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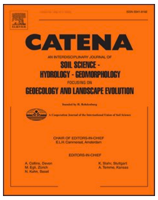

Moss cellulose ^{18}O applied to reconstruct past changes in water balance of a boreal wetland complex, northeastern Alberta

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ABSTRACT

A water and vegetation sampling program including peat coring was carried out within the McClelland Wetland, a boreal peatland complex situated within the rapidly developing oil sands mining region of northeastern Alberta, Canada. This study investigated both the current and past hydrology of the site to improve understanding of the spatiotemporal evolution of water sources, pathways, and vegetation succession prior to impending oil sands development in the western half of the watershed. The study used vegetation surveys and isotopic tracers (^{18}O, ^{2}H) for contemporary characterization of water sources and evaporation gradients, whereas flark orientation was used to identify general flow directions. Use of ^{18}O preserved in α-cellulose within moss macrofossils and wood, combined with evidence from vegetation successions in several cores, provided detailed information on historical changes in the peatland as far back as 11,300 cal. years BP. Reliability of ^{18}O archives from moss cellulose to reconstruct ^{18}O in source water was confirmed in a sub-survey conducted at 227 sites where water and moss were both sampled and analyzed to quantify isotopic fractionation in dominant moss species. Overall, the study established existence of long-term groundwater source areas around the margins of the peatland, as well as contemporary permafrost thaw zones within the peatland itself. Both contemporary (spatial) and historical (temporal) ^{18}O gradients reflect precipitation-derived origins for shallow groundwater sources with strong evaporative enrichment along the direction of flow. Historical reconstruction suggests persistence of open wet areas at the site amid several episodes of regional climatic and associated hydrologic changes.

1. Introduction

Stable isotopes of water (^{18}O and ^{2}H) have been applied in numerous studies as a basis for characterizing spatiotemporal variations in wetland water balance (e.g. Gibson et al., 2000, 2021, 2022, Clay et al., 2004, St. Amour et al., 2005, Hayashi et al., 2005, Whitfield et al., 2010, Graham et al., 2016, Ala-aho et al., 2018, Bam and Ireson, 2019). In such contemporary investigations, isotopes have been used for identification of groundwater or surface water sources, for partitioning source-water mixing and storage dynamics, as well as quantifying evaporation, infiltration, and influence of permafrost thaw. As progressive heavy isotopic enrichment often occurs due to evaporation during residency in surface storage, ^{18}O, ^{2}H, or d-excess (Dansgaard, 1964), have proven useful for mapping flowpaths and for estimating relative connectivity of complex wetland landscapes (Ala-aho et al., 2018, Graham et al., 2016). Previous studies have utilized isotopes in conjunction with solute tracers to examine complex flow distributions, surface–groundwater interaction, and evapotranspiration (Dincer et al., 1978), or in combination with remote sensing techniques to examine connectivity to streams (Brooks et al., 2018).

In addition to the advantages that isotopes may offer in contemporary investigations for site-specific and regional characterization of water balance, the preservation of isotopic signals within archival deposits has in some cases provided novel insight into past hydrological conditions. Archival records with demonstrated potential for paleoclimate or paleohydrology reconstructions include tree rings (McCarroll and Loader, 2006), aquatic sediments (Leng et al., 2006) and peat deposits (Brenninkmeijer et al., 1982; Pendall et al., 2001; Ménot-Combes

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et al., 2002, Zanazzi and Mora, 2005, Moschen et al., 2009, Jones et al., 2019, Xia and Yu, 2020). While systematic isotopic fractionation between ^{18}O in water and archival materials is the basis of this study, and for the majority of isotope-based paleoclimate investigations, ^{2}H in peat cellulose has also recently been shown to compliment past reconstructions based on ^{18}O, although requiring more complicated laboratory processing (Zanazzi and Mora, 2017). Based on our review of the published literature, moss cellulose records have not previously been used to reconstruct water balance of peatlands in western Canada including Alberta's boreal forest region.

This study was motivated by the need to develop understanding of both contemporary and past water balance for a 101 km^2 fen complex within a 202 km^2 watershed in northeastern Alberta, that is situated partially within the footprint of a planned oil sands surface mine. Due to low-relief, large extent of the wetland, and complexity of the wetland mosaic, the use of stable isotopes was initially evaluated and then adopted as a complimentary tool, along with physical and hydrochemical approaches, to understand water sources, water flow, and water balance across the site. Several objectives of this work were to develop a spatial perspective of contemporary water balance across the watershed, to develop a historical record of past water balance changes of the wetland based on ^{18}O, and to link the historical and contemporary perspectives to evaluate water balance stability and evolution, especially highlighting changes associated with vegetation succession, and if possible, fen patterning. Initially, we hoped to test the robustness of the moss-water isotopic fractionation including species effects to ensure that quantitative reconstructions were reliable and robust.

2. Mechanistic cellulose ^{18}O model

Biosynthesis of cellulose occurs by vascular plants, but also by algae, mosses, bacteria, cellular slime mold and tunicates (Saxena and Brown, 2005). Isotopic signatures in plant cellulose have been shown to depend mainly on the isotopic composition of environmental source waters used by the plant, offset by a biochemical enrichment factor reflecting the effect of exchange during hydration of carbonyl groups in cellulose formation, and physiological effects, reflecting processes such as root uptake, leaf enrichment, and evapotranspiration regulation. ^{18}O values in plant cellulose, δ_{cell}, and source water, δ_S, have been shown to be mechanistically related by:

$$\delta_{cell} = \delta_S + \varepsilon_p + \varepsilon_B \tag{1}$$

where ε_p, ε_B are the physiological and biochemical enrichment effects, respectively. A comprehensive description of the plant cellulose synthesis model can be found elsewhere (Roden et al., 2000; Shi et al., 2019). Given that mosses (i.e., bryophytes) lack stomata in photosynthetic leaves and have poorly developed vascular tissue, and therefore employ a different water use strategy, the physiological enrichment effect, ε_p, has been shown to be insignificant for these plants (Zanazzi and Mora, 2005). Importantly, experimental and observational studies have suggested near-constant values for the biochemical fractionation, ε_B, of 27 ± 3‰ (DeNiro and Epstein, 1981; Wolfe et al., 2002), although more recent compilations have argued for a weak temperature dependence (Sternberg and Ellsworth, 2011; Xia and Yu, 2020). Mosses have no roots; they do not have the ability of vascular plants to access water at depth, and so passively utilize shallow water from the acrotelm. As a result, moss is expected to utilize water in the shallow acrotelm in the immediate vicinity of the plant. While most isotopic studies of mosses seem to have focused on *Sphagnum*, an important peat-forming genus, dominant wetland species at the McClelland Wetland site also include the true mosses, *Hamatocaulis vernicosus, Tomentypnum nitens,* and *Scorpidium scorpioides.*

3. Study site

The study was conducted within the McClelland Wetland, a large boreal wetland dominated by peatlands and located near the northern extent of surface mineable bitumen adjacent to McClelland Lake (57.4871° N, 111.3197° W) (Fig. 1). Climate of the region is cool and moist, with short cool summers and long cold winters. Monthly temperatures at Fort McMurray, located 83 km to the south, range from −17.4 °C in January to 17.1 °C in July, with a mean annual temperature of 1 °C (ECCC, 2022). Annual precipitation is 419 mmm (ECCC, 2022), but is known to be annually variable (Vitt et al., 2022). Hydrology of the region is strongly influenced by low-relief and a wetland-dominated landscape dominated by bogs, fens and shallow open water bodies. Topographic highs, including regional upland plateaus, and glacial moraines, including the Fort Hills Upland, which is situated adjacent to the southern boundary of McClelland Fen, are influential surface and groundwater runoff drivers. Incised river channels connected to the lower Athabasca River, as well as an extensive network of buried paleochannels, serve as major conduits for runoff and groundwater exchange. Vertical groundwater flow is significantly inhibited in the western portion of the wetland by occurrence of shallowly emplaced bitumen deposits within poorly lithified sandstone. Present day McClelland Wetland drains eastward through a well-developed patterned fen to McClelland Lake, which is a shallow, evaporation-dominated lake with minor groundwater exchange (Zabel et al., 2022), although potential is recognized for seasonal surface water outflow during spring melt in some years, similar to other local lakes (Gibson et al., 2019a). Degrading permafrost is widespread within bogs on regional uplands but is also encountered as isolated islands within fens including within the McClelland watershed.

