# Drivers of high rates of carbon burial in a riverine-influenced freshwater marsh in the Lake Erie watershed of southern Ontario, Canada

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#### Abstract

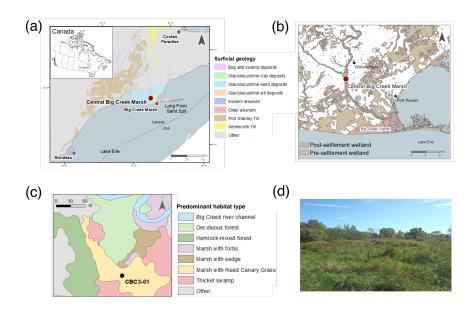
Freshwater marshes are prevalent and important stores of carbon. They bury carbon in deeper soils, although reported rates of carbon accumulation are significantly higher over recent (decadal) versus longer (centennial and millennial) timescales. Intrinsic organic matter degradation, long-term climatic and ecological changes, and recent anthropogenic impacts on sediment fluxes and organic matter production may have a role in explaining this discrepancy, yet remain poorly understood for freshwater marshes. We collected a 4-m core from a riverine-influenced marsh in the watershed of Big Creek which drains into Lake Erie in southern Ontario, Canada, and conducted radiometric dating, elemental analyses, and programmed pyrolysis for organic matter characterization. Over the past 5,710 calibrated years, burial of organic (on average  $26 \pm 34$  g C m-2 yr-1) and inorganic ( $22 \pm 25$  g C m-2 yr-1) carbon fractions has resulted in high rates of carbon accumulation. We found that elevated recent rates of organic carbon accumulation are driven by fractions that have low thermal stability and are predominantly from aquatic sources. This type of organic carbon is buried intermittently in deeper marsh sediments and corresponds to major hydro-fluvial events (e.g., Nipissing highstands), which coincide with regional marsh development. We deduce that lower fractions of labile carbon in deeper soils reflect long-term degradation, which underscores the notion that high recent rates of carbon accumulation are generally not sustained over centuries and millennia. Our research demonstrates the importance of identifying various carbon fractions in understanding carbon burial in freshwater marsh soils, and informing marsh conservation.

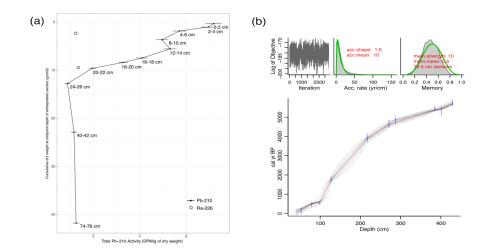
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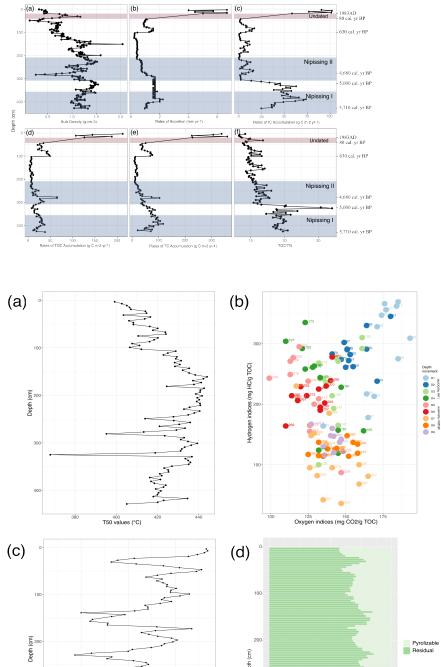
956661\_0\_art\_file\_10721459\_rq8z9c.docx available at https://authorea.com/users/544872/ articles/626884-drivers-of-high-rates-of-carbon-burial-in-a-riverine-influencedfreshwater-marsh-in-the-lake-erie-watershed-of-southern-ontario-canada

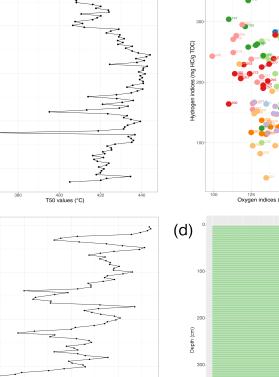
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956661\_0\_supp\_10744273\_rqnpb9.docx available at https://authorea.com/users/544872/articles/ 626884-drivers-of-high-rates-of-carbon-burial-in-a-riverine-influenced-freshwater-marshin-the-lake-erie-watershed-of-southern-ontario-canada









Hydrogen indices (mg HC/g TOC)

Proportion (%)

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2	
3	
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#### 23 Abstract

24 Freshwater marshes are prevalent and important stores of carbon. They bury carbon in deeper 25 soils, although reported rates of carbon accumulation are significantly higher over recent 26 (decadal) versus longer (centennial and millennial) timescales. Intrinsic organic matter 27 degradation, long-term climatic and ecological changes, and recent anthropogenic impacts on 28 sediment fluxes and organic matter production may have a role in explaining this discrepancy, 29 yet remain poorly understood for freshwater marshes. We collected a 4-m core from a riverine-30 influenced marsh in the watershed of Big Creek which drains into Lake Erie in southern Ontario, 31 Canada, and conducted radiometric dating, elemental analyses, and programmed pyrolysis for 32 organic matter characterization. Over the past 5,710 calibrated years, burial of organic (on average  $26 \pm 34$  g C m<sup>-2</sup> yr<sup>-1</sup>) and inorganic ( $22 \pm 25$  g C m<sup>-2</sup> yr<sup>-1</sup>) carbon fractions has resulted in 33 34 high rates of carbon accumulation. We found that elevated recent rates of organic carbon 35 accumulation are driven by fractions that have low thermal stability and are predominantly from 36 aquatic sources. This type of organic carbon is buried intermittently in deeper marsh sediments 37 and corresponds to major hydro-fluvial events (e.g., Nipissing highstands), which coincide with 38 regional marsh development. We deduce that lower fractions of labile carbon in deeper soils 39 reflect long-term degradation, which underscores the notion that high recent rates of carbon 40 accumulation are generally not sustained over centuries and millennia. Our research 41 demonstrates the importance of identifying various carbon fractions in understanding carbon 42 burial in freshwater marsh soils, and informing marsh conservation. 43

## 44 Data Availability Statement

45	Data from this research will be made available at https://doi.org/10.6084/m9.figshare.19326227
46	once the manuscript is published.
47	
48	Supporting Information
49	Supporting Information may be found in the online version of this article.
50	
51	Author Contributions
52	ALL and SAF designed the study and carried out field work. ALL prepared samples, carried out
53	laboratory analyses and assembled the datasets; OHA conducted programmed pyrolysis. ALL
54	and SAF analyzed and interpreted data from age-depth model, loss-on-ignition and elemental
55	analyses; AG and OHA analyzed and interpreted data from programmed pyrolysis. ALL
56	prepared the manuscript; all authors reviewed the results, discussed the interpretations and
57	revised the manuscript.
58	
59	Plain language summary
60	Freshwater marshes soils can contain considerable amounts of carbon stored several meters deep.
61	Analyses spanning the entire length of freshwater marsh soil profiles are uncommon and the
62	functions that enable them to sequester carbon and provide a means of mitigation against global
63	warming are poorly understood. We conducted geochemical analyses on a 4-m soil core from a

64 riverine freshwater marsh in a Lake Erie watershed to quantify and characterize carbon stores in

65 marsh soils and understand why rates of carbon burial appear markedly higher over recent

66 decades in comparison to past centuries and millennia. We found that organic and inorganic

67 carbon are buried at high rates, but easily degradable organic matter predominates at the surface

and is lost in deeper soils, which in part explains the apparent slower rates of long-term carbon
accumulation measured in marsh cores. Nonetheless, major fluctuations in Lake Erie water levels
dating back thousands of years have enhanced burial and preservation of carbon in marsh soils.
We demonstrate the importance in examining long records that capture all carbon types and the
implications of long-term decay of organic carbon. These types of analyses are critical in
assessing the role of marshes as a natural climate solution.

