pattern occurred in 2019 when fDOM trends changed from negative in the first phase (-0.002 and -0.006 RFU day⁻¹ in Zigadenus and Opabin, respectively) to positive in the second phase (0.0003 and 0.001 RFU day⁻¹ in Zigadenus and Opabin, respectively). We observed an

increasing fDOM trend in Redoubt during the first phase of 2018 ($0.0002 \text{ RFU day}^{-1}$) and a decreasing trend after the mid-September break point ($-0.003 \text{ RFU day}^{-1}$). In contrast, Sens slopes in Redoubt for 2019 were slightly negative in both phases (-0.005 and -0.0004) and did not differ significantly.

Although seasonal trends were generally similar between 2018 and 2019, fDOM magnitudes varied between years in our study lakes (Figure 3). Differences were most pronounced in Smith where July fDOM measurements were higher in 2019 than 2018 (maximum difference between years was 3.2 RFU or approximately 1.76 mg/l DOC and $3.25 \text{ m}^{-1} \text{ a320}$), but values converged by late August (Figure 3e). As similar pattern was observed for Ptarmigan but early season differences were less pronounced (maximum early season difference between years was 0.33 RFU or approximately 0.18 mg/l DOC and $0.33 \text{ m}^{-1} \text{ a320}$). The other three lakes exhibited the opposite pattern where fDOM was higher in 2018 than 2019; however, the absolute magnitude of this difference between years was relatively small. In Redoubt, interannual differences increased slightly over the course of the ice-free season peaking in late August at 0.47 RFU (Figure 3c). For Opabin and Zigadenus, the interannual difference in fDOM peaked on August 12 at 0.49 and 0.35 RFU , respectively (Figure 3a, b).

Seasonal changes in lake level followed similar trends as fDOM. In all ten time series, we detected a break or inflection point that occurred between late July and mid-September (Table 2b). The lake level break point occurred an average of 4 days after the break point for fDOM, although the relative timing varied widely among lakes and years (Table 2a, b). During the first phase, lake levels declined significantly in both years for the three non-glacially fed lakes (Table 2b, Figure 4c, d, e). The rate of change in lake level

estimated by Sens slopes was higher in Ptarmigan and Smith (-0.11 to -0.58 cm day⁻¹) than in Redoubt (~ 0.08 cm day⁻¹). In contrast, lake levels did not change significantly during the first phase in either year for glacially-fed Zigadenus (Table 2b, Figure 4a). In Opabin, lake levels declined during the first phase in 2018 (-2.74 cm day⁻¹) but not 2019 (Table 2b, Figure 4b).

In the second phase of lake level change, rates of decline in water level weakened in both years for nonglacially-fed lakes Smith, Ptarmigan, and Redoubt (Table 2b). Specifically, Sens slopes shifted from negative (declining lake level) to positive (increasing lake level) between the first and second phases in Redoubt in both years and in Ptarmigan and Smith in 2018. In contrast, Sens slopes became more negative in the second phase in both years in glacially-fed Opabin and Zigadenus (Table 2b, Figure 4a, b). Opabin exhibited the highest rate of lake level decline that we observed, with a Sens slope of -3.44 cm day⁻¹ during the second phase of 2018.

Short-term fDOM Dynamics

In addition to seasonal changes, fDOM also exhibited short-term changes in response to meteorological conditions that affected hydrologic inputs. In all time series except for Opabin in 2018, precipitation was positively correlated with changes in lake level. Cross correlations between precipitation and residual lake level (after pre-whitening with ARIMA) were significant for lags of 0 and/or 1 day for the other nine time series (Figure 5a, b). Lags of 2 days and longer were not significant for any of the time series. In glacially-fed Zigadenus, pre-whitened residual lake level was also positively correlated with residual air temperature for lags of 1 ($r_{2018}=0.31$, $r_{2019}=0.30$) and 2 days ($r_{2018}=0.31$,

$r_{2019}=0.35$). However, no significant cross correlations between air temperature and lake level were observed in Opabin, the other glacially-fed lake.

