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# Response of dissolved organic carbon dynamics to salinity in a Constructed Fen Peatland in the Athabasca Oil Sands region

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## Abstract

In northern Alberta, oil sands mining disturbs the boreal landscape, and reclamation to an ‘equivalent land capability’ is required. Industry is testing peatland construction as part of landscape reclamation. To determine if constructed peatlands can be self-sustaining, an understanding of the cycling of solutes in pore water and their interactions with dissolved organic carbon (DOC) is needed since DOC can represent an important carbon loss from peatlands. DOC is of interest due to its biotic origin and use by the microbial community and impact on carbon budgets. Additionally, salinity as a control on DOC quantity and quality may be important in oil sands reclaimed systems due to the likelihood of elevated sodium ( $\text{Na}^+$ ) from saline groundwater input derived from tailings used to construct catchments, and natural sources. For this research, DOC concentration and quality, and  $\text{Na}^+$  concentration were measured in the rooting zone (10 and 30 cm depth) of Nikanotee Fen to evaluate the role of  $\text{Na}^+$  in DOC dynamics. DOC concentration and quality suggested that DOC in the fen was largely sourced from vegetation inputs, with quality also suggesting increases in vegetation inputs between years. Elevated  $\text{Na}^+$  at 30 cm below ground surface corresponded with high concentrations of labile DOC. At 10 cm below ground surface, sampling location and temperature were the best predictors of DOC concentration and quality. With expected increases in  $\text{Na}^+$ , increased production of mobile and microbially active DOC may lead to higher rates of carbon export.

## KEYWORDS

dissolved organic carbon, peatland, reclamation, sodium, spectrophotometric indices, sulphate, water table

## 1 | INTRODUCTION

Oil sands extraction has resulted in over 953 km<sup>2</sup> of land disturbance in the Athabasca Oil Sands Region of northeastern Alberta (Alberta Environment and Parks, 2020), a region that comprised ~50% peatlands (Vitt et al., 1996). Peatlands play an important role in landscape function in this region, including contributions to soil carbon storage,

water storage and water quality (Vitt et al., 2000; Volik et al., 2020). Since oil sands companies are mandated to return the landscape disturbed by oil extraction activities to an ‘equivalent land capability’ after closure (*Conservation and Reclamation Regulation*, AB 115/93), it is important that peatland reclamation be included in the post-mining landscape. To develop an understanding of the best practices for peatland reclamation, efforts to construct (i.e. build from scratch)

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peatland ecosystems have been undertaken in the region including projects such as the Nikanotee Fen (Daly et al., 2010; Price et al., 2010) and the Sandhill Fen (Wytrykush et al., 2012). Fen peatlands have been the focus of these reclamation projects due to their prevalence in the pre-mined landscape (Vitt et al., 1996) and their design can incorporate surface and groundwater sources that help maintain sufficient water levels when precipitation inputs are low (Price et al., 2010). While this hydrological connectivity is beneficial for drought prevention, construction of fens in the post oil sands mining landscape still has many difficulties such as the design needing to account for their complex hydrology (Price et al., 2010), the potential for sodium ( $\text{Na}^+$ ) intrusion from the materials used in construction (Kessel et al., 2018), the fact that peat formation generally occurs over thousands of years (Clymo, 1983), and the drier climate of the region and need to maintain adequate wetness during fen establishment (Price et al., 2010). This study investigates the Nikanotee Fen, constructed to test fen reclamation, and hereafter referred to as the Constructed Fen. The goal of the Constructed Fen project is to restore self-sustaining ecosystem functions, including carbon accumulation, support for peat-forming vegetation and resilience to climatic stresses, while determining factors that can optimize future reclamation designs (Daly et al., 2012; Price et al., 2010). An important component of understanding fen reclamation is the biogeochemistry post-construction and in particular, the dissolved organic carbon (DOC) dynamics. This study contributes to this understanding by examining the controls on DOC quantity and quality in the rooting zone of the Constructed Fen.

DOC is defined as the carbon in organic molecules that pass through a 0.45  $\mu\text{m}$  filter (Thurman, 1985). DOC plays an important role in carbon budgets, generally accounting for 10% of total carbon released from boreal peatlands (Limpens et al., 2008). While some of this exported DOC is stored through sedimentation, it is expected that around 90% is converted to carbon dioxide ( $\text{CO}_2$ ) downstream, thus influencing downstream greenhouse gas (GHG) emissions (Evans et al., 2016). In addition to its significance in carbon storage, DOC also influences peatland and downstream chemistry by altering redox conditions and affecting the mobility of other compounds that may be abundant at reclaimed mine sites, such as heavy metals (e.g., manganese and mercury) and organic contaminants (e.g., naphthenic acids; Kalbitz et al., 1997; Kalbitz & Wennrich, 1998). Furthermore, DOC, especially that sourced from plants, can play a role in priming the microbial community for decomposition, leading to nutrient and organic matter turnover, further supporting plant and microbial communities (Neumann & Romheld, 2000). This may be especially important where highly humified peat may prevent activation of microbial processes without vegetative carbon inputs (Nwaishi et al., 2016). Thus, understanding DOC quantity and quality can help to evaluate nutrient and organic matter turnover and carbon sequestration within the fen and consider the downstream effects of constructed peatlands.

To better determine the origins, transformations and fate of DOC, information is needed on the specific carbon compounds in the DOC pool. Due to the complexity and quantity of these compounds,

it is generally not feasible to characterize every compound contributing to DOC; instead, indicators of DOC quality are often used (Peacock et al., 2014; Strack et al., 2011). Specific Ultraviolet Absorbance at 254 nm ( $\text{SUVA}_{254}$ ) and E2/E3, the ratio of absorbance at 250 and 365 nm, are parameters that are used to indicate DOC quality.  $\text{SUVA}_{254}$  is positively correlated with aromaticity, whereas E2/E3 is negatively correlated with molecular weight (Peacock et al., 2014). DOC with lower molecular weight and less aromatic character is generally more available for decomposition and more mobile (Khadka et al., 2016; Strack et al., 2015).

Environmental factors like soil temperature, water table depth, vegetation type and salinity, among other factors, can all influence DOC concentration and quality through their influence on solubility, decomposition and rhizodeposition. Some factors are well studied for their influence on DOC concentration and quality. For example, sulphate ( $\text{SO}_4^{2-}$ ) which facilitates DOC precipitation (Brouns et al., 2014; Clark et al., 2005; Jager et al., 2009), generally leads to decreased DOC concentration and increased lability. However, one of the factors least studied for its effect on DOC in Canadian peatlands is salinity (Moore, 2013; Moore et al., 2008), potentially due to saline peatlands being rare in North America's boreal region (Scarlett & Price, 2013; Trites & Bayley, 2009). However, with  $\text{Na}^+$  concentrations expected to increase in coastal peatlands due to sea level rise (Church et al., 2013; Gu  n   Nanchen et al., 2020) and an expected increase in reclamation projects in the Athabasca Oil Sands Region as sites begin to close, understanding the effects of salinity on carbon dynamics in peatlands is increasingly important. Due to the high input of solutes (especially  $\text{Na}^+$ ) in the Constructed Fen, this site provides an opportunity to better determine the effects of salinity on DOC quantity and quality. In 2015 and 2016, salinity inferred from electrical conductivity (EC), was a significant control on DOC quantity of the Constructed Fen (Irvine, 2018). However, studies considering the effect of  $\text{Na}^+$  specifically on DOC dynamics have not yet been undertaken at the Constructed Fen.

As the Constructed Fen has been extensively studied, it is already known that DOC has been largely internally produced (Irvine et al., 2021). While DOC export is largely controlled by peatland discharge (Limpens et al., 2008), internal biochemical processes, including rhizodeposition, decomposition and solubility (Moore, 2013), along with internal hydrological processes are responsible for determining DOC quality and quantity within the fen. Hydrological processes like evapoconcentration, within fen water movement, and dilution from precipitation, will alter DOC concentration at locations within the fen, but do not directly change DOC quality. Factors that influence biochemical processes, such as  $\text{Na}^+$ , however, may influence both DOC concentration and quality.

Salinity can influence DOC quantity and quality in peat soils by affecting its adsorption and desorption from the peat matrix. Specifically, ions may saturate sorption sites forcing DOC into solution and bind to DOC directly, increasing its solubility (Kalbitz et al., 2000). Or, ions may reduce charge density allowing for aggregation and precipitation of DOC (Tamamura et al., 2013). Salinity may also influence DOC production and removal by microbes (Khadka et al., 2015),

increasing activity by providing nutrients or decreasing activity from salt stress (Marschner & Kalbitz, 2003). Rhizodeposition may also be affected by salinity. Rhizodeposits are actively exuded from plant roots or released by passive diffusion as root exudates, the latter process being vulnerable to changes in root permeability (Farrar et al., 2003). As elevated salinity is expected to increase root membrane permeability (Vranova et al., 2013), salinity is expected to be positively correlated with root exudation. As DOC present in the fen has been shown to be recently produced, small and labile, it is expected that rhizodeposition plays a dominant role in determining DOC concentration and quality in the fen (Irvine et al., 2021; Khadka et al., 2016). Despite these expected relationships, it is unclear what the cumulative effect of these processes will be in the Constructed Fen.