- 75 Key words: Wetland; carbon sequestration; programmed pyrolysis; paleoecology; Nipissing
- 76 rise; Holocene; Laurentian Great Lakes

## 77 **1 Introduction**

78 There is a need to improve carbon flux quantifications in the terrestrial biosphere because of 79 their potential to mitigate or amplify anthropogenic-induced global warming; yet, land fluxes of 80 carbon remain challenging to quantify due to high spatial and temporal variability (Archer, 2010; 81 Ciais et al., 2014). In recent years, there has been a growing interest in the role of wetlands in the 82 global carbon cycle. Wetlands are recognized as a significant carbon pool with potential to take 83 up or release enough carbon to influence the global climate, while simultaneously supporting 84 bio- and cultural diversity (Heimann & Reichmann, 2008; Petrescu et al., 2015; Dinerstein et al., 85 2020; Pyke et al., 2021). Carbon stocks in wetlands are predominantly contained in wetland 86 soils, where partially-decayed biomass can be buried and stored for centuries and millennia 87 (Kayranli et al., 2010; Yu et al., 2010; Kolka et al., 2018). Wetland conservation and restoration 88 have been identified as potential natural climate solutions in the temperate region where wetland 89 alteration is widespread (e.g., Drever et al., 2021); however, carbon stocks for the entire soil 90 profile of various temperate wetlands remain poorly constrained (Kolka et al., 2018). 91 Freshwater marshes are a broad group of wetlands characterized by emergent, soft-92 stemmed herbaceous vegetation with the capacity to adapt to and tolerate saturated and dynamic 93 conditions. These marshes are especially prevalent in the temperate region yet are highly 94 susceptible to drainage and conversion for agricultural use (Zoltai, 1988; Reddy & Delaune, 95 2008; Mitsch & Gosselink, 2015). While freshwater marsh soils are generally considered 96 mineral-based with low organic matter contents, freshwater marshes support significant organic 97 carbon burial over decades, centuries and millennia, and can contain peat horizons (Loder & 98 Finkelstein, 2020). In temperate North America, estimates of short-term (past 50–100 years) apparent rates of carbon accumulation in freshwater marshes are on average 155 g C m<sup>-2</sup> yr<sup>-1</sup>; far 99

fewer measurements of long-term (over centuries and/or millennia) rates are reported (Loder & Finkelstein, 2020). Due to this paucity of data, rates of long-term carbon accumulation are poorly constrained, and it is not well known how much carbon is buried and preserved over longer time scales in freshwater marsh soils.

104 Available data suggest that recent rates are significantly higher than long-term apparent 105 rates of carbon accumulation in freshwater marsh soils. Although this difference is not well 106 characterized in freshwater marshes, it has been more thoroughly studied in coastal wetlands and 107 northern peatlands. High recent rates of carbon accumulation in coastal wetlands are often 108 attributed to accelerating relative sea level rise (e.g., McTigue et al., 2019; Rogers et al., 2019), 109 while other work suggests that factors related to human activities (including eutrophication, 110 landscape alteration and invasive species) may perturb carbon balances and elevate recent rates 111 (Bansal et al., 2019; Spivak et al., 2019; Peteet et al., 2020; Gailis et al., 2021). In northern 112 peatlands, it is well established that past apparent rates of carbon accumulation are lower than 113 recent rates because the former are measured on samples that have already undergone some 114 degree of long-term decay (e.g., Clymo, 1984), although extrinsic factors (e.g., climatic changes, 115 wildfire, hydrological change, human activity) can influence both rates (e.g., Packalen & 116 Finkelstein, 2014; Marrs et al., 2019; Young et al., 2019). For freshwater marshes, investigation 117 is required to determine how intrinsic (e.g., organic matter lability, long-term decay) and 118 extrinsic factors in temperate landscapes affect recent versus long-term rates of carbon; this will 119 help ensure that rates are accurately captured for estimates of the strengths of natural carbon 120 sinks. Otherwise, making the assumption that recent rates are sustained over the long-term may 121 result in the overestimation of the strength of these natural sinks and lead to negative outcomes

including overly generous emission offsets (Bridgham et al., 2014; Neubauer, 2014; Young etal., 2019).

124 Freshwater marshes bury and preserve autochthonous (*in situ*) and allochthonous organic 125 carbon derived from the surrounding watershed due to their variable hydrological regimes 126 (Bridgham et al., 2006; Drexler, 2011; Van de Broek et al., 2018). Consequently, carbon 127 accounting in freshwater marshes has additional complexities, as there are multiple pathways by 128 from which carbon is derived and deposited over time, and the carbon stock in marsh soils may 129 not solely reflect *in situ* production of organic matter (Bridgham et al., 2006). Furthermore, 130 freshwater marsh soils contain both organic and inorganic carbon (Mitsch & Gosselink, 2015). 131 Although inorganic carbon fractions can be negligible and are infrequently examined, carbonate 132 burial may be significant in ecosystems where allochthonous sources of carbonate (e.g., coral 133 reefs, lithogenic sources) are present (Martin, 2017; Saderne et al., 2019) and thus needs to be 134 differentiated from organic carbon burial for carbon accounting purposes. 135 This study focusses on long-term apparent rates of carbon accumulation since the 136 formation of a riverine-influenced freshwater marsh which is mineral-based, proximal to 137 intensive anthropogenic land-use activities and in a temperate region with a history of large-scale 138 hydro-climatic change associated with the Laurentian Great Lakes. The objectives of our study 139 are to: 1) characterize organic matter and quantify carbon fractions since the Middle Holocene in 140 a freshwater marsh core; 2) track long-term apparent rates (hereafter long-term rates) of carbon 141 accumulation during the Holocene, when marsh formation in temperate North America was 142 initiated (e.g., Finkelstein & Davis, 2006; Rippke et al., 2010; Drexler, 2011), in relation to local 143 and regional hydroclimatic change; and 3) evaluate factors leading to elevated recent versus 144 long-term rates of carbon accumulation. The geochemical paleorecord allows us to evaluate the

145 impacts of both intrinsic and extrinsic factors on marsh sediment and carbon accumulation. To 146 address these questions, we use radiometric dating, elemental analyses, programmed pyrolysis 147 and carbon to nitrogen (C/N) ratios to examine how organic matter composition reflected 148 hydroclimatic change and rates of carbon burial in the paleorecord, and to quantify organic and 149 inorganic fractions that make up the total carbon stock in freshwater marsh soils. Programmed 150 pyrolysis was selected as it measures the thermal stability of soil organic matter in marsh soils, 151 allowing direct evaluation of the role of organic matter lability in differentiating recent versus 152 long-term rates of carbon accumulation.

153 **2 Methods** 

## 154 **2.1 Study site**

155 Central Big Creek Marsh (42.65° N, 80.54° W) is situated on modern alluvial deposits on the 156 floodplain of Big Creek in Norfolk County, southern Ontario (Figure 1). Norfolk County is on 157 the traditional lands of the Attawandaron, Haudenosaunee and the Anishinaabe First Nations, 158 and encompassed within the Treaty lands ('Between the Lakes Purchase') of the Mississaugas of 159 the Credit. The site is located approximately 8 km from the Lake Erie shoreline and about 2 m 160 above the mean annual level of Lake Erie (~174 m asl; NOAA, 2022). At present day, the site 161 supports predominantly monotypic stands of Reed Canary Grass (*Phalaris arundinacea*); other 162 marsh plants include Schoenoplectus tabernaemontani, Sparganium eurycorpum and Nuphar 163 lutea, and Lemna spp. in pools of standing water. Surrounding ecotypes encompass thicket 164 swamp and upland Carolinian forest (Figure 1). The climate is temperate with daily mean 165 temperatures of 21.1 °C in July and minus 5.4 °C in January, and annual precipitation of 1036 166 mm (Delhi, ON, 1981–2010; Environment and Climate Change Canada, 2021). The bedrock in the Big Creek watershed is comprised of limestone carbonates, overlain by modern and older 167

alluvium around the Big Creek channel, and by carbonate-rich till and glaciolacustrine depositsof clay, sand, and silt in other parts of the watershed (Barnett, 1993).

170 Around Lake Erie, long-term fluctuations of lake levels related to differential glacial 171 isostatic adjustment have had a strong influence on wetland development over the post-glacial 172 (Coakley & Lewis, 1985; Pengelly et al., 1997; Bunting and Warner, 1998; Finkelstein & Davis, 173 2006). During the Middle Holocene, a two-pulsed event related to outlet incision and drainage 174 from the upper to lower Great Lakes caused water levels in Lake Erie to rapidly rise and decline 175 by several meters (termed the Nipissing highstands; Coakley & Lewis, 1985; Finkelstein et al., 176 2006). The first of these highstands known as Nipissing I resulted in a rapid increase in water 177 level ~5,960 cal. yr BP, followed by a decline ~5,200 cal. yr BP. Nipissing II was a subsequent 178 increase in water level which reached a maximum  $\sim$ 4,480 cal. yr BP and dropped  $\sim$ 3,770 cal. yr 179 BP (Lewis et al., 2012). Water levels in Lake Erie have since fluctuated at a lower magnitude 180 (i.e., 1–2 m) over the past 3,000 cal. yr BP (Coakley & Lewis, 1985; Pengelly et al., 1997; 181 Finkelstein & Davis, 2006; Lewis et al., 2012). Periods of high and low water stands in Lake 182 Erie during and following the Nipissing events affected water levels in coastal marshes 183 (Finkelstein & Davis, 2006), and could have caused inundation and water table levels to fluctuate 184 in low-lying riverine-influenced marshes. Thus, these events had potential to promote or reduce 185 local production and preservation of organic matter, as well as inputs of minerogenic materials, 186 and to ultimately affect sedimentation and carbon accumulation in marsh soils (Van de Broek et 187 al., 2016; Van de Broek et al., 2018).

