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1	Spatial differentiation of sediment organic matter isotopic composition and inferred
2	sources in a temperate forest lake catchment
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13	Keywords: stable isotopes; radiocarbon; lake sediment; soil carbon; freshwater carbon
14	cycling; Bayesian mixing model
15	
16	Highlights:
17	• Catchment-scale comparison of soil and sediment organic matter isotopic
18	measurements
19	• Evidence for substantial spatial variation in sediment organic matter isotopic
20	composition and origin
21	• Plant-derived organic matter is preferentially deposited in littoral lake sediments
22	• Soil microbial organic matter may be preferentially exported from the lake
23	catchment

• Lake sediment carbon isotopic composition varies markedly as a function of water depth

26

25

27 Abstract:

28 Freshwater sediments are important carbon reservoirs, but the extent to which different 29 components of soil or aquatic organic matter (OM) are deposited in these sediments is not 30 well defined. Bulk sediment carbon (δ^{13} C) and nitrogen (δ^{15} N) stable isotope ratios, as 31 well as radiocarbon, are valuable tracers for sediment OM sources, but there are few 32 studies comparing the isotopic composition of soil and sediment OM at the catchment 33 scale. We analyzed spatial variation in δ^{13} C, δ^{15} N, ¹⁴C, and C:N ratios in OM from soils, 34 stream and lake sediments, and aquatic plants and algae, in a temperate forest lake 35 catchment in southern Quebec, and used a Bayesian model to estimate source mixtures 36 for sediment OM. Sediments at the stream mouths entering the lake were characterized by high C:N ratios, high fraction modern carbon (Fm), and low δ^{13} C, indicating 37 38 preferential deposition of plant-derived OM. In contrast, sediments sampled further 39 upstream during a period of low streamflow indicated a larger proportion of microbial 40 OM based on low C:N ratios and high δ^{15} N. In lake sediments we observed zonation of 41 OM isotopic composition by water depth. Shallow sediments (0-1 m water depth) were 42 characterized by high amounts of plant-derived OM, while intermediate-depth sediments 43 (1-3 m) were characterized by high δ^{13} C, indicating an increased input of OM from aquatic plants. Deep lake sediments (> 4 m) were characterized by low δ^{13} C and Fm 44 45 values, which likely reflect greater input of phytoplankton OM. Stream sediments 46 downstream of the lake exhibited high δ^{15} N and low Fm values, implying a greater input

47	of aged microbial biomass from soils. Our results indicate catchment-scale spatial
48	differentiation in the source of OM in sediments, with zones of preferential deposition of
49	terrestrial plant, aquatic plant, phytoplankton, and soil microbial biomass.
50	
51	1. Introduction
52	Freshwater sediments are a globally important carbon reservoir that remains
53	uncertain in terms of its overall size, the source of the carbon it stores, and its sensitivity
54	to climatic and environmental change (Dean and Gorham, 1998; Mendonça et al., 2017;
55	Anderson et al., 2020). A recent study estimated that approximately 0.15 Pg of organic
56	carbon (OC) is buried in freshwater sediments annually (Mendonça et al., 2017).
57	However, this estimate is uncertain, as is the global distribution of freshwater sediment
58	OC reservoirs. Gaining a clearer understanding of this carbon reservoir, in terms of both
59	the source and amount of OC buried, is important for resolving terrestrial carbon budgets,
60	as well as to better understand the influence of human activities on aquatic carbon sinks
61	and greenhouse gas (GHG) emissions (Bastviken et al., 2011; Mendonça et al., 2017;
62	Anderson et al., 2020). Soil erosion is also considered to be an important global carbon
63	sink, and much of the carbon in eroded soils is likely redistributed to aquatic sediments
64	(Berhe et al., 2007; Wang et al., 2017; Tan et al., 2020). However, the contribution of soil
65	organic matter (OM) to freshwater sediments remains loosely defined, especially in terms
66	of empirical studies at the scale of ecosystems or catchments.
67	Identifying terrestrial carbon contributions to freshwater and marine sediments
68	using elemental, isotopic, and molecular methods have long been a focus of sedimentary

aquatic geochemistry (Hedges and Mann, 1979; Meyers, 1994; Hedges et al., 1997;

70 Hopmans et al., 2004). However, recent studies have highlighted the biogeochemical 71 complexity of soil organic matter, especially in terms of microbial processing of plant-72 derived organic matter and accumulation of microbial necromass (Marín-Spiotta et al., 73 2014; Lehmann and Kleber, 2015), suggesting that typical methods of estimating 74 terrigenous carbon inputs to lake sediments based on plant OM geochemical signatures 75 may underestimate inputs of soil organic matter. In addition, most geochemical studies of 76 lake sediments are carried out at a single point, typically the lake depocenter. Data on 77 spatial heterogeneity in sediment OM isotopic composition and inferred sources within 78 lakes or other water bodies is limited (Murase and Sakamoto, 2000; Bovee and Pearson, 79 2014; Taylor et al., 2015; Thompson et al., 2018), but could prove important in 80 understanding sediment OC budgets. In particular, littoral lake sediments are infrequently 81 studied, but are thought to contribute much more strongly to lacustrine greenhouse gas 82 (GHG) emissions relative to hypolimnetic sediments (den Heyer and Kalff, 1998; 83 DelSontro et al., 2016; Thottathil and Prairie, 2021). Relatedly, the question of how the 84 burial or respiration of OM in lakes effect the source and composition of OM transported 85 further downstream in fluvial networks has not been thoroughly examined (Goodman et 86 al., 2011).

Estimates of terrigenous carbon input to sediments also do not typically differentiate between different components of soil organic matter, including leaf litter, OM-rich topsoils, and mineral subsoils. These distinctions could be important for understanding the fate of soil carbon, and the relative contribution of plant versus microbial biomass to sediment carbon reservoirs. Subsoil carbon reservoirs typically have bulk ¹⁴C ages of thousands of years (Trumbore, 2000; Mathieu et al., 2015; van der Voort

93	et al., 2019; Shi et al., 2020; Gies et al., 2021). While there is clear evidence from
94	molecular biomarkers that some old soil carbon is exported to freshwater sediments
95	(Douglas et al., 2014; Eglinton et al., 2021; Freimuth et al., 2021), the extent to which
96	these millennial carbon reservoirs contribute to bulk sediment reservoirs remains unclear.
97	It is also widely observed that there is typically a trend of enrichment of OM 13 C and 15 N
98	with soil depth (Natelhoffer and Fry, 1988; Ehleringer et al., 2000; Billings and Richter,
99	2006; Craine et al., 2015; De Clercq et al., 2015). This pattern, combined with decreasing
100	¹⁴ C content in deeper soils, indicates the potential to distinguish the export of OM from
101	different soil components using multiple isotopic tracers (McCorkle et al., 2016; Menges
102	et al., 2020). Furthermore, OM derived from aquatic primary producers is often
103	characterized by distinctive $\delta^{13}C$ values relative to terrigenous organic matter, albeit with
104	widely varying signatures depending on inorganic carbon sources and concentration,
105	carbon fixation pathways, variation in inorganic carbon δ^{13} C, and the effects of diffusive
106	isotopic fractionation (France, 1995; Vuorio et al., 2006; De Kluijver et al., 2014; Yang
107	et al., 2014; Lammers et al., 2017). The development of Bayesian isotope mixing models
108	offers the potential to develop more quantitative estimates of sediment source
109	apportionment, and its uncertainty, on the basis of multiple isotopic parameters (Blake et
110	al., 2018; Menges et al., 2020).
111	Bulk lake sediment isotopic composition, along with the concentration and
112	isotopic composition of different lipid biomarkers, are also important proxies of
113	environmental change applied in lake sediment core studies in paleolimnology and
114	paleoclimatology (Meyers and Ishiwatari, 1993; Meyers, 1997; Talbot, 2002; Eglinton

and Eglinton, 2008; Blaga et al., 2010; Holtvoeth et al., 2019). Gaining a more detailed

116 understanding of the variables controlling these measurements, and of the sources of 117 organic matter to lake sediments, is important to improving the application of these 118 proxies (Hodell and Schelske, 1998; Lehmann et al., 2002; Torres et al., 2012). 119 Paleolimnological studies do not frequently take spatial variation in sediment OM 120 sources into account, but this could be an important consideration for accurate proxy 121 interpretation (Murase and Sakamoto, 2000; Bovee and Pearson, 2014; Taylor et al., 122 2015). 123 To investigate catchment-scale spatial variability in sediment isotopic 124 composition, and its potential to resolve OM sources, including distinct soil OM 125 reservoirs, we collected samples of soils, stream and lake sediments, and aquatic plants, 126 algae, and tree foliage, from the catchment of Lake Hertel in Southern Quebec, the site of 127 McGill University's Gault Nature Reserve (Fig. 1). Lake Hertel is a relatively 128 uncomplicated study site in that it has a small catchment with minimal human 129 disturbance, as well as homogenous vegetation and bedrock geology. Furthermore, as a 130 university field station, it has been intensively studied in terms of both terrestrial and 131 aquatic biogeochemistry (den Heyer and Kalff, 1998; Gelinas et al., 2000; Muller et al., 132 2003; Arii et al., 2005; Wironen and Moore, 2006). We analyzed the total carbon, and 133 total nitrogen content and isotopic composition ($\delta^{13}C, \delta^{15}N$) of these samples. In

134 selected soil and sediment samples we also measured ¹⁴C, expressed as fraction modern

135 carbon (Fm). Finally, we analyzed a small set of water samples for measurements of

- 136 dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and particulate
- 137 organic matter (POM) δ^{13} C values, as well as POM C:N ratios. We then used a Bayesian
- 138 mixing model (MIXSIAR) to estimate the relative contribution of different components

