

Seasonal Manganese Transport in the Hyporheic Zone of a Snowmelt-Dominated River (East
River, Colorado)

Thesis

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Abstract

Manganese (Mn) plays a critical role in river water quality since Mn-oxides serve as sorption sites for contaminant metals such as copper, zinc, and lead. Here, I measure and model annual changes in river water-groundwater interaction and $\text{Mn}_{(\text{aq})}$ transport in an alpine streambed influenced by spring snowmelt (East River, Colorado). In field observations and models, oxygenated river water containing dissolved organic carbon (DOC) mixes with groundwater rich in reduced manganese in the riverbed. The depth of mixing is greatest during spring snowmelt when river discharge is greatest, leading to an influx of DOC, dilution of $\text{Mn}_{(\text{aq})}$, and net respiration of Mn-oxides, despite an enhanced supply of oxygen. Conversely, a shift to upwelling conditions over the subsequent baseflow period allows for groundwater rich in $\text{Mn}_{(\text{aq})}$ to mix with oxygenated river water in the shallow subsurface, resulting in net accumulation of Mn-oxides until the bed freezes in winter. To explore potential responses of Mn transport to different climate-induced hydrological regimes, I model three hydrograph scenarios (Historic, Low-snow, and Storm) for the Rocky Mountain region. In a warming climate with less snowpack and a longer baseflow season, $\text{Mn}_{(\text{aq})}$ oxidation will be favored in the upper riverbed sediments over more of the year, which may increase the sorption capacity of the streambed for other metals.

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Chapter 1. Introduction

The hyporheic zone, or shallow streambed where river water and groundwater mix, hosts biogeochemical reactions that impact watershed functions and water quality [Boulton et al. 1998; Boano et al. 2014]. This thin zone disproportionately influences nutrient cycling [Triska et al. 1989; Triska et al. 1993; Mulholland and DeAngelis 2000] and contaminant fate and transport [Manamsa et al. 2016; Xu et al. 2017; Weatherill et al. 2018]. Hyporheic zones provide surface area for microbial attachment and function [Feris et al. 2003; Fischer et al. 2005], and hyporheic flow delivers a mixture of potentially limiting reactants from river water and groundwater. The mixing of these chemically distinct waters in the presence of active microbial communities makes hyporheic zones particularly efficient bioreactors [Stanford & Ward 1988; Baxter & Hauer 2000; Peralta-Maraver et al. 2018].

The respiration of microorganisms generally involves the coupling of an electron donor, such as an organic carbon compound, with a terminal electron acceptor (TEA) based on thermodynamic favorability [Jin & Bethke 2003; LaRowe & Van Cappellen 2011]. In hyporheic zones, river water can be a source of dissolved oxygen (DO), the most favorable TEA, but streambed sediments can be a source of others such as manganese (Mn) and iron (Fe), leading to vertical gradients in redox reactions in streambeds. When DO is available, microbial oxidation of reduced metals such as $Mn_{(aq)}$ (acting as an electron donor) may be thermodynamically favorable [Harvey & Fuller 1998; Robbins & Corley 2005; Butler et al. 2008]. In addition to microbial oxidation, Mn-oxides can also precipitate abiotically [Diem & Stumm 1984; Emerson 2000], but

microbial oxidation tends to dominate [Harvey & Fuller 1998; Kay et al. 2001; Fuller & Bargar 2014]. Microbial oxidation rates of $Mn_{(aq)}$ are pH-dependent, but generally increase with availability of DO, $Mn_{(aq)}$, and Mn oxidizing microbial biomass [Hem 1981; Fuller & Harvey 2000; Robbins & Corley 2005; Fuller & Bargar 2014].

Mn-oxides play an important role in adsorbing other contaminant metals such as nickel, cobalt, copper, zinc, and lead. In a field tracer study in Pinal Creek, Arizona, Fuller & Harvey [2000] concluded that dissolved heavy metals in stream water were attenuated by adsorption onto Mn-oxides in the hyporheic zone. Kay et al. [2001] conducted a column study using sediments from the same contaminated streambed and found that $Mn_{(aq)}$, cobalt, and nickel adsorbed to Mn-oxides, although the reversibility of this adsorption varied. Further batch experiments showed that zinc attenuation was controlled by Mn-oxide formation under near-neutral pH conditions [Fuller & Bargar, 2014]. Furthermore, Schaffner et al. [2015] effectively demonstrated that enriching acidic streams with Mn-oxides and hydroxides could be a cost-efficient means of remediating heavy metals such as cadmium, cobalt, nickel, and zinc.

Seasonal changes in hyporheic exchange can alter Mn-oxides via changes in river water-groundwater mixing and therefore the supply of DO, $Mn_{(aq)}$, and dissolved organic carbon (DOC) to microbial communities [Battin 1999; Wong & Williams 2009; Fellman et al. 2009]. In snowmelt-dominated rivers, large variations in stream discharge and dissolved chemical concentrations occur over the year, from low discharge during late summer and fall to high discharge during spring snowmelt [Cameron 1996]. Up to 60% of the carbon flux delivered to alpine rivers occurs during spring [Holmes et al. 2011; Raymond et al. 2007; Raymond et al. 2016; Spencer et al. 2009], which can stimulate microbial respiration and metal processing in the hyporheic zone. Baalousha et al. [2018] noted that concentrations of trace elements such as $Fe_{(aq)}$ and $Mn_{(aq)}$ declined in an

alpine stream during spring snowmelt compared to baseflow conditions, which could indicate retention in the streambed, in addition to dilution. As stream discharge increases during snowmelt, hyporheic mixing may extend deeper into the riverbed due to greater shear stresses and sediment mobilization, and groundwater flow may reverse, transporting stream-derived oxygen and metals to greater depths where they can react [Boulton et al. 1998; Harvey & Fuller 1998; Harvey et al. 2003; O'Connor & Harvey 2008].

Upland headwater catchments, such as those in the Rocky Mountains of the western US, are already experiencing accelerated rates of climate change. Under future scenarios, snow pack thickness and duration are predicted to decrease [Mann et al. 2012], and spring snowmelt is expected to occur earlier in the year [Stone et al. 2002]. Long-term decreases in snow pack thickness and annual runoff will impact river water-groundwater exchange [Cameron 1996; Wondzell 2011; Mann et al. 2012], carbon mineralization [Spencer et al. 2008; Fellman et al. 2009; Spencer et al. 2009a; Holmes et al. 2011], metal oxidation [Harvey & Fuller 1998; Robbins & Corley 2005; Butler et al. 2008], and microbial community function and dynamics [Hopkinson et al. 1998; Baker et al. 1999; Battin 1999]. Specifically, Striegl et al. [2005] predicted that DOC export will decrease disproportionately with declining stream flow as a result of increased microbial processing as residence times lengthen. Solute exchange across the sediment-water interface may also decrease, which could limit the oxidation of $Mn_{(aq)}$ [Robbins & Corley 2005; Butler et al. 2008; Spencer et al. 2008]. A longer baseflow season is expected to result in a prolonged period of upwelling groundwater, which may promote reducing conditions and further limit oxidation at depth [Battin 1999; Cardenas & Wilson 2007]. As hyporheic connectivity decreases with diminishing stream flow and the DO supply from river water declines, it is unclear how the hyporheic zone will retain metals.

In this study, my goal was to understand changes in Mn transport within an alpine hyporheic zone over the annual hydrograph and explore potential responses to changing hydrograph scenarios. To accomplish this, I monitored vertical seepage rates using temperature sensing and collected seasonal profiles of pore water chemistry from August 2016 through August 2017. I used field observations to develop a one-dimensional reactive transport model to simulate seasonal changes in Mn transport. I then modeled three potential scenarios of annual river and hyporheic flow dynamics to test the influence on Mn mobility and transport. I show that larger snowmelt events enhance Mn-oxide respiration in the shallow streambed due to deeper penetration of DOC from river water. Conversely, a longer baseflow season and smaller snowmelt event limits the supply of DOC from river water and increases the supply of $\text{Mn}_{(\text{aq})}$ from groundwater leading to a greater rate of Mn oxidation.

Chapter 2. Methods

2.1 Field Site

East River is an alpine stream that lies within the Gunnison River Basin in the southern Rocky Mountains of Colorado (Figure 1). Elevation of the watershed ranges from approximately 2445 to 4100 m [Liu et al. 2018], and most precipitation falls in the form of snow [Winnick et al. 2017]. Snowmelt is the primary source of runoff to East River, with peak discharge occurring between the months of May and July (Figure 2). Baseflow conditions prevail from August until the bed freezes in winter. The East River watershed is mostly undeveloped, apart from the city of Crested Butte [Theobald et al. 1996; Spahr 1999]. The catchment is underlain by the Cretaceous Mancos Shale formation, which mainly consists of gray siltstone and shale [Morrison et al. 2012]. The Mancos Shale is overlain by Quaternary glacial and alluvial sediments.

The study site lies northeast of Mount Crested Butte (Figure 1). Samples were collected at three locations, A, B, and C, around a characteristic meander on the East River floodplain [Winnick et al. 2017]. The site elevation is 2760 m, and the approximate channel slope is 0.008. The streambed at the site is primarily composed of gravel, with calcium-rich plagioclase feldspar and carbonate clasts.

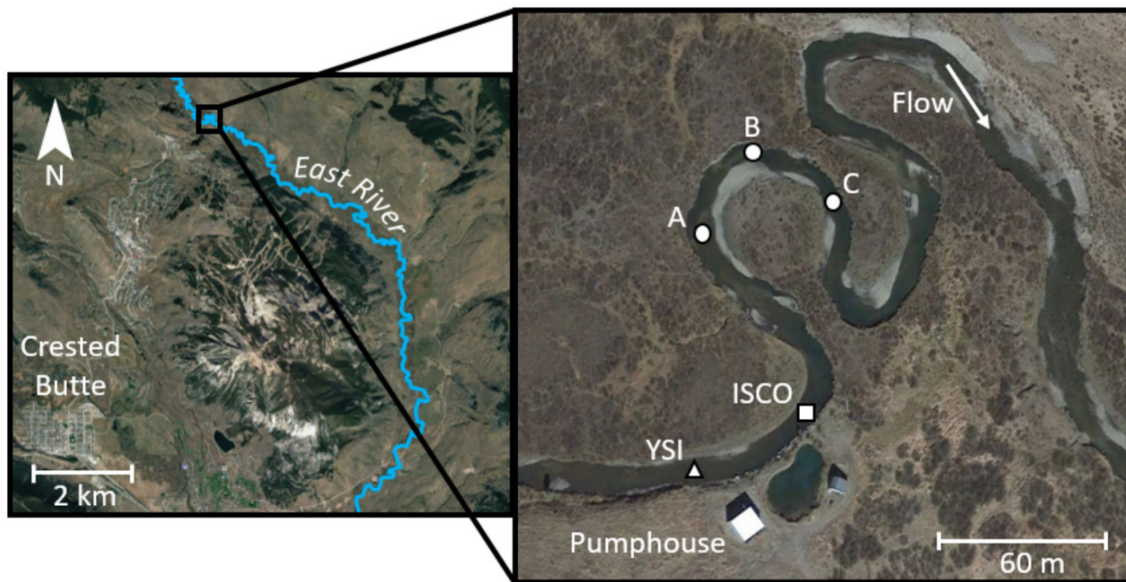


Figure 1. Aerial image of East River study site (38.923540687, -106.951006981). A, B, and C denote locations of temperature monitoring and geochemical sampling from August 21, 2016 through August 21, 2017. Daily average discharge is monitored near the Pumphouse location. The YSI and ISCO sampler are maintained by the Lawrence Berkeley National Laboratory.

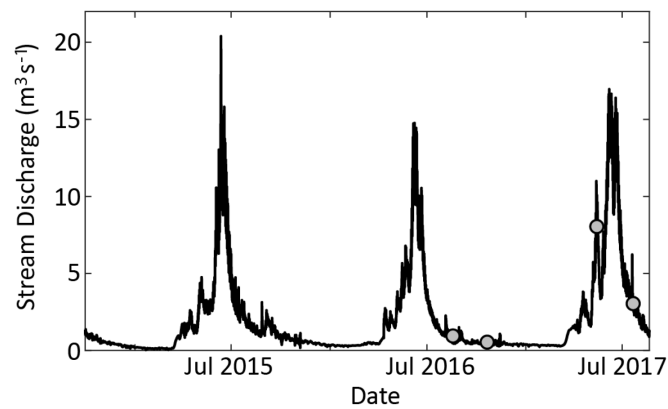


Figure 2. Stream discharge for East River from Oct. 1, 2014 through Aug. 21, 2017 measured at the Pumphouse [Carroll & Williams, 2019] (Figure 1). Grey markers represent field sampling campaigns conducted Aug. 19, 2016, Oct. 21 and 23, 2016, May 15-16 2017, and Jul. 22, 2017.

2.2 Estimating Seepage Fluxes Using Temperature Time Series

Heat was used as a tracer to quantify seasonal changes in vertical Darcy velocity through the streambed. Arrays of four temperature sensors (Onset Hobo TMC20-HD) were mounted on wooden rods and driven into the streambed at locations A, B, and C in August 2016 (Figure 1). Monitoring depths were 5, 10, 20, and 35 cm below the sediment-water interface. Temperature was recorded every 15 minutes using HOBO U-Series external-channel data loggers through August 2017. Due to changes in flow and bed movement, sensors were occasionally dislodged, inhibiting their use in heat tracing until they could be reinstalled. I utilized data from the deepest three sensors (10, 20, and 35 cm) for most locations and times because they remained undisturbed over longer intervals. However, the shallowest three probes were used for location A for August 21, 2016 through May 11, 2017 due to a faulty connection that compromised data collection at the deepest sensor.

I used 1DTempPro to determine a best fit vertical Darcy velocity (q) over 1-week intervals beginning every 3 days [Koch et al. 2015]. 1DTempPro solves the one-dimensional heat transfer equation in porous media:

$$\frac{\partial T}{\partial t} = K_e \frac{\partial^2 T}{\partial z^2} - q \frac{C_w}{C} \frac{\partial T}{\partial z}, \quad (1)$$

where T is temperature, t is time, z is depth below the sediment-water interface, K_e is the effective thermal diffusivity of the saturated sediment, q is Darcy velocity, and C_w and C are the volumetric heat capacities of the water and saturated sediment, respectively [McCallum et al. 2012]. K_e is defined as:

$$K_e = \frac{\lambda_0}{C} + \beta \left(\frac{C_w |q|}{C} \right), \quad (2)$$

where λ_0 is thermal conductivity of the bulk saturated medium, and β is thermal dispersivity [McCallum et al. 2012]. I used temperature signals at 10 and 35 cm as boundary conditions for solving Equations 1-2 at a depth of 20 cm to determine the best fitting q . Values for q are reported opposite of the sign convention used in 1DTempPro: upwelling is positive and downwelling is negative. I excluded all weeks from my analysis where the streambed was frozen, as 1DTempPro does not represent the effects of phase changes, and vertical flow was likely minimal. I considered the streambed frozen when greater than 75% of the temperature readings from one or more depths for a one-week period were less than 0.15 degrees Celsius.

To estimate thermal properties of the streambed (Table 1), I collected a grab sample of sediment with an approximate volume of 2 L near location B. I measured porosity (n) volumetrically on four splits. C was calculated from mean porosity:

$$C = C_w(n) + C_s(1 - n), \quad (3)$$

where C_s is the volumetric heat capacity of the dry sediment (chosen from Lapham [1989]), and C_w is the volumetric heat capacity of water. The calculated estimate for C is within the standard deviation of four direct measurements made on repacked saturated sediments using a KD2 Probe (Decagon Devices, WA, USA) with dual probe attachment (SH-1), but I retain the calculated value (Equation 3) rather than the direct measurement because the needles of the dual probe tended to move during insertion in coarse gravels. Using the KD2 Probe with 10 cm single needle probe (TR-1), I also measured λ_0 of the repacked, saturated sample four times (Table 1). To estimate thermal dispersivity (β , Equation 2), the least constrained parameter, I first estimated K_e using the code VFLUX2 [Gordon et al. 2012; Irvine et al. 2015] during a week beginning on Sept. 21, 2016 that had strong, upwelling, ideal sinusoidal diurnal temperature signals when β would presumably be small [McCallum et al. 2012]:

$$K_e = \frac{\Delta z^2 P^2 \ln A_r (4\pi^2 \Delta \Phi^2 - P^2 \ln^2 A_r)}{\Delta \Phi (P^2 \ln^2 A_r + 4\pi^2 \Delta \Phi^2) (P^2 \ln^2 A_r - 4\pi^2 \Delta \Phi^2)}, \quad (4)$$

where Δz is the distance between two temperature sensors, P is the period of the diurnal temperature signal, A_r is the ratio of the diurnal amplitudes, and $\Delta \Phi$ is the difference in phases of temperature maxima. I then solved for β using known q and K_e during that week (Equation 2). The value of β varied based on the selection of sensor pairings and locations, but was generally more than 1 cm, likely due to enhanced heat exchange associated with hyporheic mixing in the shallow streambed [Shanafield et al. 2011; Bhaskar et al. 2012]. Smaller values of β are often chosen in streambed heat tracing analysis in order to represent grain-scale dispersion [Molina-Giraldo et al. 2011; Voermans et al. 2018]. I therefore selected a moderate β value of 1 cm for use in estimating q .