Insight into the developmental history of the site was recently provided by Vitt et al. (2022). The site contains a diversity of landscape features, including fens, bogs, and swamps that can be shrubby, wooded, forested, graminoid-moss-dominated areas. These various site-types surround a patterned rich fen characterized by wet moss-dominated areas (flarks) associated with horizontal-oriented ridges (strings), known to generally form perpendicular to water flow (Eppinga et al., 2009). Over 114 species of bryophytes have been identified at the site, including 91 mosses and 23 hepatics (Vitt et al., 2003). The paleohydrologic setting of McClelland Lake, located downgradient of McClelland Wetland, was also recently described by Zabel et al. (2022). Notably, this study included application of ^{18}O in organic sediments and carbonate to reconstruct hydrology and temperature changes over the past 350 years.

4. Methodology

4.1. Water and moss sampling on wetland surfaces

Alpha (α-) cellulose was extracted from moss tip samples from various species at 227 sites across the surface of the wetland during 2017, 2018 and 2019, targeting collection of the two dominant species present at each site as well as paired surface water samples at each site. Water samples were considered to be representative of the acrotelm water utilized by the mosses to grow. In total, 227 near-surface moss samples were collected from 12 moss species present across the various wetland types within the McClelland Wetland, however, the majority of samples taken were *Hamatocaulis vernicosis* (characteristic of wet, lawn habitats) and *Tomentypnum nitens*, (characteristic of dry, hummocky habitats), two species that were often dominant. Less frequently, species of the genera *Sphagnum* (species of hummocks) and *Scorpidium scorpioides* (characteristic of very wet carpets and pools), were found to be dominant.

Approximately 100 g of the two dominant moss species at each site were collected and stored in paper bags for later extraction and analysis of δ^{18}O in α-cellulose. The moss was air dried, photographed, and

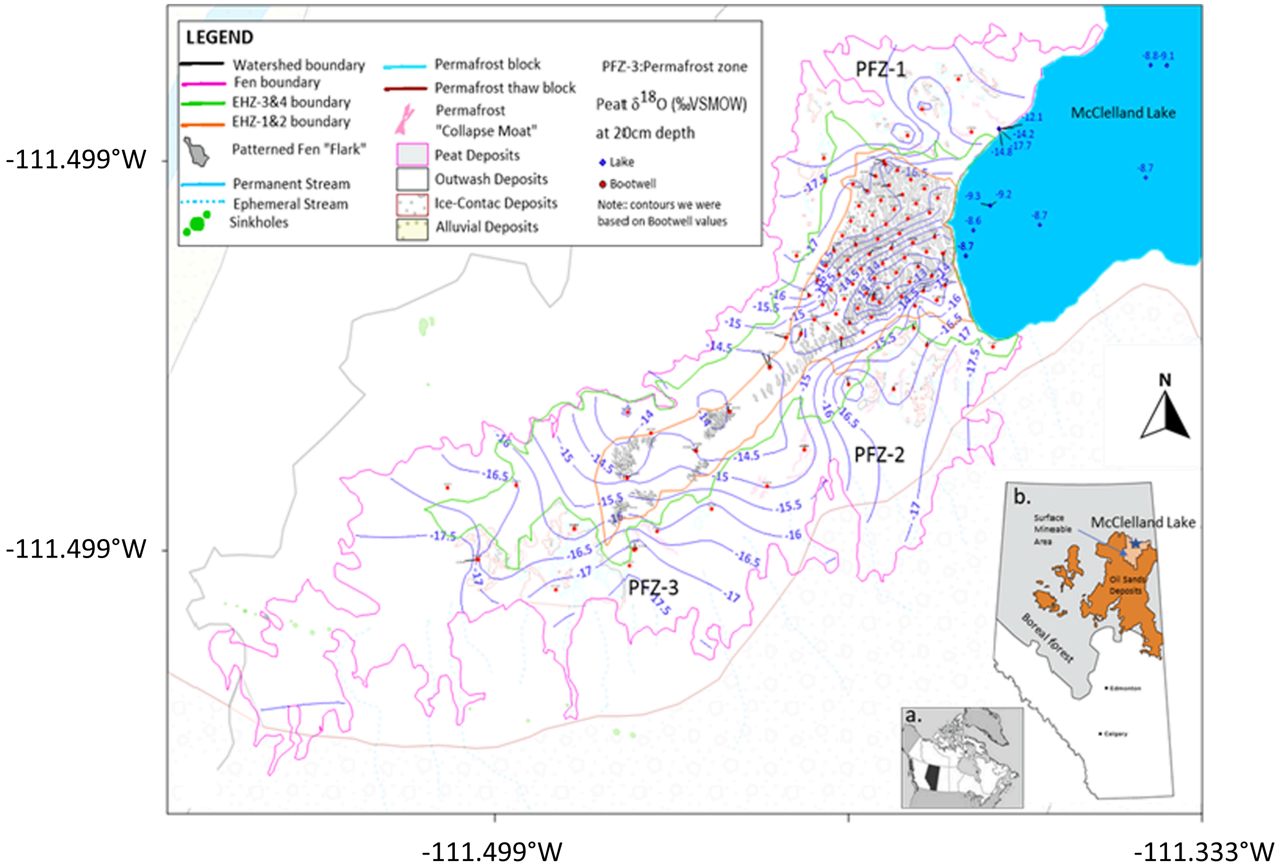

Fig. 1. Map of McClelland Wetland showing contours of $\delta^{18}O$ in water at 0.1 m depth within peat (as sampled in summer/fall 2018). Insets show (a) Province of Alberta, Canada; and (b) location of the Alberta Oil Sands Region and study site within the boreal forest region of Alberta. Selected geological features are also shown.

identified. Marl, which occurred as a residue on some samples, was noted where it occurred. The top 2 cm of the moss tips were then subsampled, placed in plastic trays, and sent to GEOTOP-UQAM for α-cellulose extraction followed by isotopic analysis.

Water samples were collected at moss collection locations for analysis of $\delta^{18}O$ and $\delta^{2}H$ of water, as well as at a broader network of surface water and groundwater monitoring stations located across the entire wetland (Fig. 1). Water samples were also tested for routine parameters including pH, temperature, electrical conductivity, and dissolved oxygen.