The objective of this study is to identify the environmental drivers of DOC quantity and quality in the rooting zone of the Constructed Fen, with a focus on the influence of  $\text{Na}^+$ . It is hypothesized that salinity will be an important control on DOC quantity and quality, with higher salinity leading to higher concentrations of DOC and more labile DOC. Given the accumulation of  $\text{Na}^+$  in the Constructed Fen and the expected high  $\text{Na}^+$  concentration in reclamation projects in the Athabasca Oil Sands region, this site provides a unique opportunity to better evaluate the influence of  $\text{Na}^+$  on DOC concentration and quality, which is little studied to date but may be crucial for understanding carbon budgets and plant health in reclaimed systems as well as peatlands influenced by sea level rise.

## 2 | MATERIALS AND METHODS

### 2.1 | Study site

This study was conducted on a constructed fen located on an oil sands lease 40 km north of Fort McMurray ( $56^{\circ}55.944'$  N  $111^{\circ}25.035'$  W). The Constructed Fen has an area of 2.9 ha and is part of a 32.1 ha reclaimed watershed (Ketcheson & Price, 2016). The pH range of the Constructed Fen is typically between 5.5 and 7.5 (Murray et al., 2017). The watershed is underlain by a geosynthetic clay liner that forces lateral water flow into the fen and prevents seepage into the underlying groundwater (Ketcheson et al., 2017; Price et al., 2010). To facilitate water movement through the watershed into the fen, an upland aquifer was created from tailings, with tailings selected as the material due to its relatively high hydraulic conductivity, abundance in the region and for reclamation of tailings. Due to the use of extraction and tailings process aids, as well as process water recycling (Hollander, personal communication, July 20, 2020) and the high initial  $\text{Na}^+$  concentration due to oil sands being marine sediments (Simhayov et al., 2017; Sui et al., 2016), the tailings sand used in the constructed watershed has a large leachable pool of  $\text{Na}^+$  that has mobilized into the Constructed Fen (Kessel et al., 2018). Evapoconcentration of mobilized  $\text{Na}^+$  within the Fen has further increased  $\text{Na}^+$  concentrations (Yang et al., 2022). The peatland itself comprises a 2 m peat layer connected laterally to the tailing sand aquifer and underlain

by a high permeability layer of petroleum coke to evenly distribute hydraulic pressure beneath the fen (Ketcheson et al., 2017). The Constructed Fen was originally vegetated in June and July 2013 using a randomized split-plot design, where a variety of vascular plants and moss species were introduced, with *Carex aquatilis* Wahlenb. and *Juncus balticus* Willd. introduced at the highest density (Borkenhagen & Cooper, 2019). These species were selected in part due to their tolerance to the salinity levels expected to occur in the Constructed Fen and their availability (Borkenhagen & Cooper, 2019). At the time of this study, 6 years after planting, the plant cover was dominated by *C. aquatilis*, with *J. balticus* and *Typha* spp. L. also being common throughout the site.

The Athabasca Oil Sands region, and thus the Constructed Fen, has a subhumid climate, where potential evapotranspiration exceeds precipitation most years (Devito et al., 2012). Since fen construction, the site has been on average becoming warmer and drier during the growing season (May–September), with average temperature ranging between  $15^{\circ}\text{C}$  and  $19^{\circ}\text{C}$  compared to the 30-year climate normal of  $13.3^{\circ}\text{C}$  and total precipitation ranging between 168 and 310 mm compared to the 30-year climate normal of 283.4 mm (Popović et al., 2022). The growing season in 2019 was generally colder (average  $15^{\circ}\text{C}$ ) and wetter (total 285 mm), than previous years since the fen's construction (Popović et al., 2022). In the present study, half-hourly precipitation measurements were taken from a Texas Electronics TE525MM/TE525M Tipping Bucket Rain Gauge connected to a Campbell Scientific CR1000 data logger set up in the upland, approximately 150 m south of the fen.

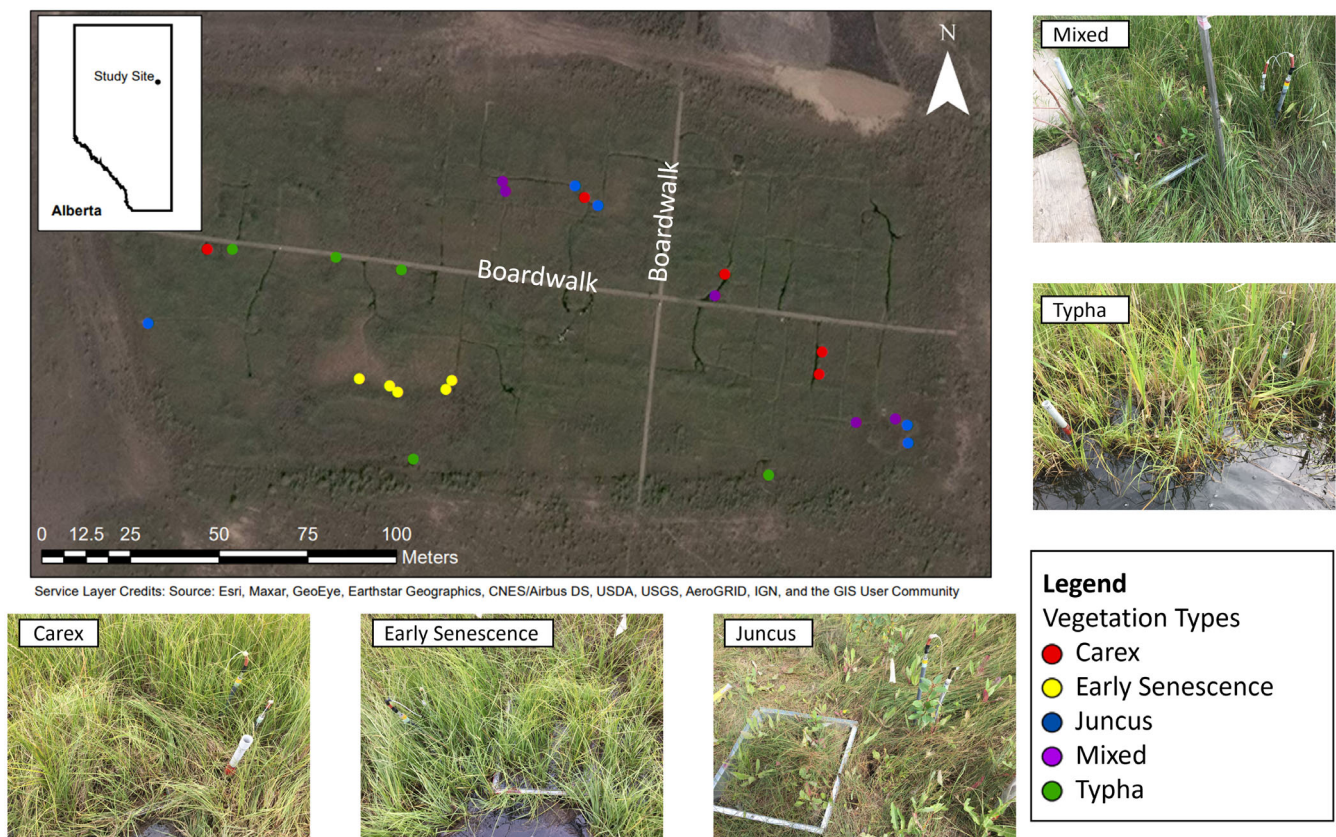
### 2.2 | Plot design

Plot locations were selected to be co-located with a subset of permanent monitoring plots where hydrological, soil temperature and vegetation community monitoring occurred allowing for consideration of these parameters in analysis. Of the available permanent plots, 25 were selected for this study. Specific plots were selected based on distribution across the fen and achieving a balanced design of dominant vegetation covers of the Constructed Fen, which are referred to as vegetation types (five plots of each vegetation type). The location of plots by vegetation type can be found in Figure 1. The vegetation types targeted were *J. balticus* (*Juncus*), *C. aquatilis* (*Carex*), *Typha* spp. (*Typha*), mixed *J. balticus* and *C. aquatilis* (Mixed) and *C. aquatilis* that showed early senescence in 2018, suggesting potential salt stress (Early Senescence).