I assessed uncertainty in q arising from uncertainty in thermal properties like β using a Monte Carlo analysis (Table 1). Because 1DTempPro does not include an option for Monte Carlo simulations, I ran Monte Carlo simulations in VFLUX2 using the analytical solution of Hatch et al. [2006] to estimate q for the week with strong downwelling diurnal temperature signals beginning on August 6, 2017 when errors associated with β would likely be greatest. I then assigned the resulting uncertainty in q of $\pm 0.026 \text{ m d}^{-1}$ to all estimates from the entire year of data from 1DTempPro. Normal distributions of all parameters were assumed, and all parameters, with the exception of λ_0 and n , were assumed to be uncorrelated.

Table 1. Parameters used in heat tracing. Mean values were used in 1DTempPro to estimate q . Standard deviations were also used in Monte Carlo analysis in VFLUX to determine error bars for q estimates.

Parameter	Mean	Standard Deviation	Units
n	0.27	0.027	-
β	0.01	0.0075	m
λ_0	1.86	0.00267	$\text{J s}^{-1} \text{m}^{-1} \text{K}^{-1}$
C_s	1872000	32600	$\text{J m}^{-3} \text{K}^{-1}$
C_w	4184000	5000	$\text{J m}^{-3} \text{K}^{-1}$

2.3 Field Methods and Chemical Analysis

Pore water samples were obtained from locations A, B, and C (Figure 1) on August 19, 2016, October 21-23, 2016, May 15-16, 2017, and July 22, 2017 (Figure 2). Samples were obtained at 10 cm intervals using a $\frac{1}{4}$ " diameter, stainless steel sipper with a 2" screen (MHE Products, MI, USA) attached to a syringe (MHE Products, MI, USA). The maximum sampling depth was generally 60 cm but varied due to challenges with penetration around large cobbles. Prior to each sample collection, 30 mL of pore water was extracted and discarded to purge the full sipper volume. Samples were filtered through a 0.22 μm Sterivex filter (Massachusetts, USA) and immediately analyzed for DO concentration using a field spectrometer (CHEMetrics, VA, USA). Because the method exposed the sample to the atmosphere, measured concentrations represent a maximum, upper bound on in-situ DO concentrations. Basic chemical parameters (pH, specific conductivity, total dissolved solids, resistivity, oxidation-reduction potential) were measured in the field using a handheld multiparameter probe (Ultrameter II, Myron L Company, CA, USA). One additional 20-mL filtered aliquot was collected from each sampling depth and location in a polyethylene vial, acidified, and placed on ice until transfer to a freezer. Preserved samples were used for cation analysis using a PerkinElmer ELAN 6000 ICP-Mass Spectrometer.

Samples were kept frozen until analysis. More details on analysis methods are provided in Saup et al. [2019].

River water specific conductivity and DOC records were obtained from the East River Data Portal. Samples and measurements were obtained near the Pumphouse using a YSI and ISCO sampler (Figure 3q and 3u) as part of the Lawrence Berkeley National Laboratory (LBNL) Watershed Function Scientific Focus Area (SFA). Stage height and stream discharge were obtained from Carroll & Williams [2019] (Figure 3a).

2.4 Reactive Transport Model

Conservative and reactive solute transport was simulated for a one-dimensional “slab” of streambed sediment with thickness of 1 m positioned such that the top of the domain is at the sediment-water interface and represents river water. Specific conductivity was chosen to represent a conservative “solute” in the unsteady advection-dispersion equation:

$$\frac{\partial C}{\partial t} = -v(t) \frac{\partial C}{\partial z} + D(z, t) \frac{\partial^2 C}{\partial z^2}, \quad (5)$$

where C is concentration (here, taken as specific conductivity, SpC), t is time, z is depth below the streambed interface, $v(t)$ is average seepage velocity, and $D(z, t)$ is effective dispersion. The unsteady one-dimensional advection-dispersion-reaction equations were used to represent transport of DO, $Mn_{(aq)}$, and DOC:

$$\begin{aligned} \frac{\partial C_{DO}}{\partial t} = & -v(t) \frac{\partial C_{DO}}{\partial z} + D(z, t) \frac{\partial^2 C_{DO}}{\partial z^2} - \beta_{ar,DO} V_{ar} X_{ar} \left(\frac{C_{DO}}{K_{DO} + C_{DO}} \right) \left(\frac{C_{DOC}}{K_{DOC} + C_{DOC}} \right) - \\ & \beta_{MnOx,DO} V_{MnOx} X_{MnOx} \left(\frac{C_{DO}}{K_{DO} + C_{DO}} \right) \left(\frac{C_{Mn(aq)}}{K_{MnOx} + C_{Mn(aq)}} \right), \quad (6) \\ \frac{\partial C_{Mn(aq)}}{\partial t} = & -v(t) \frac{\partial C_{Mn(aq)}}{\partial z} + D(z, t) \frac{\partial^2 C_{Mn(aq)}}{\partial z^2} - \beta_{MnOx,Mn} V_{MnOx} X_{MnOx} \left(\frac{C_{DO}}{K_{DO} + C_{DO}} \right) \end{aligned}$$

$$\left(\frac{C_{Mn(aq)}}{K_{MnOx} + C_{Mn(aq)}} \right) + \beta_{an,Mn} V_{an} X_{an} I \left(\frac{C_{DOC}}{K_{DOC} + C_{DOC}} \right), \quad (7)$$

$$\begin{aligned} \frac{\partial C_{DOC}}{\partial t} = & -v(t) \frac{\partial C_{DOC}}{\partial z} + D(z, t) \frac{\partial^2 C_{DOC}}{\partial z^2} - \beta_{ar,DOC} V_{ar} X_{ar} \left(\frac{C_{DO}}{K_{DO} + C_{DO}} \right) \left(\frac{C_{DOC}}{K_{DOC} + C_{DOC}} \right) - \\ & \beta_{an,DOC} V_{an} X_{an} I \left(\frac{C_{DOC}}{K_{DOC} + C_{DOC}} \right), \end{aligned} \quad (8)$$

where $\beta_{ar,DO}$, $\beta_{MnOx,DO}$, $\beta_{MnOx,Mn}$, $\beta_{an,Mn}$, $\beta_{ar,DOC}$, and $\beta_{MnOx,DOC}$ are stoichiometric coefficients, V_k is the maximum microbial rate of the k th reaction, X_k is the microbial biomass facilitating the k th reaction, and K_j is the half saturation constant for the j th species (Table 2). Model reactions include aerobic respiration (denoted with subscript *ar*), Mn-oxide respiration (*an*), and Mn_(aq) oxidation (*MnOx*) (Table 3). I assume Mn-oxides are abundant and do not limit the rate of Mn-oxide respiration. Inhibition (*I*) of Mn-oxide respiration in the presence of DO is represented as:

$$I = \frac{K_I}{K_I + DO}, \quad (9)$$

where K_I is the inhibition constant (Table 2).

Table 2. Model parameters.

Parameter	Description	Value	Source
Physical Parameters			
D_p	Mechanical diffusion at bottom boundary	$1 \times 10^{-7} \text{ (m}^2\text{s}^{-1}\text{)}$	Fitted
D_m	Molecular diffusion	$1 \times 10^{-10} \text{ (m}^2\text{s}^{-1}\text{)}$	<i>Ingebritsen & Ward [1998]</i>
G	Constant of decay for D(t,z)	$41 \text{ (m}^{-1}\text{)}$	Fitted
k	Permeability	$2.42 \times 10^{-9} \text{ (m}^2\text{)}$	Observed
n	Porosity	0.27	Observed
q_f	Darcy velocity during freezing	$0 \text{ (ms}^{-1}\text{)}$	
S	Channel slope	$0.008 \text{ (m}^1\text{m}^{-1}\text{)}$	Observed
ν_k	Kinematic viscosity of water	$1.13 \times 10^{-6} \text{ (m}^2\text{s}^{-1}\text{)}$	

Continued

Table 2 Continued

Parameter	Description	Value	Source
Reaction Kinetics			
$\beta_{an,DOC}$	Stoichiometric coefficient: DOC in anerobic respiration	1	Stoichiometry
$\beta_{an,Mn}$	Stoichiometric coefficient: $Mn_{(aq)}$ in anerobic respiration	2	Stoichiometry
$\beta_{ar,DOC}$	Stoichiometric coefficient: DOC in aerobic respiration	1	Stoichiometry
$\beta_{ar,DO}$	Stoichiometric coefficient: DO in aerobic respiration	1	Stoichiometry
$\beta_{MnOx,Mn}$	Stoichiometric coefficient: $Mn_{(aq)}$ in Mn oxidation	1	Stoichiometry
$\beta_{MnOx,DO}$	Stoichiometric coefficient: DO in Mn oxidation	0.5	Stoichiometry
C	Constant of decay for microbial biomass	3 (m ⁻¹)	Fitted
K_{DOC}	Half saturation constant for DOC	0.5 (mM)	Gue et al. [2007]; Zarnetske et al. [2012]; Sawyer [2015]; Knights et al. [2017]
K_i	Inhibition constant for Mn- oxide respiration	7.5 (μM)	Gue et al. [2007]; Zarnetske et al. [2012]; Sawyer [2015]; Knights et al. [2017]
$K_{Mn,ox}$	Half saturation constant for Mn in Mn oxidation	0.6 (μM)	Tebo & Emerson [1986]
K_{DO}	Half saturation constant for DO	0.165 (mM)	Rifai & Philip [1990]; Abrams & Loague [2000]; Gue et al. [2007]; Zarnetske et al. [2012]; Sawyer [2015]; Knights et al. [2017]
V_{an}	Maximum microbial rate of Mn-oxide respiration	0.7 (hr ⁻¹)	Abrams & Loague [2000]; Gue et al. [2007]
V_{ar}	Maximum microbial rate of aerobic respiration	1 (hr ⁻¹)	Gue et al. [2007]; Guillemette & Giorgio [2011]; Zarnetske et al. [2012]; Knights et al. [2017]
V_{MnOx}	Maximum microbial rate of Mn oxidation	0.1 (hr ⁻¹)	Harvey & Fuller [1998]; Shiller & Stephens [2005]
$X_{an,GW}$	Biomass of Mn-oxide respirers in groundwater	1 (μM)	Schallenberg & Kalff [1993]; Marmonier et al. [1995]; Hendricks [1996]
$X_{an,RW}$	Biomass of Mn-oxide respirers in river water	0.15 (mM)	Pallud & Van Cappellen [2006]; Li et al. [2010]; Dawn et al. [2012]
$X_{ar,GW}$	Biomass of aerobes in groundwater	10 (μM)	Schallenberg & Kalff [1993]; Marmonier et al. [1995]; Hendricks [1996]

Continued

Table 2 Continued

Parameter	Description	Value	Source
Reaction Kinetics			
$X_{ar,RW}$	Biomass of aerobes in river water	1.5 (mM)	Lock et al. [1984]; Battin et al. [2003]; Battin et al. [2016]; Mendoza-Lera et al. [2017]
$X_{MnOx,GW}$	Biomass of Mn oxidizers in groundwater	1 (μ M)	Schallenberg & Kalff [1993]; Marmonier et al. [1995]; Hendricks [1996]
$X_{MnOx,RW}$	Biomass of Mn oxidizers in river water	0.15 (mM)	Emerson & Moyer [1997]
River water Concentrations			
$C_{Mn(aq)}$	Concentration of $Mn_{(aq)}$	9 (nM)	Observed
C_{DO}	Concentration of DO	0.25 (mM)	Observed
Groundwater Concentrations			
C_{DOC}	Concentration of DOC	0.5 (μ M)	----
$C_{Mn(aq)}$	Concentration of $Mn_{(aq)}$	23 (μ M)	Observed
C_{DO}	Concentration of DO	25 (μ M)	Observed
C_{SpC}	Specific conductivity	500 (μ S cm^{-1})	Observed

Table 3. Reaction equations.

	Reaction
Aerobic respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
Mn-oxide respiration	$2MnO_2 + CH_2O + 2H^+ \rightarrow 2Mn^{2+} + CO_3^{2-} + 2H_2O$
Mn oxidation	$Mn^{2+} + 2OH^- + 0.5O_2 \rightarrow MnO_2 + H_2O$

Values of $v(t)$ were guided by the results of heat tracing with one significant difference: downwelling conditions were assigned to the rising limb of the spring snowmelt event, and upwelling conditions were assigned to the falling limb, despite heat tracing results that suggested more neutral to downwelling conditions (Figure 3i, dashed line). These adjustments greatly improved the match with measured specific conductivity profiles in May and July and were deemed reasonable for the following reasons: temperature sensors were disturbed by the spring snowmelt event, leading to greater uncertainties in heat tracing during that interval, and heat tracing has been shown to be biased towards downwelling conditions [Irvine et al. 2015].

$D(z, t)$ includes the effects of small-scale advective transport processes that occur within the hyporheic zone due to turbulence and bedform-current interactions [Grant et al. 2012; O'Connor & Harvey 2008; Voermans et al. 2018], as well as pore-scale mechanical dispersion. At the sediment-water interface ($z = 0$), D is assumed to be dominated by the effects of small-scale hyporheic mixing, which varies seasonally with bed shear stresses according to Equation 13 of Voermans et al. [2018]:

$$D(t, 0) = 1.9Re_K(t)^2Sc(t)D_m, \quad (10)$$

$$Sc(t) = \frac{v_k}{D_m}, \quad (11)$$

$$Re_K(t) = \frac{\sqrt{k}u^*(t)}{v_k}, \quad (12)$$

where $Re_K(t)$ is the Permeability Reynold's number, $Sc(t)$ is the Schmidt number, D_m is molecular diffusion (Table 2), v_k is kinematic viscosity of fresh water (Table 2), k is permeability (Table 2), and u^* is shear velocity:

$$u^*(t) = \sqrt{gh(t)S}, \quad (13)$$

where g is gravitational force, $h(t)$ is stage height (Figure 3), and S is channel slope (Table 2). Permeability was estimated by conducting a constant head permeameter test using a Darcy tube (Gilson Company, Inc., OH, USA) packed with sediment collected from location B. Five flow rates were measured using five unique head differences, and permeability was determined based on Darcy's Law. The above approximations assume homogenous streambed properties and uniform flow. Kinematic viscosity (v_k) is assumed to be invariant with temperature.

$D(t, z)$ is assumed to decline exponentially as the rate of small-scale hyporheic advection declines [Elliott & Brooks 1997a] and converge on a value representative of pore-scale mechanical dispersion ($D_p = 1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$) at the base of the model (Table 2). Specifically:

$$D(t, z) = (D(t, 0) - D_p) \exp(Gz) + D_p. \quad (14)$$

Facultative microbial biomasses were assumed to decline exponentially with depth by approximately 2 orders of magnitude:

$$X_k(t, z) = (X_{k,RW} - X_{k,GW}) \exp(Cz) + X_{k,GW}, \quad (15)$$

where k denotes aerobes (ar), Mn-oxide respirers (an), and $\text{Mn}_{(\text{aq})}$ oxidizers (MnOx). $X_{k,RW}$ and $X_{k,GW}$ are microbial biomasses in river water and groundwater, respectively (Table 2).