4.2. *Peat coring and moss identification*

In September 2017, a first peat core was obtained from the McClelland Wetland (Core 5) using a MacCaulay corer, a method selected to allow for collection of a continuous core from the peat while minimizing peat compression. Prior to coring, the upper 50 cm of the profile, consisting of mosses, was cut with a knife and placed in a plastic-wrapped length of PVC pipe. The corer was then inserted and advanced to extract a 50 cm interval of underlying peat. This core segment was then removed, the extracted core placed in plastic-wrapped PVC pipe, the borehole was re-entered, and the process repeated until refusal at 5.6 m depth. The cores were carefully wrapped and shipped to Southern Illinois University where preserved moss fragments were identified and sampled. Subsamples were then shipped to GEOTOP-UQAM for α-cellulose extraction and isotopic analysis. A wide variety of other characteristics were also recorded as part of concurrent study of vegetation communities at the site. During 2018–19, several additional cores were extracted using **a** 15-cm sonic corer (including Cores 6,7, 9,10). Additional cores were also sampled in 2019 targeting the main patterned fen. In general, peat cores were subsampled at 10 cm intervals and selected samples were submitted for isotopic analysis. Samples of bryophytes or wood were extracted for AMS radiocarbon dates and calibrated for calendar years BP (cal yr BP); see details in Vitt & House (2021).

4.3. *Cellulose extraction and isotope analysis*

Water samples were analyzed for $\delta^{18}O$ and $\delta^{2}H$ by isotope ratio mass spectrometry using a Thermo Scientific Delta V Advantage located at InnoTech, Victoria. Oxygen was prepared using a Gasbench II by equilibrating water and CO_2 and then introducing CO_2 into the dual inlet using an autosampler (Paul and Skrzypek, 2006). Hydrogen was analyzed by auto-injecting water into a chromium reactor heated to 875 °C in the HDevice to produce H_2, which was streamed to the dual inlet for analysis (Brand et al., 1996). Results are reported in "δ" notation in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) and normalized to the SMOW-SLAP scale, where SLAP is Standard Light Arctic Precipitation (Nelson, 2000). Laboratory analytical uncertainty estimated based on 2-σ of repeats is better than ± 0.15 for $\delta^{18}O$ and ± 0.50 for $\delta^{2}H$ ($n = 450$).

Dried moss tips (from the fen survey) or stems/fragments (in cores) were freeze-dried for 48 h and then placed into a fiberglass filter bag, heat sealed, and labelled. Based on the method of Zanazzi and Mora (2005) and Wolfe et al. (2002), α-cellulose was extracted to remove lipids, lignin, and hemicellulose. The procedure was carried out over a 6-day period in an array of Soxhlet extractors in batches of 20 samples. Briefly, lipids were removed by boiling filter bags in a toluene/ethanol mixture, dried for 24 h, rinsed, boiled in ethanol for 24 h, dried for 1 h, then boiled in deionized water for 6 h. To remove lignin, the bags were subsequently treated several times over a 2-day period with sodium chlorite and acetic acid at 70 °C. The samples were then rinsed in deionized water, rinsed with 10% NaOH solution at 60 °C, and repeated.

NaOH was then neutralized by adding 1% HCl solution until the pH was neutral. To remove hemicellulose, the bags were boiled in deionized water, placed in a bath shaker for 45 min adding NaCl and acetic acid (99%), washed multiple times in deionized water, soaked in 17% NaOH, washed again several times in deionized water, soaked in 10% acetic acid, washed again several times with deionized water, and then freeze dried. To prepare for isotope analysis, 10–15 g aliquots were placed in silver foil capsules and loaded into a PyroCube oven interfaced to an isotope ratio mass spectrometer for conversion to CO via pyrolysis at 1500 °C (see Saurer and Siegwolf, 2004).

4.4. Cellulose-water isotopic separations

$\delta^{18}O$ in α-cellulose and water were compared to evaluate cellulose/water isotopic separations ($\varepsilon^{18}O$), initially to characterize the ‘so-called’ moss-water transfer function by species; secondly, to confirm whether preserved mosses could be used reliably for reconstructing past $\delta^{18}O$ history at the site; and thirdly, to find a practical approach for routine application of the method at the McClelland Wetland and elsewhere in the region. Calculation of the biochemical enrichment was based on the apparent isotopic separation between moss and water, $\varepsilon^{18}O$:

$$\varepsilon^{18}O = \delta^{18}O_{\alpha-cellulose} - \delta^{18}O_{water}(\text{‰}VSMOW) \quad (2)$$

where $\delta^{18}O_{\alpha-cellulose}$ is the isotopic composition measured in cellulose from individual living plants or moss macrofossils in peat, and $\delta^{18}O_{water}$ is the isotopic composition measured in source water, as collected in late summer (August/September) at the surface where the moss was growing. For peat core reconstructions, $\delta^{18}O_{water}$ was inferred from Eq. (2) from the other known components. No attempt was made to infer temperature effects on isotopic fractionation, as noted by Sternberg and Ellsworth (2011) and Xia and Yu (2020), as we considered site-to-site temperature gradients to be inconsequential, and because the dominant moss species often co-existed at the same sites, suggesting that they were not differentially sensitive to local temperature, even considering that habitat and moss growth rates have been shown to be inherently