139	of soil, as well as aquatic primary producers where relevant, to stream and lake sediment
140	OM (Stock et al., 2018; Menges et al., 2020). Our analysis of these data focus on three
141	related questions: 1) do stream and lake sediment OM isotopic compositions and inferred
142	sources vary spatially within the catchment?; 2) is there a significant contribution of aged
143	subsoil carbon to stream and lake sediment OM?; and 3) is there a significant difference
144	in stream sediment isotopic composition and inferred sources upstream and downstream
145	of the lake?
146	
147	2. Materials and Methods
148	2.1 Study area
149	The Lake Hertel catchment is located at the center of Mont St. Hilaire (MSH), which is in
150	southern Quebec (45°32'N, 73°80'W), 32 km east of Montreal (Fig. 1). MSH is part of

151 the Monteregian Hills, which are a group of plutons created from the Great Meteor

152 hotspot track and exposed at the surface due to uplift and erosion (Heaman and

153 Kjarsgaard, 2000). Its maximum elevation is approximately 400 meters above the

154 surrounding St. Lawrence Lowlands (Fig. 1). MSH contains the largest remnant of

155 primeval forest in the St. Lawrence Lowlands (Arii et al., 2005; Wironen and Moore,

156 2006). MSH was designate UNESCO Nature Conservation Reserve in 1978 and is

157 currently managed both as a nature reserve and a scientific field station by McGill

158 University.

159 MSH consists of Early Cretaceous igneous intrusive rocks ranging from gabbro to 160 syenite (Webber and Jellema, 1965). The igneous bedrock has been subject to Pleistocene 161 glacial erosion resulting in a thin layer of glacial till, relatively immature soils, and a



Figure 1: A) Digital elevation model of the Gault Nature Reserve showing the
extent of the Lake Hertel Catchment, streams, sampling locations, and lake
bathymetry (1 m contour intervals. B) inset map showing location of Gault Nature
Reserve (red square) in southern Quebec relative to Montreal (yellow circle).

168 depression at the center of the mountain that forms Lake Hertel (Webber and Jellema, 169 1965; Gelinas et al., 2000; Wironen and Moore, 2006). The soils are characterized as 170 sandy loam Brunisols with a thin B horizon, and soil pH ranges from 3.0 to 5.2 (Wironen 171 and Moore, 2006). There are no detailed studies of soil erosion mechanisms at MSH, and 172 we assume that most soil erosion occurs through surface runoff. Lake Hertel is a 173 mesotrophic lake spanning approximately 0.33 square kilometers in area, at 173 meters in 174 elevation, and has a mean water depth of 4.7 m, and a maximum water depth of 8 meters 175 (den Heyer and Kalff, 1998; Muller et al., 2003) A dam was installed at the outlet of Lake 176 Hertel in 1942, which raised the water level by about 3 meters (Gelinas et al., 2000;

177 Muller et al., 2003). Two primary streams feed into the lake, one flowing from the west

and one from the north, with a lake outlet to the south (Fig. 1). The forest cover of MSH

179 is primarily composed of sugar maple (*Acer saccharum*) and American beech (*Fagus*

180 grandifolia) (Arii et al., 2005). MSH is characterized by a humid continental climate with

181 a mean annual temperature of 6.5 °C and mean annual precipitation of 1100 mm, of

182 which 180 mm falls as snow (Environment and Climate Change Canada, 2021).

183 Photographs of representative samplings sites, including soils, stream sediments, and lake

184 sediments, are provided in Supplemental File 1.

185 **2.2 Sampling methods**

186 **2.2.1 Soil sampling**

187 We sampled 7 soil sites, encompassing both the west and north stream catchments 188 (Fig. 1, Supplemental Table 1), at a range of elevations from 190 to 275 meters. All soil 189 samples were collected in June 2017. Soil sampling was designed to characterize overall 190 soil horizon OM composition across the catchment, as opposed to differences between 191 soil sites. Sample points were selected in relatively flat surfaces, and we avoided areas 192 with fallen trees, boulders and outcrops, and tree roots. At each soil site, we sampled leaf 193 litter by collecting 10 leaves, from a circular area of 10 cm diameter. The depth of the 194 litter layer was approximately 2 cm. We only sampled leaf fragments but did not assess 195 the decomposition stage of the sampled litter. We then sampled the upper 10 cm of 196 topsoils, again from a circular area with a 10 cm diameter, corresponding to the O and A 197 horizons, using a trowel. Subsoils, corresponding to the B and C horizons, were collected 198 at multiple depths with a closed-bucket hand auger, beginning at the base of the A 199 horizon. Intervals of 10-20 cm were collected with the auger and were then homogenized

in the field. The augur was cleaned with water and fully dried with Kimwipes between
sampling each depth interval. Representative foliage samples from beech and maple trees
were collected at site 7. All samples were stored in polypropylene WhirlPak bags, kept in
a cooler until transported to the lab, and then were stored at 4 °C prior to drying.

204

2.2.2. Streambed and wetland sediment sampling

205 Streambed sediments collected were collected at 14 sites along the western and 206 northern streams feeding Lake Hertel (Fig. 1), spanning a range of linear distances from 207 the stream mouths from 0 to 1375 m (Supplemental Table 1; Fig.1.). Hereafter we refer to 208 these samples as upstream sediments. Distances were measured in Google Earth 209 following the path of the streams. Three of the streambed samples collected in 2017 were 210 within a shallow beaver pond located near the mouth of the north stream. This beaver 211 pond was abandoned by the beavers in 2018 and subsequently drained. Samples were 212 collected at the inflow of the stream into the pond, in the center of the pond, and at its 213 outflow. We also collected five streambed sediment samples from the outlet stream 214 draining Lake Hertel, at a range of distances from the lake outlet spanning 65 to 700 215 meters (Supplemental Table 1; Fig. 1). Hereafter we refer to these samples as 216 downstream sediments.

We sampled streambed sediments behind log dams or other areas with relatively slow water flow to capture zones of sediment accumulation. Surficial streambed sediments were collected at each site with a trowel, up to a maximum depth of 5 cm. 11 of the streambed samples were collected in June 2017, under relatively high flow conditions, whereas 8 samples were collected in August 2018 under relatively low flow conditions. These hydrological conditions reflected slightly greater precipitation and

substantially cooler mean temperatures in the four weeks prior to sampling in June 2017
(83 mm; 13.3 °C) relative to August 2018 (71 mm; 22.9 °C) (Environment and Climate

225 Change Canada, 2021)

Two samples of surface sediments were also collected at a small wetland located on a branch of the west stream in June 2017 (Fig. 1.). The first sample was retrieved from a shallow vernal pond and the second was exposed mud sampled at the wetland surface. All sediment samples were stored in polypropylene WhirlPak bags, kept in a cooler until transported to the lab, and were stored at 4 °C prior to drying.

231 2.2.3. Lake sediment, algae, and macrophyte sampling

232 Lake sediments were collected from 15 locations spanning a range of water 233 depths (0.2 to 7.3 meters) and distances from the nearest stream mouth (20 to 350 meters, 234 measured in Google Earth) (Supplemental Table 1; Fig. 1). Surface sediments were 235 collected using an Ekman dredge from a pontoon boat. The dredge sampled the mud-236 water interface. Samples from approximately the uppermost 15 cm of sediments were 237 composited and homogenized. Water depth was measured manually with a weighted line 238 at each sampling site. 13 samples were collected in June 2017 and 2 samples were 239 collected in August 2018.

Eight samples of macrophytes and macroalgae were collected opportunistically during sampling campaigns in June 2017 and August 2018, including floating algae and plants and benthic plants collected by the sediment dredge (Supplemental Tables 1 and 2). We also sampled periphyton attached to a floating dock. All samples were stored in polypropylene WhirlPak bags, kept in a cooler until transported to the lab, and then were stored at 4 °C prior to drying.

246 **2.2.4 Dissolved and particulate carbon sampling**

247 We collected water samples for dissolved inorganic carbon (DIC), dissolved organic 248 carbon (DOC), and particulate organic matter (POM) analyses from three stream locations, 249 one each from the north stream, west stream, and outlet stream (Supplemental Table 1). 250 We also collected two samples from the lake. All water samples were collected in August 251 2018. For one sample from the lake the filter was not retained and there are no POM 252 measurements. We collected the water in 1 L acid rinsed Nalgene bottles. In the streams 253 the bottles were filled at 10 cm water depth, and in the lake the bottles were filled at 254 approximately 30 cm water depth. We filtered the water with a 0.7 µm pre-baked glass fiber filter and transferred it to three 40 mL pre-baked borosilicate amber vials with extra 255 septa for DOC and DIC concentration and δ^{13} C analyses. We freeze-dried the filters and 256 257 kept them frozen until analysis. All filtered water samples were stored in the dark at 4 °C, 258 with no fixing agent added, and were analyzed within 10 days of collection (St-Jean, 2003). 259 We did not pre-weigh the filters, and therefore do not estimate the concentration of POM.

260

2.3. Sample preparation and analysis

261 **2.3.1 Solid sample preparation**

Sediments and soil samples were homogenized by mixing in beakers with glass rods. Leaf litter and foliage samples were cut into a 1 cm-by-1 cm square using cleaned scissors. Homogenized samples and leaves were then placed in beakers and dried in a 40 ° C Lindberg Blue drying oven for 48 hours. Once dried, the sediments and soils were sieved at 2.36 mm. Pebbles, wood, leaf fragments, and root particles were separated and archived. Sieved subsamples were ground into a fine powder by a mortar and pestle, and stored in pre-combusted glass vials. Leaf litter and leaves were crushed by a spatula, ground into a
powder by a mortar and pestle, and stored in pre-combusted glass vials.

270

2.3.2. Solid sample elemental analyses

271 For elemental analyses (Supplemental Table 2), sample aliquots were weighed with 272 a microbalance, placed into tin capsules, and total carbon (TC) and total nitrogen (TN) was 273 measured using a Vario MicroCube Elemental Analyzer at the Geotop Stable Isotope 274 Laboratory at the Université du Québec à Montréal. POM samples were prepared by 275 cutting a portion of the filter. Analytical uncertainty was $\pm .07\%$ for TC and $\pm .01\%$ for TN. 276 Prior to the TC and TN measurements, three representative samples, including one soil, 277 one streambed sediment, and one lake sediment, were fumigated with 12% HCl for 24 278 hours in silver capsules, repackaged in tin capsules and measured for total organic carbon 279 (TOC). These TOC measurements were compared with TC measurements of the same 280 samples in order to determine if significant amounts or inorganic carbon were present. For 281 all three samples the difference in weight percent C was less than 0.25%, which is less than 282 the typical estimate of TC sample heterogeneity (see below). Furthermore, for the two 283 sediment samples %TOC was slightly greater than %TC, implying undetectable amounts 284 of inorganic carbon. Based on these results, combined with the absence of carbonate in 285 catchment bedrock and the low pH of catchment soils (Wironen and Moore, 2006), we 286 concluded that TC measurements are an accurate representation of TOC in our samples.