To solve equations 5-8, boundary conditions were assigned based on measured concentrations in river water and deepest pore water. River water concentrations varied with season (Figure 3), while groundwater concentrations at the lower boundary were held constant (Table 2). Reaction kinetics were guided by the literature (Table 2), and refined to achieve the best visual fit with measured reactive solute concentrations (DO and $\text{Mn}_{(\text{aq})}$). When the streambed was presumed frozen (See section 2.2), advection and reactions were halted, and the coefficient of dispersion was set to a constant equal to molecular diffusion in ice (Table 2). The transport equations were solved using COMSOL, a generic finite element solver. The mesh for the model geometry was no greater than 0.1 cm over the 1 m domain. The model reached steady annual cycles after one year of spin-up, so model results are reported from simulation year two. All model parameter values and descriptions are summarized in Table 2.

2.5 Sensitivity Study

To understand the effect of changes in hydrology on Mn cycling in the bed of East River, three scenarios were simulated: Historic, Low-Snow, and Storm (Figure 3). The Historic scenario (Figure 3, second column) reflects conditions similar to those captured during field measurements, with a long winter freezing period and a large annual snowmelt event (Figure 2). The Low-Snow (Figure 3, third column) scenario has a freezing period that is half the duration of

the Historic scenario. The annual discharge is decreased by 50% with respect to the Historic scenario, corresponding with the upper limit for the predicted change in annual discharge of Colorado alpine streams by the mid-2000's [Vano et al. 2012]. Additionally, the annual snowmelt event occurs one month earlier in the year and is smaller in magnitude and duration (Figure 3c). In the Storm scenario (Figure 3, fourth column), the annual discharge is still decreased by 50% with respect to the Historic scenario, but event flow is distributed across multiple storms in late winter through early spring instead of a large snowmelt pulse. The streambed does not freeze and summer and fall baseflow conditions are slightly lower than the Low-Snow scenario (Figure 3d). These three simulations represent a wide range of end-members that bound plausible hydrograph scenarios for the Rocky Mountains [Pederson et al. 2011; Rood et al. 2008; Stewart 2009].

In each of the three scenarios, idealized functions were chosen to represent the following time-dependent parameters: stage height ($h(t)$), stream discharge ($Q(t)$), vertical Darcy velocity ($q(t)$), effective dispersion ($D(t,0)$), specific conductivity in the river ($C_{SPC,RW}(t)$), and DOC in the river ($C_{DOC,RW}(t)$) (Figure 3). Stage and discharge were related through a rating curve (Appendix A). Darcy velocity, stream water conductivity, and stream DOC concentration were linked to changes in stage height and discharge (Appendix A). $D(t,0)$ was calculated using Equations 10-13.

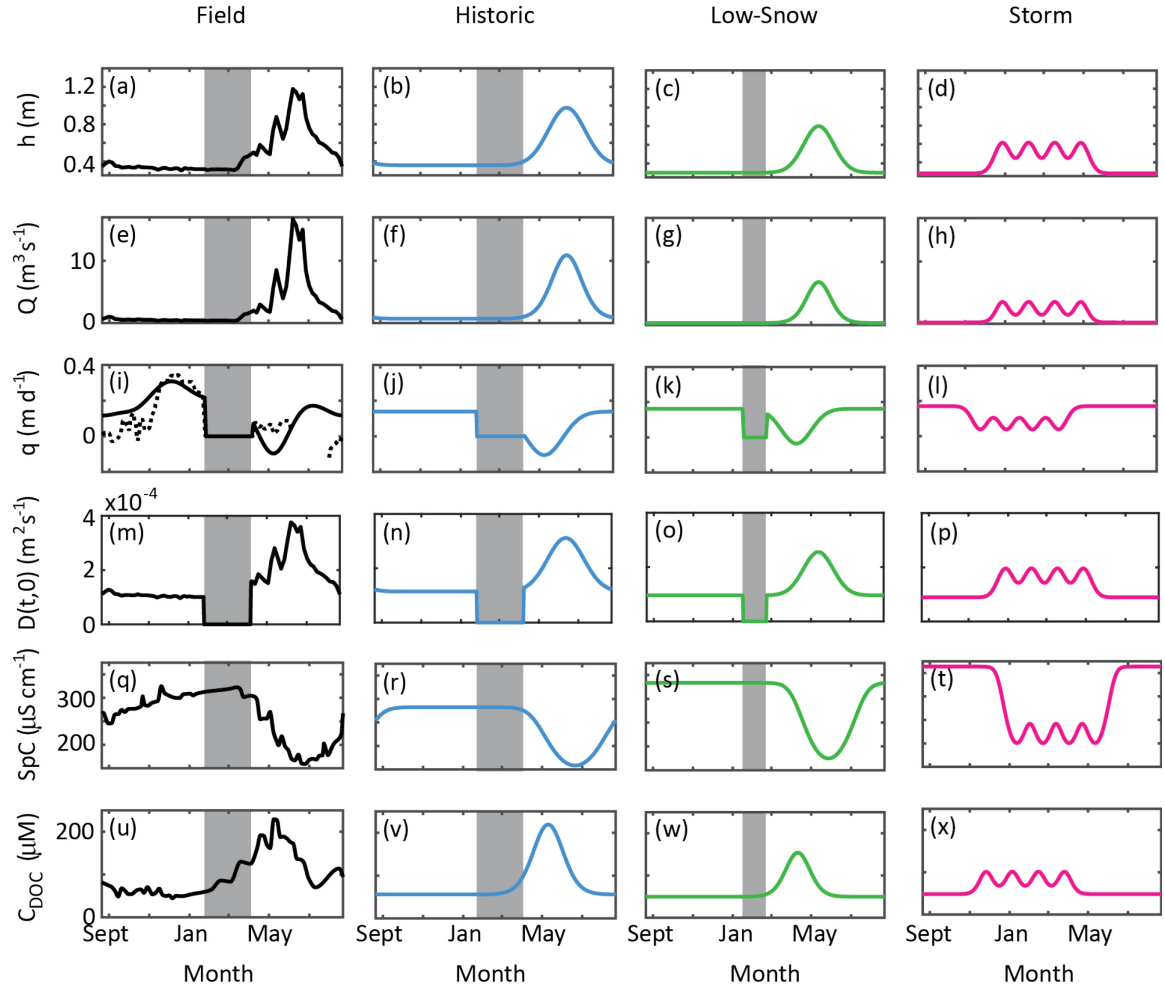


Figure 3. Idealized inputs for the field model (first column) and three climate scenarios: Historic (second column), Low-Snow (third column), and Storm (fourth column). The dotted line in (i) represents estimates made in 1DTempPro for location B. Estimates differ from prescribed values in the field model due to efforts to fit observed conservative solute profiles. Variables are defined in Table 2. Parameters are defined from August 21 to August 21 of the following year. Shaded gray regions denote periods of streambed freezing.

Chapter 3. Results

3.1 Seasonal Changes in River Water-Groundwater Interactions

Upwelling conditions dominated at the three locations over much of the year, particularly during the baseflow months (mid-August until time of freezing) (Figure 4). A switch to downwelling conditions generally occurred when stream discharge increased in the spring. Location A experienced the longest downwelling conditions from the time of thaw in April 2017 until monitoring ceased in August 2017. Location C appears to have experienced a similar period of downwelling conditions, but there was a gap in the record during flood conditions due to sensor dislodgement. At location B, downwelling initiated later in the spring snowmelt season, likely around the time of peak discharge in June. The magnitude of downwelling was also less than at locations A and C. Location B had the greatest rate of peak groundwater discharge ($0.33 \pm 0.026 \text{ m d}^{-1}$) and greatest average groundwater discharge over the year ($0.11 \pm 0.026 \text{ m d}^{-1}$).

Location B was frozen only two months, while location A was frozen for more than four months (Figure 4). All locations thawed within one week of one another, but freeze up occurred in early December at A, late December at C, and late January at B. These observations are consistent with the stronger rate of upwelling at B, which should buffer wintertime temperatures. Taken together, I interpret that location A is more river water influenced, while locations B and C are more groundwater influenced.

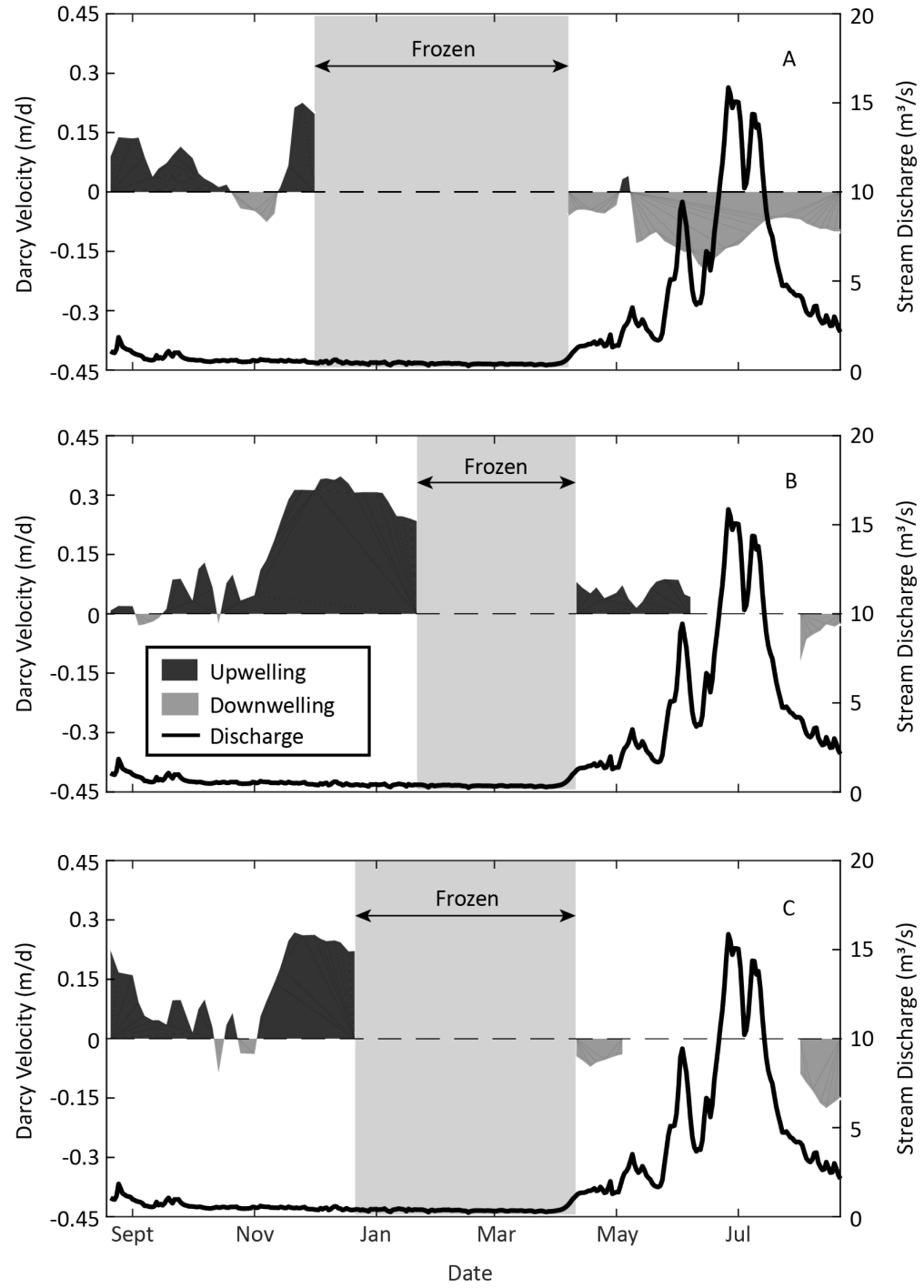


Figure 4. Rates of vertical Darcy velocity (q) at locations A, B, and C (Figure 1). Positive values indicate upwelling (shaded black), while negative values indicate downwelling (shaded dark grey). Error for estimates is $\pm 0.026 \text{ m d}^{-1}$. Periods without q estimates during the snowmelt event are due to sensor disturbance. Discharge was obtained from *Carroll & Williams [2019]*. Data published in *Bryant et al. [2019]*.

3.2 Seasonal Changes in Pore Water Chemistry

Specific conductivity generally increased with depth below the sediment-water interface (Figure 5, left column). At location A, relatively small and stable vertical gradients indicate deep mixing of low-conductivity river water across seasons. At location B, steeper gradients indicate upwelling of high-conductivity groundwater over most of the year. During the rising hydrograph in May however, river water mixed deep in the bed. At location C, specific conductivity values were generally intermediate between locations A and B. For all locations, conductivity was notably lower in May and July, compared to August and October, due to mixing of low-conductivity river water deeper in the streambed during the snowmelt event (Figure 5, left column).

Strontium-87 to Strontium-86 ($^{87}\text{Sr}/^{86}\text{Sr}$) ratios have been used as a tracer to understand hyporheic flow paths [Palmer & Edmond 1989; Lyons et al. 1994; Stewart et al. 1998] (Figure 5, second column). Location B had consistently higher ratios that may reflect groundwater influence or longer residence times, while A and C had a wider range of values that may reflect a greater portion of river-derived (hyporheic) waters with a range of residence times. Notably, August and October ratios for location C were similar to those of B, indicating older groundwater influence during the baseflow season.

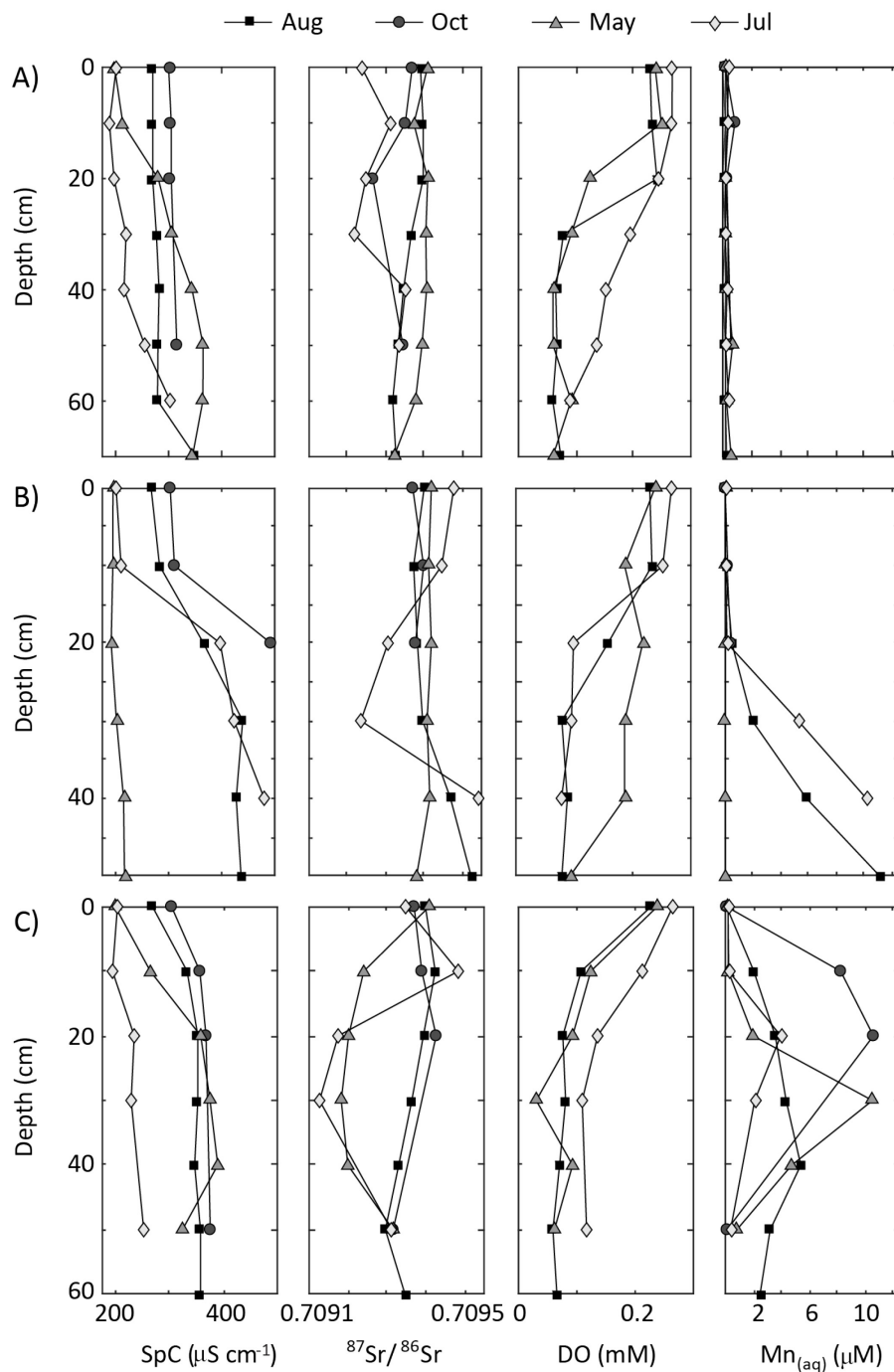


Figure 5. Depth profiles for specific conductivity (SpC), DO, Mn, and $^{87}\text{Sr}/^{86}\text{Sr}$ at locations A (top row), B (middle row), and C (bottom row). Mn_{aq} values lower than the detection limit are reported as the detection limit (Appendix C). Samples in May at location A were collected in a slightly offset location due to safety considerations with wading in high water, which may explain the seemingly groundwater-influenced profiles of higher specific conductivity and lower DO. This data was obtained from Saup et al. [2019]. Error information is provided in Appendix C.