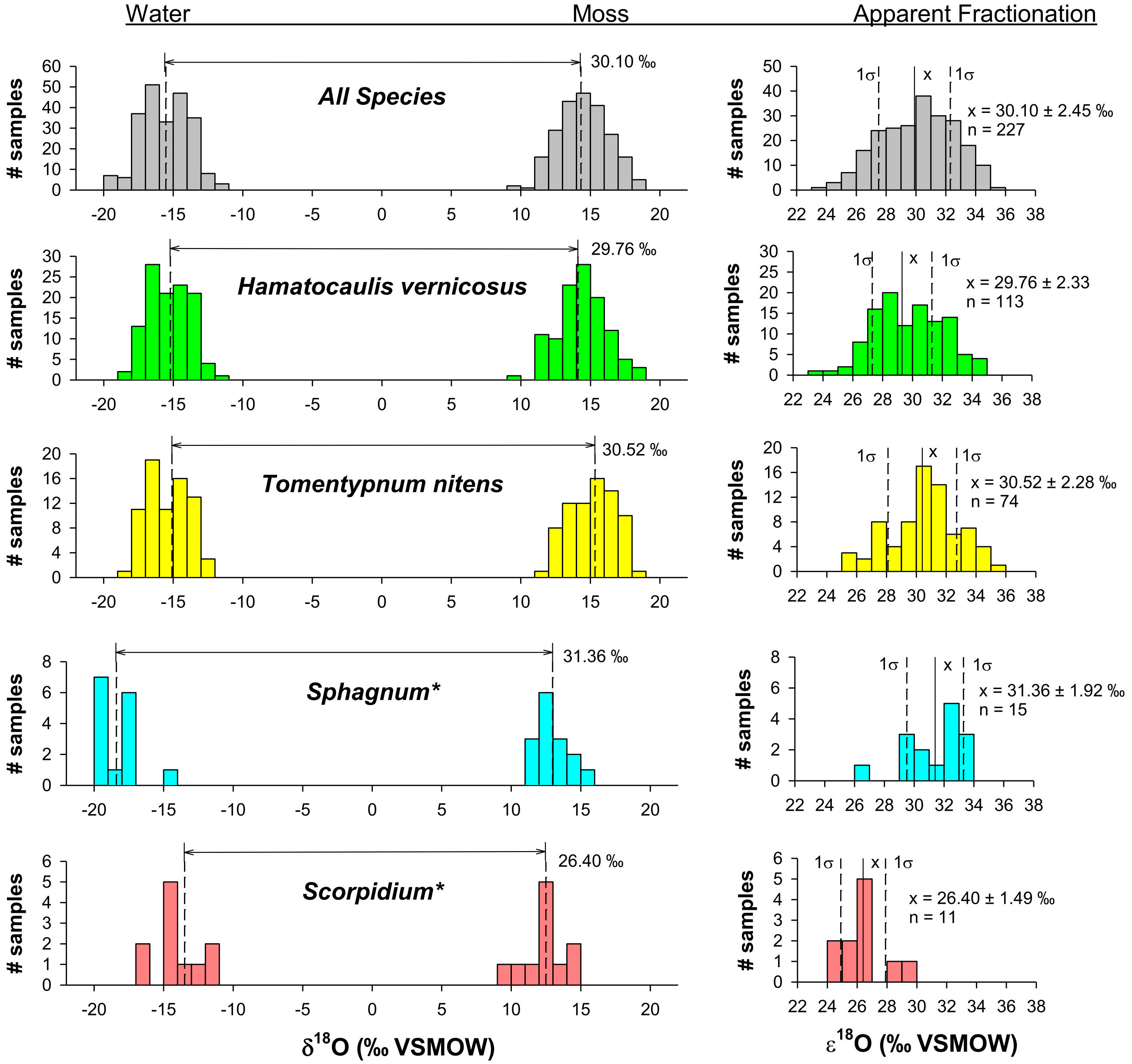

Fig. 2. Histograms illustrating distributioons $\delta^{18}O$ isotopic composition of water and moss pairs by species for the four dominant species and overall, as well as apparent moss-water isotopic fractionation for each. Average isotopic separations ($\varepsilon^{18}O$) and standard deviations are shown.

sensitive to differences in climate (Asada et al., 2003).

Statistical comparisons between $\delta^{18}O_{\alpha\text{-cellulose}}$ and $\delta^{18}O_{\text{water}}$ (Fig. 2, Table 1) highlight the overall fractionations apparent between moss and water based on all moss samples as well as individual dominant species. Results revealed very systematic moss- water isotopic separations overall. On average, moss was found to be enriched by 30.10 ± 2.45‰ (n = 227) for all species, with slight differences noted for individual species. For the two dominant species *Hamatocaulis vernicosus* and *Tomentypnum nitens*, isotopic separations were found to be very similar, 29.76 ± 2.33‰ (n = 113) *versus* 30.52 ± 2.28‰ (n = 74), respectively. Considering measured variability ranges, results are consistent with values that have been previously determined experimentally (27 ± 3‰), and most often applied in cellulose archive studies (DeNiro and Epstein, 1981; Wolfe et al., 2002; Zanazzi and Mora, 2005). Although based on fewer trials, we did note apparent isotope separations falling marginally outside this range for less common mosses, including *Sphagnum* and *Scorpidium scorpioides*, which had apparent isotopic separations of 31.36 ± 1.92‰ (n = 15) and 26.40 ± 1.49 (n = 11), respectively. It is interesting to note that species preferring drier sites, including *Sphagnum* and *Tomentypnum nitens* showed higher offset from source water than *Scorpidium scorpioides* and *Hamatocaulis vernicosus*, which prefer wetter sites. Due to negligible differences between our dominant species, we opted to carry out the reconstructionss using constant values for $\varepsilon^{18}O$. In doing so we anticipated the potential for a slight compression of the isotopic scale between dry-wet transitions, although this effect appeared to be unimportant in the reconstructions carried out, which clearly revealed the expected responses to wet and dry transitions. Overall, the systematic nature of ^{18}O signatures during water uptake into the α-cellulose was confirmed by our moss-water analysis and established a robust basis for use of moss cellulose for hydrologic reconstruction at the site.

5. Results and discussion

5.1. Contemporary water isotope systematics

Variations in stable isotope composition (^{18}O and ^{2}H) of water, both spatially and depth-wise within the wetland complex, reveal systematic patterns related to isotopic signatures in water sources overprinted by heavy isotopic enrichment due to evaporation. As shown for water sampled near surface (Fig. 1), $\delta^{18}O$ is found to range from less than −18‰ near the western, northern and southern margins of the wetland complex, to greater than −13% within the main patterned fen area

Table 1

Summary of moss and water isotopic compositions.

^{2}H water (‰ VSMOW)	n	Average	Median	stdev	max	min	Range
all	227	−127.49	−127.43	8.94	−104.88	−147.82	42.93
Hamatocaulis vernicosus	113	−126.00	−125.41	7.75	−108.05	−141.94	33.89
Tomentypnum nitens	74	−126.86	−126.66	7.10	−112.83	−139.28	26.45
*Sphagnum**	15	−142.84	−145.11	5.80	−128.56	−147.82	19.25
Scorpidium scorpioides	11	−116.73	−118.30	7.70	−104.88	−127.57	22.68
Pleurozium schreberi	4	−138.39	−138.29	2.86	−135.05	−141.94	6.88
Aulocomnium palustre	6	−137.05	−138.87	7.91	−121.73	−145.11	23.38
Plagiomnium ellipticum	1	−127.68	−127.68	–	–	–	–
Brachythecium acutum	1	−119.05	−119.05	–	–	–	–
Drepanocladus aduncus	1	−131.33	−131.33	–	–	–	–
^{18}O water (‰ VSMOW)							
all	227	−15.60	−15.84	1.71	−11.35	−19.35	8.00
Hamatocaulis vernicosus	113	−15.34	−15.48	1.49	−11.98	−18.35	6.37
Tomentypnum nitens	74	−15.43	−15.85	1.46	−12.63	−18.02	5.39
*Sphagnum**	15	−18.40	−18.84	1.19	−14.95	−19.35	4.39
Scorpidium scorpioides	11	−13.90	−14.09	1.77	−11.35	−16.62	5.27
Pleurozium schreberi	4	−17.75	−17.80	0.55	−17.02	−18.35	1.34
Aulocomnium palustre	6	−17.28	−17.53	1.34	−14.77	−18.84	4.07
Plagiomnium ellipticum	1	−15.96	−15.96	–	–	–	–
Brachythecium acutum	1	−14.20	−14.20	–	–	–	–
Drepanocladus aduncus	1	−16.24	−16.24	–	–	–	–
^{18}O moss alpha cellulose (‰ VSMOW)							
all	227	14.50	14.42	1.75	18.21	9.35	8.87
Hamatocaulis vernicosus	113	14.42	14.38	1.72	18.13	9.35	8.79
Tomentypnum nitens	74	15.10	15.18	1.58	18.21	11.92	6.30
*Sphagnum**	15	12.97	12.92	1.04	15.00	11.46	3.54
Scorpidium scorpioides	11	12.49	12.62	1.53	14.86	9.97	4.89
Pleurozium schreberi	4	15.09	14.94	0.64	15.95	14.51	1.44
Aulocomnium palustre	6	15.06	14.97	1.54	17.58	13.22	4.36
Plagiomnium ellipticum	1	13.05	13.05	–	–	–	–
Brachythecium acutum	1	16.12	16.12	–	–	–	–
Drepanocladus aduncus	1	13.52	13.52	–	–	–	–
Apparent $\varepsilon^{18}O$ (‰ VSMOW)							
all	227	30.10	30.23	2.45	35.53	23.86	11.67
Hamatocaulis vernicosus	113	29.76	29.70	2.33	34.62	23.86	10.76
Tomentypnum nitens	74	30.52	30.67	2.28	35.53	25.12	10.41
*Sphagnum**	15	31.36	32.04	1.92	33.79	26.91	6.87
Scorpidium scorpioides	11	26.40	26.30	1.49	29.24	24.23	5.01
Pleurozium schreberi	4	32.83	32.75	1.15	34.31	31.53	2.78
Aulocomnium palustre	6	32.34	32.68	1.02	33.28	30.75	2.53
Plagiomnium ellipticum	1	29.01	29.01	–	–	–	–
Brachythecium acutum	1	30.32	30.32	–	–	–	–
Drepanocladus aduncus	1	29.76	29.76	–	–	–	–

situated in the central, eastern portion of the complex. Given that heavy isotopic enrichment is generally progressive along wetland flowpaths in proportion to cumulative evaporation losses, isotopic gradients are interpreted as being indicative of water flow directions, similar to the observations of Graham et al. (2016). Isotope-inferred flow directions, which are in general agreement with flow directions deduced from hydraulic head measurements, topographic gradients, and fen patterning, suggest that flow from the southern margin and from the southern patterned fen is generally towards the eastern margin of the wetland, originating from primary inflow sources near the base of Fort Hills, an ice-thrusted morainic upland situated on the southern margin of the wetland, as well as from sandy fluvial-aeolian deposits to the north of the fen, with inflows into the northern basin (Vitt et al., 2022). Additionally, thawing permafrost within peat, detected within the north-eastern and southern marginal areas of the wetland complex is present. Three main permafrost zones are noted in Fig. 1.