Nine samples in total, including one leaf litter sample, two soils, three streambed sediments, one lake sediment, one wetland sediment and one algal sample, were analyzed in triplicate to assess compositional heterogeneity (Supplemental Table 3). For TN the pooled standard deviation was $\pm 0.02\%$, and the maximum standard deviation was $\pm 0.08\%$,

291 for a leaf litter sample. For TC the pooled standard deviation was $\pm 0.7\%$, and the maximum 292 standard deviation was $\pm 3\%$, again for a leaf litter sample. The pooled standard deviation 293 for C:N ratio was ± 0.5 , and the maximum standard deviation was ± 3.2 for a streambed 294 sample with low TN.

295

2.3.3 Solid sample stable isotope analyses

296 For stable isotope analyses (Supplemental Table 2) sample aliquots were weighed 297 and placed in tin cups, with weights determined to obtain the same amount of CO_2 and N_2 for all samples and reference materials. δ^{13} C and δ^{15} N were measured simultaneously for 298 299 samples with C:N ratios <14, and separately samples with C:N >14. The samples were 300 analyzed with a Micromass Isoprime 100 Isotope Ratio Mass Spectrometer coupled to an 301 Elementar Vario MicroCube Elemental Analyser in continuous flow mode at the Geotop Stable Isotope Laboratory. Results are expressed as δ^{13} C values in % vs. VPDB and as 302 δ^{15} N in ‰ vs. AIR (Coplen, 2011). For δ^{13} C measurements two internal reference materials 303 304 $(\delta^{13}C = -28.73\%)$ and -11.85%) were used to normalize the results on the NBS19-LSVEC scale, and a third reference material ($\delta^{13}C=-17.04\%$) was analyzed as an unknown. For 305 306 δ^{15} N two internal reference materials (δ^{15} N=-0.10‰ and +14.95‰) were used to normalize the results on the AIR scale, and a 3^{rd} reference material ($\delta^{15}N=-0.1\%$) was analyzed as an 307 unknown. The overall analytical uncertainty (1 σ) is better than ±0.1‰ for δ^{13} C and better 308 309 than $\pm 0.2\%$ for δ^{15} N.

310 To assess sample heterogeneity in stable isotope values we analyzed the same 311 sample replicates as discussed for elemental analyses above (Supplemental Table 3). For one soil sample we did not measure replicate δ^{13} C, and for one streambed sample we only 312 measured δ^{13} C in duplicate. For δ^{13} C the pooled standard deviation was $\pm 0.16\%$ for all 313

replicate samples, and the maximum standard deviation was $\pm 0.44\%$ for a leaf litter sample. For δ^{15} N the pooled standard deviation was $\pm 0.33\%$, and the maximum standard deviation was $\pm 1.17\%$ for a subsoil sample.

317

2.3.4 Radiocarbon analyses

318 24 soil and sediment samples were prepared and analyzed for ¹⁴C content 319 (Supplemental Table 4) at the A.E. Lalonde AMS Laboratory (Crann et al., 2017). Samples 320 were acid washed in HCl (1 N, 80 °C, 30 min) to remove any inorganic carbon. The samples 321 were weighed in tin cups, combusted to CO₂ using a Thermo Flash 1112 elemental analyzer 322 (EA), and the CO₂ was cryogenically separated in a breakseal. Blank tin capsules were 323 combusted between each sample to monitor the blank and to ensure no memory effect. The 324 breakseals, containing grains of silver cobaltous, were baked at 200°C to remove sulfur 325 and halogens. The CO₂ in the breakseals was reduced to graphite in the presence of Fe-H. 326 The ¹⁴C content of the resulting graphite was analyzed on a 3MV tandem accelerator mass 327 spectrometer (AMS), and the results were background corrected. Fraction modern carbon (Fm) was calculated as the ratio of the sample ${}^{14}C/{}^{12}C$ to the standard ${}^{14}C/{}^{12}C$ ratio (Reimer 328 329 et al. 2004). Both ¹⁴C/¹²C ratios are background-corrected and the result is corrected for 330 spectrometer and preparation fractionation using the AMS measured ${}^{13}C/{}^{12}C$ ratio and is 331 normalized to δ^{13} C. Typical analytical uncertainties for Fm values are 0.003. Radiocarbon 332 ages are calculated for samples with pre-modern FM values as -8033*ln(Fm) (Reimer et 333 al. 2004). Samples for radiocarbon analyses were treated with HCl, whereas samples for 334 stable isotope and elemental analyses were not, and there may be some loss of labile carbon 335 that specifically influences the radiocarbon data (Bao et al., 2019). However, this should not affect the comparison of radiocarbon data between samples, since the sample matrix

337 for all radiocarbon measurements was similar.

338 **2.3.5** Dissolved organic and inorganic carbon analyses

- 339 The concentration and δ^{13} C of DOC and DIC (Supplemental Table 2) in the water
- 340 samples were measured in the Ján Veizer Stable Isotope Laboratory (University of
- 341 Ottawa, Canada) (St-Jean, 2003; Lalonde et al., 2014). The samples in the 40 mL amber
- 342 vials and two standard solutions (KHP and sucrose) were loaded into a carousel. Then, an
- 343 aliquot was injected into a reaction chamber and acidified with 5% H₃PO₄. The released

344 gas was carried using ultra-pure helium. Water was removed and the CO₂ (DIC)

345 concentration in the gas measured by a non-destructive infrared detector (NDIR).

346 Subsequently, the δ^{13} C-CO₂ (DIC) was measured using a ThermoFinnigan DeltaPlus XP

347 isotope ratio mass spectrometer (IRMS). After the inorganic carbon was removed, a

- 348 persulfate reagent was added to the aliquot to oxidize the organic carbon (DOC) to CO₂,
- 349 which was measured for concentration and δ^{13} C as described above. The 2σ analytical

350 precision is 0.5 ppm for the concentration, and ± 0.2 ‰ for δ^{13} C.

351 2.4 Bayesian mixing model of sediment OM sources

352 We used the Bayesian modeling software MixSIAR (Stock et al., 2018),

353 implemented as an open-source R package, to derive probabilistic estimates of the

354 proportional contributions of different OM sources to specific sediment samples. The

355 basis of the MixSIAR model framework is a mixing model in which the tracer value of

the mixture is the sum of the mean value of the tracer in the source multiplied by the

357 proportional contribution to the mixture (p) as in equation 1:

$$358 Y_j = \sum_k p_k \mu_{jk}^s (1)$$

359 where the mixture tracer value, Y_{i} , for each of the j tracers is equal to the sum of the k source tracer means, μ_{ik}^{s} , multiplied by their proportional contribution to the mixture, p_{k} 360 361 (Stock et al. 2018; Stock and Semmens, 2016). The model assumes that all source 362 isotopic values are known and quantified, the isotopic tracers are conserved through the 363 mixing process, tracer values are fixed, and that the sum of the proportional contributions 364 (p) is 1. MixSIAR is a Bayesian formulation of traditional isotopic mixing models that 365 establishes a formal likelihood framework for estimating source contributions, while 366 incorporating error structures using the summary statistics of the source isotopic values, 367 namely the mean, variance, and sample size (Stock et al., 2018). MixSIAR accounts for 368 co-variation between source isotopic values by incorporating covariance matrices into the 369 model equations (Stock et al. 2018; Stock and Semmens, 2016). A discrimination factor 370 can be applied in MixSIAR in situations where a metabolic isotopic fractionation is well 371 constrained, as in dietary studies, but appropriate discrimination factors in sedimentary 372 mixing studies are not well defined (Menges et al., 2020). An example of the R code 373 used in this study, specifically for lake sediment samples, is provided in Supplemental 374 File 2.

375 We specifically estimated mixing proportions for 16 sediment samples, including 376 7 lake sediment samples and 9 streambed sediment samples, for which we have δ^{13} C, 377 δ^{15} N, and Fm measurements. We did not apply C:N ratios in MixSIAR because this 378 tracer does not mix linearly. For upstream sediments we included three sources: leaf 379 litter, topsoil, and subsoil. For lake sediments and downstream sediments, we included 380 two additional sources, macrophytes/macroalgae and phytoplankton. MixSIAR provides 381 probability distributions for source mixtures and is not inherently limited by the number

of sources relative to the number of isotopes or other tracers, or the number of sample
measurements (Stock et al., 2018; Menges et al., 2020). However, results where the
number of sources is greater than n+1 the number of tracers, as for our lake sediment and
downstream sediment samples, should be interpreted with greater caution (Stock et al.
2018; Stock and Semmens, 2016).

387 For all sources except phytoplankton, δ^{13} C and δ^{15} N signatures were estimated 388 using the mean and standard deviation (1σ) of sample measurements for those source 389 categories (Table 1). Stable isotope measurements of phytoplankton are time-intensive 390 and challenging, and we did not attempt to sample phytoplankton for this study. We 391 instead applied the mean and standard deviation of a set of paired δ^{13} C and δ^{15} N 392 measurements from lakes in temperate forests in the northern United States and Finland 393 as a best estimate (Vuorio et al., 2006; Yang et al., 2014). For Fm signatures in subsoils 394 and topsoils we applied the mean and standard deviation of sample measurements (Table 395 1). For Fm signatures in leaf litter we applied the approximate northern hemisphere 396 atmospheric values for the past decade (1.05 ± 0.05) from Turnbull et al. (2017). This is 397 supported by measurements in other temperate forests from North America, which show 398 a small difference (~0.02) between atmospheric and leaf litter Fm (Gaudinski et al., 399 2000). We did not measure the Fm of DIC in Lake Hertel, and we apply the range 400 observed other nearby Quebec lakes (1.002 ± 0.05) as the Fm signature for 401 macrophytes/macroalgae and phytoplankton (McCallister and Del Giorgio, 2008). This 402 overlaps with current atmospheric values, and therefore accounts for direct fixation of 403 atmospheric CO2 by some aquatic primary producers, while also accounting for the 404 possible incorporation of some fraction of pre-bomb DIC.