DO concentrations generally decreased with depth below the sediment-water interface (Figure 5, third column), as expected due to aerobic respiration and $\text{Mn}_{(\text{aq})}$ oxidation [Boano et al. 2010; Lensing et al. 1994; Zarnetske et al. 2012]. For most locations and months, a decline occurred around 20 to 30 cm depth. DO penetrated deepest at all locations during May (B) or July (A and C) when river discharge was high (Figure 5, third column). DOC concentrations were not measured due to limited sample volume, but Nelson et al [2019] found pore water concentrations ranged from below 0.92 (detection limit) to 7.8 mg L⁻¹ and averaged 2.1 mg L⁻¹ within the study reach.

$\text{Mn}_{(\text{aq})}$ concentrations at location A were very low (< 7.5 μM) compared to locations B and C (Figure 5, fourth column). At location B, $\text{Mn}_{(\text{aq})}$ was only low in May, when DO penetrated deeper in sediments during flood stage. In July and August, discharging groundwater carried $\text{Mn}_{(\text{aq})}$ toward the sediment-water interface, and the Mn-oxidation front shifted upward in July and August (Figure 5, fourth column). A seasonal shift in the Mn oxidation front was also evident at location C: the peak $\text{Mn}_{(\text{aq})}$ concentration shifted upward from 30 cm in May to 20 cm in October, towards the end of the baseflow season (Figure 5). In general, $\text{Mn}_{(\text{aq})}$ concentrations were low when DO was high and increased with specific conductivity, used here as a proxy for groundwater influence (Figure 6a). For comparison, dissolved chromium exhibited an opposite relationship with DO, as the soluble form is the oxidized form, unlike Mn (Figure 6b). pH varied over a small range, generally falling between 7.5 and 8.5 (Figure 7).

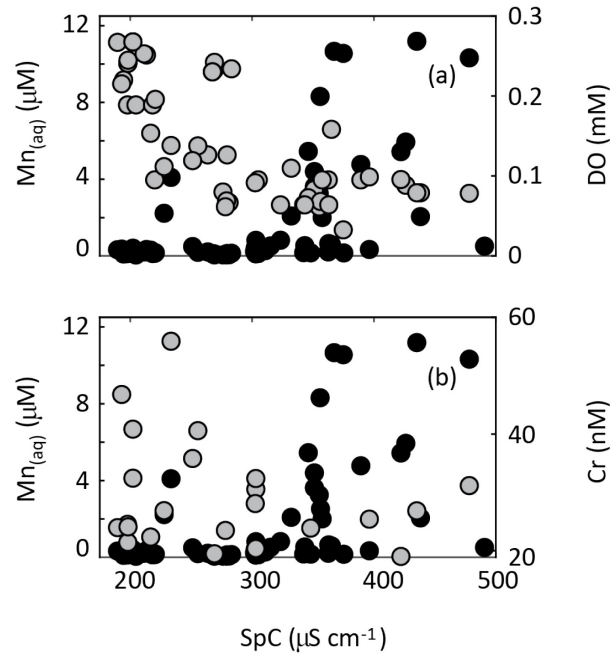


Figure 6. $Mn_{(aq)}$ compared to DO (a), and chromium (Cr) (b) for all locations (A, B, and C) and seasons (August, October, May, and July) along a mixing line between river water (low SpC) and groundwater (high SpC). $Mn_{(aq)}$ values lower than the detection limit are reported as the detection limit (Appendix C). This data was obtained from Saup et al. [2019]. Error information is provided in Appendix C.

Trace metals such as zinc, lead, and copper tended to have lower concentrations in the baseflow season (~ 0.05 - $0.06 \mu M$) that increased during spring snowmelt (May and July) in both river water and pore water (up to $0.4 \mu M$) (Figure 7). Copper had the highest concentrations of the three metals (up to $0.4 \mu M$), while lead had significantly lower concentrations for all months, depths, and locations (up to $0.03 \mu M$). Because concentrations tended to increase in both river water and deep pore water during the hydrograph peak, both river water and groundwater may serve as metal sources to the hyporheic zone. Copper concentrations were generally lower between 10 to 30 cm below the sediment-water interface, suggesting potential immobilization in shallow sediments, perhaps on Mn-oxides [Fuller & Harvey 2000; Kay et al. 2001; Schaffner et al. 2015] (Figure 7).

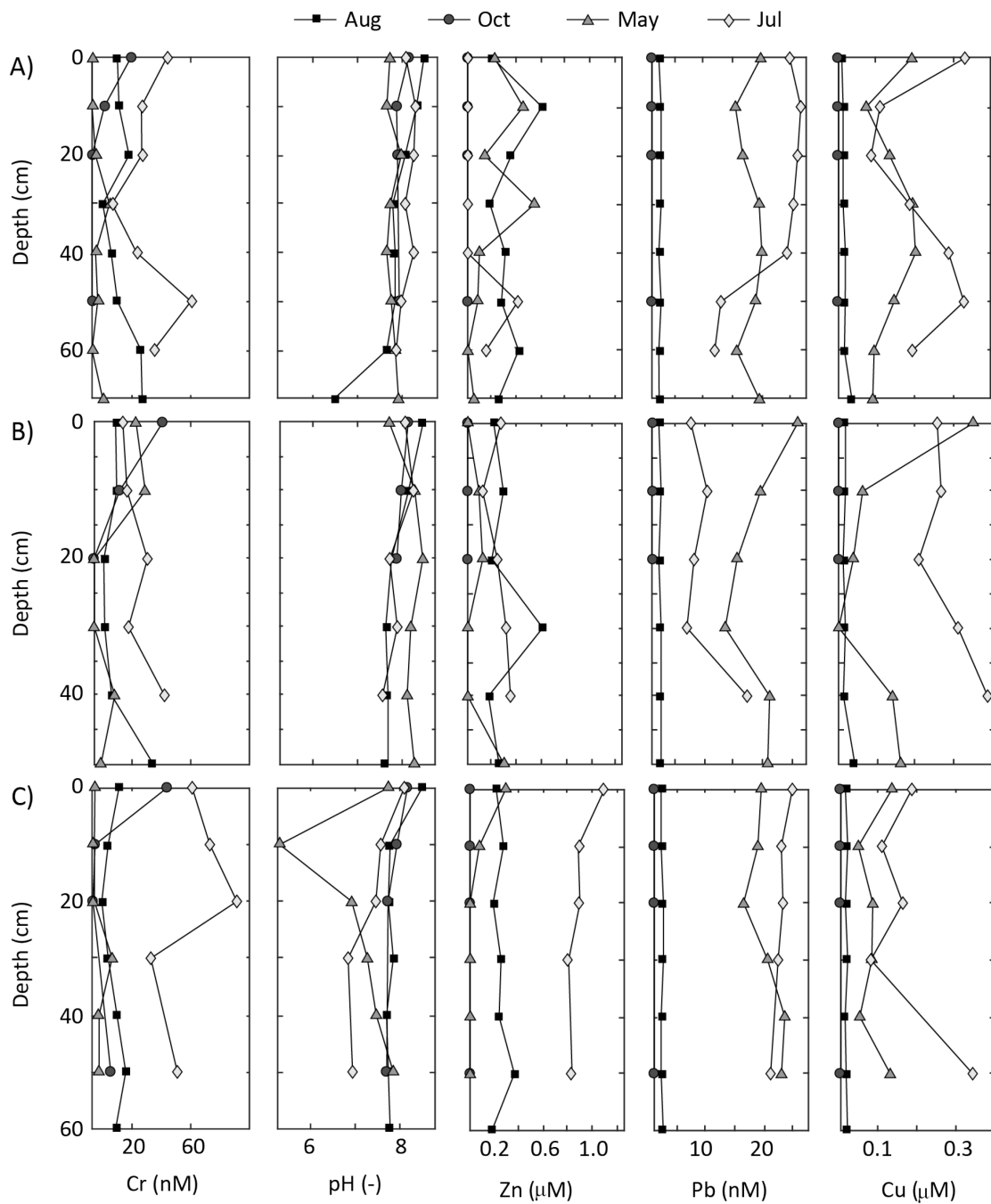


Figure 7. Depth profiles for chromium (Cr), pH, zinc (Zn), lead (Pb), and copper (Cu), at locations A (top row), B (middle row), and C (bottom row). Values lower than the detection limit are reported as the detection limit (Appendix C). A, B, and C refer to locations A, B, and C, respectively. This data was obtained from Saup et al. [2019]. Error information is provided in Appendix C.

3.3 Model Comparison with Observations

Location B was identified as an ideal site for model development because it was well represented by one-dimensional transport. Location A was not simulated because concentrations of $\text{Mn}_{(\text{aq})}$ remained low over all sampled depths and seasons. At location C, concentrations peaked at an intermediate depth, suggesting the possibility of multiple geochemical end members or multidimensional flow not well captured by a one-dimensional model. A gravel layer mapped by Malenda [2018] may focus horizontal flow near location C.

All modeled specific conductivity profiles at location B were in good agreement with measurements (Figure 8, left). Specific conductivity decreased in May as stream water intruded during the rising limb of the spring snowmelt event, then increased in association with groundwater upwelling (Figure 8, left). The model also captured the increase in DO and decrease in $\text{Mn}_{(\text{aq})}$ in May during downwelling conditions (Figure 8, center). Although modeled DO concentrations decayed faster with depth than observations (especially in May), the sampling technique exposed samples to DO from the atmosphere, so measured DO concentrations represent maximum estimates of in-situ concentrations. The model accurately characterized shifts in the $\text{Mn}_{(\text{aq})}$ concentration profile over July and August (Figure 8, right).

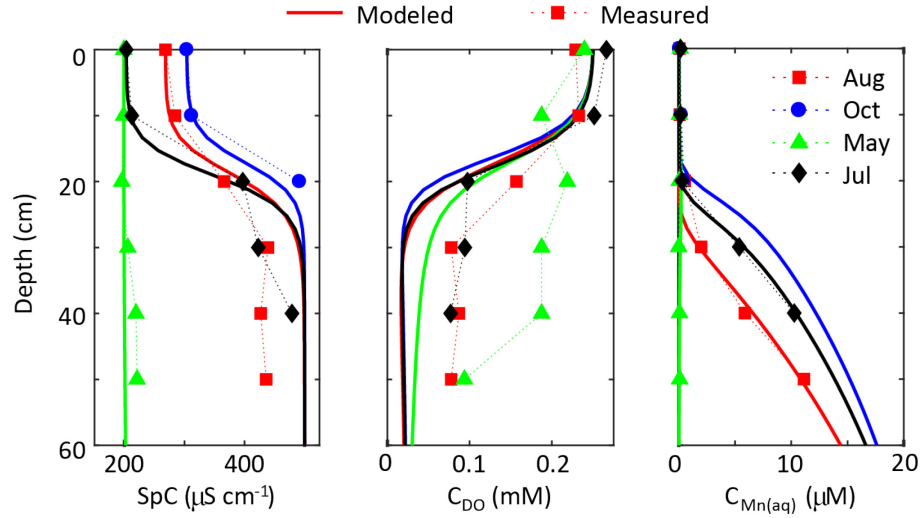


Figure 8. Comparison between measured and modeled results for specific conductivity (SpC), DO, and $Mn_{(aq)}$ using the field model at location B.

3.4 Model Hydrograph Scenarios

Under the Historic scenario, or idealized present day conditions, low-conductivity river water mixes deep into the streambed over the rising limb of the spring snowmelt (April through mid-May) (Figure 9d). DO penetrates deep into the streambed (>50 cm) (Figure 9g), while $Mn_{(aq)}$ concentrations decline abruptly in pore water (Figure 9j). This decline is primarily driven by the advective transport of low- $Mn_{(aq)}$, low-specific conductance river water down through the profile. The result is a decline in the $Mn_{(aq)}$ oxidation rate, calculated as the magnitude of the third term on the right side of Equation 7 (Figure 9p). In mid-May, as DOC concentrations increase in the upper 25 cm of the streambed (Figure 9m), aerobic respiration restricts the depth of DO penetration (Figure 9g). Rates of Mn-oxide respiration also increase slightly with the enhanced supply of DOC, leading to a small region of elevated $Mn_{(aq)}$ (<0.4 μM) near 20 cm. This subtle increase in $Mn_{(aq)}$ concentrations allows for a small region where Mn-oxides form between 15 and 30 cm (Figure 9p). In June, declining DOC concentrations (Figure 9m) limit aerobic and anaerobic respiration, leading to a brief increase in DO between 20 and 50 cm (Figure 9g). Rates of Mn

oxidation (Figure 9p) are low due to a limited supply of $Mn_{(aq)}$ from declining rates of Mn-oxide respiration. Over the recession and baseflow season (mid-June through Feb), river water penetrates less deeply to about 20 cm (Figure 9d), and upwelling groundwater supplies $Mn_{(aq)}$ to shallower pore water below 20 cm (Figure 9j). DO and DOC only mix to depths of approximately 20 and 15 cm, respectively (Figure 9g and 9m). As upwelling groundwater transports $Mn_{(aq)}$ up through the streambed profile (Figure 9j), Mn oxidation rates increase, peaking between 15 and 25 cm (Figure 9p). Above 15 cm, $Mn_{(aq)}$ concentrations are low due to dilution with low- $Mn_{(aq)}$ river water and oxidation of $Mn_{(aq)}$ from groundwater, leading to low rates of Mn oxidation despite high DO concentrations (Figure 9g). During frozen conditions, solute concentrations remain nearly steady due to negligible transport and reactions.