The isotopic signatures of wetland waters, their offset from source water signatures, and the role of evaporation become clear when the background isotope data are shown in $\delta^{18}O$-$\delta^{2}H$ dual isotope space (Fig. 3). As illustrated, water isotope signatures in the wetland generally plot on or below the meteoric water line (MWL) defined for Canada by Gibson et al. (2005), for the Athabasca region by Baer et al. (2016) and subsequently refined by Chad et al. (2022) (Table 2).

Falling close to this MWL bundle, winter precipitation in the region typically ranges between –22 and –32‰ in $\delta^{18}O$ (−170 and −250‰ in $\delta^{2}H$), whereas rainfall typically ranges between −10 and −20‰ in $\delta^{18}O$ (−80 and −170‰ in $\delta^{2}H$) (Gibson et al., 2015; Baer et al., 2016; Chad et al., 2022). Shallow groundwaters in Quaternary aquifers within the Athabasca region typically range between −15 and −21‰ in $\delta^{18}O$ (−160 and −130‰ in $\delta^{2}H$) (see Gibson et al., 2015; Birks et al., 2019), and generally plot close to the MWL reflecting that they originate from various mixtures of snow and rainfall recharge. We note a similar lower limit for isotope values in wetland waters from McClelland Wetland compared to these shallow groundwaters, but also observe that isotope values in the wetland reach upper limits as high as −12‰ for $\delta^{18}O$ (−105‰ for $\delta^{2}H$), with significant offset from the MWL. For comparison, isotopic enrichment in McClelland Lake was found to reach values close to −9‰ for $\delta^{18}O$ (−95‰ for $\delta^{2}H$).

While shallow groundwaters (and also formation waters) typically plot close to the MWL, often varying along regression lines with slopes approaching 7 or 8 (see Meteoric Waters, Table 2), wetland waters are found to plot along evaporation lines with slope approaching 5 (see McClelland Wetland waters, Table 2). We note that offset from the MWL arises as a direct result of higher evaporation/inflow, and this offset has been widely used to estimate water balance of lakes and wetlands in the region and elsewhere (see Gibson et al., 2015, 2016a, 2022). In particular, the highest enrichment observed in the McClelland Wetland occurs in areas with standing water that are primarily associated with string-flark patterning.

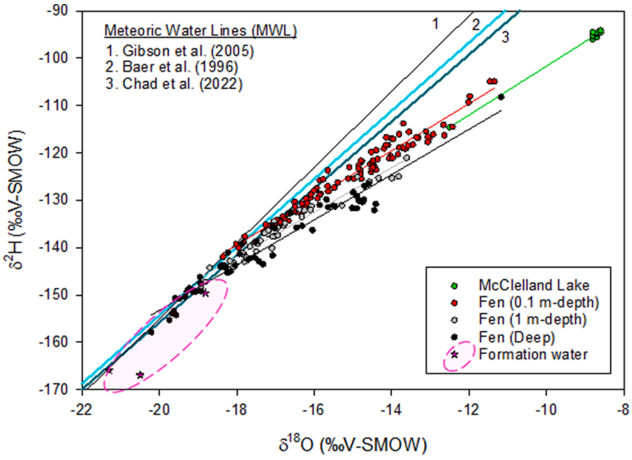

Fig. 3. Dual isotope plot showing sub-parallel isotopic enrichment patterns of fen porewaters at various depths in relation to the local meteoric water line bundle defined in previous studies (see Table 2). Fen waters fall along slopes close to 5 indicating evaporative modification as compared to 8 for the MWL (i.e., precipitation). McClelland Lake and examples of bedrock formation water sampled within the McClelland Watershed are shown. (See above-mentioned references for further information.)

For McClelland Wetland waters, isotopic enrichment is shown to define distinct, subparallel evaporation trajectories for three stratified depth classes (Fig. 3), as follows: (i) peat surface waters sampled within the acrotelm (<0.1-m depth), (ii) peat pore waters sampled from piezometers installed within the shallow catotelm (1-m depth), and (iii) peat pore waters sampled from piezometers installed within the deep catotelm (1 to 8-m depth). Because evaporation is a surface process restricted to the acrotelm, we postulate that occurrence of evaporated water signatures at depth within the shallow and deep catotelm (anaerobic zone) implies widespread net downward advection–dispersion of porewater from surface across the acrotelm/catotelm interface. While there is little distinction evident between the slope of surface waters (4.80), upper catotelm pore waters (4.70) and deep catotelm porewaters (4.78), a systematic depth-wise shift to lower ^{18}O,^{2}H intercept is evident, and is found to be statistically significant (Table 2).

Several possible mechanisms were initially contemplated to explain the depth-wise depletion in ^{18}O and ^{2}H. Firstly, depleted signatures were thought to potentially indicate mixing with heavy-isotope depleted groundwater sources including: (i) upwelling surficial aquifer water (ii) formation water, or (iii) preferential recharge of freshet snowmelt via depressions or macropores. While these hypotheses were considered possible, the low hydraulic conductivity of highly-compacted catotelm peat would likely limit the degree and extent of this process. Whereas fens are generally understood to be minerotrophic, i.e., groundwater-fed, inflows can be expected to decline exponentially with depth, implying only potential for shallow-seated groundwater inputs. This did not appear to explain the observations.

Another factor potentially contributing to systematic depth-wise decline in ^{18}O is selective water use by mosses compared to vascular plants; mosses being preferentially reliant on shallow capillary fringe or unsaturated zone water, whereas vascular plants have a propensity to exploit saturated acrotelm water sources, with water use distributions being determined by rooting depth, as noted in previous studies (Rasmussen and Kulmatiski, 2021). Vascular plants were not expected to tap into the catotelm, it being anoxic. From studies conducted in boreal peatlands in the region, rooting depth has been shown to be positively correlated with water table depth for *Picea* and *Larix laricina* but may also respond to occurrence of frost (Lieffers and Rothwell, 1987). Slight elevation increases and deeper water tables are often characteristic of hummocks and strings in patterned fens. While untested, a selective water use scenario we considered is that mosses efficiently evaporate water from saturated or standing water on flark surfaces, whereas by a combination of evaporation and transpiration, mosses and vascular plants may together be more efficient at removing water from strings. The fraction removed via transpiration of vascular plants from strings is expected to occur without isotopic fractionation, if drawn from the saturated acrotelm, or fractionated if drawn from adjacent flark pools, which makes the overall selective water supply effect difficult to predict without direct experimental evidence.