Changes in lake level were in turn associated with changes in fDOM. In all five lakes, cross correlations between residual lake level and residual fDOM were positive and significant in 2019 for 0 and/or 1 day lags but not lags of 2 days or more (Figure 6b). In 2018, no cross correlations were significant for any lags (Figure 6a). The connection between precipitation events and fDOM responses in 2019 was also supported by cross correlations directly between the two variables. For Smith lake, the cross correlation was significant ($p<0.05$) with a 0-day lag ($r=0.22$), and for Ptarmigan, Opabin, and Zigadenus the 1-day lag was significant ($r_{\text{Ptarmigan}}=0.22$, $r_{\text{Opabin}}=0.22$, $r_{\text{Zigadenus}}=0.35$). Redoubt was the only lake that did not have any significant cross correlations between precipitation and fDOM. Cross correlations between residual air temperature and fDOM were not significant at any lag for any lake-year combination.

Although all five lakes had significant fDOM responses to precipitation in 2019, the magnitude of fDOM responses to changes in lake level differed among lakes. Linear regressions of residual lake level (for the lag with the highest correlation in that lake) as the predictor vs. residual fDOM differed in slope across the five study lakes (Figure 7). Smith Lake had the highest slope, indicating this lake had the largest change in fDOM per unit change in lake level (0.07 RFU cm^{-1}). Ptarmigan had the second highest slope, followed by Redoubt, Zigadenus, and Opabin which was two orders of magnitude lower than Smith but still significantly different from zero ($F_{1,71}=17.07$, $p<0.001$).

DISCUSSION

Despite experiencing similar climatic conditions, fDOM dynamics varied widely among lakes. These among-lake differences in fDOM dynamics corresponded with variation in catchment vegetation coverage. Smith Lake (80% vegetation coverage) exhibited the highest variability in fDOM between years, over the ice-free season, and in short-term responses to hydrologic inputs. Ptarmigan Lake (40% vegetation coverage) had intermediate levels of variation at annual, seasonal, and short-term time scales, and Redoubt, Opabin, and Zigadenus Lakes (<25 vegetation coverage) all had low fDOM variability. Because these lakes represent a chronosequence of increasing vegetation coverage predicted over the next century, our results suggest DOM inputs will become more dynamic as mountain landscapes respond to climate change. This change in DOM dynamics has potentially important implications for lake ecosystems. For example, DOM strongly regulates water transparency, particularly in the UV range. As DOM inputs increase, primary production may increase due to a reduction in UV-induced photoinhibition (Elser et al. 2020), whereas the amplitude of zooplankton diel vertical migration may decrease (Fischer et al. 2015). Higher DOM inputs may also stimulate heterotrophic bacterial production in spring when primary production is low and through the summer below the thermocline (Sadro et al. 2011a, b).

Seasonal fDOM Dynamics: In both years, all five lakes exhibited a two-phase trend in fDOM dynamics. fDOM decreased during the first phase, which generally lasted until late July or mid-August and corresponded to the time period following spring snow melt in the region (Pomeroy and Whitfield. 2016). In other high latitude or elevation systems, DOM concentrations peak during spring snowmelt and decline over the course of the season

(Boyer et al. 1997, Finlay et al. 2006, Ågren et al. 2010). As the accumulated snowpack melts, DOM derived from terrestrial plant growth the preceding summer is flushed through saturated soils to streams and freshets (Ågren et al. 2008, Laudon et al. 2011) and subsequently to lakes. Following this pulse, fDOM decreased in the first phase, likely due to a combination of consumption by heterotrophic bacteria (Sadro et al. 2011a, b) and photodegradation (Cory et al. 2014). Because substantial snowmelt precedes ice breakup on mountain lakes (Caldwell et al. 2021), large quantities of DOM can be delivered before lakes become ice free (Cortes et al. 2017). Although we deployed sensors within a week of ice off, we may have missed the initial increase in DOM to a spring peak. Nevertheless, we did observe declines in DOM fluorescence during the first phase that were highest in Smith Lake and decreased as a function of catchment vegetation coverage in the other study lakes.