### 2.3 | Water sampling analysis

Suction Lysimeters (Model 1900 Soil Water Sampler, SoilMoisture Equipment Corp., Santa Barbara, California and retrofitted tensiometers) were installed on May 27, 2019 (Day of Year [DOY] = 147) to sample pore water from the Constructed Fen. These lysimeters are made with a high fire silica body ceramic cup that has been found not





**FIGURE 1** Locations of suction lysimeters in the Constructed Fen. Colours of points (see legend) indicate the vegetation type: Carex—*C. aquatilis*, Carex Senescence—*C. aquatilis* early senescence in 2018, Juncus—*J. balticus*, Mixed—mixed *C. aquatilis* and *J. balticus*, Typha—*Typha* spp. Images of representative sites for each vegetation type are shown for reference and were taken on 14 August 2019.

to significantly absorb DOC (Lilienfein et al., 2004). Suction lysimeters were installed at 10 and 30 cm depths, to obtain samples representative of the rooting zone of the fen. Though root depths extended to at least 0.75 m in 2018, over 90% of root biomass was in the top 30 cm with 67% found in the first 10 cm alone (Messner et al., n.d.). Thus, the top 30 cm was considered the rooting zone.

Water sampling from suction lysimeters was conducted on 30 May, 4 June, 18 June, 2 July, 17 July, 26 July, 1 August and 14 August 2019 (DOY = 150, 155, 169, 183, 198, 207, 213 and 226; respectively). The day before sampling, lysimeters were suctioned using a vacuum pump to  $-75$  kPa. All lysimeters were suctioned within a 2-h period to reduce the impact of temporal variability in samples. Initial samples were collected the morning of sampling by connecting a three-way valve to the Tygon™ tubing of the lysimeter and using a 60 mL syringe to extract the sample. Samples were placed into 120 mL sample bottles and lysimeters were suctioned again to  $-75$  kPa. The depth to water table at each location was measured from a 50 cm depth well located within 1 m of the lysimeters. After the first round of sampling, all lysimeters were sampled within approximately 4 h with the new sample being added to the same 120 mL bottle as the first sample.

Immediately after samples were placed in the 120 mL bottle, pH and EC were measured using an Orion Star™ A325 pH/Conductivity

multiparameter meter with an Orion 8107UWMMMD Ultra pH/ATC Triode and a Thermo Scientific™ Orion™ Conductivity and Temperature Probe. This was done after the first round of sampling with the initial sample and repeated on the combined sample. The combined sample values were used in analysis as no significant changes in pore water electrical conductivity were found between sampling rounds (paired *t*-test,  $t(365) = -0.40$ ,  $p = 0.69$ ). Probes were calibrated for pH with pH 4, 7 and 10 standards and calibrated for EC with 1413 and 12 880  $\mu\text{S cm}^{-1}$  standard solutions on the day of sampling. pH values from the lysimeters were higher than the range of pH values from adjacent 30 cm piezometers found in proximity to many lysimeters. This was attributed to the applied vacuum shifting the  $\text{CO}_2$  equilibrium of the water, degassing  $\text{CO}_2$  and increasing the pH of the sample. As the measured pH was not representative of the water in situ, pH was not considered in the analysis. While the multiparameter probe did provide temperature, the measured temperature was not representative of pore water as samples were pulled into the lysimeter hours before sampling and thus could equilibrate with surface temperature. Temperature of samples was thus taken as a biweekly average temperature ( $T_{\text{avg}}$ ) using a thermocouple temperature probe at 10 and 30 cm depths from the co-located monitoring plots. This corresponded to the use of approximately four temperature measurements to calculate the average for each sampling date.

Samples were stored in a cooler during the day and were placed in a 4°C refrigerator within 10 h of sampling. Within 24 h of sampling, samples were filtered using vacuum filtration through 0.45 µm nitrocellulose filters. Between 3 and 10 mL of filtered sample was then used to measure the Na<sup>+</sup> concentration of the water using an Orion Star™ A324 pH/ISE multiparameter meter with a ROSS Sodium Sure Flow Electrode (model 8611BNWP). The probe was calibrated before use and after every 2 h of use using 10, 100 and 1000 ppm standards. The electrode slope was also confirmed to be between 54 and 60 mV dec<sup>-1</sup> after each calibration to ensure proper function of the probe.

## 2.4 | DOC concentration and quality

Samples were analysed for DOC concentration with a Shimadzu TOC analyser using the Non-Purgeable Organic Carbon method at the University of Calgary and were diluted by a factor of 10 to avoid instrument saturation. Since the samples were filtered prior to analysis this represents the dissolved fraction of organic carbon. Samples were also analysed for absorbance using a Thermo Scientific™ GENESYS™ 10S UV-Vis Spectrophotometer at 250, 254, 365, 400, 465 and 665 nm wavelengths. Using absorbance data, SUVA<sub>254</sub> and E2/E3 were calculated using Equations (1) and (2). E4/E6 is related to the degree of humification of organic matter, with ratios between 2 and 5 indicating mature humic acids and less mature fulvic acids having ratios between 5.5 and 17 (Grayson & Holden, 2012; Thurman, 1985). While E4/E6 was also determined it was excluded from further analysis due to debates on its usefulness (Peacock et al., 2014) and the low absorbance at 665 nm in this study which led to high E4/E6 variability. The E4/E6 linear mixed effects models are included in the Supporting Information for completeness (Table S2).

$$\text{SUVA}_{254} = \frac{\text{Absorbance at 254 nm (cm}^{-1}\text{)}}{[\text{DOC}] \text{ (mg L}^{-1}\text{)}} \times 100 \text{ (cm m}^{-1}\text{)} \quad (1)$$

$$\frac{\text{E2}}{\text{E3}} = \frac{\text{Absorbance at 250 nm}}{\text{Absorbance at 365 nm}} \quad (2)$$

## 2.5 | Vegetation survey

A vegetation survey was completed within 50 cm of the suction lysimeters on August 9, 2019. This survey used 60 × 60 cm quadrats and recorded percentage cover of *J. balticus*, *C. aquatilis*, *Typha* spp., forbs, shrubs, moss, litter and water. Total sedge and rush cover including the presence of the species considered individually, was recorded for each quadrat. Since suction lysimeters were installed into peat with similar vegetation coverage to quadrats, these vegetation surveys are considered representative of vegetation cover over suction lysimeters.

## 2.6 | SO<sub>4</sub><sup>2-</sup> concentration

Due to the effect of SO<sub>4</sub><sup>2-</sup> on redox and DOC solubility shown in other peatlands (Clark et al., 2005; Fenner et al., 2011), SO<sub>4</sub><sup>2-</sup>

concentration was measured for consideration in models. Samples of SO<sub>4</sub><sup>2-</sup> concentration were measured in the field to minimize oxidation of sulfide gas, that could contribute to measured SO<sub>4</sub><sup>2-</sup>. This required SO<sub>4</sub><sup>2-</sup> sampling and DOC sampling to occur on separate days, due to time constraints and the need to retrieve sufficient volume for analysis. SO<sub>4</sub><sup>2-</sup> samples were collected six times throughout the summer from 30 cm suction lysimeters on 11, 21 and 28 June, 9 and 23 July and 7 August (DOY = 162, 172, 179, 190, 204 and 219; respectively). Immediately after sample collection, 0.25 mL of sample was pipetted into a sample cell and mixed with one Hach SulfaVer 4 powder pillow, stoppered and allowed to react for 5 min. After 5 min, 9.75 mL of ultrapure deionized (UPDI) water was pipetted into the sample cell to bring the volume to the 10 mL needed for measurement. During reaction, a blank was prepared where 0.25 mL of sample and 9.75 mL of UPDI were pipetted into an additional sample cell and stoppered. This led to a 40 times sample dilution of the blank and sample and was required to keep output SO<sub>4</sub><sup>2-</sup> concentration below the 70 mg L<sup>-1</sup> detection maximum. The blank and sample were analysed on a Hach DR2800 spectrophotometer using method 680, with the output concentration multiplied by 40 to obtain the sample concentration. Given the temporal difference between SO<sub>4</sub><sup>2-</sup> and DOC sample results, values were averaged over the summer within a plot, for analysis. While this averaging does have limitations by masking temporal variation, it was deemed to be reasonably appropriate due to similarities in variation among plots and among sampling dates.