A third mechanism, and one that is likely a contributing factor to depth-wise depletions in ^{18}O and ^{2}H under both of the above scenarios, is that deep catotelm porewaters are ancient, being recharged under colder climate conditions. At nearby Mariana Lakes, a recent survey of porewater sampled in piezometers installed to depths ranging from 1 to 8 m depth at bog and fen sites, found that tritium was absent below 4 m, suggesting these waters predated the 1950′s tritium peak, and at 8-m depth, may have been recharged between 1200 and 2400 cal. years

Table 2

Summary of regional meteoric water lines and fen water lines.

	Description		Reference	Equation	N	r^2	p
	Meteoric Waters						
1	Canadian Meteoric Water Line (Monthly weighted)		Gibson et al., 2005	$\delta^2H = 8.0(\pm0.050)\cdot\delta^{18}O + 8.5(\pm1.04)$	289	0.990	<0.001
2	Mildred Lake Water Line (Amount weighted)		Baer et al., 2016	$\delta^2H = 7.20\cdot\delta^{18}O - 10.3$	106	0.983	<0.001
3	Mildred Lake Water Line (revised, Amount weighted)		Chad et al., 2022	$\delta^2H = 7.07\cdot\delta^{18}O - 14.4$	435	0.994	<0.001
	McClelland Wetland waters						
	0.1 m depth	Fen surface water	This study	$\delta^2H = (4.80 \pm 0.095)\cdot\delta^{18}O - (49.821 \pm 1.45)$	104	0.965	<0.001
	1 m depth	Shallow piezo-meters in peat		$\delta^2H = (4.70 \pm 0.18)\cdot\delta^{18}O - (57.27 \pm 3.00)$	37	0.951	<0.001
	1–8 m depth	Deep piezo- meters in peat		$\delta^2H = (4.78 \pm 0.15)\cdot\delta^{18}O - (57.61 \pm 2.65)$	57	0.947	<0.001

*refers to labels in Fig. 3; n = no.samples; r^2 = correlation coefficient; p= =significance.

BP based on apparent rates of water movement (Gibson et al., 2021).

Variations in wetland $\delta^{18}O$ during the growing season are also expected based on the described seasonality inherent in the isotopic signatures of snow and rain that are propagated to varying degrees through the recharge process and via mixing with insitu water storage. While the full range of growing season variability was not captured during the limited water-moss pairs sampling program at McClelland Wetland, longer $\delta^{18}O$ monitoring records for wetlands, lakes, rivers, and groundwater are available for the Athabasca region which provide some background on expected variations (Fig. 4).

We note that typical variations in fens at a selection of sites ranges from 6 to 12‰ in $\delta^{18}O$, with larger ranges observed for wetlands associated with evaporation-controlled hydrologic settings, or in the case of groundwater, snowmelt-driven recharge.

Comparison with the range of $\delta^{18}O$ values reconstructed from the current moss-water survey at McClelland Fen is also shown, and is informative for interpretation of our cellulose results described below.

5.2. Core ^{18}O reconstruction

Historical reconstruction of source water ($\delta^{18}O_{water}$) over time was carried out for 5 peat cores based on analysis of α-cellulose extracted from moss stem/leaf fragments preserved within sequential layers of the peat cores. Such peat chronologies are generally ideal for historical reconstruction as living plants, including mosses, die on the wetland, are partially decomposed, and become deposited within the anoxic catotelm, where plant fragments are preserved for thousands of years. Wood from vascular plants is also frequently preserved, and so can be used to characterize co-existing woody vascular plants in wetlands or to delimit depositional periods characterized by forest aggradation or forest fire.

A constant cellulose-water isotopic separation ($\varepsilon^{18}O$) of 30.1‰ was used for the McClelland reconstructions (Fig. 5) as justified previously. We acknowledge that species-specific reconstructions may be a worthwhile refinement of our approach under some circumstances, especially in cases where the dominant moss species at a site may change significantly over time. This was not the case for the McClelland Wetland, but

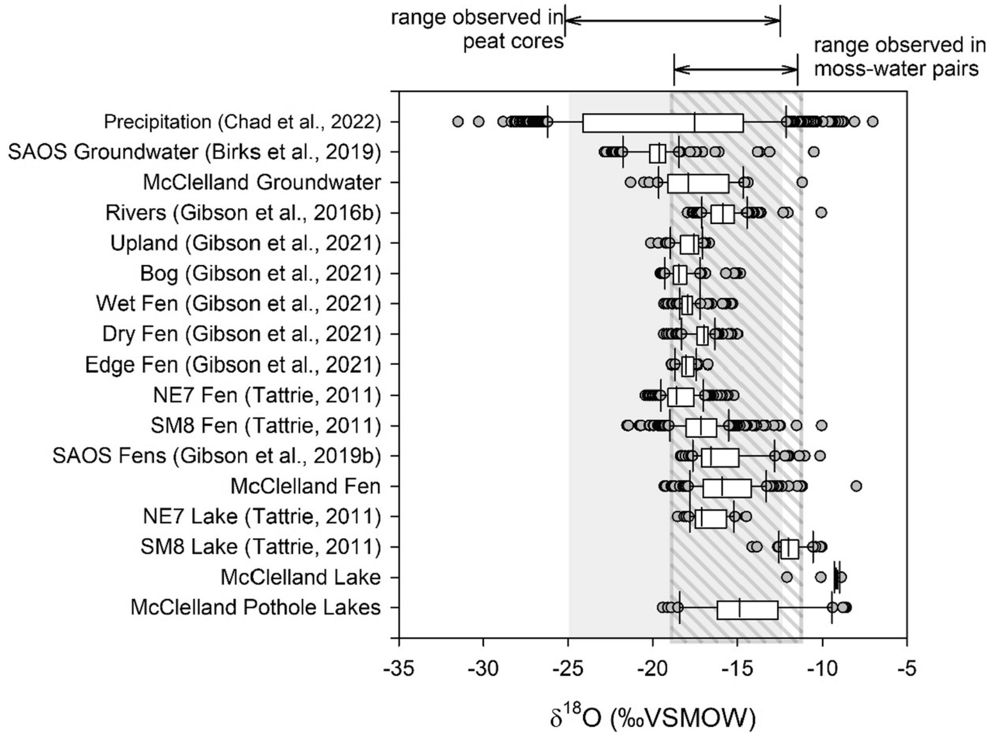

Fig. 4. Natural range of ^{18}O in selected waters based on previous studies, from peat core reconstruction, and contemporary water sampling conducted in the McClelland Wetland complex. Boxes indicate median, 25th and 75th percentiles; whiskers indicate 10th and 90th percentiles; individual outliers are shown. SAOS-South Athabasca Oil Sands region. (See above-mentioned references for further information.)