Source	δ^{15} N	σ	$\delta^{13}C$	σ	Fm	σ
Litter	-4.9 ^a	1.9	-28.5 ^a	0.5	1.05 ^b	0.04
Topsoil	1.3 ^a	2.8	-26.9 ^a	0.8	1.02 ^a	0.04
Subsoil	5.8 ^a	2.6	-25.8 ^a	0.4	0.87 ^a	0.07
Macrophyte/						
Macroalgae	1.0 ^a	2.4	-18.0 ^a	4.0	1.002 ^c	0.05
Phytoplankton	3.6 ^d	2.8	-27.6 ^d	4.8	1.002 ^c	0.05

405 Table 1: OM signatures and uncertainties for MixSIAR model

406 407 408

^aBased on mean±1σ standard deviation of data measured in this study (Supplementary Table 2)

^bBased on approximate value of northern hemisphere atmospheric CO₂ for the past decade (Turnbull et al., 2017) ^oBased on measurements of DIC in southern Quebec lakes (McCallister and Del Giorgio, 2008)

4ŎЎ 410 ^dBased on measurements of phytoplankton in North American and Finnish lakes (Vuorio et al., 2006; Yang et al., 2014) 411 We used an uninformed prior, as has been applied in previous applications of

412 MixSIAR to sediment OM (Menges et al., 2020), since we do not have independent

413 constraints on the contribution of these sources. Using an uninformative prior may bias

414 the model results towards a relatively uniform distribution of sources (Stock et al., 2018).

415 As we modeled source contributions to single sediment samples the model was run with

416 process error, but no residual error (Stock et al., 2018; Menges et al., 2020). Model

417 convergence was estimated using the Gelman Rubin (Gelman et al., 2003) diagnostic test

418 for Monte Carlo Markov Chain (MCMC) model convergence. Convergence was reached

419 after the "very long" (for streambed sediments) or "extreme" (for lake sediments)

420 MixSIAR model run with a burn-in of 250,000 or 1,500,000, a chain length of 1,000,000

421 or 3,000,000 and 3 chains.

422 There are several key caveats associated with the application of MixSIAR in this

423 study, which we briefly summarize here. First, we do not account for diagenetic alteration

424 in sediments, which is more likely to effect lake sediments than stream sediments

425 (McCorkle et al., 2016; Menges et al., 2020; Lehmann et al., 2002; Gälman et al., 2009).

426 The isotopic effects of lake sediment diagenesis are difficult to predict, especially for

427	δ^{15} N, and can vary both in sign and magnitude as a function of redox chemistry and the
428	availability of different electron acceptors (Lehmann et al., 2002; Gälman et al., 2009).
429	Therefore, we have not attempted to incorporate diagenetic effects into the model, but we
430	discuss this source of error in section 4.3. Second, we do not explicitly account for
431	enrichment of ¹⁵ N or ¹³ C in heterotrophic biomass, which could be a significant source of
432	OM to lake sediments (Elser et al., 1995). Since $\delta^{15}N$ enrichment is likely to be more
433	pronounced in heterotrophic biomass we include uncertainty in the MixSIAR $\delta^{15}N$
434	discrimination factor of ± 1 %. Third, we do not account for possible primary production
435	within stream environments, because the small surface area of the streams and the
436	generally high flow rates (James and Roulet, 2009), suggest that accumulation of
437	autochthonous OM in these streams is minor relative to inputs from soil OM. Fourth, we
438	do not account for molecular differentiation of bulk source material, particularly topsoils
439	and subsoils, during OM export, transport, and deposition (Tiessen et al., 1984;
440	Gaudinski et al., 2000; Schmidt and Gleixner, 2005; Van der Voort et al., 2017). Our
441	estimates of isotopic variability in bulk soil OM (Table 1) likely encompass much of the
442	variation between soil fractions, but enrichment of certain soil OM fractions in sediments
443	could bias our inferences when compared with bulk soil OM isotopic source
444	compositions.

3. Results

3.1. Total carbon and dissolved carbon measurements

447 Total carbon (TC), which we infer to represent organic carbon (see section
448 2.3.2), varied by two orders of magnitude across all soil and sediment samples, from 48.6
449 to 0.3 % (Figs. 2A, 3A). Within soil profiles there was a consistent decrease in TC with



Figure 2: Depth profiles of TC (A); TN (B); C:N (C); δ^{13} C (D); δ^{15} N (E) and Fm (F) for the seven soil sampling sites, alongside measured values in foliage from Site 7. Litter values are plotted at a depth of 0 cm, and topsoil samples at a depth of 10 cm. Dashed line in F indicates the division between pre-bomb and post-bomb carbon. Analytical uncertainties are smaller than points for all data.



Figure 3: Sediment TC (A); TN (B); C:N (C); δ^{13} C (D); δ^{15} N (E) and Fm (F) as a 457 458 function of distance from the stream mouths entering Lake Hertel. Positive 459 (negative) distances indicate distance downstream (upstream) of the stream 460 mouths. Values for source OM categories (mean±1_o standard deviation) are 461 plotted as bars. DOC (filled squares) and POM (filled diamonds) measurements 462 are color-coded following the legend for the sediment samples. Black dots 463 indicate samples collected in August 2018. Analytical uncertainties are smaller 464 than points for all data.

465	depth from litter (45.2 \pm 3.2%; mean \pm 1 σ standard deviation), to topsoils (15.5 \pm 9.2%), to
466	subsoils (1.6±1.1%) (Fig. 2A). TC in upstream sediments ranged from 0.32 to 8.1%, with
467	notably higher values at the stream mouths (Fig. 3A). Downstream sediment samples
468	demonstrated a similar range (0.4 to 9%), with the highest value in the sample nearest to
469	the lake outlet. Lake sediment samples were consistently higher in TC than stream
470	sediments (13.7±3%) (Figs. 3A, 4A). There was not a clear relationship between TC and
471	either lake water depth or distance from the streams. Dissolved organic carbon
472	concentrations were highest in the lake (2.9 to 4.3 ppm), intermediate downstream of the
473	lake (2.5 ppm), and lowest upstream of the lake (1.1 to 1.4 ppm).
474	3.2 Total nitrogen measurements
475	TN also spanned two orders of magnitude across all samples, from 4.6 to 0.04
476	weight % (Figs. 2B,3B). There was a similar range in leaf litter ($1.0\pm0.1\%$) and topsoil
477	(0.95±0.4%), reflecting very large variability in the nitrogen content of topsoil (Fig. 2B).
478	Subsoils were uniformly lower in TN than topsoils and litter (0.1 \pm 0.06%). TN in
479	upstream sediments ranged from 0.03 to 0.44%, with markedly higher values at the
480	stream mouth, similar to TC (Fig. 3B). Similarly, downstream sediment TN, which
481	ranged from 0.04 to 0.73, was highest nearest to the lake outflow. Similar to TC, TN was
482	higher in lake sediments (1.4 \pm 0.4%) than almost all stream sediments (Fig. 3B). TN
483	increased in lake sediments with water depth, especially between 0.2 to 3 meters (Fig.
484	4B).
485	3.3 C:N ratios
486	C:N ranged from 74.5 to 8.2 across all samples (Figs. 2C, 3C). The highest values

487 were found in leaf litter (57.4±8.6), and the lowest values in macroalgae (minimum 10.3),



488

Figure 4: Lake sediment TC (A); TN (B); C:N (C); δ^{13} C (D); δ^{15} N (E) and Fm (F) as a function of water depth. DOC (squares) and POM (diamonds) measurements are plotted by the depth of the water column at the point of sampling. The dashed black line indicates the depth of the hypolimnion. Analytical uncertainties are smaller than points for all data.

494 lake sediments (minimum 9.9), and lacustrine POM (8.2). C:N was markedly higher in 495 leaf litter relative to topsoils (19.7 ± 2.2) and subsoils (20.4 ± 3.5) (Fig. 2C). C:N ratios in 496 upstream sediments (19.7 \pm 4.7) were highest at the stream mouths (Fig. 3C). Downstream 497 sediments exhibited highly variable C:N (16±5.6), without a clear spatial pattern. C:N in 498 lake sediments (13.1 ± 3.4) were uniformly lower than stream sediments, with the 499 exception of the two samples closest to the stream mouths (Figs. 3C). C:N decreased with 500 water depth in lake sediments, with the largest decrease between 0-1 m (Fig. 4C). Stream 501 POM C:N was within the range of streambed sediments (14.9 ± 3.6) (Fig. 3C), while lake 502 POM C:N (8.2) was lower than observed in the lake sediments.

503 3.4. δ^{13} C measurements

504 δ^{13} C values varied from -31.5‰ (foliage) to -13.6‰ (benthic macrophyte) (Figs 505 2D, 3D). δ^{13} C values increased with depth in soils, with the lowest values in litter (-506 $28.5\pm0.5\%$), intermediate values in topsoil (-26.9±0.75), and highest values in subsoil (-25.8±0.4‰) (Fig. 2D). δ^{13} C in upstream sediments (-27.7±0.8‰) exhibited the lowest 507 508 values at the stream mouths (Fig. 3D). Downstream sediment δ^{13} C was more variable (-509 26.4±2.2), with one notably high outlier (-22.8‰), but with no clear relationship with distance downstream. Lake sediment δ^{13} C (-27.2±2.0‰) varied widely and non-linearly 510 511 with water depth, with values increasing up to 3 meters water depth, and then decreasing 512 to 7 meters (Fig. 4D). Macrophytes and macroalgae spanned a wide range of relatively 513 high δ^{13} C values (-18±4‰). POM δ^{13} C was lowest in the upstream waters (-30±0.2‰), 514 highest in the lake waters (-25.6‰), and intermediate in the downstream waters (-515 29.4‰). δ^{13} C of DOC was consistently higher than POC but followed a similar pattern,

with relatively low values in upstream waters (-27.1±0.4‰), and higher values in lake
waters (-25.1±0.4‰) and downstream waters (-25‰).