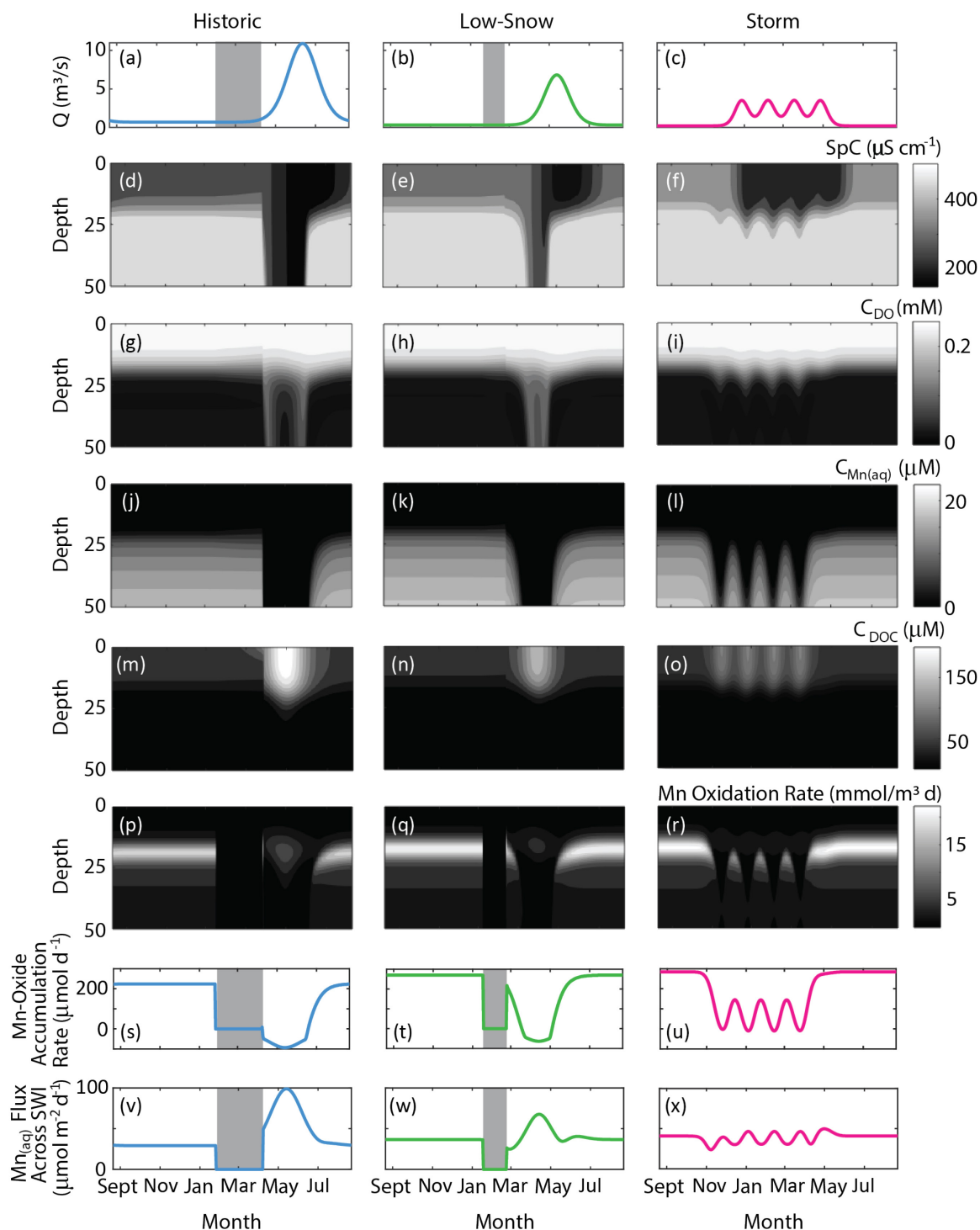


Figure 9. Model results for three climate scenarios: Historic (left column), Low-Snow (middle column), and Storm (right column). Stream discharge (Q) for the three scenarios is shown on the top row for comparison. Results are shown over a one year period from August 21 to August 21 of the following year. Models were allowed a one year ramp up period.

I calculated the accumulation rate of Mn-oxides beneath a unit area of streambed as the integral with depth of the difference between Mn oxidation and Mn-oxide respiration over the upper 50 cm of the streambed. Positive values indicate more oxidation than Mn-oxide respiration, or net sequestration of Mn as Mn-oxides (Figure 9s). Over the rising limb of the spring snowmelt, $Mn_{(aq)}$ is released (net Mn-oxide respiration occurs) as oxidation is limited by the supply of $Mn_{(aq)}$ from groundwater, and Mn-oxide respiration is enhanced by the supply of DOC from river water. The maximum rate of Mn mobilization is $-93.6 \mu\text{mol d}^{-1}$ (Figure 9s). Mn-oxides then accumulate over the falling limb of the hydrograph as Mn-oxide respiration becomes limited by declining DOC concentrations and Mn oxidation is enhanced by an increase in $Mn_{(aq)}$ supply from groundwater. The maximum accumulation rate of $224 \mu\text{mol d}^{-1}$ is maintained over most of the baseflow season. The yearly average Mn-oxide accumulation rate is $113 \mu\text{mol d}^{-1}$.

$Mn_{(aq)}$ flux, calculated as the integral of the total flux of $Mn_{(aq)}$ across the sediment water interface, is always positive, or directed from the aquifer to the stream (Figure 9v). During spring, the downward-directed advective flux is compensated for by an increase in dispersive flux due to the increase in shear stress at the sediment-water interface (Equations 10-13). A maximum flux of $98.9 \mu\text{mol m}^{-2} \text{d}^{-1}$ occurs in May despite low $Mn_{(aq)}$ concentrations in the upper 15cm of streambed. The flux decreases to $29.2 \mu\text{mol m}^{-2} \text{d}^{-1}$ during the baseflow season as dispersion due to hyporheic mixing decreases. Assuming a streambed area with an average width of 8.5 m and homogeneous streambed properties, the yearly flux to the river is $105.6 \text{ mmol m}^{-1}$ of linear channel. It is important to note that these fluxes to the stream are very small. For comparison, the downstream flux of $Mn_{(aq)}$ in the river during baseflow is $\sim 1.4 \text{ mol/d}$ at the Pumphouse.

In the Low-Snow scenario with a smaller spring snowmelt event and shorter freezing period, baseflow conditions persist for a greater portion of the year, about 9 months instead of 7

for the Historic scenario (Figure 9e). During spring snowmelt, DOC from river water is restricted to shallower depths of 20 cm (Figure 9n) compared to 25 cm for the Historic scenario, leading to a shorter period of net Mn-oxide respiration in April and a less negative rate of Mn-oxide accumulation ($-63.8 \mu\text{mol d}^{-1}$ versus $-93.6 \mu\text{mol d}^{-1}$) (Figure 9t). During baseflow, Mn-oxide accumulation rates are greater compared to the Historic scenario ($270 \mu\text{mol d}^{-1}$ versus $224 \mu\text{mol d}^{-1}$) (Figure 9t) due to a greater rate of groundwater upwelling, which supplies $\text{Mn}_{(\text{aq})}$ for oxidation (Figure 9k). Averaged over the year, the Mn-oxide accumulation rate is significantly greater than the Historic scenario ($182.4 \mu\text{mol d}^{-1}$ versus $113.2 \mu\text{mol d}^{-1}$) due to consistently greater accumulation rates during non-frozen conditions and a shorter frozen period.

$\text{Mn}_{(\text{aq})}$ fluxes across the sediment-water interface in the Low-Snow scenario are significantly lower during peak downwelling conditions compared to the Historic scenario ($67.7 \mu\text{mol d}^{-1} \text{ m}^{-2}$ versus $98.9 \mu\text{mol d}^{-1} \text{ m}^{-2}$) due to a decrease in dispersive mixing (Figure 9w). Fluxes are slightly greater during baseflow compared to the Historic scenario ($36.6 \mu\text{mol d}^{-1} \text{ m}^{-2}$ versus $29.3 \mu\text{mol d}^{-1} \text{ m}^{-2}$) due to an increase in advective flux associated with more groundwater upwelling and relatively similar dispersive flux (Figure 9w). It is important to note that I assume lower stage height during baseflow in a Low-Snow year will result in greater rates of groundwater upwelling (Appendix A). This relationship may not hold true and is hard to predict given complex interactions between the hydrosphere and biosphere. Over the entire year, the flux to the river is slightly greater than the Historic scenario ($110.9 \text{ mmol m}^{-1}$ versus $105.6 \text{ mmol m}^{-1}$) because the increased flux during a longer baseflow season is balanced by decreased flux during snowmelt.

In the Storm scenario with distributed, small precipitation events, baseflow conditions span only half the year. The depth of river water mixing is more constant over the year and is limited to ~ 30 cm during storm events (Figure 9f). DO and DOC only penetrate to depths of ~ 25

and 15 cm, respectively, during storm events (Figure 9i and 9o), and each storm event dilutes $Mn_{(aq)}$ concentrations in the upper 50 cm of the streambed (Figure 9l). The net effect is a decline in rates of both Mn-oxide respiration during the peak of each storm event and Mn oxidation immediately after each storm event (Figure 9r) compared to the snowmelt event of the Historic scenario (Figure 9p). Brief periods of net Mn-oxide respiration occur (Mn-oxide accumulation rate of $-10.2 \mu\text{mol d}^{-1}$) during each storm (Figure 9u). In between storm events, upwelling groundwater delivers $Mn_{(aq)}$ to streambed sediments, and Mn oxidation rates are greatest around 15-25 cm (Figure 9r). Over the baseflow season, the Mn-oxide accumulation rate is slightly greater than in the Low-Snow scenario ($284 \mu\text{mol d}^{-1}$ versus $270 \mu\text{mol d}^{-1}$) due to a greater rate of groundwater upwelling, which supplies $Mn_{(aq)}$ (Figure 9u). Averaged over the year, the Mn-oxide accumulation rate is $189.1 \mu\text{mol d}^{-1}$, which is greater than the Low-Snow scenario.

Over the year, the flux of $Mn_{(aq)}$ to the river is more steady in the Storm scenario, with multiple small fluctuations (Figure 9x). Peak $Mn_{(aq)}$ fluxes during storm events are less than peak fluxes during snowmelt events in the Historic and Low-Snow scenarios. During the rising limb of the first storm event, there is a decrease in flux associated with the groundwater flow reversal (Figure 3l) that precedes the peak in stage (Figure 3d) and dispersive mixing (Figure 3p). At this time, the lowest $Mn_{(aq)}$ flux occurs ($23.7 \mu\text{mol d}^{-1} \text{m}^{-2}$). The flux then increases as dispersive mixing peaks with stage (Figure 9x). These fluctuations repeat over each storm cycle until the last streamflow recession, when dispersion-like hyporheic mixing and advection associated with groundwater discharge are both large, leading to a maximum $Mn_{(aq)}$ flux to the stream of $49.8 \mu\text{mol d}^{-1} \text{m}^{-2}$. During baseflow, flux of $Mn_{(aq)}$ across the sediment-water interface is $40.8 \mu\text{mol d}^{-1} \text{m}^{-2}$ (slightly greater than in Historic and Low-Snow scenarios) due to greater advective flux and similar dispersive flux (Figure 9x). The yearly $Mn_{(aq)}$ flux to the river is $121.6 \text{ mmol m}^{-1}$.

Chapter 4. Discussion

4.1 River Water-Groundwater Interactions and Mn Fate in a Changing Climate

Under current “typical” hydrograph conditions, East River, Colorado experiences large seasonal shifts in river water-groundwater mixing that lead to large seasonal changes in $Mn_{(aq)}$ flux and Mn-oxide formation. Rates of Mn-oxide formation are greatest in the summer baseflow season, zero in frozen winter conditions, and negative in spring snowmelt, when net Mn-oxide respiration and mobilization are driven by a greater DOC supply to the hyporheic zone. Fluxes of $Mn_{(aq)}$ to the river are moderate during the baseflow season, zero in frozen winter conditions, and greatest during spring snowmelt due to significant hyporheic mixing. These findings differ from studies of mining-impacted streams. For example, Robbins & Corley [2004] observed increases in the concentration of Mn-oxides in spring and summer months in the hyporheic zone of an alpine stream in Arizona, rather than summer and fall. Similar to Robbins & Corley [2004], August et al. [2002] demonstrated that an alpine wetland impacted by acid mine drainage functioned as a net sink of Mn during spring snowmelt, while the East River streambed is a source. In these studies, $Mn_{(aq)}$ concentrations in river water ranged up to 1 mM. At East River, river water concentrations are generally $\sim 1 \mu M$, and the main source of $Mn_{(aq)}$ to the hyporheic zone is groundwater. Spring snowmelt conditions result in downwelling river water, which limits the supply of $Mn_{(aq)}$ and enhances the supply of DOC, leading to Mn-oxide respiration. During baseflow conditions however, reduced groundwater supplies $Mn_{(aq)}$ to the oxygenated, shallow streambed. The Mn oxidation rates are greatest during this baseflow period. Consequently, a

shift towards a longer baseflow period under a warmer climate should result in the sequestration and immobilization of Mn and other metals in pristine riverbeds like that of East River.

My relatively simple model scenarios suggest that a shift towards less snowpack and a more subdued annual hydrograph will diminish annual fluctuations in Mn cycles and also influence annual average transport behavior. Warmer, drier conditions in the model favor higher average rates of Mn-oxide accumulation in the upper 50 cm of the streambed, potentially by 60% for a 50% decrease in annual stream discharge (Low-Snow scenario). Moreover, less $Mn_{(aq)}$ is mobilized during a smaller spring snowmelt event because Mn-oxide respiration is diminished by a smaller supply of DOC from river water to the hyporheic zone. The yearly $Mn_{(aq)}$ flux from the aquifer to the river may only change by ~5% in response to a smaller snowmelt event. The subdued change in flux is primarily due to tradeoffs between a smaller flux during the spring snowmelt event but a longer non-frozen period when the $Mn_{(aq)}$ flux is towards the river. Under a more storm-dominated hydrological regime with the same 50% decline in annual stream discharge, average rates of Mn-oxide accumulation may increase by 67%, and $Mn_{(aq)}$ flux to the river may increase by 15%, but the timing of accumulation and flux is distributed more evenly over the year. Frequent penetration of DOC-rich river water facilitates short intervals of Mn-oxide respiration and mobilization. A greater increase in $Mn_{(aq)}$ flux to the river for the storm-dominated regime is primarily due to the lack of frozen streambed conditions. With greater accumulation rates of Mn oxidation under a warmer, drier climate, other contaminant metals may be more readily adsorbed and immobilized in the streambed of East River and similar pristine alpine streams.

4.2 Model Considerations

Several biogeochemical processes were simplified in my models. I assumed that the microbial communities remained steady in all scenarios. These communities are likely to respond to a changing hydrograph. Danczak et al. [2016] show that microbial communities in the hyporheic zone of the Colorado River change seasonally over the event, which could result in changes in Mn processing [Clements et al. 2008]. Microbial communities and activities can also be affected by changes in temperature, which were not incorporated in these models [Kaplan & Bott 1989; Storey & Williams 2004]. However, Battin [2000] showed that hyporheic microbial activity was not well correlated with temperature over an annual range similar to that of East River. I also did not account for non-linear, unexpected changes in the quality or quantity of DOC in stream water, which may occur in a changing climate [O'Donnell et al. 2010; Mann et al. 2012]. Such biogeochemical changes would undoubtedly impact Mn transport and processing in this system, but are outside the scope of this study and should be assessed in future work. I assumed that DOC is limiting in groundwater and did not include organic matter as a source of DOC in the hyporheic zone [Zarnetske et al. 2012; Knights et al. 2017]. Given the significant pulse of DOC in the river water during spring snowmelt and coarse nature of streambed gravels, sediment sources of DOC are unlikely to play a major role in alleviating DOC limitations on Mn-oxide respiration. It is possible that groundwater contains Mancos-shale derived DOC, but many studies have shown such groundwater DOC to be less labile than terrestrially-derived DOC in river water [Grøn et al. 1992; Schindler & Krabbenhoft 1998; Sobczak & Findlay 2002].

This study took a one dimensional approach to represent hyporheic transport. As such, my models did not explicitly incorporate multidimensional flow paths. For example, bedforms have been shown to promote downwelling conditions that deliver more oxygen to streambed

sediments on the leeward side [Shen et al. 1990; Elliott & Brooks 1997], resulting in horizontal gradients in aerobic respiration and nitrate removal [Harvey & Bencala 1993; Boano et al. 2012]. Additionally, at the scale of meanders, lateral hyporheic flow paths connect recharge zones on the upslope edge of the meander with discharge zones on the opposite side of the bend [Boano et al. 2010]. Such trends will likely have a predictable effect on Mn transport and transformation at the reach scale. Future field observations and streambed mapping could support the development of multidimensional hyporheic transport models to explore heterogeneity in Mn transport.

I did not measure Mn-oxide concentrations or mineral composition, which would have required destructive sampling of my monitoring sites. Measuring changes in Mn-oxide concentrations and composition over seasons is an important area for future study. Furthermore, my model does not capture multiphase transport during frozen conditions [Kalousová et al. 2014]. No sampling campaigns were conducted during winter due to difficulty extracting samples from the frozen subsurface. This is a time when microbial activity [Zelles et al. 1991; Liang et al. 2003] and fluxes [Cherkauer & Lettenmaier 1999] are likely minimal.