## 2.7 | Data analysis

Data were analysed using R 3.6.2 (R Core Team, 2019) and R studio (RStudio team, 2016). The lme function from the nlme package (Pinheiro et al., 2018) was used to create linear mixed effect models explaining variation in DOC concentration, SUVA<sub>254</sub>, E2/E3 and E4/E6. Models were created separately for 10 and 30 cm depth as the processes contributing to DOC variability at these depths were expected to differ. Vegetation type, Na<sup>+</sup> concentration, water table and T<sub>avg</sub> and all two-way interactions were considered in linear mixed effects (LME) models and plot was included as a random factor to account for repeated measures. Stepwise General Linear Model selection was used to select models with the lowest Akaike information criterion (AIC). EC data was not included in LME models as Na<sup>+</sup> and EC were correlated with Na<sup>+</sup> being a contributor to EC. A separate LME model revealed that EC was a significant predictor of Na<sup>+</sup> concentration (LME, F<sub>1,365</sub> = 328.28, p < 0.001), but that the correlation was moderate between these variables with an R<sup>2</sup> of 0.46. Thus, EC was considered in separate LME models with EC as a fixed effect and plot nested within vegetation type as random effects once interactions between EC and vegetation type were confirmed to be non-significant. Since percent sedge and rush cover and SO<sub>4</sub><sup>2-</sup> concentration were not available with the same temporal resolution as DOC data, they were compared as averages by plot in additional LME models. For comparison of percent sedge and rush cover, DOC concentration, SUVA<sub>254</sub> and E2/E3 averaged from 1 to 14 August were used as over this period sedge and rush cover was fairly stable at the surveyed

**TABLE 1** Mean ( $\pm$  standard deviation) of environmental variables at 10 and 30 cm depth for vegetation type categories over the summer of 2019 at the Constructed Fen.

	EC ( $\mu\text{S cm}^{-1}$ )		Na <sup>+</sup> (mg L <sup>-1</sup> )		T <sub>avg</sub> (°C)		SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	WL (cm)
	10 cm	30 cm	10 cm	30 cm	10 cm	30 cm	30 cm	
C	3379 (1040) <sup>a*</sup>	2982 (851) <sup>a*</sup>	240 (52) <sup>a*</sup>	183 (42) <sup>a*</sup>	13.8 (3.6) <sup>a*</sup>	10.6 (4.5) <sup>a*</sup>	1525 (610) <sup>a</sup>	-5.63 (6.66) <sup>ab</sup>
CS	3543 (661) <sup>a*</sup>	3085 (529) <sup>a*</sup>	258 (97) <sup>a*</sup>	219 (98) <sup>a*</sup>	16.9 (2.3) <sup>c*</sup>	14.4 (2.5) <sup>b*</sup>	1372 (382) <sup>a</sup>	-1.91 (5.01) <sup>ac</sup>
J	4262 (1124) <sup>a</sup>	4329 (767) <sup>a</sup>	290 (150) <sup>a*</sup>	270 (122) <sup>a*</sup>	16.2 (2.8) <sup>bc*</sup>	13.9 (3.1) <sup>b*</sup>	2168 (565) <sup>b</sup>	-15.26 (12.59) <sup>b</sup>
M	4203 (801) <sup>a*</sup>	3163 (875) <sup>a*</sup>	279 (92) <sup>a*</sup>	175 (56) <sup>a*</sup>	14.5 (3.5) <sup>ab*</sup>	12.3 (4.2) <sup>ab*</sup>	1487 (590) <sup>a</sup>	-7.82 (7.63) <sup>ab</sup>
T	3554 (641) <sup>a*</sup>	2912 (538) <sup>a*</sup>	282 (97) <sup>a*</sup>	212 (69) <sup>a*</sup>	13.6 (3.7) <sup>a*</sup>	10 (4.5) <sup>a*</sup>	1600 (746) <sup>a</sup>	7.97 (10.12) <sup>c</sup>

Note: The letters representing vegetation types are: C—*C. aquatilis*, CS—*C. aquatilis* early senescence in 2018, J—*J. balticus*, M—mixed *C. aquatilis* and *J. balticus*, T—*Typha* spp. WL represents water table. Significance letters are indicated in superscript and indicate differences between vegetation type categories within an environmental variable and within depths. Vegetation types sharing a letter indicates that there is no significant difference. Asterisk indicates a significant difference between depth within vegetation type ( $p < 0.05$ ).

value. All LME models were visually assessed for normality and homogeneity of variance using residuals and were log transformed to meet test assumptions when necessary (DOC concentration and EC were log transformed for models where they were the response variable). LME models were tested for significance using a type III ANOVA to account for unequal sample sizes due to missing data and significance was determined at  $p < 0.05$ . The `ghlt` function with method 'Tukey' from the `multcomp` package (Bretz et al., 2020) and the 'emmeans' function from the `emmeans` package (Lenth et al., 2020) were used to evaluate which vegetation types were significantly different and to compare slopes between categories when interactions were significant, respectively. The  $R^2$  for models was determined using the `r.squaredGLMM` function from package `MuMIn` (Barton, 2019) and  $R^2$  for fixed effects using the `r2beta` function from package `r2glmm` (Jaeger, 2017).

To consider the dominant environmental influences on DOC concentration, SUVA<sub>254</sub> and E2/E3, redundancy analyses (RDA) were performed on data averaged over the summer by plot for 10 and 30 cm using the `vegan` package (Oksanen et al., 2019). Environmental parameters considered were Na<sup>+</sup> concentration, water table, T<sub>avg</sub>, percent sedge and rush cover, SO<sub>4</sub><sup>2-</sup> concentration and vegetation type. Prior to the RDA all variables were standardized using the `scale` function. The final model was selected using the `ordistep` function with forward selection. For a parameter to enter the model, a  $p$ -value below 0.05 was needed, whereas a  $p$ -value above 0.10 allowed the parameter to be removed from the model.

### 3 | RESULTS

#### 3.1 | Environmental conditions

While most vegetation types had similar percent sedge and rush cover at peak season, *Typha* plots had lower cover than all vegetation types but *Juncus* plots (LME,  $F_{4,20} = 4.27$ ,  $p = 0.01$ ). There were significant differences in water table between vegetation types (LME,  $F_{4,20} = 6.60$ ,  $p = 0.001$ ), with *Typha* plots having a higher water table

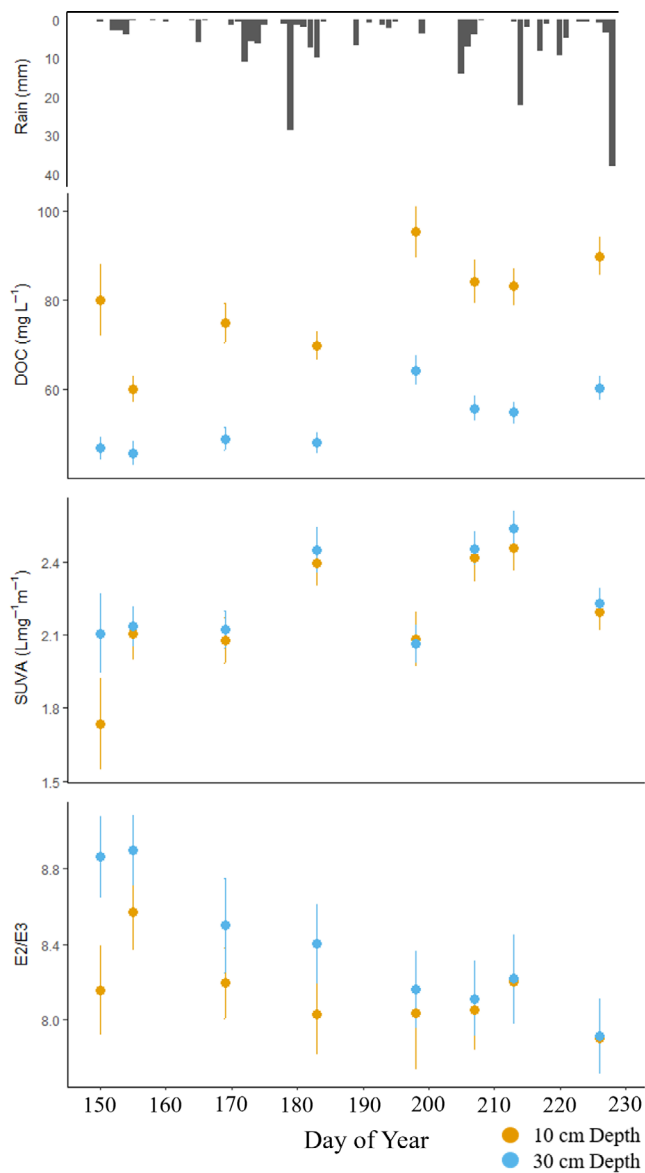
relative to the peat surface than *Carex*, *Juncus* and Mixed, and *Juncus* plots having a deeper water table than Early Senescence and *Typha* plots (Table 1). Average plot temperature differed between vegetation types at both 10 and 30 cm (LME,  $F_{4,20} = 7.09$ ,  $p = 0.001$ ; LME,  $F_{4,20} = 7.60$ ,  $p < 0.001$ ; respectively). Generally, Early Senescence and *Juncus* plots were warmer than other plots (Table 1). SO<sub>4</sub><sup>2-</sup> concentration was only measured at 30 cm and was similar between most plot types, apart from *Juncus* plots that had significantly higher concentration than other vegetation types (Table 1). Neither EC nor Na<sup>+</sup> were significantly different among vegetation types at both 10 cm (LME,  $F_{4,20} = 1.30$ ,  $p = 0.305$ ; LME,  $F_{4,20} = 0.19$ ,  $p = 0.940$ ; respectively) and 30 cm (LME,  $F_{4,20} = 2.28$ ,  $p = 0.096$ ; LME,  $F_{4,20} = 0.87$ ,  $p = 0.499$ ; respectively).