Although decreasing fDOM during the first phase was observed in both 2018 and 2019, there were interannual differences that were most pronounced in Smith and Ptarmigan. In these two lakes, the first phase lasted approximately two weeks longer and fDOM declined 20% more slowly in 2019. In contrast, interannual differences in slopes and in the first phase were minor for the other three lakes. Winter precipitation was higher in 2018, but warmer temperatures in May likely initiated earlier snowmelt. Consequently, the decline in fDOM and water level during the first phase started and ended sooner in 2018 compared to 2019. The effects of an earlier spring would be most apparent in Smith and Ptarmigan, where more vegetated catchments have the potential to deliver significant quantities of allochthonous DOM during spring snowmelt.

In contrast to the first phase, seasonal changes in DOM fluorescence were more variable among lakes and years during the second phase. In Smith, fDOM increased over time in both years despite the fact that lake levels increased in 2018 but decreased in 2019. These fDOM increases partly reflect pulsed inputs of organic matter from the catchment during precipitation events (see *Short-term fDOM Dynamics* below). Increased summer temperatures also likely accelerated the breakdown of terrestrial vegetation in the catchment (Mzobe et al. 2018, Wen et al. 2020). In addition, DOM stored in the hypolimnion since spring could move to surface waters during mixing events or as the lake turns over in September (Osburn et al. 2001). In Ptarmigan, fDOM stabilized in the second phase regardless of trends in lake level. The lack of an increase in fDOM relative to Smith is again consistent with lower levels of vegetation catchment coverage, as either less DOM was stored in the hypolimnion or transported during precipitation events. In the other three lakes, fDOM continued to slowly decline in the second phase of 2018, and stayed stable or increased slightly in 2019. The patterns for lakes in these rocky catchments suggest that inputs of DOM to surface water from the catchment or hypolimnion during the second phase were limited.

Short-term fDOM Dynamics: In all five study lakes, we observed short-term changes in fDOM in response to precipitation events. However, these responses were only observed in 2019, the year with higher precipitation totals in June, July, and August. Lake levels did increase with precipitation in 2018 for all lakes but Opabin (which is fed via groundwater rather than surface inflows), indicating that there were hydrological responses. However, no concurrent or subsequent changes in fDOM were observed in any lake that year. Dry conditions can decrease terrestrial decomposition rates (Zhang et al. 2008) and alter

groundwater flowpaths through deeper soil horizons where organic matter is less prevalent (Boyer et al. 1997, Somers and McKenzie 2020). In addition, dry conditions can reduce or eliminate cryptic wetlands that can be important sources of DOM to mountain lakes (Winn et al. 2009). Each of these responses would reduce DOM inputs during and after precipitation events. Dry antecedent conditions can also reduce DOM export during minor precipitation events by reducing hydrologic connectivity (Tulaney et al. 2016, Szokakan-Emilson et al. 2017). Conversely, dry antecedent conditions can enhance DOM export during large storm events due to increased overland flow over dry, hardened soils (Jane et al. 2017, McMillan et al. 2018). That likely happened in August 2018 in Redoubt, Opabin, and Zigadenus. Each of the sharp increases in fDOM occurred as >8 mm of precipitation fell that day and the day before, following eight or more consecutive days of minimal precipitation (<2 mm in total).

Although all lakes responded to precipitation with increases in fDOM in 2019, the magnitude of fDOM responses varied among lakes as a function of vegetation catchment coverage. Smith Lake had the largest change in fDOM per unit change in lake level, followed by Ptarmigan, Redoubt, Zigadenus, and Opabin. Previous studies have demonstrated a relationship between the composition and coverage of catchment vegetation and DOM variability in streams (Hood et al. 2006, Cool et al. 2014, Schwab et al. 2017). In particular, trees can be a significant source of DOM during rainfall events via throughfall and litter leachates (Van Stan and Stubbins 2018). Smith Lake had the highest vegetation coverage and was the only study lake below treeline. Those two factors together help explain the three-fold higher fDOM response to lake level change in Smith compared to the other study lakes. In contrast, fDOM levels changed relatively little in

response to hydrologic events in the three lakes with sparsely-vegetated catchments. The minimal fDOM response in Opabin was also likely affected by much larger fluctuations in lake level compared to the other lakes. Without a surface outlet, lake levels in Opabin fluctuated over a 3 m range whereas the other study lakes varied in lake level by less than 10 cm.