Chapter 5. Conclusion

The timing and magnitude of snowmelt events in alpine river systems has a large impact on Mn transformation and mobility. During baseflow conditions when groundwater upwelling restricts the depth of hyporheic mixing, Mn oxidation occurs at shallow depths. A reversal to downwelling conditions during spring snowmelt results in a decrease in pore-water concentrations of $Mn_{(aq)}$ and an increase in DOC, simultaneously restricting Mn oxidation and enhancing Mn-oxide respiration. In years with less snowmelt, a diminished supply of DOC to the upper streambed during spring should limit Mn-oxide respiration, and a longer baseflow season should increase the supply of $Mn_{(aq)}$ from groundwater for Mn-oxide formation, leading to greater rates of Mn-oxide accumulation. In the absence of a frozen bed and large snowmelt event, a more subdued annual hydrograph is expected to result in smaller annual disturbances to streambed chemistry and microbial communities. With less hyporheic mixing under more persistent groundwater upwelling, DO and DOC from river water will only reach microbial communities in the uppermost sediments. Persistent supply of $Mn_{(aq)}$ from groundwater will result in further increases in Mn-oxide accumulation rates, immobilizing the metal and creating additional sorption sites for other trace metals.

While many hyporheic modeling studies have focused on carbon and nitrate, models of dynamic Mn transport in hyporheic zones are limited. My models, developed from field observations in a pristine river, show that dynamic hyporheic mixing has large effects on Mn fate in streambeds. Future research should focus on two- and three-dimensional observations

and models to understand the role that lateral flowpaths play in Mn transport and transformation. As climate changes and anthropogenic metal contamination in riverine systems intensifies, it will be imperative to understand the fate of Mn in alpine rivers and their sediments to better predict changes in metal mobility and water quality.

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Appendix A. Idealized Flow Conditions

Stage height and stream discharge data were recorded at the Pumpouse location and obtained from the East River Data Portal site. Idealized stage height (h) for each hydrograph scenario was represented as the sum of normal Gaussian distribution curves, denoted $N(\mu, \alpha^2)$ where μ is the timing of the peak event and α^2 characterizes the event length:

$$h_l(t) = h_{base,l} + h_{amp,l} \sum_{n=-1} N(\mu_l - 365n, \alpha_l^2).$$

Subscript l denotes Historic (*hist*), Low-Snow (*low*), and Storm (*stm*) scenarios. $h_{base,l}$ is average stage height at baseflow (Table 3), $h_{amp,l}$ is the amplitude of peak stage, n is the simulation year, t is time in days, μ_l is the time of peak stage, and α_l is half of the duration of the event. Simulation year one is represented by $n=0$. For the Storm scenario, the timing of the peak of the first storm event is provided in Table 3, and subsequent events each occur 30 days after the previous event. Stage was related to discharge using the rating curve for the Pumpouse location:

$$Q(t)[\text{m}^3\text{s}^{-1}] = 14.975(h(t)[\text{m}])^2 - 3.4558(h(t)[\text{m}]).$$

Specific conductivity in river water becomes diluted during the spring snowmelt event, but the minimum lags peak discharge by about 15 days:

$$C_{SPC,RW}(t)[\mu\text{S cm}^{-1}] = 261.2[\mu\text{S cm}^{-1}](Q(t[\text{d}] - 15[\text{d}])[\text{m}^3\text{s}^{-1}])^{-0.2095}.$$

DOC concentration in river water increases, but the peak precedes the peak in discharge by about 32 days:

$$C_{DOC,RW}(t)[\text{mM}] = 0.045[\text{mM}] + 0.016[\text{mM}](Q(t[\text{d}] + 32[\text{d}])[\text{m}^3\text{s}^{-1}]).$$

Darcy velocity across the bed also precedes the snowmelt event (34 days). I related Darcy velocity to river stage through Darcy's Law:

$$q(t)[\text{md}^{-1}] = 0.46[\text{md}^{-1}] - K[\text{md}^{-1}] \frac{h_d[\text{m}] + h(t[\text{d}] + 34[\text{d}])[\text{m}]}{dx[\text{m}]},$$

where K is hydraulic conductivity (Table 3), and h_d is hydraulic head at a depth of dx . Parameters h_d and dx were measured using a manometer during baseflow [Nelson et al., in prep]. This relationship implies that an increase in stage drives a reversal in groundwater flow. At low stage, groundwater flow is toward the stream, and the flux during baseflow in the Historic scenario is consistent with estimates from heat tracing. The relationship also implies that in drier scenarios with lower stage in late summer, the groundwater discharge rate is greater. In other words, drier scenarios with lower stage have higher rates of baseflow. In practice, the groundwater discharge rate is difficult to predict in a changing climate and will vary along reaches due to geologic controls on spring locations and over time due to feedbacks in recharge and vegetation.

In the field scenario, Darcy velocity was represented as the sum of multiple idealized, Gaussian curves. The behavior is similar to estimates from heat tracing but was modified to improve fits between modeled and measured specific conductivity profiles. Specifically:

$$\begin{aligned} q_{field}(t)[\text{md}^{-1}] = & 0.0864[\text{md}^{-1}] - 0.181[\text{md}^{-1}] \sum_{n=-1} N(260.4[d] - 365n, 33.8[d]^2) - \\ & 0.0302[\text{md}^{-1}] \sum_{n=-1} N(355[d] - 365n, 31.5[d]^2) + \\ & 0.242[\text{md}^{-1}] \sum_{n=-1} N(251[d] - 365n, 29.2[d]^2). \end{aligned}$$

All idealized curves and measured parameters are shown in Figure 3.

Table 4. Idealized curve parameters.

Parameter	Description	Value
α_{hist}	Half duration of snowmelt event for Historic scenario	39.6 (d)
α_{low}	Half duration of snowmelt event for Low-Snow scenario	32.6 (d)
α_{stm}	Half duration of each storm event for Storm scenario	17 (d)
μ_{hist}	Time of peak snowmelt event for Historic scenario	294.4 (d)
μ_{low}	Time of peak snowmelt event for Low-Snow scenario	264.4 (d)
μ_{stm}	Time of peak of first storm event for Storm scenario	129 (d)
dx	Depth of hydraulic head measurement	0.38 (m)
$h_{amp,hist}$	Stage amplitude of snowmelt event for Historic scenario	0.6177 (m)
$h_{amp,low}$	Stage amplitude of snowmelt event for Low-Snow scenario	0.5 (m)
$h_{amp,stm}$	Stage amplitude of storm events for Storm scenario	0.332 (m)
$h_{base,hist}$	Stage at baseflow for Historic scenario	0.3588 (m)
$h_{base,low}$	Stage at baseflow for Low-Snow scenario	0.3 (m)
$h_{base,stm}$	Stage at baseflow for Storm scenario	0.28 (m)
h_d	Hydraulic head at depth	0.45 (m)
K	Hydraulic conductivity	0.15 (m d ⁻¹)

Appendix B. Field Model Code

```
% Generated by Comsol v. 5.2 and run using Matlab Livelink for Comsol

function out = model
%
% BaseModel.m
%
% Model exported on Apr 14 2019, 21:30 by COMSOL 5.2.0.220.

import com.comsol.model.*
import com.comsol.model.util.*

model = ModelUtil.create('Model');

model.modelPath('C:\Users\bryant.1694\Box
Sync\research\Data_Workflow\reactive_model\12_fin');

model.label('BaseModel.mph');

model.comments(['Untitled\n\n']);

model.param.set('Dp', '1*10^-7 [m^2/s]', 'Mechanical diffusion at
bottom boundary');
model.param.set('Dm', '1*10^-10 [m^2/s]', 'Molecular diffusion');
model.param.set('Dm_gw', '0.5*10^-10 [m^2/s]', 'Molecular diffusion at
bottom boundary');
model.param.set('G', '41 [1/m]', 'Constant of decay for D(t,z)');
model.param.set('K', '2.42*10^(-9) [m^2]', 'Permeability');
model.param.set('n', '0.27', 'Porosity');
model.param.set('q_F', '0 [m/s]', 'Darcy velocity during freezing');
model.param.set('S', '-0.008', 'Channel Slope');
model.param.set('v_k', '1.13*10^(-6) [m^2/s]', 'Kinematic viscosity of
water');
model.param.set('w', '8.5 [m]', 'Channel width');
model.param.set('L', '1 [m]', 'Domain length');
model.param.set('g', '-9.81 [m/s^2]', 'Gravity');
model.param.set('Ban_DOC', '1', 'Stoichiometric coefficient: DOC in Mn-
oxide respiration');
model.param.set('Ban_Mn', '2', 'Stoichiometric coefficient: Mn(aq) in
Mn-oxide respiration');
model.param.set('Bar_DOC', '1', 'Stoichiometric coefficient: DOC in
aerobic respiration');
model.param.set('Bar_DO', '1', 'Stoichiometric coefficient: DO in
aerobic respiration');
```

```

model.param.set('Bmnox_Mn', '1', 'Stoichiometric coefficient: Mn(aq) in
Mn oxidation');
model.param.set('Bmnox_DO', '0.5', 'Stoichiometric coefficient: DO in
Mn oxidation');
model.param.set('C', '3 [1/m]', 'Constant of decay for microbial
biomass');
model.param.set('K_DOC', '.5 [mmol/L]', 'Half saturation constant for
DOC');
model.param.set('K_i', '0.0075 [mmol/L]', 'Inhibition constant for Mn-
oxide respiration');
model.param.set('K_mnox', '6*10^-4[mmol/L]', 'Half saturation constant
for Mn in Mn oxidation');
model.param.set('K_DO', '.165[mmol/L]', 'Half saturation constant for
DO');
model.param.set('V_an', '.7 [h^-1]', 'Maximum rate of Mn-oxide
respiration');
model.param.set('V_ar', '1 [h^-1]', 'Maximum rate of aerobic
respiration');
model.param.set('V_mnox', '.1 [h^-1]', 'Maximum rate of Mn oxidation');
model.param.set('Xan_gw', '1*10^-3 [mmol/L]', 'Biomass of Mn-oxide
respirers in groundwater');
model.param.set('Xan_rw', '.15 [mmol/L]', 'Biomass of Mn-oxide
respirers in river water');
model.param.set('Xar_gw', '1*10^-2 [mmol/L]', 'Biomass of aerobes in
groundwater');
model.param.set('Xar_rw', '1.5 [mmol/L]', 'Biomass of aerobes in river
water');
model.param.set('Xmnox_gw', '1*10^-3 [mmol/L]', 'Biomass of Mn
oxidizers in groundwater');
model.param.set('Xmnox_rw', '.15 [mmol/L]', 'Biomass of Mn oxidizers in
river water');
model.param.set('DOCrw', '0.0762914 [mmol/L]', 'DOC concentration for
river water at t=0');
model.param.set('Mnrw', '0.000009[mmol/L]', 'Mn(aq) concentration for
river water');
model.param.set('DOrw', '0.25 [mmol/L]', 'DO concentration for river
water');
model.param.set('SpCrw', '267[mmol/L]', 'SpC for river water at t=0,
actually uS/cm');
model.param.set('DOCgw', '.0005 [mmol/L]', 'DOC concentration for
groundwater');
model.param.set('Mngw', '0.023[mmol/L]', 'Mn(aq) concentration for
groundwater');
model.param.set('DOgw', '.025 [mmol/L]', 'DO concentration for
groundwater');
model.param.set('SpCgw', '500[mmol/L]', 'SpC for groundwater, actually
uS/cm');

model.modelNode.create('comp1');

model.geom.create('geom1', 2);

model.file.create('res1');

```

```

model.file.create('res3');
model.file.create('res4');

model.func.create('an1', 'Analytic');
model.func.create('an3', 'Analytic');
model.func.create('an5', 'Analytic');
model.func.create('an6', 'Analytic');
model.func.create('an7', 'Analytic');
model.func.create('an8', 'Analytic');
model.func.create('an11', 'Analytic');
model.func.create('an12', 'Analytic');
model.func.create('an16', 'Analytic');
model.func.create('an17', 'Analytic');
model.func.create('int1', 'Interpolation');
model.func.create('int3', 'Interpolation');
model.func.create('an18', 'Analytic');
model.func.create('int4', 'Interpolation');
model.func.create('an42', 'Analytic');
model.func.create('an43', 'Analytic');
model.func.create('an44', 'Analytic');
model.func.create('an51', 'Analytic');
model.func.create('an53', 'Analytic');
model.func('an1').set('expr', '-(SpCgw-SpCrw)*x+SpCrw');
model.func('an1').set('plotargs', {'x' '-1' '0'});
model.func('an1').set('funcname', 'SpC_IC');
model.func('an3').set('expr', '14.975*(h(x))^2-3.4558*h(x)');
model.func('an3').set('plotargs', {'x' '0' '31536000*5'});
model.func('an3').set('funcname', 'Q');
model.func('an5').set('expr', 'w*h(x)');
model.func('an5').set('plotargs', {'x' '0' '31536000*5'});
model.func('an5').set('funcname', 'A');
model.func('an6').set('expr', 'Q(x)/A(x)');
model.func('an6').set('plotargs', {'x' '0' '31536000*5'});
model.func('an6').set('funcname', 'u');
model.func('an7').set('expr', 'sqrt(g*h(x)*S)');
model.func('an7').set('plotargs', {'x' '0' '31536000*5'});
model.func('an7').set('funcname', 'shear');
model.func('an8').set('expr', '(sqrt(K)*shear(x))/v_k');
model.func('an8').set('plotargs', {'x' '0' '31536000*5'});
model.func('an8').set('funcname', 'Re');
model.func('an11').set('expr', 'v_k/Dm');
model.func('an11').set('plotargs', {'x' '0' '31536000*5'});
model.func('an11').set('funcname', 'Sc');
model.func('an12').set('expr', '1.9*((Re(x))^2)*Sc(x)*Dm');
model.func('an12').set('plotargs', {'x' '0' '31536000*1'});
model.func('an12').set('funcname', 'D_top');
model.func('an16').set('expr', '-(DOgw-DOrw)*x+DOrw');
model.func('an16').set('plotargs', {'x' '-1' '0'});
model.func('an16').set('funcname', 'DO_IC');
model.func('an17').set('expr', '-(DOCgw-DOCrw)*x+DOCrw');
model.func('an17').set('plotargs', {'x' '-1' '0'});
model.func('an17').set('funcname', 'DOC_IC');
model.func('int1').label('Int 1');

```

```

model.func('int1').set('funcs', {'SpC_top' '1'});
model.func('int1').set('filename', 'C:\Users\bryant.1694\Box
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model.func('int1').set('interp', 'piecewisecubic');
model.func('int1').set('source', 'file');
model.func('int3').label('Int 3');
model.func('int3').set('funcs', {'h' '1'});
model.func('int3').set('filename', 'C:\Users\bryant.1694\Box
Sync\research\Data_Workflow\reactive_model\h_5yr_red7.txt');
model.func('int3').set('source', 'file');
model.func('an18').set('expr', '-0.0000021*exp(-(x-
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0.0000021*exp(-(x-85572000)^2/(2922304^2))-0.00000035*exp(-(x-31536000-
10*86400)^2/(2722304^2))-0.00000035*exp(-(x+0-10*86400)^2/(2722304^2))-
0.00000035*exp(-(x-63072000-10*86400)^2/(2722304^2))-0.00000035*exp(-(
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9*86400)^2/(2522304^2))+0.0000028*exp(-(x+22465600-
9*86400)^2/(2522304^2))+0.0000028*exp(-(x-40606400-
9*86400)^2/(2522304^2))+0.0000028*exp(-(x-72142400-
9*86400)^2/(2522304^2))');
model.func('an18').set('plotargs', {'x' '0' '31536000*1'});
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model.func('int4').set('funcs', {'DOC_top' '1'});
model.func('int4').set('filename', 'C:\Users\bryant.1694\Box
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model.func('int4').set('interp', 'piecewisecubic');
model.func('int4').set('source', 'file');
model.func('an42').set('args', {'x' 'y'});
model.func('an42').set('expr', '(Xan_rw-Xan_gw)*exp(C*y)+Xan_gw');
model.func('an42').set('plotargs', {'x' '0' '31536000*3'; 'y' '-1'
'0'});
model.func('an42').set('funcname', 'Xan');
model.func('an43').set('args', {'x' 'y'});
model.func('an43').set('expr', '(Xmnox_rw-
Xmnox_gw)*exp(C*y)+Xmnox_gw');
model.func('an43').set('plotargs', {'x' '0' '31536000*3'; 'y' '-1'
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model.func('an43').set('funcname', 'Xmnox');
model.func('an44').set('args', {'x' 'y'});
model.func('an44').set('expr', '(Xar_rw-Xar_gw)*exp(C*y)+Xar_gw');
model.func('an44').set('plotargs', {'x' '0' '31536000*3'; 'y' '-1'
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model.func('an44').set('funcname', 'Xar');
model.func('an51').set('expr', '-(Mngw-Mnrw)*x+Mnrw');
model.func('an51').set('plotargs', {'x' '-1' '0'});
model.func('an51').set('funcname', 'Mn_IC');
model.func('an53').set('args', {'x' 'y'});
model.func('an53').set('expr', '(D_top(x)-Dp)*exp(G*y)+Dp');
model.func('an53').set('plotargs', {'x' '0' '31536000*3'; 'y' '-1'
'0'});
model.func('an53').set('funcname', 'D');