While Na<sup>+</sup> and EC were not significantly different between vegetation types, they did exhibit depth dependency with 10 cm having higher EC and Na<sup>+</sup> than 30 cm (LME,  $F_{1,369} = 106.16$ ,  $p < 0.001$ ; LME,  $F_{1,369} = 198.23$ ,  $p < 0.001$ ; respectively). Na<sup>+</sup> at 10 cm was higher under all vegetation types, while EC did not significantly differ between depths under *Juncus* plots. Average temperature was shown to be depth dependent with 10 cm having higher temperature than 30 cm under all vegetation types (LME,  $F_{1,342} = 58.10$ ,  $p < 0.001$ ).

#### 3.2 | DOC concentration and quality

DOC concentration, SUVA<sub>254</sub> and E2/E3 varied over the summer of 2019 with 10 cm and 30 cm values having similar temporal patterns (Figure 2). The largest difference in DOC between 10 and 30 cm was on 30 May with 10 cm DOC having a higher concentration, lower aromaticity and higher molecular weight (Figure 2). DOC concentrations remained higher at 10 cm for the remainder of the summer, but quality parameters were comparable between 10 and 30 cm from June to August. DOC concentration increased over the summer with a steep increase in concentration between measurements on July 2 (DOY = 183) and 17 (DOY = 198), coinciding with a period of low precipitation during peak growing season (Figure 2). Between measurements on 2 and 17 July, there was a steep decrease in SUVA<sub>254</sub>,





**FIGURE 2** Average DOC concentration,  $SUVA_{254}$  and E2/E3 and their confidence intervals of standard error for each DOC sampling event at the Constructed Fen in 2019. Cumulative daily precipitation is shown in the top panel.

while E2/E3 continued to decrease as observed between previous measurements (Figure 2).  $SUVA_{254}$  generally increased over the summer, while E2/E3 decreased throughout the summer. Overall, while DOC concentration increased over the summer, lability decreased.

Vegetation type was not a significant control on DOC concentration and  $SUVA_{254}$  at 10 cm but was a significant control on E2/E3 (Table 2). Specifically, only Typha plots had higher E2/E3 than Carex plots at 10 cm ( $p = 0.040$ ). At 30 cm there was significant variability in all DOC variables with vegetation types. DOC concentration was higher under Mixed plots than Early Senescence ( $p < 0.001$ ) and  $SUVA_{254}$  was higher at Carex plots than at Early Senescence plots ( $p = 0.018$ ). E2/E3 again showed more overall variability than other DOC measures with Juncus plots having higher E2/E3 than Carex and

Mixed plots, and Mixed plots having significantly lower E2/E3 than Early Senescence plots (Figure 3).

DOC concentration differed significantly with depth, with higher concentrations at 10 cm than 30 cm (LME,  $F_{1,372} = 275.01$ ,  $p < 0.001$ ; Figure 2). This relationship was significant under all vegetation types. Differences in  $SUVA_{254}$  with depth were only significant under certain vegetation types. Specifically, Early Senescence and Mixed plots had higher  $SUVA_{254}$  at 30 cm (LME,  $F_{1,74} = 13.86$ ,  $p < 0.001$ ; LME,  $F_{1,67} = 4.65$ ,  $p = 0.035$ ; respectively), whereas Juncus plots had higher  $SUVA_{254}$  at 10 cm (LME,  $F_{1,73} = 5.59$ ,  $p = 0.021$ ) and  $SUVA_{254}$  did not vary significantly with depth at Carex and Typha plots (LME,  $F_{1,73} = 0.73$ ,  $p = 0.394$ ; LME,  $F_{1,74} = 0.01$ ,  $p = 0.904$ ; respectively). The relationship between depth and E2/E3 also differed with vegetation type, where Carex and Juncus plots had higher E2/E3 at 30 cm (LME,  $F_{1,73} = 31.55$ ,  $p < 0.001$ ; LME,  $F_{1,73} = 48.86$ ,  $p < 0.001$ ; respectively), Mixed plots had lower E2/E3 at 30 cm (LME,  $F_{1,67} = 15.08$ ,  $p < 0.001$ ) and Early Senescence and Typha plots were not significantly different between depths (LME,  $F_{1,74} = 0.001$ ,  $p = 0.973$ ; LME,  $F_{1,74} = 0.28$ ,  $p = 0.600$ ; respectively).

### 3.3 | Controls on DOC concentration and quality

$Na^+$  concentration significantly explained DOC concentration and quality at 30 cm, but only variation in  $SUVA_{254}$  at 10 cm (Table 2; Figure 4). The relationship of  $SUVA_{254}$  and E2/E3 with  $Na^+$  was dependent on vegetation type (Table 2). While most vegetation types showed negative  $SUVA_{254}$  and  $Na^+$  relationships, Early Senescence plots had a positive slope despite this slope not differing significantly from other vegetation type slopes (Table S2). Despite the overall positive trend of E2/E3 with  $Na^+$ , this relationship was driven by the positive slopes of Mixed and Carex plots, as Early Senescence, Juncus and Typha plots had negative slopes that significantly differed from the positive slopes (Table S2). At 30 cm depth in the Constructed Fen, plots with higher salinity tended to have higher DOC concentrations with the DOC characterized by lower aromaticity and lower molecular weight.

Though EC and  $Na^+$  are closely related, they did exhibit differences in their relationships with DOC quantity and quality. DOC concentration was weakly and positively correlated with EC at both 10 and 30 cm (LME,  $F_{1,169} = 39.73$ ,  $p < 0.001$ ; LME,  $F_{1,174} = 42.35$ ,  $p < 0.001$ ).  $SUVA_{254}$  was negatively correlated to EC at 30 cm (LME,  $F_{1,174} = 5.92$ ,  $p = 0.016$ ), and E2/E3 was positively correlated with EC at 10 cm (LME,  $F_{1,163} = 6.25$ ,  $p = 0.013$ ). Despite these differences between  $Na^+$  and EC, both show overall trends of increases in DOC quantity and a shift to lower aromaticity and molecular weight with increasing salinity.

Water table was weakly and negatively correlated to both DOC concentration and E2/E3 at 10 cm (Table 2). With water table typically varying between 5 and 10 cm below surface (Table 1), peat at 10 cm depth was subject to periods above and below the water table. DOC concentration was weakly and positively correlated to  $T_{avg}$  at 30 cm under all vegetation types (Table 2). E2/E3 was weakly and