Our results suggest that catchment composition, specifically vegetation coverage, plays a key role in fDOM dynamics. In contrast, catchment size and areal vegetation coverage was not strongly related to fDOM dynamics, as evidenced by the fact that Smith Lake was most dynamic despite having the smallest catchment and similar or lower amounts of vegetation coverage than other lakes (18 ha for Smith vs. 10-15 ha for Redoubt, Opabin, and Zigadenus and 59 ha for Ptarmigan). Olson et al. (2018) also found that variation in catchment composition, specifically percent vegetation coverage, caused wide variation in a_{320} across 33 mountain lakes. Because lake size (surface area and depth) were positively correlated with catchment size, a_{320} was better explained by catchment composition rather than areal coverage.

In contrast to vegetation, the presence of glaciers appeared to have little influence on fDOM dynamics. Both Opabin and Zigadenus had similar seasonal trends as Redoubt, which also had little vegetation coverage but no glacier in its catchment. These similarities in fDOM dynamics occurred despite the fact that seasonal hydrological patterns in the two glacially-fed lakes differed from nonglacially-fed lakes. In addition, lake levels in Zigadenus increased in response to higher air temperatures, presumably due to higher rates of glacial melt. However, fDOM changed relatively little over the course of the ice-free seasons. In both Zigadenus and Opabin, glacial meltwater flows through moraines that are largely

devoid of vegetation before entering the lake. Lafrenière and Sharp (2004) also found that most DOC in a glacial meltwater inflow to Bow Lake, Alberta was of microbial origin and little was derived from terrestrial vegetation. Similarly, Hood and Scott (2008) found lower DOC concentrations in streams fed by glaciers compared to nonglacially-fed streams. Although glacial meltwater can influence other biogeochemical cycles in lakes (Slemmons et al. 2013), effects on DOM appear to be minimal. Therefore, glacial loss may have less of a direct impact on DOM dynamics in lakes. However, indirect effects of glacial loss via an increase in habitat suitable for vegetation growth could be substantial (Williamson et al. 1999).

In our analyses, we quantified DOM dynamics using high frequency measurements of DOM fluorescence. The fluorescing component of DOM is a subset of CDOM, which is derived largely from the decomposition of terrestrial plant matter (Zhang et al. 2021) and reflects both the quantity and freshness of DOM in lakes (Hansen et al. 2016). Although autochthonous DOM is generally low in mountain lakes (Rose et al. 2015), concentrations peak in summer when algal production is highest (Miller and McKnight 2010). In our study lakes, residuals of regressions between fDOM and DOC were positively correlated with Julian date, suggesting there were additional sources of DOC as the season progressed that were not reflected in fDOM. Therefore, the patterns reported here are more applicable to allochthonous DOM inputs.

Mountain ecosystems are particularly sensitive to the effects of climate change (Moser et al. 2019, Sadro et al. 2019). Increasing temperatures and altered precipitation regimes are impacting mountain landscapes by advancing treelines, and enhancing vegetation growth (Rogora et al. 2018, Winkler et al. 2018). These changes will affect

mountain lakes by increasing inputs of allochthonous DOM, particularly in higher elevation lakes where catchment vegetation will increase the most. Our results suggest that these inputs will also become more dynamic. In addition to experiencing larger seasonal declines following snowmelt and more variability between years, lake DOM levels will change more dramatically in response to hydrologic events. This loss of resistance, a key component of ecological resilience (Folke et al. 2004), could have important consequences for foodwebs, light and thermal profiles, and other aspects of ecosystem structure and function.

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Table 1. Physical characteristics of study lakes. Vegetation coverage is from Olson et al. (2018) and glacier coverage is based on 2010 LandSat images. Banff CS, Pika Run, and Skoki Mountain meteorological stations are operated by the Alberta Ministry of Agriculture and Forestry. Daily mean temperature and precipitation measurements are publicly available at <https://agriculture.alberta.ca/acis/>. The Opabin Plateau meteorological station is part of the Lake O’Hara Alpine Hydrology Observatory (He and Hayashi 2019).