Based on soil maps, topographic, hydrological data, and land cover information, marsh and swamp habitat were extensive in Norfolk County prior to European settlement and 82% of wetlands have since been lost in this region (Snell, 1987; Ducks Unlimited Canada, 2010; Byun

191 et al., 2018; Figure 1). Widespread marshland had established across the Big Creek watershed 192 due to low-lying topography, the low permeability of glaciolacustrine deposits and riverine influence (Byun et al., 2018). Europeans arrived in Norfolk County during the mid-17<sup>th</sup> century, 193 194 and the first significant period of European settlement took place between 1790 and 1820 AD 195 (Chapman & Putnam, 1984). Shortly after, large-scale deforestation, drainage and intensive 196 landscape alterations occurred primarily in support of agricultural development and continued into the 20<sup>th</sup> century, resulting in massive increases in rates of erosion (Bunting et al., 1997; 197 198 Riley, 2013).

199 **2.2 Sampling** 

200 A 430-cm sediment core (CBC3-01) was recovered from Central Big Creek Marsh in October 201 2019 using a Russian peat corer of barrel length 50 cm (Eijkelkamp Soil and Water, Giesbeek, 202 the Netherlands) to minimize compaction. Like other minerogenic marsh cores (e.g., Drexler et 203 al., 2009; Peteet et al., 2020), we did not observe sediment compaction upon examining the soil 204 cores. Standing water was not present at the time of sampling. Core samples were stored in 205 plastic split tubes, kept in the dark and refrigerated at 4 °C in the University of Toronto 206 Paleoecology Laboratory until sub-sectioning began. The CBC3-01 sediment core was subsampled at contiguous 2-cm intervals. Samples of 6.28 cm<sup>3</sup> from every subsection were dried 207 208 and weighed to constant mass for bulk density measurements.

209

# 2.3 Radiocarbon and <sup>210</sup>Pb dating

210

Radiocarbon dates were obtained from wood samples (*N*=9) and plant macrofossils (*N*=1;

Table 1). Samples were washed with reverse-osmosis water, dried at ~60 °C to constant mass,

and sent to the A.E. Lalonde AMS Laboratory (Ottawa, Ontario, Canada) for radiocarbon dating

213 via Accelerator Mass Spectrometry (AMS). An age-depth model was developed for CBC3-01 at

1-cm increments using the rbacon package (Bayesian age-depth modelling) in R (Version 3.6.3;
Goring et al., 2012) to infer rates of vertical accretion (hereafter rates of accretion) accounting
for both inorganic and organic sediments. Ages were calibrated using OxCal 4.4 (Bronk Ramsey,
2009) with the IntCal20 calibration curve (Reimer et al., 2020), and are expressed as calendar

218 years before present (hereafter cal. yr BP) in relation to 1950 AD.

Contiguous sediment samples were analyzed for lead-210 (<sup>210</sup>Pb) activities in more 219 220 recently deposited sediments. Dried material (~0.5 g) was allocated from each 2-cm subsection of the top 0–30 cm of CBC3-01 for supported <sup>210</sup>Pb activities (i.e., background levels) by 221 examining radium-226 (<sup>226</sup>Ra), and for unsupported <sup>210</sup>Pb activities by subtracting the supported 222 <sup>210</sup>Pb activities from the total <sup>210</sup>Pb activities. These samples were ground to fine powder using a 223 224 ball mill and sent to Flett Research Ltd. (Winnipeg, Manitoba, Canada) for analysis of <sup>210</sup>Pb activity. Total <sup>210</sup>Pb activity was measured via polonium-210 by alpha spectrometry and 225 supported <sup>210</sup>Pb activity (in secular equilibrium with Ra-226) was determined by radon-222 226 227 emanation.

#### 228 **2.4 Elemental analyses and programmed pyrolysis**

Dried material from every second 2-cm increment of CBC3-01 was ground to fine powder using
a ball mill for elemental analyses and programmed pyrolysis. The first allocation was analyzed
for total carbon and total nitrogen (TN; ~400 mg ground sample) using a LECO CHN628
elemental analyzer in the Radiochronology Laboratory at the Centre for Northern Studies at
Université Laval.

The second allocation was used for programmed pyrolysis (~70 mg ground sample) using HAWK TOC analyzer at the Geological Survey of Canada (Calgary, Alberta, Canada) to measure total organic carbon (TOC) content and inorganic carbon (in carbonates), and to

237 characterize organic matter type. Programmed pyrolysis was originally developed for petroleum 238 exploration (LaFargue et al., 1998; Behar et al., 2001), but has started to be applied to surficial 239 soils for characterizing organic matter, discerning lability and differentiating organic versus 240 inorganic carbon fractions (Carrie et al., 2012; Hare et al., 2014; Galloway et al., 2018; Kemp et 241 al., 2019). More specifically, programmed pyrolysis measures different organic matter fractions, 242 and their thermal stability and potential for decomposition, making it an ideal method to evaluate 243 the effects of organic carbon lability on recent- versus long-term rates of carbon burial in 244 freshwater marsh soils (Soucémarianadin et al., 2020; Kanari et al., 2022; Zhang et al., 2023). 245 Spectroscopic methodologies that characterize wetland soil organic matter such as Fourier-246 Transform Infrared Spectroscopy (FTIR) identify chemical bonds of organic carbon, but do not 247 directly quantify labile versus recalcitrant organic carbon, or inorganic carbon fractions. During 248 pyrolysis, soil samples were subjected to iso-temperature heat at 300 °C for three minutes to 249 determine the total free (labile) hydrocarbon released (S1 fraction). The temperature was 250 subsequently ramped up to 650 °C at 25 °C per minute to release, through thermal cracking, 251 thermal-stable hydrocarbons and the oxygen contained in pyrolizable kerogen (S2 fraction, mg 252 HC/g sediment, and S3 fraction, mg CO<sub>2</sub>/g sediment, respectively). Samples were then 253 automatically transferred to the oxidation oven and heated from 300 °C to 850 °C with the 254 heating rate of 20 °C per minute to measure the residual inert organic carbon (S4 fraction, mg 255 CO and CO<sub>2</sub>/g sediment and residual carbon, weight %) and the mineral (inorganic) carbon 256 fraction. Total organic carbon is quantified as the sum of the total quantity of organic matter 257 released during the pyrolysis and the oxidation steps. The hydrogen index (HI) is the ratio of S2 258 to TOC and is proportional to H/C, while the oxygen index (OI) is calculated by normalizing the 259 quantity of the pyrolizable  $CO_2$  (S3) to TOC and is proportional to the elemental O/C ratio of

organic matter (Lafargue et al., 1998; Behar et al., 2001). The thermal stability of organic matter
in the soil samples was examined by identifying the temperatures at which half of the pyrolizable
hydrocarbon (S1 and S2) was released during pyrolysis (hereafter T50 measurements; Gregorich
et al., 2015). Finally, ratios of 'generative' (S1, S2 and S3) and 'non-generative' (S4) organic
carbon in relation to TOC were calculated to estimate the proportions of pyrolizable versus
residual fractions of organic carbon down core in CBC3-01.

266 To verify our organic and inorganic carbon measurements from programmed pyrolysis, 267 we allocated a portion of unground material from every second 2-cm increment of CBC3-01 for 268 standard loss-on-ignition (LOI) analyses (see Supporting Information for more on methods and 269 for results). Furthermore, we allocated an additional ~150-200 mg of ground material from 13 270 increments from CBC3-01 to measure inorganic carbon using an SSM-5000A Solid Sample 271 Combustion Unit in a Shimadzu TOC-L Analyzer at the Analytical Laboratory for 272 Environmental Science Research and Training (ANALEST) at the University of Toronto (see 273 Appendix A for results). Carbon to nitrogen ratios have been used in lake and wetland 274 ecosystems to determine the extent to which aquatic (C/N < 10; attributed to algae and aquatic 275 plants that are enriched in lipids and proteins) and/or terrestrial (C/N > 20; attributed to terrestrial 276 and vascular plants that are enriched in lignin and cellulose) production contribute to organic 277 matter preserved in bulk sediments in paleoenvironments (Meyers & Teranes, 2001; Kim, 2003; 278 Khan et al., 2015). Given the significance of inorganic carbon in the sediments of CBC3-01, we 279 calculated C/N values using the ratio of TOC to TN (hereafter TOC/TN) fractions to examine 280 whether the organic matter was derived from aquatic versus terrestrial environments. 281 Organic, inorganic and total carbon densities were calculated for every 2-cm increment

using the bulk density measurements and were used in conjunction with rates of accretion to

- 283 calculate rates of carbon accumulation (e.g., Bao et al., 2011; Drexler, 2011; Jones et al., 2014;
- 284 Delaune et al., 2018). Soil core data from this manuscript is available at Loder et al. (2022).