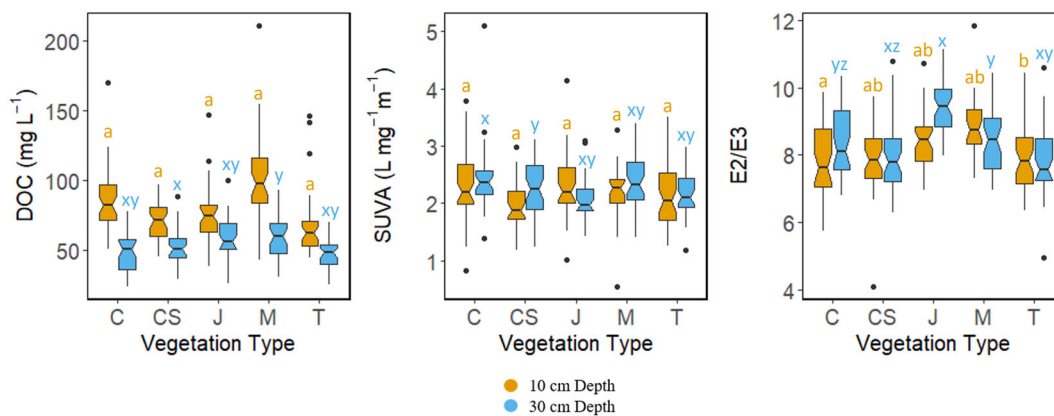
Model	Effect	F	p	R <sup>2</sup> <sub>m</sub>	R <sup>2</sup> <sub>c</sub>
log([DOC]) 10 cm	Vegetation type	$F_{4,20} = 0.23$	0.920	0.50	0.67
	Na <sup>+</sup>	$F_{1,135} = 0.24$	0.625		
	<b>WL</b>	<b><math>F_{1,135} = 5.46</math></b>	<b>0.021</b>		
	$T_{avg}$	$F_{1,135} = 0.01$	0.934		
	Vegetation type × Na <sup>+</sup>	$F_{4,135} = 1.76$	0.141		
	Vegetation type × WL	$F_{4,135} = 1.51$	0.204		
	Vegetation type × $T_{avg}$	$F_{4,135} = 2.39$	0.054		
	<b>Na<sup>+</sup> × WL</b>	<b><math>F_{1,135} = 5.50</math></b>	<b>0.020</b>		
	<b>Intercept</b>	<b><math>F_{1,135} = 105.61</math></b>	<b>&lt;0.001</b>		
log([DOC]) 30 cm	<b>Vegetation type</b>	<b><math>F_{4,20} = 4.03</math></b>	<b>0.015</b>	0.41	0.84
	<b>Na<sup>+</sup></b>	<b><math>F_{1,150} = 27.93</math></b>	<b>&lt;0.001</b>		
	WL	$F_{1,150} = 1.46$	0.228		
	<b><math>T_{avg}</math></b>	<b><math>F_{1,150} = 12.27</math></b>	<b>&lt;0.001</b>		
	<b>Vegetation type × <math>T_{avg}</math></b>	<b><math>F_{4,150} = 3.56</math></b>	<b>&lt;0.001</b>		
	<b>Intercept</b>	<b><math>F_{1,150} = 493.73</math></b>	<b>&lt;0.001</b>		
SUVA <sub>254</sub> 10 cm	Vegetation type	$F_{4,20} = 0.54$	0.711	0.25	0.71
	<b>Na<sup>+</sup></b>	<b><math>F_{1,138} = 4.10</math></b>	<b>0.045</b>		
	WL	$F_{1,138} = 3.15$	0.080		
	<b><math>T_{avg}</math></b>	<b><math>F_{1,138} = 17.15</math></b>	<b>&lt;0.001</b>		
	Vegetation type × Na <sup>+</sup>	$F_{4,138} = 0.28$	0.891		
	<b>Intercept</b>	<b><math>F_{1,138} = 25.00</math></b>	<b>&lt;0.001</b>		
SUVA <sub>254</sub> 30 cm	<b>Vegetation type</b>	<b><math>F_{4,20} = 3.17</math></b>	<b>0.036</b>	0.32	0.56
	<b>Na<sup>+</sup></b>	<b><math>F_{1,146} = 8.57</math></b>	<b>0.004</b>		
	WL	$F_{1,146} = 2.03$	0.157		
	$T_{avg}$	$F_{1,146} = 0.003$	0.955		
	<b>Vegetation type × Na<sup>+</sup></b>	<b><math>F_{4,146} = 2.79</math></b>	<b>0.028</b>		
	<b>Intercept</b>	<b><math>F_{1,146} = 75.07</math></b>	<b>&lt;0.001</b>		
E2/E3 10 cm	Vegetation type	$F_{4,20} = 2.50$	0.075	0.20	0.81
	<b>Na<sup>+</sup></b>	<b><math>F_{1,138} = 3.18</math></b>	<b>0.077</b>		
	<b>WL</b>	<b><math>F_{1,138} = 5.79</math></b>	<b>0.017</b>		
	$T_{avg}$	$F_{1,138} = 0.66$	0.418		
	<b>Vegetation type × <math>T_{avg}</math></b>	<b><math>F_{4,138} = 4.46</math></b>	<b>0.002</b>		
	<b>Intercept</b>	<b><math>F_{1,138} = 119.54</math></b>	<b>&lt;0.001</b>		
E2/E3 30 cm	<b>Vegetation type</b>	<b><math>F_{4,20} = 4.92</math></b>	<b>0.006</b>	0.47	0.74
	<b>Na<sup>+</sup></b>	<b><math>F_{1,150} = 5.03</math></b>	<b>0.026</b>		
	WL	$F_{1,150} = 2.55$	0.112		
	<b><math>T_{avg}</math></b>	<b><math>F_{1,150} = 25.59</math></b>	<b>&lt;0.001</b>		
	<b>Vegetation type × Na<sup>+</sup></b>	<b><math>F_{4,150} = 5.49</math></b>	<b>&lt;0.001</b>		
	<b>Intercept</b>	<b><math>F_{1,150} = 83.03</math></b>	<b>&lt;0.001</b>		

Note: The final models are shown and were selected by achieving the lowest Akaike Information Criterion. DOC concentration was log transformed to achieve normality. WL represents water table. Significant variables and interactions are bolded.

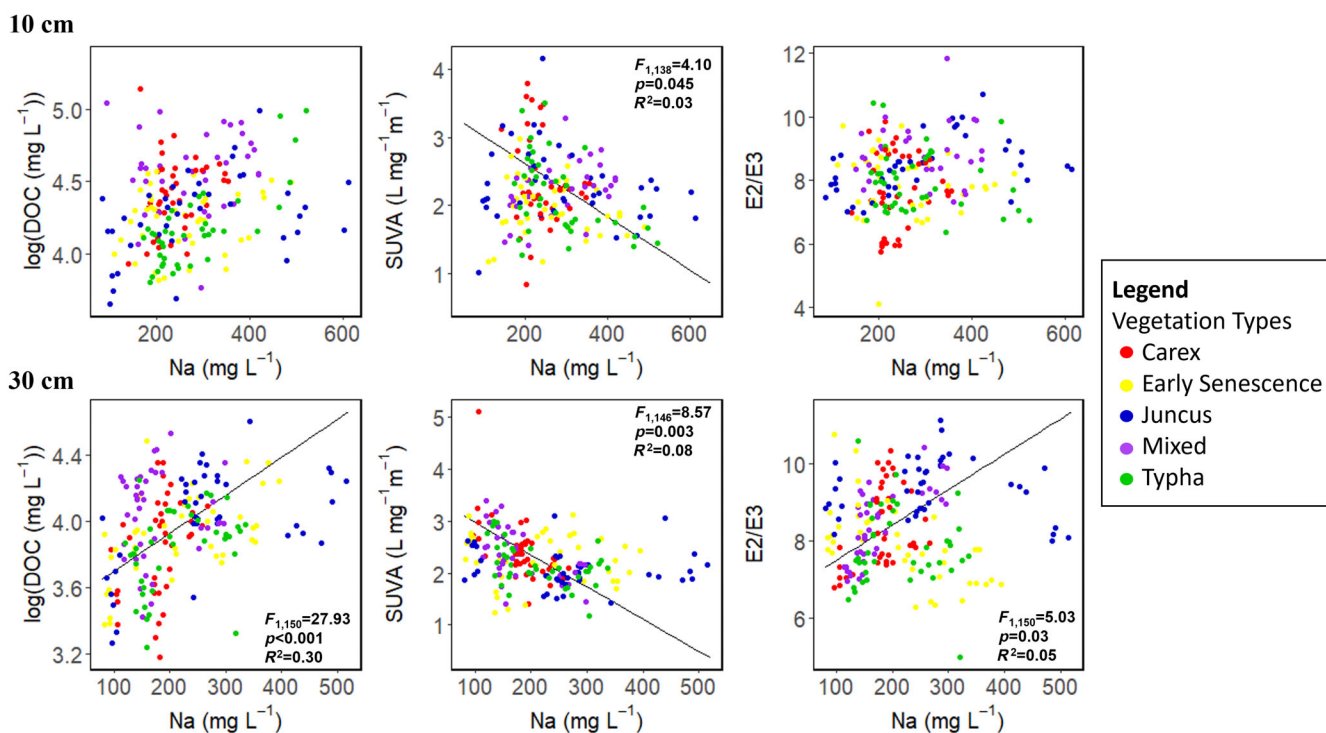
negatively correlated to  $T_{avg}$  at 30 cm (Table 2). At 10 cm, SUVA<sub>254</sub> was weakly and positively correlated with  $T_{avg}$  (Table 2), while E2/E3's relationship with  $T_{avg}$  was dependent on the vegetation type

with Carex and Juncus plots having positive slopes and Early Senescence, Mixed and Typha plots having negative slopes (Table S2). The overall E2/E3 correlation with  $T_{avg}$  at 10 cm was not significant.

**TABLE 2** Results of linear mixed effect model for environmental variables correlated to DOC concentration, SUVA<sub>254</sub> and E2/E3 at 10 and 30 cm in the Constructed Fen over the summer of 2019.



**FIGURE 3** DOC, SUVA<sub>254</sub> and E2/E3 under the different vegetation types of the Constructed Fen 2019. Pairwise comparison significance letters are shown above plots with ‘ab’ used for 10 cm and ‘xyz’ used for 30 cm. Box width is proportional to the square root of the sample size. The letters representing vegetation types are: C—*C. aquatilis*, CS—*C. aquatilis* early senescence in 2018, J—*J. balticus*, M—mixed *C. aquatilis* and *J. balticus*, T—*Typha* spp. Vegetation types sharing a letter indicates no significant difference.