Lake	Latitude/ Longitude	Elevation (m a.s.l.)	Surface Area (ha)	Maximum Depth (m)	Volume (X 10 ⁴ m ³)	Catchment Area (ha)	% Vegetation Coverage in Catchment	% Glacier Coverage in Catchment	Nearest Meteorological Station (km from lake)
Zigadenus	51° 30' 02" 116° 05' 03"	2283	14.0	22.0	165.7	256	4.9	13.1	Skoki Mountain (4.8)
Opabin	51° 20' 27" 116° 18' 44"	2270	3.2	10.9	7.2	262	4.0	4.3	Opabin Plateau (0.7)
Redoubt	51° 29' 04" 116° 04' 38"	2393	19.1	11.0	85.4	68	22.9	0	Pika Run (3.4)
Ptarmigan	51° 28' 25" 116° 04' 24"	2332	28.0	21.3	195.0	151	39.3	0	Pika Run (3.7)
Smith	51° 14' 58" 115° 55' 32"	1560	3.0	9.7	16.7	22	83.0	0	Banff CS (26.8)

Table 2. Results of a) fDOM and b) lake level time series trend analysis. Date of phase change for fDOM and lake level were determined by Pettitt's test, which were significant for all 10 time series ($U > 772$, $p < 0.01$ in all cases). Significance of trends in each phase were determined by Mann-Kendall test and are reported as approximated Z-scores. Significant ($p < 0.05$) results are indicated by asterisks. Slopes and 95% confidence intervals were based on Sens slope estimators. Units for fDOM are in RFU/Day. Units for lake level are in cm/Day. Changes in slope between the first and second phase were determined using confidence intervals.

a) fDOM

Lake	Year	Date of Change	First Phase		Second Phase		Change in Slope
			Slope (95% Conf. Int.)	Z-Score	Slope (95% Conf. Int.)	Z-Score	
Zigadenus	2018	10-Aug	-0.001 (-0.0016/-0.0006)	-3.85*	-0.003 (-0.004/-0.0025)	-8.07*	Yes
	2019	21-Aug	-0.002 (-0.003/-0.001)	-4.14*	+0.0003 (0.000/+0.0001)	1.14	Yes
Opabin	2018	10-Aug	-0.001 (-0.0023/-0.0007)	-3.25*	-0.003 (-0.004/-0.0026)	-8.10*	Yes
	2019	28-Jul	-0.006 (-0.007/-0.005)	-5.03*	+0.001 (+0.0007/+0.002)	+4.70*	Yes
Redoubt	2018	14-Sep	+0.0002 (-0.0003/+0.01)	+0.93	-0.003 (-0.004/-0.0026)	-5.62*	Yes
	2019	20-Aug	-0.005 (-0.006/-0.004)	-6.67*	-0.0004 (-0.006/0.000)	-2.01*	No
Ptarmigan	2018	26-Jul	-0.021 (-0.023/-0.020)	-7.11*	+0.0003 (-0.001/+0.001)	+0.56	Yes
	2019	8-Aug	-0.015 (-0.017/-0.013)	-7.57*	-0.0004 (-0.001/+0.0002)	+1.36	Yes
Smith	2018	24-Jul	-0.086 (-0.098/-0.074)	-6.33*	+0.006 (+0.005/+0.008)	+6.90*	Yes
	2019	18-Aug	-0.074 (-0.089/-0.052)	-6.96*	+0.004 (+0.001/+0.007)	+2.32*	Yes