```

```

model.mesh.create('mesh1', 'geom1');

model.geom('geom1').create('r1', 'Rectangle');
model.geom('geom1').feature('r1').set('size', {'1' '1'});
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model.geom('geom1').run();

model.physics.create('thaw', 'DilutedSpeciesPorousMedia', 'geom1');
model.physics('thaw').identifier('thaw');
model.physics('thaw').field('concentration').field('cSpC');
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'cMn' 'cDOC'});
model.physics('thaw').create('reac1', 'Reactions', 2);
model.physics('thaw').feature('reac1').selection.set([1]);
model.physics('thaw').create('concl', 'Concentration', 1);
model.physics('thaw').feature('concl').selection.set([2]);
model.physics('thaw').create('conc2', 'Concentration', 1);
model.physics('thaw').feature('conc2').selection.set([3]);

model.mesh('mesh1').create('size1', 'Size');
model.mesh('mesh1').create('ftri1', 'FreeTri');
model.mesh('mesh1').feature('size1').selection.geom('geom1', 1);
model.mesh('mesh1').feature('size1').selection.set([2 3]);

model.result.table.create('tbl1', 'Table');

model.view('view1').axis.set('abstractviewxscale',
'0.003611610271036625');
model.view('view1').axis.set('ymin', '-1.0223249197006226');
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model.view('view1').axis.set('abstractviewbratio', '-
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model.view('view1').axis.set('abstractviewratio',
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model.view('view1').axis.set('abstractviewrratio',
'3.1296675205230713');
model.view('view1').axis.set('xmin', '-1.0416666269302368');
model.view('view1').axis.set('abstractviewlratio', '-
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model.view('view1').axis.set('ymax', '0.027675092220306396');

model.physics('thaw').prop('EquationForm').set('form', 'Transient');
model.physics('thaw').feature('pmtpl').set('epsilon_p_mat', 'userdef');
model.physics('thaw').feature('pmtpl').set('epsilon_p', 'n');
model.physics('thaw').feature('pmtpl').set('FluidDiffusivityModelType',
'UserDefined');
model.physics('thaw').feature('pmtpl').set('minput_velocity', {'0';
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model.physics('thaw').feature('pmtpl').set('DF_cSpC', {'D(t,y)*n'; '0';
'0'; '0'; 'D(t,y)*n'; '0'; '0'; '0'; '0'; 'D(t,y)*n'});

```

```

model.physics('thaw').feature('pmtpl').set('DF_cMn', {'D(t,y)*n'; '0';
'0'; '0'; 'D(t,y)*n'; '0'; '0'; '0'; 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDOC', {'D(t,y)*n'; '0';
'0'; '0'; 'D(t,y)*n'; '0'; '0'; '0'; 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDO', {'D(t,y)*n'; '0';
'0'; '0'; 'D(t,y)*n'; '0'; '0'; '0'; 'D(t,y)*n'});
model.physics('thaw').feature('init1').set('initc', {'SpC_IC(y)';
'DO_IC(y)'; 'Mn_IC(y)'; 'DOC_IC(y)'});
model.physics('thaw').feature('reac1').set('R_cMn',
'n*(K_i/(K_i+cDO))*Ban_Mn*V_an*Xan(x,y)*(cDOC/(K_DOC+cDOC))-
n*Bmnox_Mn*V_mnox*Xmnox(x,y)*(cDO/(K_DO+cDO))*(cMn/(K_mnox+cMn))');
model.physics('thaw').feature('reac1').set('R_cDOC', '-
n*Bar_DOC*V_ar*Xar(x,y)*(cDO/(K_DO+cDO))*(cDOC/(K_DOC+cDOC))-
n*(K_i/(K_i+cDO))*Ban_DOC*V_an*Xan(x,y)*(cDOC/(K_DOC+cDOC))');
model.physics('thaw').feature('reac1').set('R_cDO', '-
n*Bar_DO*V_ar*Xar(x,y)*(cDO/(K_DO+cDO))*(cDOC/(K_DOC+cDOC))-
n*Bmnox_DO*V_mnox*Xmnox(x,y)*(cDO/(K_DO+cDO))*(cMn/(K_mnox+cMn))');
model.physics('thaw').feature('conc1').set('species', {'1'; '1'; '1';
'1'});
model.physics('thaw').feature('conc1').set('c0', {'SpCgw'; 'DOgw';
'Mngw'; 'DOCgw'});
model.physics('thaw').feature('conc1').label('BCbottom');
model.physics('thaw').feature('conc2').set('species', {'1'; '1'; '1';
'1'});
model.physics('thaw').feature('conc2').set('c0', {'SpC_top(t)'; 'DOrw';
'Mnrw'; 'DOC_top(t)'});
model.physics('thaw').feature('conc2').label('BCtop');

model.mesh('mesh1').feature('size').set('hauto', 4);
model.mesh('mesh1').feature('size').set('custom', 'on');
model.mesh('mesh1').feature('size').set('hmax', '0.02');
model.mesh('mesh1').feature('size1').set('custom', 'on');
model.mesh('mesh1').feature('size1').set('hmaxactive', true);
model.mesh('mesh1').feature('size1').set('hmax', '0.005');
model.mesh('mesh1').run;

model.frame('material1').sorder(1);

model.result.table('tbl1').comments('Surface Integration 1
(n*(K_i/(K_i+cDO))*Xmnox_Mn*V_mnox*Bmnox(x,y)*(cDO/(K_DO+cDO))*(cMn/(K_
mnox+cMn))-
n*(K_i/(K_i+cDO))*Xan_Mn*V_an*Ban(x,y)*(cDOC/(K_DOC+cDOC))');

model.study.create('std1');
model.study('std1').create('time', 'Transient');
model.study.create('std2');
model.study('std2').create('time', 'Transient');
model.study.create('std3');
model.study('std3').create('time', 'Transient');
model.study.create('std4');
model.study('std4').create('time', 'Transient');
model.study.create('std5');
model.study('std5').create('time', 'Transient');

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model.study.create('std6');
model.study('std6').create('time', 'Transient');

model.sol.create('sol1');
model.sol('sol1').study('std1');
model.sol('sol1').attach('std1');
model.sol('sol1').create('st1', 'StudyStep');
model.sol('sol1').create('v1', 'Variables');
model.sol('sol1').create('t1', 'Time');
model.sol('sol1').feature('t1').create('fc1', 'FullyCoupled');
model.sol('sol1').feature('t1').create('d1', 'Direct');
model.sol('sol1').feature('t1').feature.remove('fcDef');
model.sol.create('sol2');
model.sol('sol2').study('std2');
model.sol('sol2').attach('std2');
model.sol('sol2').create('st1', 'StudyStep');
model.sol('sol2').create('v1', 'Variables');
model.sol('sol2').create('t1', 'Time');
model.sol('sol2').feature('t1').create('fc1', 'FullyCoupled');
model.sol('sol2').feature('t1').create('d1', 'Direct');
model.sol('sol2').feature('t1').feature.remove('fcDef');
model.sol.create('sol3');
model.sol('sol3').study('std3');
model.sol('sol3').attach('std3');
model.sol('sol3').create('st1', 'StudyStep');
model.sol('sol3').create('v1', 'Variables');
model.sol('sol3').create('t1', 'Time');
model.sol('sol3').feature('t1').create('fc1', 'FullyCoupled');
model.sol('sol3').feature('t1').create('d1', 'Direct');
model.sol('sol3').feature('t1').feature.remove('fcDef');
model.sol.create('sol4');
model.sol('sol4').study('std4');
model.sol('sol4').attach('std4');
model.sol('sol4').create('st1', 'StudyStep');
model.sol('sol4').create('v1', 'Variables');
model.sol('sol4').create('t1', 'Time');
model.sol('sol4').feature('t1').create('fc1', 'FullyCoupled');
model.sol('sol4').feature('t1').create('d1', 'Direct');
model.sol('sol4').feature('t1').feature.remove('fcDef');
model.sol.create('sol5');
model.sol('sol5').study('std5');
model.sol('sol5').attach('std5');
model.sol('sol5').create('st1', 'StudyStep');
model.sol('sol5').create('v1', 'Variables');
model.sol('sol5').create('t1', 'Time');
model.sol('sol5').feature('t1').create('fc1', 'FullyCoupled');
model.sol('sol5').feature('t1').create('d1', 'Direct');
model.sol('sol5').feature('t1').feature.remove('fcDef');
model.sol.create('sol6');
model.sol('sol6').study('std6');
model.sol('sol6').attach('std6');
model.sol('sol6').create('st1', 'StudyStep');
model.sol('sol6').create('v1', 'Variables');

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model.sol('sol6').create('t1', 'Time');
model.sol('sol6').feature('t1').create('fc1', 'FullyCoupled');
model.sol('sol6').feature('t1').create('d1', 'Direct');
model.sol('sol6').feature('t1').feature.remove('fcDef');

model.result.numerical.create('int1', 'IntSurface');
model.result.numerical.create('int2', 'IntLine');
model.result.numerical('int1').selection.set([1]);
model.result.numerical('int1').set('probetag', 'none');
model.result.numerical('int2').selection.set([3]);
model.result.numerical('int2').set('probetag', 'none');
model.result.create('pg1', 'PlotGroup2D');
model.result.create('pg2', 'PlotGroup1D');
model.result.create('pg3', 'PlotGroup2D');
model.result.create('pg4', 'PlotGroup2D');
model.result.create('pg5', 'PlotGroup2D');
model.result.create('pg6', 'PlotGroup2D');
model.result.create('pg7', 'PlotGroup2D');
model.result('pg1').create('surf1', 'Surface');
model.result('pg2').set('data', 'dset2');
model.result('pg2').create('lng1', 'LineGraph');
model.result('pg2').feature('lng1').set('data', 'dset6');
model.result('pg2').feature('lng1').set('xdata', 'expr');
model.result('pg2').feature('lng1').selection.set([1]);
model.result('pg3').create('surf1', 'Surface');
model.result('pg4').set('data', 'dset3');
model.result('pg4').create('surf1', 'Surface');
model.result('pg5').set('data', 'dset4');
model.result('pg5').create('surf1', 'Surface');
model.result('pg6').set('data', 'dset5');
model.result('pg6').create('surf1', 'Surface');
model.result('pg7').set('data', 'dset6');
model.result('pg7').create('surf1', 'Surface');

model.study('std1').feature('time').set('rtol', '0.0001');
model.study('std1').feature('time').set('tlist', '0,13651200');
model.study('std1').feature('time').set('rtolactive', true);
model.study('std2').feature('time').set('solnum', 'last');
model.study('std2').feature('time').set('useinitsol', 'on');
model.study('std2').feature('time').set('rtol', '0.0001');
model.study('std2').feature('time').set('tlist', '13651200,19785600');
model.study('std2').feature('time').set('rtolactive', true);
model.study('std2').feature('time').set('initstudy', 'std1');
model.study('std2').feature('time').set('initmethod', 'sol');
model.study('std3').feature('time').set('solnum', 'last');
model.study('std3').feature('time').set('useinitsol', 'on');
model.study('std3').feature('time').set('rtol', '0.0001');
model.study('std3').feature('time').set('tlist', '19785600,31363200');
model.study('std3').feature('time').set('rtolactive', true);
model.study('std3').feature('time').set('initstudy', 'std2');
model.study('std3').feature('time').set('initmethod', 'sol');
model.study('std4').feature('time').set('solnum', 'last');
model.study('std4').feature('time').set('useinitsol', 'on');

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model.study('std4').feature('time').set('rtol', '0.0001');
model.study('std4').feature('time').set('tlist',
'31363200,31762800,36860400,45100800');
model.study('std4').feature('time').set('rtolactive', true);
model.study('std4').feature('time').set('initstudy', 'std3');
model.study('std4').feature('time').set('initmethod', 'sol');
model.study('std5').feature('time').set('solnum', 'last');
model.study('std5').feature('time').set('useinitsol', 'on');
model.study('std5').feature('time').set('rtol', '0.0001');
model.study('std5').feature('time').set('tlist', '45100800,51321600');
model.study('std5').feature('time').set('rtolactive', true);
model.study('std5').feature('time').set('initstudy', 'std4');
model.study('std5').feature('time').set('initmethod', 'sol');
model.study('std6').feature('time').set('solnum', 'last');
model.study('std6').feature('time').set('useinitsol', 'on');
model.study('std6').feature('time').set('rtol', '0.0001');
model.study('std6').feature('time').set('tlist',
'51321600,54648000,60530400,63072000');
model.study('std6').feature('time').set('rtolactive', true);
model.study('std6').feature('time').set('initstudy', 'std5');
model.study('std6').feature('time').set('initmethod', 'sol');

model.sol('sol1').attach('std1');
model.sol('sol1').feature('t1').set('maxstepbdf', '60*15');
model.sol('sol1').feature('t1').set('initialstepbdfactive', true);
model.sol('sol1').feature('t1').set('atolmethod', {'comp1_cSpC'
'global' 'comp1_cDOC' 'global' 'comp1_cDO' 'global' 'comp1_cMn'
'global'});
model.sol('sol1').feature('t1').set('tstepsbdf', 'strict');
model.sol('sol1').feature('t1').set('atol', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol1').feature('t1').set('maxstepbdfactive', true);
model.sol('sol1').feature('t1').set('atoludotactive', {'comp1_cSpC'
'off' 'comp1_cDOC' 'off' 'comp1_cDO' 'off' 'comp1_cMn' 'off'});
model.sol('sol1').feature('t1').set('tlist', '0,13651200');
model.sol('sol1').feature('t1').set('initialstepbdf', '60');
model.sol('sol1').feature('t1').set('maxorder', '2');
model.sol('sol1').feature('t1').set('atolglobal', '0.000001');
model.sol('sol1').feature('t1').set('atoludot', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol1').feature('t1').set('rtol', '0.0001');
model.sol('sol1').feature('t1').feature('fc1').set('jtech', 'once');
model.sol('sol1').feature('t1').feature('fc1').set('damp', '0.9');
model.sol('sol1').feature('t1').feature('fc1').set('maxiter', '8');
model.sol('sol1').feature('t1').feature('d1').set('linsolver',
'pardiso');
model.sol('sol2').attach('std2');
model.sol('sol2').feature('v1').set('initsol', 'sol1');
model.sol('sol2').feature('v1').set('solnum', 'last');
model.sol('sol2').feature('v1').set('initmethod', 'sol');
model.sol('sol2').feature('v1').set('notsolmethod', 'sol');
model.sol('sol2').feature('v1').set('notsol', 'sol1');
model.sol('sol2').feature('v1').set('notsolnum', 'last');

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model.sol('sol2').feature('t1').set('maxstepbdf', '60*15');
model.sol('sol2').feature('t1').set('initialstepbdfactive', true);
model.sol('sol2').feature('t1').set('atolmethod', {'comp1_cSpC'
'global' 'comp1_cDOC' 'global' 'comp1_cDO' 'global' 'comp1_cMn'
'global'});
model.sol('sol2').feature('t1').set('tstepsbdf', 'strict');
model.sol('sol2').feature('t1').set('atol', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol2').feature('t1').set('maxstepbdfactive', true);
model.sol('sol2').feature('t1').set('atoludotactive', {'comp1_cSpC'
'off' 'comp1_cDOC' 'off' 'comp1_cDO' 'off' 'comp1_cMn' 'off'});
model.sol('sol2').feature('t1').set('tlist', '13651200,19785600');
model.sol('sol2').feature('t1').set('initialstepbdf', '60');
model.sol('sol2').feature('t1').set('maxorder', '2');
model.sol('sol2').feature('t1').set('atolglobal', '1e-6');
model.sol('sol2').feature('t1').set('atoludot', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol2').feature('t1').set('rtol', '0.0001');
model.sol('sol2').feature('t1').feature('fc1').set('jtech', 'once');
model.sol('sol2').feature('t1').feature('fc1').set('damp', '0.9');
model.sol('sol2').feature('t1').feature('fc1').set('maxiter', '8');
model.sol('sol2').feature('t1').feature('d1').set('linsolver',
'pardiso');
model.sol('sol3').attach('std3');
model.sol('sol3').feature('v1').set('initsol', 'sol2');
model.sol('sol3').feature('v1').set('solnum', 'last');
model.sol('sol3').feature('v1').set('initmethod', 'sol');
model.sol('sol3').feature('t1').set('maxstepbdf', '60*15');
model.sol('sol3').feature('t1').set('initialstepbdfactive', true);
model.sol('sol3').feature('t1').set('atolmethod', {'comp1_cSpC'
'global' 'comp1_cDOC' 'global' 'comp1_cDO' 'global' 'comp1_cMn'
'global'});
model.sol('sol3').feature('t1').set('tstepsbdf', 'strict');
model.sol('sol3').feature('t1').set('atol', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol3').feature('t1').set('maxstepbdfactive', true);
model.sol('sol3').feature('t1').set('atoludotactive', {'comp1_cSpC'
'off' 'comp1_cDOC' 'off' 'comp1_cDO' 'off' 'comp1_cMn' 'off'});
model.sol('sol3').feature('t1').set('tlist', '19785600,31363200');
model.sol('sol3').feature('t1').set('initialstepbdf', '60');
model.sol('sol3').feature('t1').set('maxorder', '2');
model.sol('sol3').feature('t1').set('atolglobal', '1e-6');
model.sol('sol3').feature('t1').set('atoludot', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol3').feature('t1').set('rtol', '0.0001');
model.sol('sol3').feature('t1').feature('fc1').set('jtech', 'once');
model.sol('sol3').feature('t1').feature('fc1').set('damp', '0.9');
model.sol('sol3').feature('t1').feature('fc1').set('maxiter', '8');
model.sol('sol3').feature('t1').feature('d1').set('linsolver',
'pardiso');
model.sol('sol4').attach('std4');
model.sol('sol4').feature('v1').set('initsol', 'sol3');
model.sol('sol4').feature('v1').set('solnum', 'last');
model.sol('sol4').feature('v1').set('initmethod', 'sol');

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model.sol('sol4').feature('t1').set('maxstepbdf', '60*15');
model.sol('sol4').feature('t1').set('initialstepbdfactive', true);
model.sol('sol4').feature('t1').set('atolmethod', {'comp1_cSpC'
'global' 'comp1_cDOC' 'global' 'comp1_cDO' 'global' 'comp1_cMn'
'global'}));
model.sol('sol4').feature('t1').set('tstepsbdf', 'strict');
model.sol('sol4').feature('t1').set('atol', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'}));
model.sol('sol4').feature('t1').set('maxstepbdfactive', true);
model.sol('sol4').feature('t1').set('atoludotactive', {'comp1_cSpC'
'off' 'comp1_cDOC' 'off' 'comp1_cDO' 'off' 'comp1_cMn' 'off'}));
model.sol('sol4').feature('t1').set('tlist',
'31363200,31762800,36860400,45100800');
model.sol('sol4').feature('t1').set('initialstepbdf', '60');
model.sol('sol4').feature('t1').set('maxorder', '2');
model.sol('sol4').feature('t1').set('atolglobal', '1e-6');
model.sol('sol4').feature('t1').set('atoludot', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'}));
model.sol('sol4').feature('t1').set('rtol', '0.0001');
model.sol('sol4').feature('t1').feature('fc1').set('jtech', 'once');
model.sol('sol4').feature('t1').feature('fc1').set('damp', '0.9');
model.sol('sol4').feature('t1').feature('fc1').set('maxiter', '8');
model.sol('sol4').feature('t1').feature('d1').set('linsolver',
'pardiso');
model.sol('sol5').attach('std5');
model.sol('sol5').feature('v1').set('initsol', 'sol4');
model.sol('sol5').feature('v1').set('solnum', 'last');
model.sol('sol5').feature('v1').set('initmethod', 'sol');
model.sol('sol5').feature('t1').set('maxstepbdf', '60*15');
model.sol('sol5').feature('t1').set('initialstepbdfactive', true);
model.sol('sol5').feature('t1').set('atolmethod', {'comp1_cSpC'
'global' 'comp1_cDOC' 'global' 'comp1_cDO' 'global' 'comp1_cMn'
'global'}));
model.sol('sol5').feature('t1').set('tstepsbdf', 'strict');
model.sol('sol5').feature('t1').set('atol', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'}));
model.sol('sol5').feature('t1').set('maxstepbdfactive', true);
model.sol('sol5').feature('t1').set('atoludotactive', {'comp1_cSpC'
'off' 'comp1_cDOC' 'off' 'comp1_cDO' 'off' 'comp1_cMn' 'off'}));
model.sol('sol5').feature('t1').set('tlist', '45100800,51321600');
model.sol('sol5').feature('t1').set('initialstepbdf', '60');
model.sol('sol5').feature('t1').set('maxorder', '2');
model.sol('sol5').feature('t1').set('atolglobal', '1e-6');
model.sol('sol5').feature('t1').set('atoludot', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'}));
model.sol('sol5').feature('t1').set('rtol', '0.0001');
model.sol('sol5').feature('t1').feature('fc1').set('jtech', 'once');
model.sol('sol5').feature('t1').feature('fc1').set('damp', '0.9');
model.sol('sol5').feature('t1').feature('fc1').set('maxiter', '8');
model.sol('sol5').feature('t1').feature('d1').set('linsolver',
'pardiso');
model.sol('sol6').attach('std6');
model.sol('sol6').feature('v1').set('initsol', 'sol5');
model.sol('sol6').feature('v1').set('solnum', 'last');

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model.sol('sol6').feature('v1').set('initmethod', 'sol');
model.sol('sol6').feature('t1').set('maxstepbdf', '60*15');
model.sol('sol6').feature('t1').set('initialstepbdfactive', true);
model.sol('sol6').feature('t1').set('atolmethod', {'comp1_cSpC'
'global' 'comp1_cDOC' 'global' 'comp1_cDO' 'global' 'comp1_cMn'
'global'});
model.sol('sol6').feature('t1').set('tstepsbdf', 'strict');
model.sol('sol6').feature('t1').set('atol', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol6').feature('t1').set('maxstepbdfactive', true);
model.sol('sol6').feature('t1').set('atoludotactive', {'comp1_cSpC'
'off' 'comp1_cDOC' 'off' 'comp1_cDO' 'off' 'comp1_cMn' 'off'});
model.sol('sol6').feature('t1').set('tlist',
'51321600,54648000,60530400,63072000');
model.sol('sol6').feature('t1').set('initialstepbdf', '60');
model.sol('sol6').feature('t1').set('maxorder', '2');
model.sol('sol6').feature('t1').set('atolglobal', '1e-6');
model.sol('sol6').feature('t1').set('atoludot', {'comp1_cSpC' '1e-3'
'comp1_cDOC' '1e-3' 'comp1_cDO' '1e-3' 'comp1_cMn' '1e-3'});
model.sol('sol6').feature('t1').set('rtol', '0.0001');
model.sol('sol6').feature('t1').feature('fc1').set('jtech', 'once');
model.sol('sol6').feature('t1').feature('fc1').set('damp', '0.9');
model.sol('sol6').feature('t1').feature('fc1').set('maxiter', '8');
model.sol('sol6').feature('t1').feature('d1').set('linsolver',
'pardiso');

model.result.numerical('int1').set('table', 'tbl1');
model.result.numerical('int1').set('expr',
'n*(K_i/(K_i+cDO))*Xmnox_Mn*V_mnox*Bmnox(x,y)*(cDO/(K_DO+cDO))*(cMn/(K_
mnox+cMn))-
n*(K_i/(K_i+cDO))*Xan_Mn*V_an*Ban(x,y)*(cDOC/(K_DOC+cDOC))');
model.result.numerical('int1').set('unit', '');
model.result.numerical('int1').set('descr',
'n*(K_i/(K_i+cDO))*Xmnox_Mn*V_mnox*Bmnox(x,y)*(cDO/(K_DO+cDO))*(cMn/(K_
mnox+cMn))-
n*(K_i/(K_i+cDO))*Xan_Mn*V_an*Ban(x,y)*(cDOC/(K_DOC+cDOC))');
model.result.numerical('int2').set('expr', 'tds.tflux_cMny');
model.result.numerical('int2').set('unit', '');
model.result.numerical('int2').set('descr', 'Total flux, y component');
model.result.numerical('int1').setResult;
model.result('pg1').label('Concentration (tds)');
model.result('pg1').feature('surf1').set('expr', 'cMn');
model.result('pg2').set('xlabel', 'Concentration (mol/m<sup>3</sup>)');
model.result('pg2').set('ylabel', 'y-coordinate (m)');
model.result('pg2').set('showlegends', 'off');
model.result('pg2').set('ylabelactive', false);
model.result('pg2').set('xlabelactive', false);
model.result('pg2').feature('lngr1').set('expr', 'y');
model.result('pg2').feature('lngr1').set('xdataexpr', 'cMn');
model.result('pg2').feature('lngr1').set('descr', 'y-coordinate');
model.result('pg2').feature('lngr1').set('unit', 'm');
model.result('pg3').label('Concentration (tds) 1');
model.result('pg4').label('Concentration (tds) 2');

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model.result('pg5').label('Concentration (tds) 3');
model.result('pg6').label('Concentration (tds) 4');
model.result('pg7').label('Concentration (thaw)');

model.sol('sol1').runAll;

model.result('pg1').run;

model.physics('thaw').feature('reac1').active(false);
model.physics('thaw').feature('pmtpl').set('minput_velocity', {'0'
'q_F' '0'});
model.physics('thaw').feature('pmtpl').set('DF_cSpC', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDO', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});
model.physics('thaw').feature('pmtpl').set('DF_cMn', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDOC', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});

model.sol('sol2').runAll;

model.result('pg2').run;

model.physics('thaw').feature('reac1').active(true);
model.physics('thaw').feature('pmtpl').set('minput_velocity', {'0'
'flux(t)' '0'});
model.physics('thaw').feature('pmtpl').set('DF_cSpC', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDO', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cMn', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDOC', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});

model.sol('sol3').runAll;

model.result('pg4').run;

model.sol('sol4').runAll;

model.result('pg5').run;

model.physics('thaw').feature('reac1').active(false);
model.physics('thaw').feature('pmtpl').set('minput_velocity', {'0'
'q_F' '0'});
model.physics('thaw').feature('pmtpl').set('DF_cSpC', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDO', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});