**FIGURE 4** Significant relationships between DOC concentration, SUVA<sub>254</sub> and E2/E3 with Na<sup>+</sup> concentration at the Constructed Fen over the summer of 2019 at 10 and 30 cm depth. Relationships were extracted from LME models with F statistic, p-value and the R<sup>2</sup> attributed to variation in Na<sup>+</sup> are shown. DOC concentrations were log transformed to meet assumptions of normality.

Plots with high SO<sub>4</sub><sup>2-</sup> had high DOC lability, with SUVA<sub>254</sub> being negatively, and E2/E3 being positively correlated to SO<sub>4</sub><sup>2-</sup> concentration (LME,  $F_{1,19} = 14.36, p = 0.001$ ; LME,  $F_{1,19} = 18.12, p < 0.001$ ; respectively). There was no significant correlation between SO<sub>4</sub><sup>2-</sup> and DOC concentration (LME,  $F_{1,19} = 2.93, p = 0.103$ ). However, as discussed in the Section 2, there are limitations to these results due to averaging of data over the growing season, especially in the consideration of SUVA<sub>254</sub>. Percent sedge and rush cover did not significantly correlate with any DOC variable at 10 cm, though DOC concentration at 30 cm positively correlated with percent vegetation cover (LME,

$F_{1,19} = 7.54, p = 0.012$ ). Correlations were generally weak suggesting a variety of factors influenced DOC quantity and quality at the Constructed Fen and/or factors not measured during the current study may have had a dominant effect on DOC quantity and quality.

The effect of environmental factors on the multivariate indicators of DOC quantity and quality was further evaluated with redundancy analysis for 10 and 30 cm. This was done to support the results of the LMEs, assess overall drivers of DOC quantity and quality together, and assess the role of variables that did not have high enough temporal resolution to be considered in the LME (percent sedge and rush

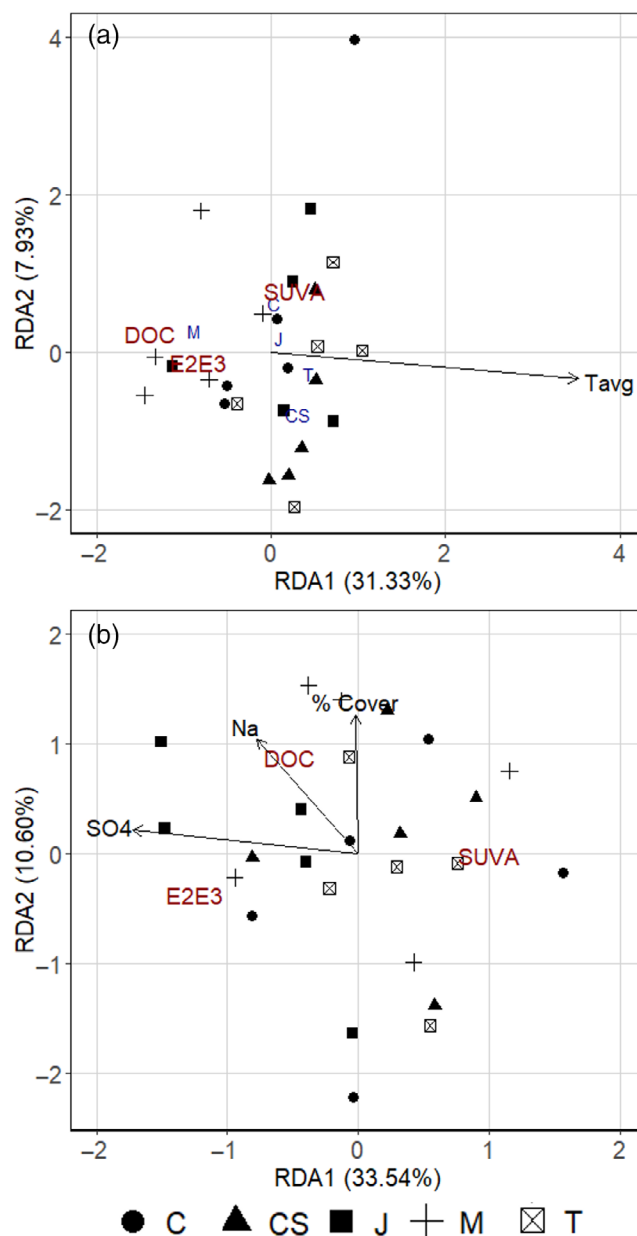
cover and  $\text{SO}_4^{2-}$  concentration). At 10 cm the RDA explained 42.3% of variation over three RDA axes (RDA,  $F_{5,19} = 2.79$ ,  $p = 0.003$ ), while at 30 cm 47.6% was explained over three axes (RDA,  $F_{3,21} = 6.35$ ,  $p < 0.001$ ). At 10 cm depth, temperature and vegetation type were the only significant variables retained, with increases in temperature correlated to lower DOC concentration and higher molecular weight DOC (Figure 5a). Vegetation types were correlated with different RDA axes and exhibited no clear clustering (Figure 5a). At 30 cm depth,  $\text{SO}_4^{2-}$  was strongly correlated with RDA1, with higher concentrations associated with higher E2/E3 and lower  $\text{SUVA}_{254}$  (Figure 5b). Both  $\text{Na}^+$  and percent sedge and rush cover were moderately correlated with RDA2 with higher  $\text{Na}^+$  concentration and percent sedge and rush cover associated with higher DOC concentration. The relationship between percent sedge and rush cover and DOC concentration is further supported by the LME displayed in Figure S1. There was no clear clustering according to vegetation type at 30 cm depth.

## 4 | DISCUSSION

As hypothesized,  $\text{Na}^+$  was found to explain variation in DOC concentration and quality at the Constructed Fen, but only at 30 cm depth, where higher  $\text{Na}^+$  concentration was correlated with higher DOC concentrations and lower DOC aromaticity and molecular weight. However,  $\text{Na}^+$  concentration alone could not explain DOC concentration and quality at the Constructed Fen, with multiple factors needed to explain the overall trends, especially at 10 cm depth where spatial variability was high.

### 4.1 | Biochemical controls of DOC concentration and quality

At the Constructed Fen, we observed that  $\text{Na}^+$  concentration was a control on DOC concentration and quality at 30 cm depth (Figures 4 and 5b). This result could potentially be explained by the influence of  $\text{Na}^+$  on increasing rhizodeposition or decreasing decomposition. Monovalent cations like  $\text{Na}^+$  can influence DOC concentration and quality by increasing the permeability of root membranes, leading to an increase in root exudation (Vranova et al., 2013). Root exudation releases low molecular weight compounds that are thought to have low aromaticity (Farrar et al., 2003; Kane et al., 2014). Additionally, as the compounds released from plant roots are generally highly available to the microbial community, in solution they are decomposed to smaller and less aromatic products, and may prime the microbial community for increased decomposition of other sources (Basiliko et al., 2012; Jones et al., 2004).  $\text{Na}^+$  can decrease decomposition rate through salt stress or increase decomposition rate due to flocculation promoting microbial attachment (Chambers et al., 2014; Marschner & Kalbitz, 2003; Mavi et al., 2012). The balance of these processes will determine the net effect on DOC quantity and quality in the field. Mavi et al. (2012) report that  $\text{SUVA}_{254}$  decreased as salinity increased, which they attributed to protection of labile aliphatic compounds from decomposition at high salinity. Future work should directly



**FIGURE 5** RDAs for 10 (a) and 30 (b) cm investigating environmental controls (black text and arrows) on DOC concentration,  $\text{SUVA}_{254}$  and E2/E3 (red text). Plot positions on the RDA are shown as points, with the symbol indicating vegetation type. Centroids for categorical variables are shown in blue text indicating the vegetation type as C—*C. aquatilis*, CS—*C. aquatilis* early senescence in 2018, J—*J. balticus*, M—mixed *C. aquatilis* and *J. balticus*, T—*Typha* spp. RDAs were scaled into two dimensions to account for the third RDA axis. At 10 cm depth, average temperature ( $T_{\text{avg}}$ ) and vegetation type were the only variables retained in the model after forward model selection. At 30 cm depth,  $\text{Na}^+$  (Na),  $\text{SO}_4^{2-}$  ( $\text{SO}_4$ ) and percent sedge and rush cover (% Cover) were the only variables retained after forward model selection.

measure the impact of  $\text{Na}^+$  on rhizodeposition and decomposition to assess if these mechanisms can explain the observed effect of  $\text{Na}^+$  on DOC concentration and quality at the Constructed Fen.