518 **3.5.** δ^{15} N measurements

519 δ^{15} N values varied from -8.8‰ to +9.1‰, with the lowest values in fresh leaves 520 and leaf litter, and the highest values in subsoils. $\delta^{15}N$ values increase with depth in soil 521 profiles (Fig. 2E), with the lowest values in leaf litter ($-4.9\pm1.9\%$), intermediate values in 522 topsoils (+1.3 \pm 2.7‰), and the highest values in subsoils (+5.8 \pm 2.6‰). δ^{15} N in upstream 523 sediments (+1.7±1.6‰) varied non-linearly with distance, with the maximum values 524 between 660 to 800 m upstream (Fig. 3E). The upstream samples with the highest $\delta^{15}N$ 525 values were sampled in August 2018 under low flow conditions. Downstream sediments had significantly higher δ^{15} N values (+4.3±1.1‰) than upstream sediments, and δ^{15} N in 526 downstream sediments increased linearly with distance downstream ($R^2 = 0.81$, p = 0.04). 527 528 δ^{15} N in lake sediments was generally lower than stream sediments (+0.8±1‰). Lake sediment $\delta^{15}N$ was positively correlated with distance from the inflow stream mouths (R² 529 530 = 0.3, p=0.02; Fig. 3D), but was not significantly correlated with water depth (Fig. 4E). 531 Macrophyte and macroalgae spanned a relatively wide range of δ^{15} N values (+1±2.4‰). 532 3.6 Fm measurements 533 Fm measurements in selected soil and sediment samples ranged from 1.09 to 0.77.

534 The lowest values, indicating the oldest carbon, was found in subsoils $(0.872\pm0.07,$

535 corresponding to 1100 ± 650 ¹⁴C years BP), which is similar to values found in other

- temperate forest subsoils (Gaudinski et al., 2000). Topsoil values (1.02±0.04) overlapped
- 537 recent atmospheric values (~1.05; Turnbull et al., 2017). These values likely indicate a
- 538 mixture of decadal and centennial cycled carbon in topsoils (Gaudinski et al., 2000). Fm

539	measurements in upstream sediments were primarily within the range of post-bomb
540	carbon (1.04±0.04; Fig. 3F), with one sample indicating a pre-bomb mean composition
541	(0.98, 147 ¹⁴ C years BP). Downstream sediments on average contained a greater
542	proportion of pre-modern carbon (0.98 ± 0.04), with one sample in particular having a low
543	value (0.94, 500 14 C years BP). This sample (DS2) was also characterized by an
544	anomalously high δ^{13} C value (-22.8‰). This could indicate an influence from
545	anthropogenic fossil carbon sources, but alternatively could represent aged carbon
546	derived in part from aquatic macrophytes that was stored in lake sediments prior to
547	export. We included this sample in our analyses, but interpreted it with caution. Lake
548	sediment samples consistently demonstrate Fm values greater than 1 (1.05 ± 0.03). Fm
549	decreased linearly with water depth, and more weakly with distance from the stream
550	mouths (Figs. 3F, 4F).
551	3.7 Co-variation between isotopic measurements and C:N ratios
552	Across all soil horizons δ^{15} N is strongly positively correlated with δ^{13} C (Fig. 5),
553	as has been observed in other forest soils (Natelhoffer and Fry, 1988; Billings and
554	Richter, 2006). Within soil subcategories, $\delta^{15}N$ is significantly correlated with $\delta^{13}C$ in
555	topsoils, but not in leaf litter or subsoils. δ^{13} C is strongly negatively correlated with δ^{15} N

556 in macrophytes and macroalgae (Fig. 5).

557 We observe a strong negative correlation between δ^{13} C and Fm in topsoil and 558 subsoil samples (Fig 6A). This relationship is consistent with two mechanisms proposed 559 for δ^{13} C enrichment with depth in soils: 1) the Suess effect, which would lead to more 560 depleted δ^{13} C in SOM fixed during the industrial period when fossil fuel emissions have 561 led to¹³C and ¹⁴C depletions in atmospheric CO₂; or 2) older carbon in deeper soils being





563 Figure 5: Scatter plot of δ^{15} N vs. δ^{13} C for foliage, litter, soil, sediment,

564 macrophyte/macroalgae and foliage samples. Significant regression relationships

and their statistics are shown. Dotted lines indicate regression 95% confidence

566 intervals. Analytical uncertainties are smaller than points for all data.

567

568 subject to repeated microbial degradation and recycling, leading to a loss of ¹³C depleted

569 carbon in the form of respired CO₂ (Ehleringer et al., 2000). δ^{13} C and Fm are also

570 negatively correlated in stream sediments, with a somewhat flatter slope than in soils.

571 Excluding the outlying downstream sediment sample (DS2) does not significantly change

572 this regression relationship. We also observe significant negative relationships between

573 δ^{15} N and Fm in all soil samples (including topsoils and subsoils), and in stream samples

574 (Fig. 6B). The slopes of these regression relationships are similar, but the stream





577 Figure 6: Scatter plot of (A) δ^{13} C vs. Fm and (B) δ^{15} N vs. Fm for soil and sediment 578 samples. Significant regression relationships and their statistics are shown. 579 Dotted lines indicate regression 95% confidence intervals. Dashed lines indicate 580 division between pre-bomb and post-bomb Fm values. Analytical uncertainties are 581 smaller than points for all data.

sediment relationship is offset to higher Fm values. We do not observe a significant

584 relationship between $\delta^{15}N$, $\delta^{13}C$, or Fm for lake sediments.

585 δ^{13} C was significantly negatively correlated with C:N ratios in upstream

- 586 sediments and topsoils, but not in other samples (Fig. 7A). $\delta^{15}N$ is also negatively
- 587 correlated with C:N ratios in upstream sediments and topsoils (Fig. 7B). We do not
- 588 observe a significant linear relationship between Fm and C:N ratios in any of the sample

589 categories.





592 Figure 7: Scatter plot of (A) C:N vs. δ^{13} C and (B) C:N vs. δ^{15} N for soil and sediment 593 samples. Significant regression relationships and their statistics are shown.

594 Dotted lines indicate regression 95% confidence intervals. POM values are plotted

as filled diamonds in (A), with colors corresponding to sampling location.

596 Analytical uncertainties are smaller than points for all data.

597

598 **3.8 Mixing model results**

599 MixSIAR results are presented as probability distributions for the proportional 600 contribution of each relevant OM source to a particular sediment sample. For most 601 samples the probability distributions of OM source contributions overlap substantially, 602 indicating that OM source isotopic compositions are not sufficiently differentiated, or 603 there are too many possible sources relative to the number of tracers, to fully resolve 604 source mixtures. Despite this, the probability distributions are informative about the 605 606 likelihood of different source contributions. In the text we primarily focus on the median607 probability contribution by OM sources to sediment samples.

608 Results for upstream sediment samples indicated that topsoils were likely to be 609 the dominant source of sediment OM in all samples (Fig. 8A). Median contributions 610 of topsoil OM ranged from 60 to 70%. The probability distribution of litter OM 611 contribution varied widely between samples, with the median contribution ranging from 612 18 to 33%. Subsoils were consistently estimated be the smallest contributor to upstream 613 sediments, with median contributions ranging from 5 to 10%. 614 In lake sediments, the MixSIAR model estimated a more even distribution of OM 615 sources than in upstream sediments, and no OM source had a median contribution above 616 50% (Fig. 8C). Phytoplankton was most likely to be the largest source in six of seven 617 samples, with the median contribution ranging from 30 to 40%. Litter was likely to be the 618 second largest OM source in most samples, with median contributions between 36 to 619 28%. Estimated macrophyte/macroalgae contributions to lake sediments were generally 620 low (7-12%), with the highest values in intermediate depth samples with high δ^{13} C 621 values. Estimated topsoil contributions were relatively constant across samples, with 622 median contributions between 13 to 17%. Estimated subsoil contributions were 623 consistently low, with median contributions from 2 to 3%. Based on the mean 624 contribution of the three soil source categories (litter, topsoil, and subsoil), we estimate 625 that approximately $53\pm 24\%$ of lake sediment OM has a terrigenous source, implying 626 subequal contributions of terrigenous and aquatic OM to sediments throughout the lake. We note that the much larger variance for δ^{13} C values for 627 628 macrophytes/macroalgae and phytoplankton (Table 1), relative to the soil OM sources,



Figure 8: Boxplots of MixSIAR probability distributions of OM source fractional contributions for individual sediment samples for (A) upstream sediments; (B) downstream sediments; and (C) lake sediments. Box centers indicate the median contribution for each source category, box edges indicate the 25th and 75th percentile, and whiskers indicate 5th and 95th percentiles. In (A) samples are arranged by distance from the stream mouths. In (B) samples are arranged by distance from the lake outlet. In (C) samples are arranged by water depth.

638	likely has an important influence on the MixSIAR model results. The 1σ range in δ^{13} C
639	for phytoplankton, in particular, spans all lake sediment values, and therefore the model
640	could be overestimating the input of phytoplankton OM, and potentially underestimating
641	the contribution of macrophytes/macroalgae. Inclusion of Fm in the model could also
642	bias our estimates of macrophytes/macroalgae and phytoplankton, since we did not
643	directly measure Fm in these sources. We analyzed an alternate version of the model
644	using only only $\delta^{13}C$ and $\delta^{15}N$ as source tracers, which resulted in somewhat higher
645	median contributions of macrophytes/macroalgae in intermediate water sediments (20-
646	26%, Supplementary Table 5). However, this difference does not change our
647	interpretations about the relative importance of different sources of lake sediment OM.
648	We argue that Fm values are important for differentiating inputs from subsoil OM, and
649	we focus our interpretation on the model results that include Fm.
650	In downstream sediments the model predicted highly variable compositions
651	between samples, and very wide probability distributions. In two out of three downstream
652	samples, topsoil and subsoil contributions are likely to be dominant. Subsoil median
653	contributions range from 1 to 24% and increase with distance downstream. In one sample
654	macrophyte/macroalgae and phytoplankton OM are estimated to be dominant, with
655	median contributions of 30% and 20% respectively. Since this sample (DS2) exhibits
656	anomalous $\delta^{13}C$ and Fm values we interpret it with caution. The model results are also
657	compatible with a large phytoplankton contribution to all three downstream sediment
658	samples. Estimated litter contributions are uniformly low, with median contributions less
659	than 1%. We estimate that approximately 60±43% of downstream sediment OM has a

660 terrigenous source, with the large uncertainty reflecting the wide probability distributions

661 for the different source categories.