```

```

model.physics('thaw').feature('pmtpl').set('DF_cMn', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDOC', {'Dm*n' '0' '0'
'0' 'Dm*n' '0' '0' '0' 'Dm*n'});

model.sol('sol5').runAll;

model.result('pg6').run;

model.physics('thaw').feature('reac1').active(true);
model.physics('thaw').feature('pmtpl').set('minput_velocity', {'0'
'flux(t)' '0'});
model.physics('thaw').feature('pmtpl').set('DF_cSpC', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDO', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cMn', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});
model.physics('thaw').feature('pmtpl').set('DF_cDOC', {'D(t,y)*n' '0'
'0' '0' 'D(t,y)*n' '0' '0' '0' 'D(t,y)*n'});

model.sol('sol6').runAll;

model.result('pg7').run;

out = model;

```

Appendix C: Detection Limits, Errors, and Additional Cation Depth Profiles

Table 5. Detection limits and accuracy/error of cation analyses. Samples were run using inductively coupled plasma mass spectrometry (ICP-MS). Analysis details are provided by Saup et al. [2019]. Error was calculated from the standard deviation of standards run on the PerkinElmer ELAN 6000. No error estimate is available for U.

Parameter	Detection Limits	Error
Cr (ppb)	0.377	0.703
Mn (ppb)	0.042	0.081
Cu (ppb)	0.466	5.837
Zn (ppb)	0.166	16.682
As (ppb)	0.911	0.655
Sr (ppb)	0.119	1.589
Mo (ppb)	0.022	0.033
Hg (ppb)	1.043	0.183
Pb (ppb)	10.983	1.243
U (ppb)	0.226	-

Table 6. Manufacturer reported instrument accuracy for basic water quality parameters. All parameters were measured using a Myron L Company Ultrameter II[®] Model 6PFCE, with the exception of dissolved oxygen (DO), which was measured using a Chemetrics V-2000 Multi-Analyte Photometer for Water Quality Analysis. Actual measurement accuracy associated with field sampling protocols is presumably greater.

Parameter	Error
pH	± 0.01
Conductivity ($\mu\text{S cm}^{-1}$)	± 1%
Temperature ($^{\circ}\text{C}$)	± 0.1
ORP (mV)	± 1
TDS (ppm)	± 1%
DO (mg L^{-1})	± 1.5

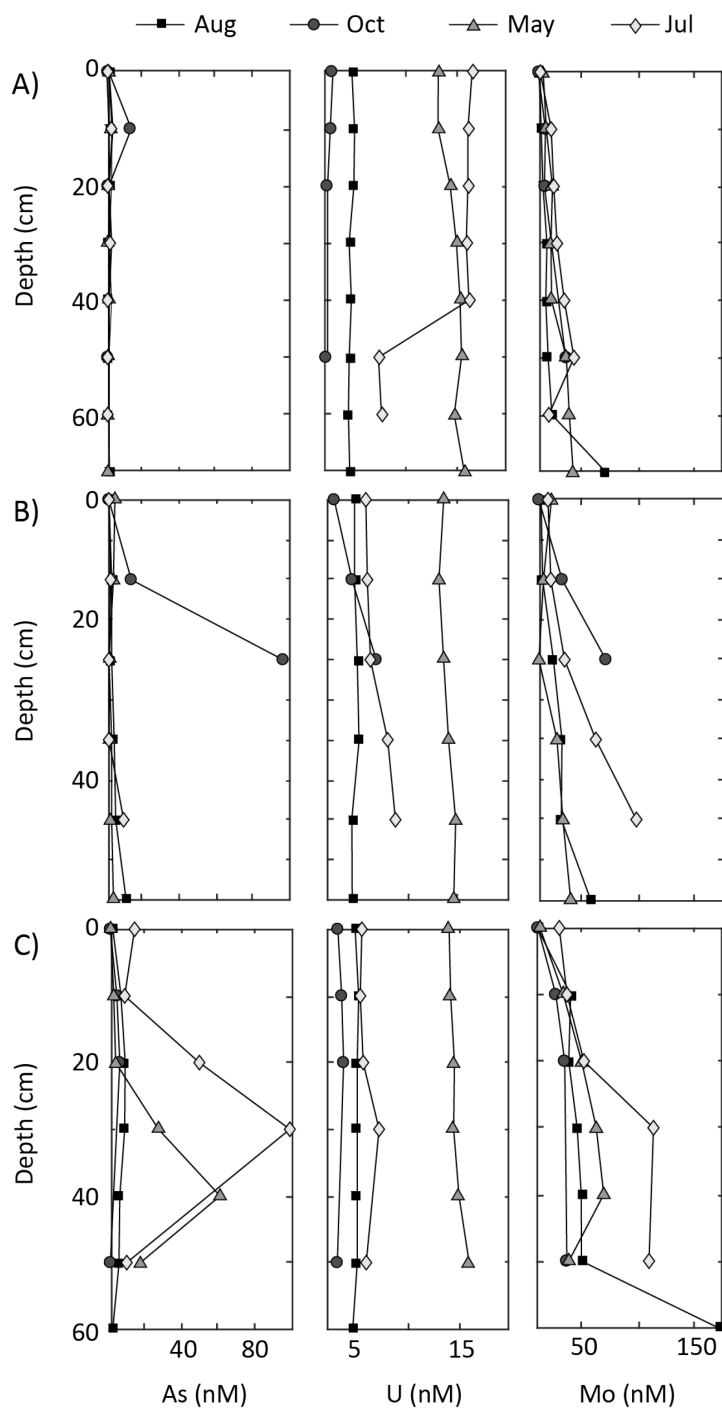


Figure 10. Depth profiles for arsenic (As), uranium (U), and molybdenum (Mo) at locations A (top row), B (middle row), and C (bottom row). Values lower than the detection limit are reported as the detection limit (Appendix C). A, B, and C refer to locations A, B, and C, respectively. This data was obtained from Saup et al. [2019]. Error information is provided in Appendix C.