At 30 cm depth,  $\text{SO}_4^{2-}$  concentration correlated with increased DOC lability in the Constructed Fen (Figure 5b). Increasing  $\text{SO}_4^{2-}$

concentration may increase DOC lability by operating as a terminal electron acceptor for decomposition (Fenner et al., 2011); however, given the high concentration of  $\text{SO}_4^{2-}$  at the Constructed Fen it is unlikely to be the limiting factor in decomposition.  $\text{SO}_4^{2-}$  has been shown to decrease DOC solubility through facilitated precipitation of DOC (Brouns et al., 2014; Clark et al., 2005; Jager et al., 2009) and decreasing pH, which decreases DOC solubility (Clark et al., 2012). Larger DOC compounds are generally preferentially adsorbed and precipitated, which would be expected to lead to an increase in DOC lability where DOC solubility is decreased. This mechanism is supported by the results at the Constructed Fen, however, given the temporal difference between DOC and  $\text{SO}_4^{2-}$  sampling, the implications of these results should be taken with caution. Further work should evaluate the influence of  $\text{SO}_4^{2-}$  concentration on the solubility of DOC compounds at the Constructed Fen to assess this potential mechanism. Furthermore, with the potential role of pH in impacting DOC solubility, pH should also be considered in any future studies evaluating this mechanism.

From 2013 to 2016, DOC concentrations increased through time in the near surface (Irvine et al., 2021; Khadka et al., 2016); however, this study found similar DOC concentrations to those recorded in 2016 (average  $\sim 55\text{--}60\text{ mg L}^{-1}$  at 30 cm in 2016; Figure 2). The quality of DOC continued to increase in lability with average  $\text{SUVA}_{254}$  decreasing slightly from  $\sim 2.6$  to  $2.3\text{ L mg}^{-1}\text{ m}^{-1}$  and E2/E3 increasing from  $\sim 6.5$  to  $8.4$  from 2016 to 2019 (Irvine et al., 2021; Figure 3). This suggests that the mechanisms of DOC production and removal have not yet stabilized or are not stable interannually.  $\text{SO}_4^{2-}$  concentration has been increasing at the Constructed Fen from  $\sim 1000\text{ mg L}^{-1}$  in 2017 (Osman, 2018) to  $\sim 1600\text{ mg L}^{-1}$  in 2019, and  $\text{Na}^+$  concentration has also been increasing at the Constructed Fen (Kessel et al., 2018). In previous years, increasing DOC lability interannually had been attributed to increased vascular plant cover (Khadka et al., 2016). At the time of the present study, plant cover had roughly stabilized at the Constructed Fen (Borkenhagen & Cooper, 2019), suggesting additional mechanisms may be contributing to the continued interannual changes in DOC lability in the Constructed Fen. This study suggests that increased  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  concentrations could contribute to these observed interannual changes.

## 4.2 | Hydrological and physical controls of DOC concentration and quality

DOC concentrations at the Constructed Fen were found to be higher at 10 cm over 30 cm depth (Figure 3). Kalbitz et al. (2000) found substantial evidence that DOC concentrations increased following rewetting and suggest that dissolution of built-up microbial products from reduced decomposition during dry periods and cell lysis following rewetting contribute to this increase. As the water table was found to generally fluctuate around 10 cm depth, the method described by Kalbitz et al. (2000) may have led to the higher DOC concentration at 10 cm depth compared to 30 cm depth, where water table was consistently above 30 cm depth for most plots. However, evapoconcentration of DOC at the surface, as has been found for  $\text{Na}^+$  at the

Constructed Fen (Yang et al., 2022), and a greater presence of labile compounds for decomposition from fresh litter input could also explain higher DOC concentrations at 10 cm. It is likely that multiple compounding factors contributed to the observed result. With many conflicting studies on the influence of water table on DOC dynamics and further debate on the mechanism (Clark et al., 2005, 2012; Davidson et al., 2019; Dieleman et al., 2016; Fenner et al., 2011; Khadka et al., 2015; Strack et al., 2015), this study suggests water table variability should be studied to better understand the relationship between DOC and water table.

Temperature has generally been identified as a positive control on DOC concentration due to stimulation of the microbial community at higher temperature (Dieleman et al., 2016; Irvine et al., 2021; Kane et al., 2014; Khadka et al., 2015; Moore & Dalva, 2001), and this was supported at 30 cm depth. As 2016 had a warmer average growing season air temperature than 2019 (Popović et al., 2022), the cooler temperatures in 2019 may have also contributed to the lack of increase in DOC concentration between years at 30 cm depth, despite increases in variables positively correlated with DOC concentration like  $\text{Na}^+$  concentration between years. However, at 10 cm, DOC concentration correlated negatively with temperature in the RDA, where E2/E3 also correlated negatively with temperature (Figure 5a). This suggests that at 10 cm, plots that were on average warmer had higher net consumption of DOC over production leading to lower average DOC concentration and higher molecular weight. At 10 cm, therefore, the net effect of temperature on production and consumption of DOC may be important in determining DOC quantity and molecular weight.

## 4.3 | Implications

Climatic conditions at the Constructed Fen, since its construction, have been on average drier and warmer than the 30-year normal (Popović et al., 2022) and these trends are expected to continue with climate change in the Athabasca Oil Sands Region (Welham & Seely, 2012). Based on the results of this study, lowering of zone of water table variability closer to 30 cm depth, due to dry conditions, and higher temperature may increase DOC concentration at 30 cm depth. However, with temperature being negatively correlated with DOC concentration at 10 cm depth, and climatic trends leading to conditions at 30 cm depth being more similar in water table and temperature to those of 10 cm depth in 2019, there may be a reversal in the impact of temperature leading to differing results.

Overall, with  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  concentrations continuing to rise in the Constructed Fen (Kessel et al., 2018), continued increases in DOC lability may be expected. Having higher concentrations of smaller and less-aromatic DOC may lead to enhanced decomposition of DOC and thus higher gaseous carbon fluxes from the fen (Khadka et al., 2015). This labile carbon source may also prime the microbial community allowing for enhanced microbial degradation of peat and recalcitrant DOC (Basiliko et al., 2012) further increasing carbon loss from the Constructed Fen. Additionally, with labile DOC being more mobile (Strack et al., 2015), greater aqueous DOC export from the site can be expected. With less complex DOC compounds generally forming



organometallic complexes, mobilizing heavy metals (Steinberg, 2003), increased DOC lability may also mobilize contaminants, making them bioavailable for the microbial and vegetation community at the Constructed Fen. This presents an area for future research into the mobility of DOC-bound contaminants. Furthermore, when reclaimed systems are hydrologically connected to the landscape, this mobilization of contaminants may impact downstream ecosystems unless appropriate measures are taken to reduce efflux, such as biological filtration.

Though DOC is becoming more labile over time at the Constructed Fen, the seasonal changes in DOC over the growing season may create conditions where DOC is least labile when DOC export is highest. Specifically, DOC was observed to be most recalcitrant in the late summer when there is higher precipitation (Figure 1) and thus DOC export is likely to be higher (Limpens et al., 2008). While the DOC pool at the Constructed Fen is still trending towards becoming more labile through time, slightly more recalcitrant DOC when export is highest may help retain DOC, and the compounds it complexes, within the fen. However, with DOC concentrations also being highest at the end of the summer the net effect may still lead to greater carbon export.

## 5 | CONCLUSION

In this study, we report on the DOC dynamics of the rooting zone of the Constructed Fen. DOC spectrophotometric properties at the Constructed Fen indicated low molecular weight, low aromaticity and low humification, suggesting largely inputs from vegetation to the DOC pool. Variation in DOC quantity and quality at 30 cm below the peat surface was explained by  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  concentration and percent sedge and rush cover. Elevated  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  led to more labile DOC, with elevated  $\text{Na}^+$  and higher percent sedge and rush cover contributing to higher DOC concentrations. This work has implications for peatland construction as a part of landscape reclamation and for understanding DOC dynamics under the effects of sea level rise in coastal peatlands.

Due to the high DOC concentrations at the Constructed Fen and the inferred mobility of DOC from its lability, it is recommended that industry monitor DOC outflow for consideration in carbon budgets. Additionally, with DOC concentration and lability rising at the Constructed Fen and expected to rise as  $\text{Na}^+$  concentrations continue to increase, monitoring of metal transport is suggested. DOC is known to bind and transport metals, which may be abundant in reclaimed systems, with labile DOC having a higher binding affinity and mobility than recalcitrant compounds. As connectivity between reclaimed systems will be implemented in final reclamation plans, ecosystems constructed downstream of peatlands should be tolerant to high DOC concentrations and the potential for elevated metal concentrations.

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## CONFLICT OF INTEREST STATEMENT

The authors declare that there is no conflict of interest that could be perceived as prejudicing the impartiality of the research reported.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in 2019 Nikanotee Fen DOC Data at <https://doi.org/10.5683/SP3/MMQDBC>.

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## SUPPORTING INFORMATION

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