b) Lake Level

Lake	Year	Date of Change	First Phase		Second Phase		Change in Slope
			Slope (95% CI)	Z-Score	Slope (95% CI)	Z-Score	
Zigadenus	2018	26-Aug	-0.014 (-0.029/+0.001)	-1.86	-0.070 (-0.088/-0.049)	-5.03*	Yes
	2019	17-Aug	-0.011 (-0.035/+0.015)	-0.96	-0.093 (-0.115/-0.073)	-6.18*	Yes
Opabin	2018	13-Aug	-2.739 (-3.975/-1.589)	-5.51*	-3.441 (-4.174/-2.867)	-7.24*	No
	2019	28-Jul	-0.553 (-2.350/+0.500)	-1.27	-2.425 (-2.888/-1.825)	-5.54*	Yes
Redoubt	2018	9-Sep	-0.077 (-0.092/-0.055)	-5.51*	+0.050 (-0.004/+0.109)	1.75	Yes
	2019	29-Jul	-0.085 (-0.184/-0.011)	-2.28*	+0.014 (+0.003/+0.025)	+2.38*	Yes
Ptarmigan	2018	13-Aug	-0.575 (-0.606/-0.544)	-7.70*	+0.105 (+0.081/+0.122)	+5.53*	Yes
	2019	21-Aug	-0.265 (-0.318/-0.236)	-8.04*	-0.031 (-0.050/-0.012)	-2.86*	Yes
Smith	2018	10-Aug	-0.108 (-0.129/-0.086)	-6.39*	+0.033 (+0.019/+0.048)	+4.07*	Yes
	2019	22-Aug	-0.562 (-0.690/-0.431)	-7.82*	-0.062 (-0.074/-0.048)	-6.78*	Yes

Figure 1. a) Monthly mean air temperature and b) monthly total precipitation for 2018 and 2019. Mean air temperature and monthly precipitation are averaged across the four meteorological stations in close proximity to study lakes. Time series are plotted from October to September to correspond to winter and summer seasons. Error bars represent ± 1 standard deviation across the four meteorological stations. Grey bars represent period during which sensors were deployed.

254x190mm (72 x 72 DPI)

Figure 2. a) Scatter plots of mean daily fDOM (RFU) measured with optical sensors vs. a) DOC concentration (mg/l) and b) a₃₂₀ absorbance (m⁻¹) in water samples collected the same day. Symbols represent study lakes. Lines represent best fit linear regressions as a function of fDOM for both direct measures of dissolved carbon (DOC concentration: $Y=0.45 + 0.55X$, a₃₂₀: $Y=0.38 + 0.1.01X$).

254x190mm (72 x 72 DPI)

Figure 3. Daily mean DOM fluorescence (RFU) vs. date in 2018 and 2019 for a) Zigadenus Lake, b) Opabin Lake, c) Redoubt Lake, d) Ptarmigan Lake, and e) Smith Lake.. Mean values are based on hourly measurements taken in a calendar day. Shaded symbols correspond to observations in the first phase and open symbols correspond to observations in the second phase, as estimated using Pettit's tests (Table 2a). Note differences in scale of Y axes.

190x254mm (96 x 96 DPI)

Figure 4. Daily mean lake level (m a.s.l.) vs. date in 2018 and 2019 for) Zigadenus Lake, b) Opabin Lake, c) Redoubt Lake, d) Ptarmigan Lake, and e) Smith Lake. Mean values are based on measurements taken at 30 minute intervals in a calendar day. Shaded symbols correspond to observations in the first phase and open symbols correspond to observations in the second phase, as estimated using Pettit's tests (Table 2b).

190x254mm (96 x 96 DPI)

Figure 5. Cross correlation functions for time lags of 0 and 1 day between precipitation and lake level in a) 2018 and b) 2019. Daily mean lake levels were pre-whitened using ARIMA and residuals were used in cross correlation analysis. Because daily precipitation was not autocorrelated, raw values were used in cross correlation analysis. Dashed horizontal line indicates the critical value of r for significance at $p < 0.05$. Lags of 2 days or more were not significant for any lake in either year.

254x190mm (72 x 72 DPI)

Figure 6. Cross correlation functions for time lags of 0 and 1 day between lake level and fDOM in a) 2018 and b) 2019. Both daily mean lake level and daily mean fDOM were pre-whitened using ARIMA and residuals were used in cross correlation analysis. Dashed horizontal line indicates the critical value of r for significance at $p < 0.05$. Lags of 2 days or more were not significant for any lake in either year.

254x190mm (72 x 72 DPI)

Figure 7. Slopes of linear regressions between change in fDOM (RFU) vs. change in lake level (cm) for five study lakes in 2019. Both variables are residuals of ARIMA pre-whitening. Error bars represent standard errors of slope estimates.

254x190mm (72 x 72 DPI)