**3 Results** 

#### **3.1 Chronology and rates of accretion**

The chronology of CBC3-01 was obtained from the unsupported <sup>210</sup>Pb profile (0–20 cm depth; 287 Figure 2(a)) and a model of <sup>14</sup>C dates (40–429 cm depth; Figure 2(b)). We developed the rbacon 288 289 model for CBC3-01 solely based on the radiocarbon dates and applied the model between 40 and 429 cm depth. In the top-of-core section, total<sup>210</sup>Pb activity decreases exponentially with depth 290 291 from 0 cm down to 20 cm in CBC3-01. In this same interval, dry bulk density measurements are <0.50 g cm<sup>-3</sup>, but rapidly increase below 20 cm to a high of 1.17 g cm<sup>-3</sup> at 33 cm and drop below 292 0.50 cm<sup>-3</sup> at 41 cm (Figure 3). Radium-226 measurements were 1.22 and 1.29 DPM/g at 6-8 cm 293 and 20–22 cm, respectively, both of which are lower than total <sup>210</sup>Pb activities between 0–22 cm 294 yet higher than the total <sup>210</sup>Pb activity at 22–24 cm. The total <sup>210</sup>Pb activities at 40–42 cm and 295 74-76 cm are not significantly different than the <sup>226</sup>Ra activities and indicate background 296 297 (supported) levels.

298 We infer that core CBC3-01 does not contain a continuous profile of 110+ years of accumulated sediments needed to build an accurate <sup>210</sup>Pb inventory, and that sediment 299 300 accumulation processes between 20-40 cm are uncertain and were likely affected by truncation and/or atypical imports of material older than 110 years. However, given the sufficiently linear 301 trend in unsupported <sup>210</sup>Pb activities between 0–20 cm, we can approximate sediments at 20 cm 302 depth to be less than 2 half-lives of <sup>210</sup>Pb (45 years). We use a constant rate of supply model 303 (calibrated against the linear regression model) to apply <sup>210</sup>Pb age modelling to the top 20 cm of 304 305 CBC3-01. We consider 0-20 cm as the datable, post-settlement section in CBC3-01 and leave

306 20–40 cm undated. Dates between 40–52 cm are extrapolated from the rbacon model and thus
307 should be interpreted with caution (Figure 2).

308 Basal sediments in CBC3-01 date to 5,710 cal. yr BP (Table 1) and correspond to 309 Nipissing I of Lake Erie associated with widespread wetland initiation and marsh establishment 310 in coastal zones of the lower Great Lakes (Finkelstein and Davis, 2006; Lewis et al., 2012). Rates of accretion in Central Big Creek Marsh ranged between 0.2–6.7 mm yr<sup>-1</sup> (Figure 3), 311 312 which are similar to rates in other local lacustrine-influenced marshes located on the shores of the lower Great Lakes including Cootes Paradise (1.0–7.1 mm yr<sup>-1</sup>; Finkelstein et al., 2005) and 313 Lower Big Creek Marsh (1.8 mm yr<sup>-1</sup>; Bunting et al., 1997; Figure 1). Between 5,710–4,640 cal. 314 yr BP rates of accretion at CBC3-01 were greater than 1.0 mm yr<sup>-1</sup> but subsequently dropped and 315 316 steadily declined down to 0.2 mm yr<sup>-1</sup> by 1,670 cal. yr BP. Rates of accretion sharply rose after 630 cal. yr BP and varied between 0.9 and 1.5 mm yr<sup>-1</sup> until ~80 cal. yr BP. These rates increased 317 several-fold in the most recent part of the record, with the highest values (up to  $6.7 \text{ mm yr}^{-1}$ ) 318 319 between 1983 and 2019 AD.

# 320 **3.2 Rates of carbon accumulation**

321 Organic carbon burial has been occurring at Central Big Creek Marsh since its formation 5,710 322 cal. yr BP with an average ( $\pm$  standard deviation) long-term rate of organic carbon accumulation 323 of 26  $\pm$  34 g C m<sup>-2</sup> yr<sup>-1</sup>. Rates of inorganic carbon accumulation were notably high following 324 initiation, but declined after 4,970 cal. year BP.

High rates of organic carbon accumulation were sustained during the Nipissing highstands (Figure 3). During Nipissing I, rates of organic carbon accumulation in Central Big Creek Marsh reached 37 g C m<sup>-2</sup> yr<sup>-1</sup> and declined following the highstand. At the time of Nipissing II, a short-term peak in organic carbon burial (65 g C m<sup>-2</sup> yr<sup>-1</sup>) occurred around 4,680

cal. yr BP, which coincided with the approximate time of initiation of marshes in adjacent coastal areas of Lake Erie (e.g., Finkelstein & Davis, 2006). Following Nipissing II, rates of organic carbon accumulation dropped and remained  $<10 \text{ g C m}^{-2} \text{ yr}^{-1}$  between 4,160 cal. yr BP and 630 cal. yr BP.

Rates of organic, inorganic, and total carbon accumulation increased around 630 cal. yr BP and remained elevated until present day. However, rates of organic carbon accumulation were high and variable between 1983–2019 AD and coincided with maximum rates of sediment accretion. During this 36-year period (0–20 cm depth), rates of total carbon accumulation were between 225 and 359 g C m<sup>-2</sup> yr<sup>-1</sup>, which comprised both organic and inorganic fractions of carbon; these rates are 1–2 orders of magnitude higher than any recorded during the Holocene in this record (Figure 3).

#### 340 3.3 TOC/TN ratios

341 Between 5,710–4,930 cal. yr BP, TOC/TN ratios varied between 15 and 24, except for an

342 increase to 34 at 5,000 cal. yr BP during the lowstand after Nipissing I (Figure 3). These are the

343 highest TOC/TN values in the CBC3-01 paleorecord and are driven by low TN contents. Since

this lowstand and through the Late Holocene, TOC/TN ratios have fluctuated between 6 and 16.

345 Values of TOC/TN in CBC3-01 are predominantly <10 in sediments deposited over the past 400

cal. yr BP.

#### 347 **3.4 Thermal stability of carbon fractions**

348 The S1, S2 and S3 values derived from programmed pyrolysis and TOC content follow

- each other closely in CBC3-01 (see Figure S6 in Supporting Information). Samples are
- 350 predominantly comprised of S2 thermal-stable hydrocarbons (range of 0.13–37.07 mg HC/g soil;
- 351 mean [ $\pm$  standard deviation] equal to  $6.73 \pm 7.64$  mg HC/g soil), with smaller proportions of S3

pyrolizable organic matter (range of  $0.51-18.88 \text{ mg CO}_2/\text{g soil}$ ; mean equal to  $3.95 \pm 3.87 \text{ mg}$ CO<sub>2</sub>/g soil) and more minor proportions of S1 labile hydrocarbons (range of 0.02-5.46 mg HC/gsoil; mean equal to  $0.79 \pm 1.13 \text{ mg HC/g soil}$ ).

Temperature measurements of T50 generally increase down core in CBC3-01 (Figure 4). Between 5,710–5,150 cal. yr BP, T50 values ranged from 405°C (at the basal sediments) to 435°C. However, T50 values subsequently became highly variable, with temperatures as low as 368°C (at 325 cm) and 395°C (at 281 cm), until 2,300 cal. yr BP. The rapid decline in T50 values at 281 cm and subsequent up-core variability matches the variability in S1 values (Figure S6). Overall, T50 values were generally lowest (between 399–424°C) in sediments deposited over the past 630 cal. yr BP.