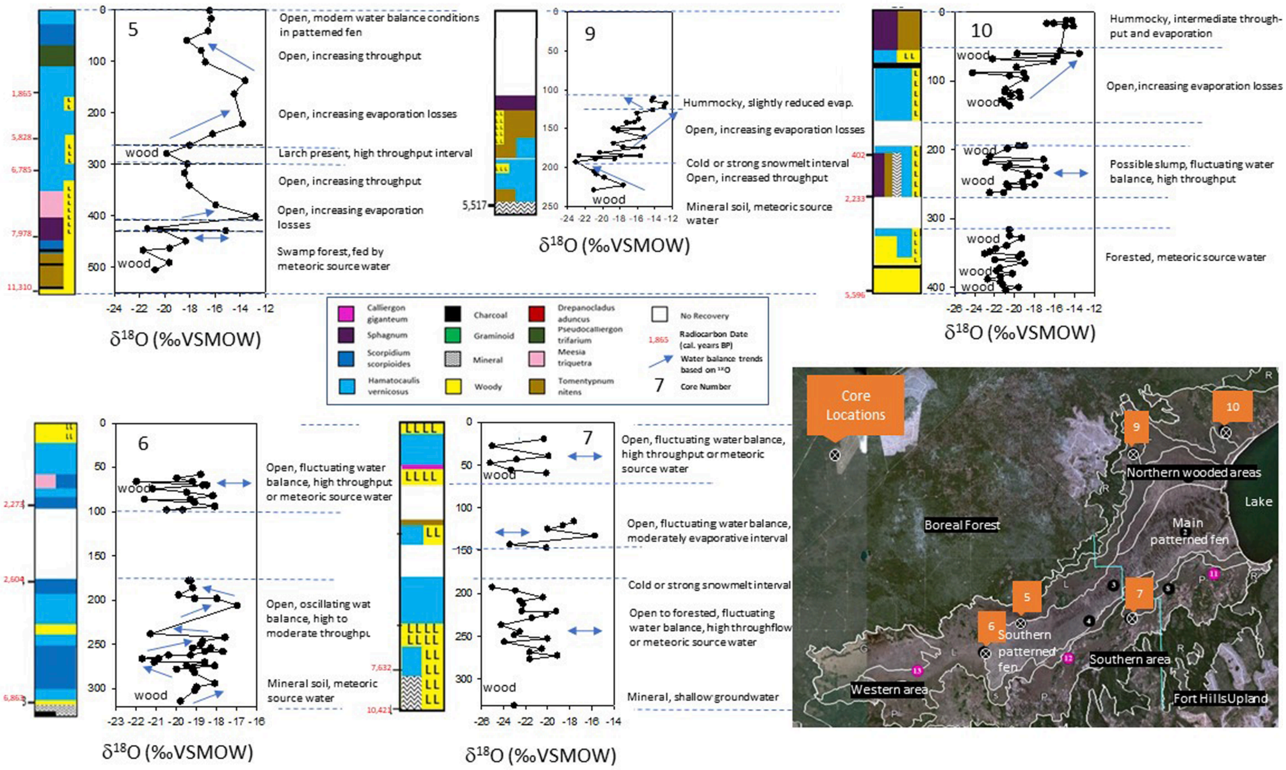

Fig. 5. Age-dated peat core species chronologies aligned with δ^{18}Owater as reconstructed α-cellulose in preserved mosses, McClelland Fen. Inferred conditions and water balance changes are noted. Inset shows core locations used in this analysis. Species chronologies are modified from Vitt and House (2021). L = Larix laricina.

may be important for reconstructions at other sites in the region. In some circumstances, it may be practical to target a single species of moss in a core to simplify application of the method. As for cellulose ^{18}O archives in general, we note that use of constant values of ε^{18}O has been the most commonly applied strategy in previous wetland paleohydrology investigations (Ménot-Combes et al., 2002, Zanazzi and Mora, 2005, Moschen et al., 2009, Kaislahti Tillman et al., 2010, Daley et al., 2010, Jones et al., 2019). A similar α-cellulose approach was recently used to reconstruct lakewater δ^{18}O over the past 350 years in adjacent McClelland Lake, based on both aquatic cellulose and authigenic carbonate in lake sediments (Zabel et al., 2022). Use of dual archives permitted estimation of lake temperature, which revealed gradual warming of the lake since 1900 (Zabel et al., 2022).

5.3. *Wetland water balance variations*

Depth-wise variations in $\delta^{18}O_{water}$ in the peat cores are shown in combination with species chronologies in Fig. 5. Comments are provided at various intervals throughout each peat core to broadly identify our interpretation of wetland status based on vegetation observations and isotopic changes. A detailed description of species and vegetation succession throughout the cores was conducted as part of a separate investigation (Vitt and House, 2021), however, selected features of the vegetation record are described here to assist in constraining the isotopic interpretations.

Median ages (cal. years BP) based on radiocarbon dating of wood or moss are shown for each peat core (in red) (Fig. 5). Core 5, which is a 560 cm core extracted from the northern edge of the southern patterned area of the fen, reveals earlier and thicker peat accumulation than the marginal cores (Cores 6,7,9,10, which recovered from 250 to 410 cm of core). Peat accumulation appears to have originated in the central basin following glacial drainage by 11,310 years BP, with paludification leading to peat accumulation and expansion to marginal areas over the next 1,000 to 6000 years (Vitt and House, 2021). Peat deposition along the southern margin of the wetland adjacent to Fort Hills appears to significantly precede deposition along on the northern and western margins. Shallow groundwater and runoff from Fort Hills is inferred to be a primary source of water supply to the wetland early on in fen development, a role it continues to fulfill based on evidence of modern δ^{18}O gradients across the wetland (Fig. 1). Both modern gradients and architecture of the basin suggest that source water originates mainly from the southern margins of the fen, and flows through the central and eastern areas of the fen to McClelland Lake. Degrading permafrost is present in both the northeastern and southern marginal bogs and peat plateaus, but was not found in the central wetland corridor.

The reconstructed $\delta^{18}O_{water}$ from the cores was found to range from −25‰ to −13‰, which spans a similar range to meteoric waters and groundwaters observed across the Athabasca region (Fig. 4), and specifically aligns with contemporary fen isotope results (Fig. 3). This agreement appears to confirm that the approach used for reconstructing $\delta^{18}O_{water}$ is in reasonable agreement with known variations at the site and across the region. From modern observations across the wetland, we note that water balance appears to be the primary driver of variations in $\delta^{18}O_{water}$, and so is inferred to be useful as an indicator of historical conditions. A general interpretation of $\delta^{18}O_{water}$ variations in each core is provided prior to presenting an integrated interpretation and perspective on the overall evolution of wetland water balance.

5.3.1. *Southern patterned fen*

With a basal radiocarbon date of 11,310 cal. Years BP, Core 5 is located at the northern edge of the southern patterned fen (Fig. 5). Peat formation above the mineral soil contact was initially *Tomentypnum nitens* dominant, with abundant evidence of larch (*Larix laricina*) in the form of wood debris and charcoal (reflecting episodes of forest fire). This interval is consistent with a hummocky paludifying forested swamp. $\delta^{18}O_{water}$ values during this interval are found to range from −20 to −18‰, close to values expected for meteoric water, i.e., precipitation or shallow groundwater, with negligible evaporation. A likely wetting trend, marked by transition from *Scorpidium scorpioides* to *Sphagnum* by 7,978 cal. years BP and then to *Meesia triquetra*, a species indicative of open wet conditions, captures a significant historical change in the system, that is accurately captured by $\delta^{18}O_{water}$ values, which shift dramatically to values representative of modern wet lawn areas (−13‰), indicating significant open-water and bryophyte-mediated evaporation losses. By slightly earlier than 6,785 cal. years BP, *Hamatocaulis vernicosis* becomes dominant, another moss species commonly associated with rich fen lawns, and this species substantially dominates from its appearance until the present day, apart from a brief interval beginning around 1 m depth when *graminoids* and *Scorpidium*, which are associated with wet carpets in rich fens, emerge dominant. Despite open conditions for much of the period from ~8,000 years to present, $\delta^{18}O_{water}$ values are remarkably variable, suggesting that water balance continued to systematically cycle between wet and dry conditions. Shortly after the appearance of *Hamatocaulis vernicosis* there is a brief episode of larch (*Larix laricina*) increase which aligns directly with a local minimum in $\delta^{18}O_{water}$ at ~6,000 cal. years BP, which reaches −20‰, inferred to reflect drier conditions and reduced evaporation losses. Immediately following this interval, a second wetting cycle without significant vegetation changes begins, characterized by increase in $\delta^{18}O_{water}$ from −20‰ to −14‰, which remains until after ~1,800 cal. years BP. The second shift appears to occur during what has been termed the Mid-Holocene warm period (Bartlein et al., 2010). Based on the shift to more enriched $\delta^{18}O_{water}$, and considering the resilient water supply feeding the southern fen, we infer that this interval may reflect higher evaporation losses at the site during this period, perhaps with slightly reduced source water supply, similar to the interval following initial formation of open conditions at ~ 8,000 cal. years BP. A return to higher throughflow and reduced evaporation losses is suggested by the subsequent major shift in $\delta^{18}O_{water}$ from −14‰ to −18‰, which appears to suggest a cooler than modern phase, most probably the Little Ice Age (~900–1300 years BP). The remaining core, extending from ~ 50 cm to surface, likely represents the entire Anthropocene period (i.e., several hundred years BP), but shows little apparent change, in contrast to the nearby McClelland Lake sediment core which recorded significant warming during this period (Zabel et al., 2022). Overall, given the significant hydrologic and climatic changes implied by the isotopic record at the site, and notwithstanding a few forested incursions, it appears that vegetation was fairly stable at the site and reflective of graminoid-moss-dominated lawn habitats since about ~ 8,000 cal. years BP.