662 **4. Discussion**

663 **4.1 Organic matter isotopic differentiation in soil horizons**

Elemental and isotopic variability observed in the soil profiles is generally
consistent with patterns observed in other temperate forest soils (Natelhoffer and Fry,
1988; Ehleringer et al., 2000; Gaudinski et al., 2000; Billings and Richter, 2006; Craine
et al., 2015; Ostrowska and Porębska, 2015). Our results show clear changes in elemental
and isotopic composition with depth between litter, topsoil, and subsoil layers, but

669 inconsistent or minimal differences with increasing depth in subsoils (Fig. 2).

670 The observed decrease in the TC and C:N ratios, and increase in δ^{13} C, between 671 the litter and topsoil horizons is consistent with a loss of plant-derived macromolecules, 672 such as lignin, during pedogenesis and litter decomposition (Klotzbücher et al., 2011). Lignin is characterized by high C:N ratios and low δ^{13} C values (Benner et al., 1987). As 673 674 discussed below (Sections 4.2 and 4.3), we infer that a proportion of this plant-derived 675 OM is flushed into the streams and lake during periods of high runoff (Schiff et al., 1997; 676 Dalzell et al., 2007; Smith et al., 2013), and is preferentially deposited at the stream 677 mouths and in shallow lake sediments. It is likely that a portion of this plant-derived OM 678 is also mineralized within litter and in streams (Baldy and Gessner, 1997; Klotzbücher et 679 al., 2011).

680 The observed correlations between δ^{13} C, δ^{15} N, and C:N ratios in the topsoil 681 samples are consistent with differentiation between plant-derived and microbial OM in 682 this horizon. Specifically, we infer that this reflects varying mixtures of a plant OM end-

683	member with low $\delta^{13}C$ and $\delta^{15}N$ and high C:N, and a microbial OM end-member with
684	high δ^{13} C and δ^{15} N and low C:N (Figs. 5 and 7) (Natelhoffer and Fry, 1988; Ehleringer et
685	al., 2000; Craine et al., 2015; Philben et al., 2018). Co-variation between δ^{13} C, δ^{15} N, and
686	C:N is not evident in subsoil horizons (Figs. 5 and 7). We suggest that topsoils are the
687	primary locus for the transformation of plant OM to microbial biomass in these temperate
688	forest soils. In contrast, in subsoils we observe a wide range of C:N ratios, but less
689	variable isotopic compositions, especially in terms of δ^{13} C. This difference could imply a
690	large molecular diversity in subsoil OM that is not directly linked to the processes of
691	plant OM decomposition and accumulation of microbial biomass that are driving the
692	isotopic co-variation observed in topsoils (Salome et al., 2010). Processes involving
693	mineral adsorption and DOM transport may be particularly important in controlling C:N
694	ratios and isotopic compositions in subsoil OM (Rumpel and Kögel-Knabner, 2011).
695	The ¹⁴ C data indicate there is a substantial pool of millennial-aged carbon in the
696	catchment subsoils (Fig. 2F). Negative correlations between Fm and both $\delta^{13}C$ and $\delta^{15}N$
697	in soils (Fig. 6), including both topsoils and subsoils, are consistent with older soil carbon
698	reservoirs being associated with a greater proportion of microbial necromass, likely
699	associated with mineral surfaces (van der Voort et al., 2019; Gies et al., 2021). However,
700	the absence of a correlation between Fm and C:N complicates this association. The
701	variation in our topsoil (± 0.07) and subsoil (± 0.07) sample Fm values is about twice as
702	large as plot-level spatial variation in a regional study in Switzerland (± 0.035) (van der
703	Voort et al., 2016), and likely reflects substantial catchment-scale spatial heterogeneity in
704	the relative abundance of decadal- and millennial-aged carbon pools .

705	We derived approximate estimates for the carbon and nitrogen mass in litter,
706	topsoil, and subsoil based on our measured values for TC and TN, measured horizon
707	depths, and values for bulk soil density derived from Wironen and Moore (2006). We
708	estimate C masses of 0.3 \pm 0.1 kg/m ² for litter, 16 \pm 5 kg/m ² for topsoil, and 12 \pm 6 kg/m ² for
709	subsoil. N mass estimates are 0.007 \pm 0.002 kg/m ² for litter, 1 \pm 0.3 kg/m ² for topsoil, and
710	0.7 ± 0.3 kg/m ² for subsoil. These estimates imply that only about 1% of soil carbon and
711	0.3% of soil nitrogen are contained in litter, whereas topsoil and subsoil C and N
712	reservoirs are subequal when considering the uncertainties in the mass estimates.
713	Comparison of these estimates of soil carbon stocks to the modeled contribution to
714	sediments (Fig. 8) suggests that litter OM is disproportionately transported to upstream
715	and lake sediments, since its median contribution ranges from 18 to 36%. In contrast, this
716	comparison suggests that subsoil OM is underrepresented in upstream and lake sediments
717	relative to its proportion of total soil OM, since its median contribution ranges between 2
718	to 10%, and its maximum contribution is consistently less than 15%. The median
719	contributions of litter and subsoil OM in downstream sediments are more consistent with
720	their relative abundance in soils (Fig. 8C).

721 **4.2 Soil organic matter export to upstream sediments**

The isotopic and elemental composition of the upstream sediments is largely similar to that of topsoils (Figs. 3, 5, 6, 7). We infer from this similarity that topsoils are the dominant source of upstream OM. This is consistent with the MixSIAR modeling results, which estimate median topsoil contributions to upstream OM between 60-70% (Fig. 8). However, there are some key differences between topsoil and upstream sediment OM. Notably, upstream sediment OM has generally lower δ^{13} C values than topsoil OM

728	(Figs. 4D, 5), with especially low values in the sediments closest to the stream outlets.
729	We suggest three possible mechanisms that could explain this difference in δ^{13} C: 1) a
730	significant contribution of litter OM with low δ^{13} C values in stream sediments; 2) a
731	selective deposition of topsoil OM components with low $\delta^{13}C$ values, such as lignin or
732	other plant structural compounds; and 3) in-situ OM production or decomposition within
733	streambed environments leading to lower δ^{13} C than OM inputs. The MixSIAR model
734	predicts a significant contribution of litter OM to upstream sediments, with median
735	contributions ranging from 18 to 33%, but as discussed in section 2.4 the model cannot
736	explicitly account for the latter two mechanisms.
737	Negative co-variance between C:N ratios and both $\delta^{13}C$ and $\delta^{15}N$ in upstream
738	sediments are consistent with varying proportions of plant-derived OM and microbial
739	OM, similar to the relationships described for topsoils in Section 4.1. Spatially, we
740	observe the strongest signal of plant-derived OM in the stream sediments close to the lake
741	outlet (Fig. 4C,D,E). In contrast, we observe the clearest signal of microbial OM in
742	samples at an intermediate distance from the lake outlet, and primarily in samples
743	collected in August 2018. Our sampling protocol does not allow us to identify whether
744	this is primarily a spatial or a temporal difference, since the residence time of streambed
745	sediments is typically less than a year (Gartner et al., 2012). August 2018 was somewhat
746	drier and much hotter than May and June 2017, leading to lower streamflow. While
747	spatial and temporal variability are conflated in this dataset, our measurements are
748	consistent with hydrological variability driving upstream sediment geochemical variation.
749	Fm values in upstream sediments are primarily greater than 1, although one
750	sample has a pre-bomb value. This suggests that some pre-bomb C is exported to stream

751 sediments from soils, although post-bomb C is generally predominant. We infer that the 752 observed variability in Fm values primarily reflects varying admixtures of pre-bomb C 753 from soils, with lower values indicating a greater proportion of pre-bomb C. This is 754 consistent with lower Fm values in stream sediments being correlated with higher $\delta^{13}C$ and δ^{15} N values (Fig. 6), which reflects greater microbial processing of OM that has a 755 756 longer soil residence time. We note that stream sediment OM generally has higher Fm 757 values than soil OM, even when δ^{15} N values are similar (Fig. 6B). This could be 758 explained by the observation that water extractable organic carbon, which is more likely 759 to be exported to streams, is composed of microbial metabolites but tends to be cycled 760 more quickly and have higher Fm values than bulk soil OM (van der Voort et al., 2019). 761 We observe relatively high Fm values in stream sediments near the lake outlets, consistent with this OM being dominated by plant-derived OM with relatively short soil 762 763 residence times.