362 Hydrogen and oxygen indices range between 36-369 mg HC/g TOC and 99-193 mg 363  $CO_2/g$  TOC, respectively, in CBC3-01 (Figure 4). Between 5,710–4,900 cal. yr BP (below 300 364 cm depth), HI values were typically low (<150 mg HC/g TOC) while OI indices ranged between 365 125–165 mg CO<sub>2</sub>/g TOC. Between 4,900–2,270 cal. yr BP, OI values were generally lower than 366 in the Middle Holocene soils, while HI values were generally higher through the Late Holocene 367 (top 200 cm of CBC3-01). Hydrogen indices gradually increased between 2,280–630 cal. yr BP 368 and thus decrease with depth between 100–150 cm. Since 630 cal. yr BP, both HI and OI values 369 were elevated. Recently-deposited sediments in the top 100 cm of CBC3-01 comprise some of 370 the highest HI and OI values up to 369 and 193, respectively, except for disturbed samples 371 between 20–40 cm which have the lowest HI values. 372

Proportions of residual versus pyrolizable organic carbon vary down core in CBC3-01
but are predominated by the residual fraction (between 57–89 %; Figure 4). Following marsh
initiation and during Nipissing I, the residual fraction of organic carbon was predominantly >80

375 %, but began to decline (while the pyrolizable fraction simultaneously increased) during

376 Nipissing II and reached a minimum of 68 %. Proportions of pyrolizable organic carbon have

377 generally been higher (up to 43 %) since 630 cal yr BP, with lower values in the undated

378 sediments between ~80 cal. yr BP and 1983 AD.

379 4 Discussion

## 380 4.1 Composition and origins of carbon stocks

381 Carbon stocks in whole-profile soils of freshwater marshes are rarely considered in soil carbon 382 inventories to date due to a lack of data. In this study, we demonstrate that non-tidal freshwater 383 marshes bury carbon at high rates on decadal, centennial and millennial scales. These marshes 384 have potential to stabilize several meters of carbon in their soils over thousands of years when 385 connected to a large network of freshwater ecosystems (e.g., the Great Lakes) and when situated 386 on a riverine floodplain where deposition rates are high. Furthermore, we show that while long-387 term rates of carbon accumulation were elevated during major water level rises in Lake Erie, 388 recent rates of carbon accumulation are several-fold higher than long-term rates calculated 389 through the Middle and Late Holocene.

390 Organic carbon stores in Central Big Creek Marsh are predominantly comprised of a 391 'residual' or inert fraction which is resistant to pyrolysis. When transported through the 392 sedimentary environment, the residual fraction is often coupled with or bound to the mineral 393 fraction in fluvial sediments, and consequently is physically stable and protected from further 394 biological degradation (Mudd et al., 2009; Van de Broek et al., 2018; Repasch et al., 2021). 395 Because the residual fraction is deposited in downstream lowlands (Repasch et al., 2021) and is 396 suited for preservation over hundreds to thousands of years, we deduce that this fraction has a 397 strong, positive influence on long-term rates of organic carbon accumulation in riverine-

398 influenced freshwater marshes. The proportion of pyrolizable organic carbon relative to the 399 residual fraction of organic carbon decreases with depth throughout the core, suggesting that 400 organic carbon deposits in surface sediments are less thermally stable than deeper deposits due to 401 organic matter breakdown via microbial processes. We therefore conclude that recent 402 accumulations of organic carbon in freshwater marshes are susceptible to and undergo biological 403 degradation, and that a more resistant fraction remains with increasing depth. This corroborates 404 the relationships observed between increased thermal stability and the loss of labile organic 405 matter in other environments (e.g., arable versus fallow agricultural fields, surface versus buried 406 organic matter in Arctic hummocks; Gillespie et al., 2014; Gregorich et al., 2015). Even in the 407 absence of human impacts, short-term rates are very likely to be elevated relative to longer-term 408 rates.

409 Our analysis shows that labile organic carbon stores are not only present in recent 410 deposits, but also in distinct layers at depth in freshwater marsh soils. During the Middle to Late 411 Holocene transition, layers of organic carbon with low thermal stabilities were buried 412 intermittently among more stable layers of organic carbon in deeper soils, notably at 325 cm 413 (5,000 cal. yr BP), 281 cm (4,710 cal. yr BP) and 249 cm (4,320 cal. yr BP) depths (Figure 4). 414 The latter two depths are also characterized by high levels of the most thermolabile fraction of 415 organic carbon (S1 and S2), demonstrating that pockets of undecomposed and highly labile 416 material are preserved in the marsh profile. Deeper soils, thus, cannot be discounted in carbon 417 inventories of freshwater marshes given their potential to comprise significant organic carbon 418 stocks that can readily degrade if disturbed (i.e., drained) and exposed to oxygen.

Ratios of TOC/TN measured in bulk sediments can be used to differentiate those that
 contain predominantly aquatic- versus terrestrially-derived organic matter because aquatic

421 organic matter comprises N-rich proteins and H-rich lipids, and terrestrial organisms typically 422 contain cellulose-rich structural tissue (Meyers & Teranes, 2001; Khan et al., 2015). Using 423 TOC/TN values, we found that recently-deposited sediments comprise a significant proportion of 424 labile organic matter with low TOC/TN values which was likely produced by aquatic organisms 425 (Meyers and Teranes, 2001; Carrie et al., 2012; Khan et al., 2015). This result may additionally 426 reflect added nutrient influxes due to intensive agricultural activity in the watershed and/or the 427 presence of invasive Phalaris arundinacea in Central Big Creek Marsh. Nevertheless, organic 428 matter characterizations through the paleorecord suggest that Central Big Creek Marsh 429 accumulated higher proportions of organic matter derived from aquatic sources throughout the 430 Late Holocene. Conversely, organic matter stores from the Middle Holocene differ in 431 composition and show comparatively higher TOC/TN values. This organic matter was likely 432 derived primarily from terrestrial sources (Figure 4). Terrestrial organic matter comprises 433 predominantly lignin and cellulose which are more resistant to decomposition than lipids and 434 proteins in autochthonous organic matter (Reddy & Delaune, 2008; Carrie et al., 2012). 435 Therefore, these organic fractions that were deposited in Central Big Creek Marsh during the 436 Middle Holocene may have good potential for long-term preservation in undisturbed marsh 437 environments, and require consideration when discerning differences in rates of organic carbon 438 accumulation throughout the paleorecord.

Most studies rely only on quantifications of organic carbon or find that the inorganic carbon fraction is negligible in marsh soil samples (Loder & Finkelstein, 2020). In our study, we found that both organic and inorganic fractions of carbon drive elevated rates of total carbon accumulation in this freshwater marsh. The Big Creek watershed is underlain by glacial sediments from the Wentworth and Port Stanley tills (Figure 1), which are rich in carbonates

444 (mean contents of 36 % and 37.0 %, respectively). These tills are further underlain by limestone 445 associated with the Dundee Formation (Barnett, 1993; Lewis et al., 2012). Through erosional 446 processes and/or water infiltration, these deposits are the major source of carbonates in the Big 447 Creek watershed and contribute to elevated carbonate burial in Central Big Creek Marsh. Coastal 448 ecosystems have recently been recognized for their potential to enhance carbon sequestration 449 because local calcification processes and resultant carbon dioxide (CO<sub>2</sub>) outputs are minimal, 450 and marine-derived carbonates may be accrued from local lithogenic sources and modern coral 451 reefs and undergo dissolution in coastal ecosystems (requiring the removal of CO<sub>2</sub>; Martin, 2017; 452 Saderne et al., 2019). More research is required to determine whether carbonate burial could 453 enhance carbon sequestration in freshwater marshes through similar processes that have been 454 identified in marine-influenced wetlands.

#### 455 **4.2 Implications of hydroclimatic events on carbon burial in wetlands**

456 We found three major shifts in organic carbon composition and burial in the CBC3-01 457 paleorecord which coincided with past hydroclimatic events. The first occurred during the 458 lowstand following Nipissing I (Figure 3) and is characterized by a marked increase in labile 459 organic carbon and more terrestrially-derived organic carbon. Central Big Creek Marsh is 460 situated 2 m above lake level at present day; based on glacial isostatic adjustment, the core top of 461 CBC3-01 would have been about 0.5–1 m above lake level during the Middle Holocene (Lewis 462 et al., 2012; Lewis et al., 2021). We conclude that the rise in Lake Erie water levels by several 463 meters during Nipissing I caused inundation and elevated the water table at the CBC3-01 site, 464 and ultimately triggered the formation of marshland. The lowering of lake water levels following 465 Nipissing I likely reduced inundation and decreased water table levels, and may have resulted in

466 a decline in aquatic primary productivity which was compensated by an apparent increase in467 terrestrial production and inputs at Central Big Creek Marsh.

468 The second shift occurred at the time of Nipissing II (4,680 cal. yr BP; 277 cm depth), 469 and is characterized by a marked increase in degradable organic carbon and rates of organic 470 carbon accumulation. In this case, we conclude that the highstand of Nipissing II again caused 471 inundation and increased the water table level at Central Big Creek Marsh. Coupled with warmer 472 temperatures during the Middle Holocene in southern Ontario (Yu et al., 1996), these conditions 473 would have stimulated aquatic primary productivity and organic carbon production. We also 474 speculate that Central Big Creek Marsh served as a depositional environment during Nipissing II 475 for rapid influxes of minerogenic sediments upon erosion and flooding from the Big Creek River 476 channel. These minerogenic influxes can help bury and preserve in situ organic carbon by 477 advecting organic matter to deeper sediment layers by rapid rates of accretion, and by reducing 478 the time of exposure to diagenesis at the surface (Mudd et al., 2009; Van de Broek et al., 2016; 479 Van de Broek et al., 2018; Kemp et al., 2019; Spivak et al., 2019).