5.3.2. Northern wooded areas

Located on the northern fringe of the wetland in degrading permafrost terrain (Fig. 5), Cores 9 and 10 represent similar time intervals although deposition rates appear to be higher for core 10. Basal dates reveal that paludification did not reach the sites until approximately 5,500 cal. years BP. The earliest dominant species were *Tomentypnum nitens* (Core 9) and *Hamatocaulis vernicosis* (Core 10). Both sites contained basal woody material, although more so for Core 10, which appears to have been forested and likely corresponds closely to the larch interval in Core 5 above 300 cm. $\delta^{18}O_{water}$ in both cores, ranging from −18 to –22‰, appears similar albeit variable up to about 200 cm in each core, and shifts to peak values close to −12‰ (Core 9) and −14‰ (Core 10) near the top of each core. As in core 5, shifts to more enriched $\delta^{18}O_{water}$ are inferred to reflect a more evaporative status and presumably warmer climate conditions. Vegetation changes at the sites are mostly indicative of shifts in dominance of *Hamatocaulis vernicosis* and *Tomentypnum nitens*, both indicators of open conditions, although *Hamatocaulis vernicosis* occurs in emergent lawn habitats whereas *Tomentypnum nitens* favors drier hummocky conditions associated wooded or forested conditions including strings (Vitt, 2014). We note that shifts to more evaporative conditions also appear to ultimately favour *Tomentypnum nitens* in both cores, although *Sphagnum* also ascends near the top of each core. Dominance of *Sphagnum* near the top of Core 9 is accompanied by a small decrease in $\delta^{18}O_{water}$, which may be reflective of less evaporative conditions associated with hummocks and a deeper acrotelm which are typical for *Sphagnum*. While age dates are limited near the top of these cores, and significant non-recovery intervals were encountered, it is likely that shifts to more evaporative conditions coincide with the Mid-Holocene warm period, as noted for Core 5.

5.3.3. Southern and western site-types

Peat cores extracted along the southern and western site-types that border on the patterned area of McClelland Fen including Cores 6 and 7, are distinguished from the cores previously described by lack of evidence of any significant evaporative episodes based on $\delta^{18}O_{water}$, which generally ranged between −18 and –23‰ (excepting 1 sample that attained −16‰), reflecting meteoric water or shallow groundwater sources. Core 6 was extracted from along the drainage divide between eastern flowing water into the patterned area and western flowing water to the graminoid-moss fen to the west, along the edge of the southern patterned fen, and Core 7 was extracted near a likely secondary water source.

Cores 6 and 7, as with the previous cores, were found to be dominated by macrofossils of *Hamatocaulis vernicosis,* but in this case Core 6 also contained intervening intervals of *Scorpidium scorpioides,* the latter occurrences corresponding to local minima in $\delta^{18}O_{water}$, ranging from –22 to −25‰, that may reflect wetter, cooler conditions than present. A brief evaporative interval is also noted for Core 7, which could be concurrent with the initial evaporative episode noted for Core 5. Cores 6 and 7 appear to be very stable over time, since these areas appear to be fairly unchanging with respect to source signatures and water balance over the past 7,000 to 10,000 years, despite significant climate changes occurring during the Holocene. Combined, the vegetation and $\delta^{18}O_{water}$ provide valuable evidence of ecosystem stability and resilience in the fen system in the areas monitored despite apparent hydroclimatological perturbations.

6. Concluding remarks

Modern $\delta^{18}O$ variations measured across the McClelland Wetland, including a moss-water sampling program, and a peat coring program, provide the basis for reconstructing historical water balance trends at the site, and assist in establishing important water source areas and water balance differences associated with the observed vegetation succession at the site. A controlled experiment confirmed the magnitude and systematic nature of isotopic fractionation associated with source water uptake in mosses, including species effects, and provides additional confidence in use of preserved moss material from peat cores for paleohydrology reconstructions. Accounting for moss-water biochemical fractionations, historical isotope variations measured in mosses from five peat cores were used to reconstruct $\delta^{18}O_{water}$, and were found to be consistent with modern $\delta^{18}O$ values measured in representative wetland zones, indicating temporal changes in water balance in various zones across the wetland. Notably, open conditions and high evaporation losses were found at ~ 8,000 cal. years BP and again after 5,000 cal. years BP, the latter likely in response to the mid-Holocene warm period.

Throughout all five of the investigated cores, considerable variation in climate-driven water balance is present. In comparison, the lack of associated vegetation change present in the five cores suggests that vegetation has strong resilience to climatically induced variation in water balance, given long-term stable sources of groundwater and surface water inputs.

We have described natural variations in stable water isotopes across a major wetland complex in the Athabasca Oil Sands region, and in doing so have established a basic framework for extending contemporary application of isotopes into a study of the past. Wetland monitoring programs operated by the Alberta Biodiversity Monitoring Institute (ABMI) and Alberta's Oil Sands Monitoring (OSM) program are presently evaluating and implementing new approaches for regional monitoring of wetlands, including similar isotope-based methods for determining site-specific water balance and for classification of important environmental controls such as groundwater reliance status or role of wetlands in regulating streamflow during floods and droughts. A recent study, isoABMI, determined water balance from isotope surveys in over 1022 open-water wetlands across Alberta (see Gibson et al., 2022) and demonstrated potential inflow and outflow partitioning methods capable of improving regional water balance assessment. While much interest to date has been on contemporary characterization, it is interesting to note that the study of historical water balance based on isotopes and vegetation succession in peat cores, as we have shown, may serve as a complementary tools for expanding understanding of the natural range of variability in wetland water balance monitoring, and thereby expediently develop a retroactive baseline without the prerequisite for decades of water sampling prior to meaningful results being obtained. Such records, based on short peat cores, could be accurately age dated using ^{210}Pb so that cores could be extracted that represent deposition over the entire Antropocene, thereby capturing a baseline history that predates and spans the era of development in the region. In addition to water isotopes, vegetation succession, nutrients, nutrient isotopes, geochemical indicators, and other important wetland health indicators could also be included. There is also great potential for wider application of the peat cellulose approach to study the holistic evolution and hydrologic interaction between wetlands, lakes, groundwaters and rivers over the course of the Holocene under changing climate and under changing permafrost conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2022.106116.

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