764 We suggest that hydrological processes largely control the isotopic and elemental 765 variation in upstream sediments. Specifically, we infer that during periods of high runoff 766 and streamflow, plant-derived OM from topsoils and litter containing primarily post-767 bomb C is preferentially flushed downstream and deposited at the stream mouth and in 768 shallow lake sediments. In contrast, during low-flow periods microbial biomass from 769 topsoil and subsoil containing a greater proportion of pre-modern C is exported through 770 shallow groundwater. This OM accumulates in mid-stream sediments since there is 771 limited stream power to export this material downstream. This hypothesis is consistent 772 with previous studies showing an association between greater streamflow and the 773 transport of plant biomass that is enriched in lignin (Dalzell et al., 2007) or depleted in

774	δ^{13} C (Smith et al., 2013). It is also consistent with the lower Fm observed in groundwater
775	DOC as opposed to stream DOC in Canadian lake catchments (Schiff et al., 1997).
776	Our limited upstream POM measurements are characterized by low δ^{13} C values
777	and relatively low C:N ratios that are distinct from sediment OM (Fig. 4D, 7A). Given
778	that POM was sampled during a period of low flow (August 2018), we suggest that it
779	may represent a fraction of microbial OM exported via groundwater that is depleted in
780	$^{13}\mathrm{C}$ relative to sediment OM. In contrast, upstream DOC is enriched in $\delta^{13}\mathrm{C}$ relative to
781	most sediments (Fig. 4D). The distinct δ^{13} C values for sediments, POC, and DOC suggest
782	isotopic differentiation between these OM fractions that merits further study. Sediment
783	OM δ^{13} C is intermediate to that of POM and DOC, and it is possible that sediments
784	represent a mixture of sedimented POM and flocculated DOM. Measurements of $\delta^{15}N$ in
785	POM and dissolved organic nitrogen (DON) would help to better understand the distinct
786	sources of these stream OM fractions.
787	4.3 Variability in lake sediment OM composition and organic matter sources
788	We observe substantial variability in lake sediment isotopic composition and C:N
789	ratios, particularly in littoral sediments at less than 6 meters water depth. Relatively low
790	δ^{13} C and high C:N values in shallow water (< 1 m water depth) sediments (Figs. 4C,D)
791	likely represents a large contribution of terrestrial-plant-derived OM, with a similar
792	composition to what is observed in the stream sediments near the stream mouths. With
793	progressively greater water depths we observe a substantial increase in $\delta^{13}C$ coupled with
794	a decrease in C:N. We infer that this represents a strong increase in the contribution of
795	OM from aquatic sources. In particular, input from macrophytes and macroalgae is likely
796	important in contributing to the high δ^{13} C values between 2-3 m water depth. Similar

797	enrichment in δ^{13} C in lake sediment at intermediate water depths has been observed in a
798	number of lakes in China (Jiang et al., 2021). In that study, biomarker evidence also
799	supports a large contribution of macrophyte OM to sediment. We argue that the
800	maximum in δ^{13} C values between 2-3 m water depth likely reflects the zone of maximum
801	macrophyte biomass in the lake basin. Based on an empirical model of macrophyte
802	biomass as a function of water transparency (Chambers and Kaiff, 1985), and on Secchi
803	disk measurements at Lake Hertel of 3.1 m (Hanna and Peters, 1991), we estimate
804	maximum macrophyte biomass at approximately 2 meters water depth. The increase in
805	the slope of the lake bed between 2 to 6 meters water depth (Fig. 1) may also act to
806	decrease macrophyte biomass at depths greater than 3 m (Duarte and Kalff, 1986).
807	The decrease in sediment OM δ^{13} C from 3 to 7 m water depth (Fig. 4D) could be
808	a result of 1) a greater contribution of terrigenous OM input, specifically from litter or
809	topsoil; 2) a greater contribution of phytoplankton OM with low δ^{13} C values; or 3) the
810	effect of diagenetic alteration of sedimentary OM. Diagenetic alteration in both oxic and
811	anoxic lake sediments can lead to depletion of sediment $\delta^{13}C$, with shifts on the order of
812	2 to 3‰ (Lehmann et al., 2002). However, Lehmann et al. (2002) observed similar
813	decreases in POM $\delta^{13}C$ under oxic and anoxic conditions, suggesting that diagenetic
814	effects would be similar above and below the hypolimnion. Therefore, the low $\delta^{13}C$ in
815	hypolimnetic sediments most likely reflects a more ¹³ C-depleted OM source mixture than
816	epilimnetic sediments. The consistently low C:N in sediments deeper than 3 m water
817	depth suggests an important contribution from autochthonous OM. Therefore, we infer
818	that the most likely explanation of this trend is an increasing contribution of
819	phytoplankton, as is implied by the MixSIAR results. A similar decline in the $\delta^{13}C$ of

lake sediments between 0-20 m water depth was observed in Lake Biwa, Japan, and was
attributed to an increasing contribution of autochthonous OM (Murase and Sakamoto,
2000).

823 δ^{15} N values in lake sediments show a large degree of variability that is positively 824 correlated with distance from stream outlets (Fig. 3E). We infer that this is likely the 825 result of greater heterotrophic microbial recycling of sediment OM as a function of 826 distance from the stream outlet, possibly as a function of greater mean OM residence time within the lake. The effect of early diagenesis on OM δ^{15} N in lakes can be highly 827 828 variable in magnitude and sign depending on redox conditions, denitrification rates, and 829 the relative importance of selective preservation of OM and accumulation of microbial 830 biomass (Hodell and Schelske, 1998; Lehmann et al., 2002; Gälman et al., 2009). Our 831 data indicate the potential for substantial spatial variation in δ^{15} N in lake sediments (Fig. 832 4E), which is likely influenced by complex interactions between variation in source 833 contributions and differential effects of diagenetic alteration under different redox 834 conditions. This spatial variation, if observed more widely, may pose complications for 835 the interpretation of δ^{15} N in lake sediment cores.

The Fm of lake sediment OM is consistently greater than 1, implying a dominance of post-bomb carbon in surficial sediments (Fig. 4F). This implies a limited contribution of aged subsoil OM to lake sediments, which is also consistent with lake sediment stable δ^{15} N values (Fig. 5), as well as the MixSIAR results (Fig. 8B). Fm decreases significantly with water depth (R² = 0.69, p = 0.02). Interpretation of variability in sediment Fm values >1 is complicated by the non-linear variation in atmospheric ¹⁴C in the 20th century. Values higher than the contemporary value of the atmosphere (~1.05) are

indicative of a component of decadally cycling carbon fixed between 1950 and 2010.
This suggests that there could be a time lag on the order of 10 to 50 years between the
production of organic matter in terrigenous environments and their deposition in littoral
lake sediments. We note that studies of terrigenous biomarkers, such as leaf wax lipids,
have found evidence for substantially longer time lags on the order of hundreds to
thousands of years (Douglas et al., 2014; Freimuth et al., 2021). Time lags for the
transport and deposition of terrigenous OM could affect the signal recorded in
paleolimnological proxy data and should be considered when interpreting these data.
Lower Fm values between 1 and 1.05 in deeper water sediments could either be
the result of a greater admixture of pre-bomb carbon, or a predominance of contemporary
carbon. The water depth trend in Fm is consistent with increasing input of phytoplankton,
particularly if DIC in Lake Hertel is characterized by relatively low Fm values around 1,
as has been observed in other lakes in southern Quebec (McCallister and Del Giorgio,
2008). Alternately, lower Fm in deeper water sediments could reflect a greater input of
pre-modern C from soils, although the C:N and $\delta^{15}N$ data are not consistent with an
increasing input of soil OM with water depth. A third possible explanation is that
decreasing Fm with water depth is controlled by the timescales of sediment resuspension
and focusing within the lake. This scenario would imply that OM deposited in
hypolimnetic sediments have a mean resuspension transit time of at least 70 years, in that
they contain a mean Fm signal of carbon preceding the peak of the bomb spike. However,
radionuclide studies indicate that lacustrine sediment focusing redistributes sediments on
timescales of 10-20 years (Wieland et al., 1991; Crusius and Anderson, 1995), and
therefore an OM transit time of >70 years within Lake Hertel seems implausible.

866	Overall, the lake sediment data present a picture of highly variable OM isotopic
867	and elemental composition, with the greatest variation in littoral sediments between 0-4
868	meters water depth. This differentiation implies a relatively large contribution of
869	terrestrial plant derived OM in shallow water sediments near the stream outlets (< 1 m
870	water depth), an increasing contribution of macrophyte and macroalgae OM in
871	intermediate water sediments (1-3 m), and an increasing contribution of a ¹³ C-depleted
872	and low C:N OM source in deeper water sediments, which we infer is most likely
873	phytoplankton. This inference will require phytoplankton isotopic measurements to
874	confirm. Despite the apparent signal of an increasing contribution of phytoplankton OM
875	with water depth, our mixing model estimates a consistently important contribution of
876	terrigenous OM within uncertainty of 50%, primarily from litter and topsoil, at all water
877	depths. The substantial changes in OM characteristics between 3 and 4 m water depth,
878	including lower %C and %N, lower C:N, lower δ^{13} C, and higher δ^{15} N, may be partly the
879	result of the increasing slope of the lake bed, which would act to inhibit macrophyte
880	growth (Duarte and Kalff, 1986), and could also limit the accumulation of detrital
881	terrigenous sediment, leading to a relative concentration of microbial or phytoplankton
882	biomass settling from the water column.
883	There are few studies that have examined intra-lake variation in sediment isotopic
884	composition (Murase and Sakamoto, 2000; Bovee and Pearson, 2014; Taylor et al.,

- 885 2015), and there is a general assumption that depocenter sediment isotopic compositions
- are representative of the lake basin. Our data suggest this assumption is not uniformly
- valid, and that isotopic values for sediment can be highly variable within a lake,
- 888 especially in terms of δ^{13} C. In terms of understanding the long-term burial of OM, the

889	composition and source of hypolimnetic sediments are probably most important. In
890	contrast, a number of studies have implied that littoral sediments are critically important
891	for OM decomposition and greenhouse gas emissions (den Heyer and Kalff, 1998;
892	Juutinen et al., 2003; DelSontro et al., 2016). The large isotopic variation in Lake Hertel
893	littoral sediments implies major OM compositional and source diversity and suggests that
894	terrestrial plant litter and macrophyte/macroalgae biomass may be disproportionately
895	fueling GHG emissions in this lake, relative to their contribution to depocenter sediments.
896	The large $\delta^{13}C$ variation in littoral lake sediments could be useful as a tracer in incubation
897	studies focused on understanding which OM sources are being predominantly respired by
898	microbes (Mahmoudi et al., 2017). We suggest that spatial surveys of littoral lake
899	sediment isotopic composition in a broader range of lakes would be of value in
900	determining whether spatial variability in isotopic and OM source is a widespread
901	phenomenon.
902	4.4 Lacustrine influence on downstream sediment organic matter