480 Lastly, there was a prolonged period between 4,200–630 cal. yr BP (100–240 cm depth) 481 during which rates of organic carbon accumulation were reduced and less variable. The decline 482 in rates of accretion after Nipissing II coincided with the drop in water levels in Lake Erie 483 (Lewis et al., 2012). In tidal marshes, the long-term accumulation of organic carbon in soils is 484 controlled by sediment supply and is not solely related to local biomass production (Mudd et al., 485 2009; Van de Broek et al., 2016; Van de Broek et al., 2018). Thus, we speculate that water levels 486 were lower and hydrological inputs reduced in Central Big Creek Marsh during this prolonged 487 period, and that these conditions lead to higher rates of decomposition, and lower rates of 488 organic carbon production and burial. In contrast, the Nipissing highstands in Lake Erie would

have enhanced bank erosion of marsh creeks and increased the sediment supply into Central Big
Creek Marsh, thereby increasing the potential for burial and preservation of organic carbon (Yu
et al., 2017; Van de Broek et al., 2018; Spivak et al., 2019; Repasch et al., 2021).

492 Like organic carbon, rates of inorganic carbon burial in Central Big Creek Marsh were 493 also likely influenced by hydro-fluvial changes associated with the Nipissing highstands. Higher 494 rates of inorganic carbon accumulation in the bottom 1-m of CBC3-01 are likely attributed to 495 conditions during the Middle Holocene when temperatures were warmer and carbonate 496 concentrations were higher in Lake Erie waters (Lewis et al., 2012). Upon the highstand of 497 Nipissing I and formation of Central Big Creek Marsh, carbonate-rich waters likely inundated 498 and precipitated in situ at CBC3-01 when water residence times were long enough. During 499 Nipissing II, water that inundated Central Big Creek Marsh from Big Creek may have comprised 500 fewer carbonates because the waters in the Lake Erie basin at that time had been transferred from 501 the upper Great Lakes and more northern latitudes, were cooler in temperature and were diluted 502 (Lewis et al., 2012). Alternatively, or in combination with the former, Lake Erie water and its 503 carbonate supply may have been restricted at the mouth of the Big Creek river channel upon 504 formation of the Long Point sand spit (Barnett et al., 1985), thereby reducing carbonate burial.

#### 505 **4.3 Recent versus long-term rates of carbon accumulation**

Recent rates of organic and total carbon accumulation are high while long-term rates are generally slower in CBC3-01. Both recent and long-term rates can be comparable to rates in salt marshes and peatlands. This demonstrates that riverine-influenced freshwater marshes with high rates of vertical accretion and biomass production provide an important means for carbon storage. Although we largely attribute the marked difference between recent and long-term rates of organic carbon accumulation in Central Big Creek Marsh to losses of labile fractions over the

512 long-term, we suspect that other factors are contributing to this difference and require further513 investigation.

514 Hydroclimatic conditions associated with the Little Ice Age may have promoted higher 515 rates of organic carbon accumulation. Around 630 cal. yr BP (100 cm depth), there was a notable 516 increase in rates of accretion and carbon accumulation at Central Big Creek Marsh. Peat 517 accumulation began around 650 cal. yr BP at Lower Big Creek Marsh (Bunting et al., 1997) and 518 a cluster of short paleorecords from four separate sloughs have basal ages of approximately 700 519 cal. yr BP at the Rondeau Marshes (Finkelstein & Davis, 2006; Figure 1). All these events are 520 attributed to higher water levels in eastern Lake Erie during the Little Ice Age when conditions 521 were wetter in the eastern Great Lakes region of southern Ontario (Pengelly et al., 1997; 522 Finkelstein & Davis, 2006), and collectively may have elevated water levels, rates of accretion 523 and organic carbon accumulation in Central Big Creek Marsh.

524 In the more recent record, high and variable rates of accretion, and organic, inorganic and 525 total carbon accumulation over the past 36 years collectively suggest that major landscape 526 alterations affected rates of accretion and carbon accumulation. Even when accounting for 527 different dating methods and errors covering different timespans, rates of alluvium accretion 528 (associated with erosion) across North America are shown to have increased 10-fold post-529 European settlement due major landscape alterations and clearance for agriculture (Kemp et al., 530 2020). Because subsoils comprised of carbonates are increasingly exposed and eroded from 531 landscapes that have experienced intensive farming, carbonate availability and deposition in 532 proximate watersheds has been used as an indicator for tillage erosion (Papiernik et al., 2002; 533 Zamanian et al., 2020). We suspect that elevated recent rates of accretion and inorganic carbon accumulation in Central Big Creek Marsh have resulted from increases in erosion and soil loss in 534

535 parts of the Big Creek watershed where intensive agricultural activity has taken place. Further 536 research is required to discern the extent to which elevated recent rates of organic carbon 537 accumulation are driven by the accumulation of labile fractions versus anthropogenic pressures 538 in temperate wetlands.

Although differences in the timespan of measurements (e.g., <sup>210</sup>Pb versus <sup>14</sup>C dating 539 540 techniques) have potential to cause discrepancies between short- versus long-term rates of 541 accretion (Kemp et al., 2020), our geochemical analyses on core CBC-01 demonstrate 542 continuous accretion through the dated sections of the paleorecord and elevated recent rates of 543 accretion when dating errors are considered (as per Binford et al., 1990). Applying rates of mass 544 accumulation instead of accretion when calculating rates of carbon accumulation can further 545 increase the accuracy in rate measurements (Arias-Ortiz et al., 2018), and thus requires 546 consideration in future research alongside the limitations in dating techniques when comparing 547 short- versus long-term rates of carbon accumulation in freshwater marshes.

548 **5** Conclusion

549 Non-tidal freshwater marshes have potential to bury and store considerable amounts of organic 550 and inorganic carbon. We demonstrate that elevated rates of organic carbon accumulation in 551 temperate freshwater marshes are episodic, yet can be as high as recent rates in salt marshes and 552 as high as those in peatlands in the long-term when high rates of vertical accretion and local 553 biomass production are sustained. These rates fluctuate in relation to major hydroclimatic events 554 that caused water levels in the lower Great Lakes to fluctuate through the Holocene. 555 Furthermore, they are vulnerable to anthropogenic-induced activities (e.g., land use, the presence 556 of invasive species, nutrient loading) in the temperate region, which have potential to affect 557 recent rates of organic carbon burial.

558 We show that organic carbon fractions in surface marsh soils are predominantly labile 559 and will be subjected to decay in the ensuing centuries and millennia, thereby lowering long-560 term rates of organic carbon accumulation. Our finding that recent rates of organic carbon 561 accumulation are attenuated over hundreds to thousands of years due to long-term decay 562 corroborates findings in the coastal (tidal) wetland and peatland literature, and concerns that the 563 extrapolation of recent rates over centuries and millennia leads to erroneous assumptions in 564 wetland carbon budgets (Mudd et al., 2009; Bridgham et al., 2014; Young et al., 2019). Because 565 of long-term decay and the various contents and properties of carbon fractions throughout the 566 marsh paleorecord, it is critical to consider the entire profile and all carbon fractions when 567 quantifying the climate mitigation potential of freshwater marsh soils and their role as a natural 568 climate solution. Otherwise, high recent rates of organic carbon accumulation in freshwater 569 marsh soils may provide a false sense of success in mediating the climate crisis if applied as 570 carbon offsets over longer time scales.