903 The downstream sediment samples are isotopically and compositionally distinct 904 from the upstream sediments. Specifically, they are characterized by generally higher average δ^{13} C and δ^{15} N values, lower C:N ratios, and lower Fm. The difference in δ^{15} N in 905 906 particular is statistically significant on the basis of a Kruskal-Wallis test (p = 0.004). Aside from one sample with anomalous δ^{13} C and Fm values (DS2), the downstream 907 sediment data are consistent with the observed correlations between $\delta^{13}C$ and $\delta^{15}N$ and 908 909 both C:N and Fm identified in upstream sediments (Figs. 6,7). The distribution of 910 downstream sediments relative to upstream sediments in Figs. 6 and 7 suggests that downstream sediments contain a greater proportion of microbial OM and a greater 911

912	proportion of pre-bomb soil C. This is consistent with our interpretation that upstream
913	sediments sampled in August 2018 with relatively high $\delta^{15}N$ contain a relatively greater
914	proportion of microbial soil OM exported through shallow groundwater (see Section 4.2).
915	The mixing model estimates a relatively high median contribution of subsoil OM to
916	downstream sediments (Fig. 8), consistent with a greater input of older and microbially
917	processed OM. However, the mixing model results for the downstream sediments are
918	particularly uncertain, and a large contribution of lacustrine phytoplankton OM is also
919	possible. The downstream POC and DOC measurements are also high in δ^{13} C relative to
920	upstream measurements, and the POM is also characterized by a lower C:N ratio. The
921	downstream DOC- δ^{13} C in particular is quite similar to lake DOC- δ^{13} C, whereas the
922	downstream POM- δ^{13} C is much lower than lacustrine POM- δ^{13} C.
923	The downstream sediment dataset is small, but the results suggest that the
924	presence of Lake Hertel has a significant influence on downstream OM isotopic and
925	elemental composition. Notably, terrestrial plant OM appears to be much less prominent
926	in the downstream sediments. We suggest that lake sediments act as a trap for litter and
927	plant-derived soil OM, and that very little plant OM from the Lake Hertel catchment is
928	transported downstream of the lake. In contrast our results suggest that microbial soil OM
929	is transported to downstream sediments. It is possible that soil OM adsorbed on fine
930	mineral particles could remain suspended in lake waters and is then exported at the lake
931	outlet. Periods of low flow may promote the deposition of these fine mineral particles in
932	downstream sediments. We note that 3 of 5 downstream sediments were sampled during
933	a low-flow period. Additionally, the lake may act as a hydrological buffer for high-flow
934	storm transport of plant OM.

935	There is also a clear potential for lacustrine OM to contribute to downstream
936	sediment. This is especially true for one sample with a very high $\delta^{13}C$ value, although, as
937	discussed above, it is possible that this sample (DS2) is contaminated with anthropogenic
938	C. However, downstream sediment δ^{15} N values are uniformly higher than in lake
939	sediments, implying a significant contribution of soil OM with high $\delta^{15}N$ to downstream
940	sediments. To our knowledge there are few studies comparing sediment OM upstream
941	and downstream of a lake. Studies of DOM find that there is substantial export of
942	lacustrine DOM to outflowing streams (Goodman et al., 2011), consistent with our
943	measurements of downstream DOC δ^{13} C.
944	It is unclear how far downstream the distinctive isotopic signal in downstream
945	sediments would persist, as it may be progressively diluted by inputs from downstream
946	catchment soils and plants. However, the spatial pattern observed with our limited
947	downstream sediment dataset is that $\delta^{15}N$ values increase significantly with distance
948	downstream. Unfortunately, it will be difficult to further study this question at Mont Saint
949	Hilaire since our most downstream sampling point was at the limit of the Gault Nature
950	Reserve, and beyond this point there is a much stronger anthropogenic influence from
951	agriculture and suburban residential development.
952	4.5 Implications for catchment scale OM transport and storage

953 Overall, our results indicate key differences in the export of different components 954 of soil organic matter to sediments. Litter is disproportionately transported to sediments, 955 compared on its relative abundance in soils. We observe a strong concentration of plant 956 OM, likely derived from both litter and topsoil, at the stream outlets and shallow lake

957 sediments. We infer that this deposition is driven by periods of high surface runoff that958 have the stream power to transport plant OM to the lake basin.

959 In contrast subsoil OM appears to be much less prevalent in sediments relative to 960 its abundance in catchment soils. Since this catchment is not undergoing major erosion, 961 subsoil OM reservoirs appear to be minimally exported by surface transport. However, 962 we do see a stronger input of microbial soil OM in some upstream sediments sampled 963 during periods of low streamflow, and more prominently in downstream sediments. It is 964 likely that this microbial soil OM is derived from both topsoil and subsoil. We infer that 965 this material may be largely transported by shallow groundwater and may only be 966 apparent in sediments that have not been affected by high-streamflow transport and 967 sedimentation. Combining these results with a more detailed study of soil erosion 968 mechanisms, and with groundwater OM characteristics, would be valuable in confirming 969 these inferences.

970 Within the lake we observe a strong signal of terrigenous plant OM in shallow 971 sediments that is then overprinted with a signal of macrophyte OM at intermediate water 972 depths and phytoplankton OM at deeper water depths. It is unclear whether plant OM 973 delivered to shallow lake sediments is primarily decomposed, and therefore not 974 transported to deeper water sediments, or instead we are simply observing progressive 975 dilution with aquatic OM in deeper water sediments. The MixSIAR results imply that 976 there is a substantial contribution of litter and topsoil OM to deeper water sediments, 977 albeit with a declining proportion relative to phytoplankton. Regardless, given that littoral 978 sediments have been shown to contribute dominantly to GHG emissions at Lake Hertel

979 (den Heyer and Kalff, 1998), we infer that a substantial proportion of the terrigenous980 plant OM deposited in littoral sediments is mineralized.

981 Regardless of the fate of terrigenous plant OM in littoral sediments, it appears that 982 these sediments are the primary locus of terrigenous plant OM deposition in the 983 catchment, and that this material is not exported from the lake in substantial quantities. 984 This suggests that the presence of lakes in a landscape could play an important role in the 985 fluvial transport of terrigenous plant OM by preferentially trapping, and either burying or 986 decomposing, this material. Similarly, our analysis suggests that the presence of a lake 987 may enhance the relative abundance of older subsoil OM transported downstream. Our 988 results are based on one catchment and more study is needed to determine if these 989 patterns occur widely. Lake Hertel represents a specific context of a relatively stable 990 forested environment with minimal human disturbance, recent deglaciation, and limited 991 soil development. A catchment with greater human disturbance might produce greater 992 erosive input of topsoil and subsoil to sediments. Likewise, a catchment with more 993 developed soils might have a larger flux of subsoil OM exported via groundwater. 994 Therefore, the relatively high contribution of litter to upstream and lake sediments in this 995 environment may be specific to this relatively pristine environment with limited soil 996 development. However, we suggest that the catchment-scale trapping of litter and plant-997 derived soil OM in littoral lake sediments is likely a common phenomenon. In general, 998 these results suggest that greater consideration of littoral lake sediments, and the ultimate 999 fate of the OM they contain, could be important in linking soil and sediment OM budgets, 1000 and clarifying the long-term fate of terrigenous carbon reservoirs.

1001

1002 **5. Conclusions**

1003

1004 composition, we found major variability across the Lake Hertel catchment. Increasing

In this in-depth analysis of soil and sediment organic matter isotopic and elemental

1005 OM δ^{13} C and δ^{15} N and decreasing C:N between litter, topsoil, and subsoil horizons is

1006 consistent with a progressive enrichment in microbial biomass, but we do not observe

- 1007 consistent changes in OM composition with depth in subsoils. Topsoils contain carbon
- 1008 that cycles on decadal to centennial timescales, while subsoils contain a large proportion
- 1009 of carbon that cycles on millennial timescales.

1010 Stream sediment OM δ^{13} C and δ^{15} N co-vary with both Fm and C:N ratios,

1011 indicating a continuum of compositions between older OM enriched in microbial biomass

1012 and younger OM enriched in plant biomass. Plant-derived OM is concentrated at the

1013 stream outlets, which we infer is related to flushing of this material from litter and

1014 topsoils during periods of high surface runoff. In contrast, sediments at more upstream

1015 locations sampled during a period of relatively low flow were enriched in microbial OM,

1016 which we infer is transported via groundwater-derived baseflow. Plant-derived OM is

1017 also concentrated in shallow water littoral lake sediments adjacent to stream mouths but

1018 is progressively diluted with autochthonous OM with low C:N ratios in deeper water

1019 sediments. This includes both macrophyte-derived OM with high δ^{13} C values in

1020 intermediate depth sediments from 1 to 4 m water depth, and probable phytoplankton

1021 derived OM with low δ^{13} C in deeper water sediments, including hypolimnetic sediments.

1022 Our results indicate substantial δ^{13} C variation in lake sediments of >6‰, and we suggest

1023 that exploration of similar isotopic variation in a wider set of lake basins would be of

1024 value in understanding lake carbon budgets, including the role of plant and soil OM in

lake GHG emissions and long-term sediment burial. Our isotopic mixing model cannot
fully resolve lake sediment sources, but our results suggest that approximately half of the
OM in hypolimnetic sediments is terrigenous in origin. Spatial variation in bulk lake
sediment isotopic values is also important to consider in paleolimnological studies that
are based on these measurements.

1030 Downstream sediments have notably high δ^{15} N and low Fm values, which we 1031 attribute to a combination of exported lacustrine OM and microbial soil OM that is either 1032 transported by groundwater or is transported across the lake. Based on our mixing model, 1033 leaf litter probably makes up a disproportionately large component of sediment OM in 1034 upstream and lake sediments, relative to its abundance in soil profiles. However, lake 1035 sediments appear to be an effective trap for litter and plant-derived soil OM, and there is 1036 minimal export of this material to stream sediments downstream of the lake. Therefore, 1037 we suggest that the presence of lakes limits the fluvial transport of plant-derived 1038 sedimentary OM, while enriching fluvial systems in aquatic and microbial OM, including 1039 a greater proportion of aged soil OM. This hypothesis will require further testing in a 1040 broader range of lake catchments.

1041

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1050	
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1053	
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