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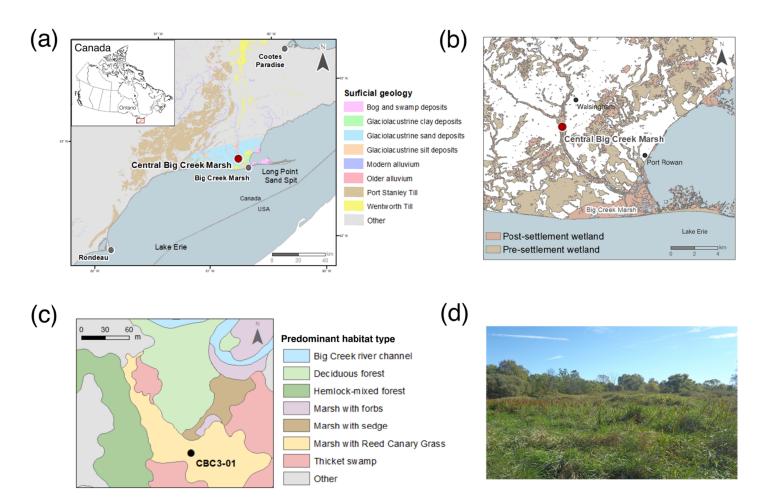
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- 848 **Figures and tables**
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## 850

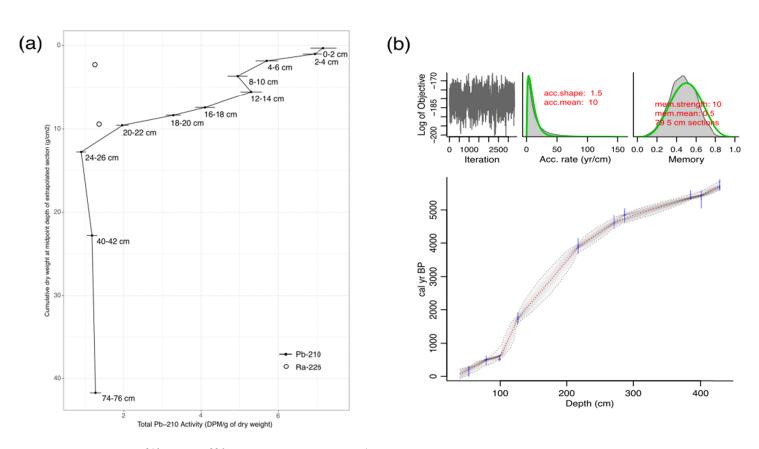
851 Figure 1. Maps and photos of Central Big Creek Marsh where core CBC3-01 was retrieved in southern Ontario, 852 Canada. Central Big Creek Marsh is situated on the traditional lands of the Attawandaron, Haudenosaunee and 853 the Anishinaabe First Nations, and within the Treaty lands ('Between the Lakes Purchase') of the Mississaugas of the Credit. a) Location of Central Big Creek Marsh relative to Ontario, Canada, and other local freshwater 854 855 marshes (Rondeau, Big Creek Marsh and Cootes Paradise). Surficial geology is shown for the Big Creek watershed and other areas of Norfolk County as mapped in the Quaternary Geology of Ontario dataset (Ontario 856 Ministry of Northern Development, Mines, Natural Resources and Forestry, 2012). b) Location of Central Big 857 858 Creek Marsh within the Big Creek watershed. Both pre-European settlement wetlands (i.e., wetland that has been drained and altered since European settlement in the region) and post-European settlement wetlands (i.e., 859 wetland that remains intact at present day) are shown from Byun et al. (2018). All present-day wetlands are 860 861 considered to have also been wetlands during the pre-settlement period. c) Predominant habitat types as identified and mapped by the Nature Conservancy of Canada in 2010 within the Central Big Creek Marsh, and 862 location where CBC3-01 was extracted. d) Ground-level image of Central Big Creek Marsh. 863 864

865 Table 1. AMS radiocarbon dates from sediment core CBC3-01, collected from Central Big

866 Creek Marsh in Southern Ontario, Canada. Dates were calibrated using OxCal 4.4 with the

867	IntCal20 calibration curve (Bronk Ramsey, 2009; Reimer et al., 2020). Raw radiocarbon dates
868	can be used to generate age-depth model with 95% confidence intervals in rbacon (Figure 2(b)).

Depth (cm)	Material dated	<sup>14</sup> C age (yr BP)	Calibrated age 2σ (yr BP)	Median age (yr BP)	Lab number
52–54	Wood	145 ± 26	281–170 (40 %) 154–126 (10 %) 120–56 (27 %) 47 (19 %)	140	UOC-12338
78–80	Wood	463 ± 26	537-491 (95 %)	510	UOC-15387
98–100	Wood	506 ± 25	549-506 (95 %)	530	UOC-14899
126–128	Wood	1,844 ± 26	1,826–1,704 (95 %)	1,750	UOC-12339
216–218	Wood	3,603 ± 26	3,976–3,844 (95 %)	3,910	UOC-12340
270–272	Wood	4,140 ± 25	4,823–4,745 (31 %) 4,734–4,572 (65 %) 4,538–4,535 (<1 %)	4,690	UOC-12341
286–288	Wood	4,301 ± 27	4,960–4,929 (9 %) 4,912–4,899 (2 %) 4,887–4,830 (85 %)	4,860	UOC-12342
384–386	Twig	4,692 ± 23	5,477–5,435 (25 %) 5,422–5,321 (70 %)	5,380	UOC-12343
400–402	Plant macrofossil	4,634 ± 26	5,462–5,375(74 %) 5,358–5,346 (3 %) 5,333–5,308 (19 %)	5,410	UOC-13435
426–429	Wood pieces	4,991 ± 27	5,884–5,825 (14 %) 5,754–5,650 (73 %) 5,631–5,604 (8 %)	5,710	UOC-13436



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Figure 2. (a) Total <sup>210</sup>Pb and <sup>226</sup>Ra activities (DPM g<sup>-1</sup> of dry weight) plotted against the cumulative dry weight at the midpoint depth for several extrapolated sections (g cm<sup>-2</sup>) from CBC3-01. Error bars represent +/- one standard deviation. Errors for <sup>226</sup>Ra activities are

 $^{872}$  solution several extrapolated sections (g cm<sup>-</sup>) non energy of the bars represent  $^{172}$  one standard deviation. Energy of the act act  $^{873}$  <0.08 DPM g<sup>-1</sup> and not visible at the scale of the plot. Sediments deposited between 0–20 cm depth are dated using <sup>210</sup>Pb age

874 modelling. (b) Bayesian age-depth model developed for 40–429 cm of CBC3-01 using <sup>14</sup>C dates in rbacon. Confidence intervals

875 (95%) are shown in the grey shading. Sediments deposited between 20–40 cm are undated.

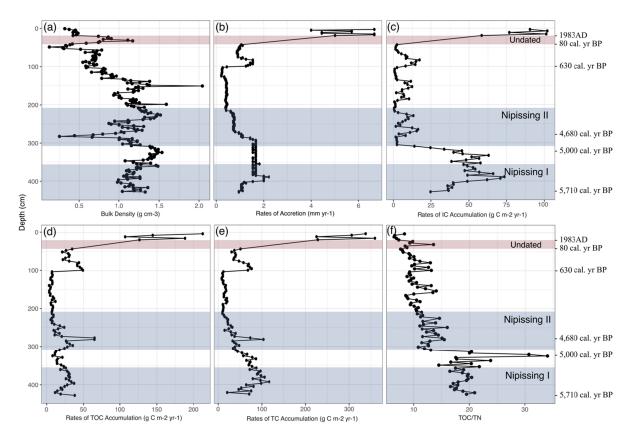
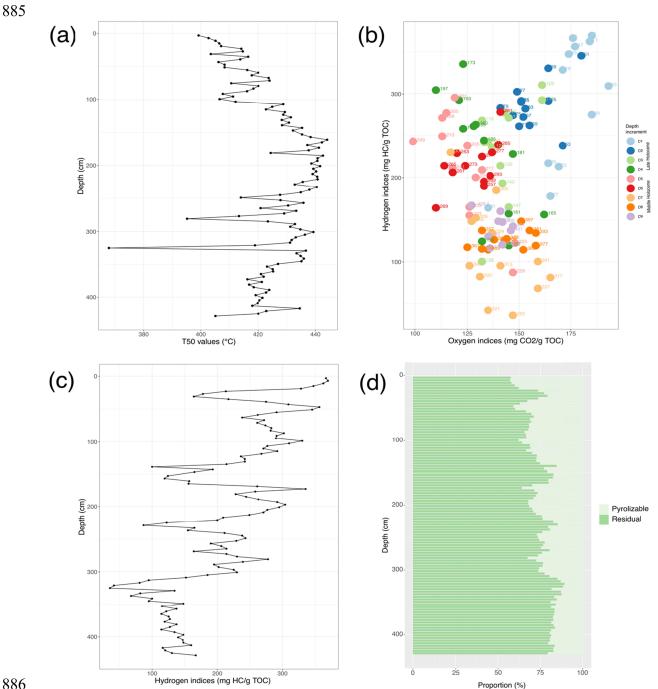


Figure 3. Bulk density (a), rates of accretion (b), rates of inorganic carbon (IC) accumulation (via programmed pyrolysis; c), rates of total organic carbon (TOC) accumulation (via programmed pyrolysis; (d)), rates of total carbon (TC) accumulation (via CHN elemental analyses with precision range of 0.5% for TC content; (e)) and TOC/TN ratios (via programmed pyrolysis for TOC and CHN elemental analyses for TN; (f)). Red boxes highlight undated sediments that are disturbed, and blue boxes highlight sediments deposited during Nipissing I and II. Mean calibrated ages derived from the age-depth model (Figure 2(b)) for key transitions are shown on the right-hand margin in the geochemical proxies plotted here. Radiocarbon dates are provided in Table 1.



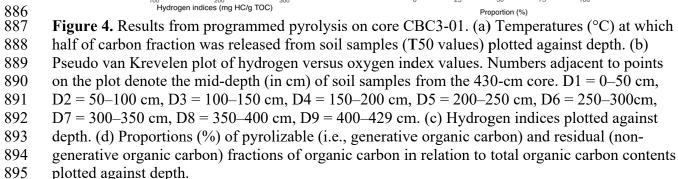
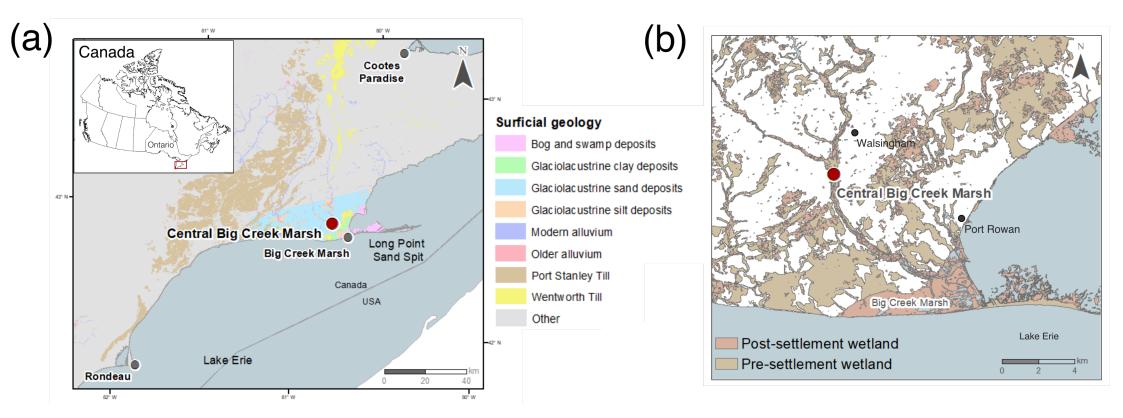
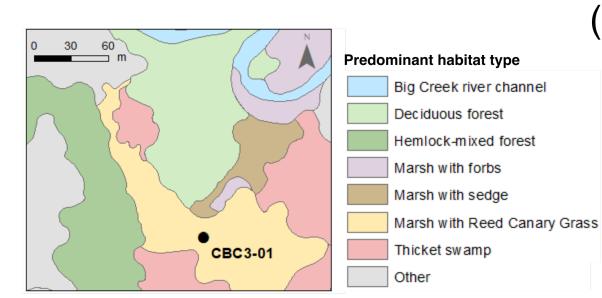


Figure 1.



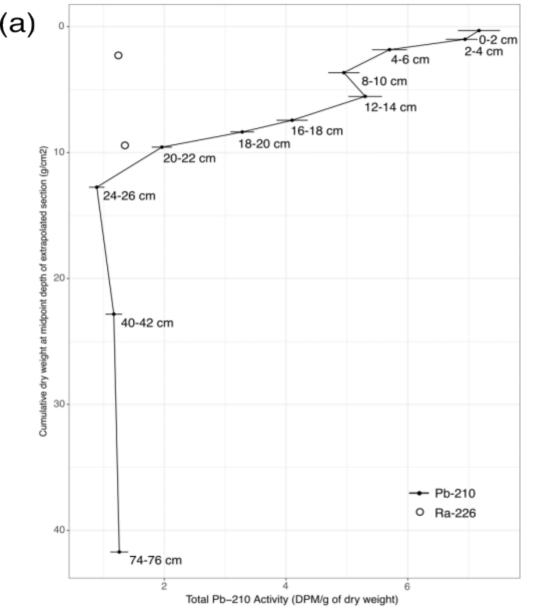


(C)

## (d)



Figure 2.



(b)

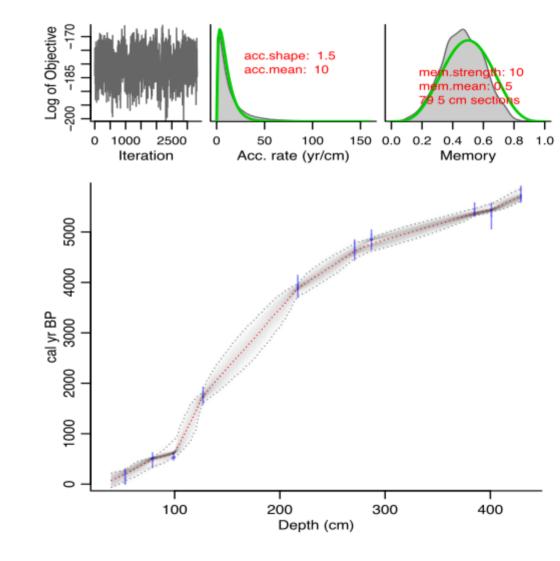


Figure 3.

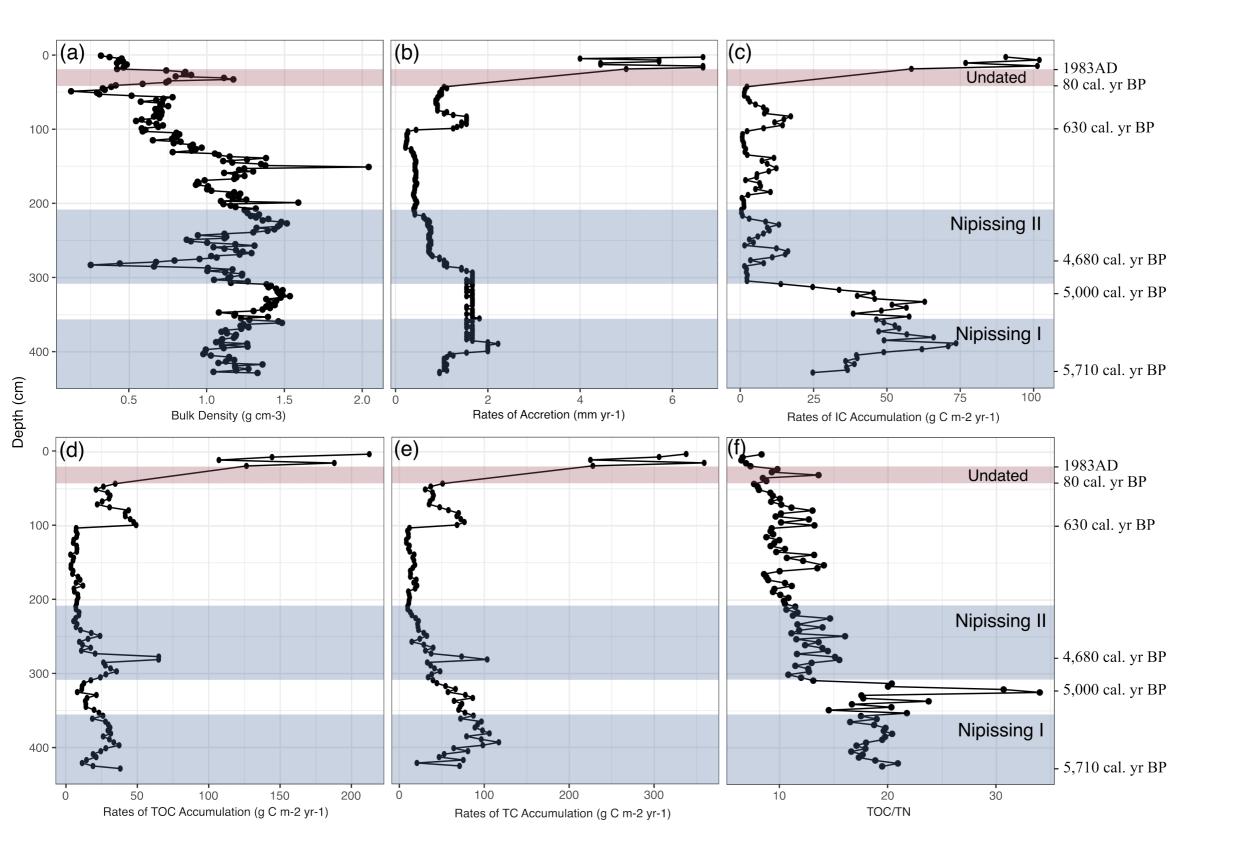


Figure 4.

