

Soil hydrology, physical and chemical properties and the distribution of carbon and mercury in a postglacial lake-plain wetland

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ABSTRACT

Northern wetland soils hold globally significant carbon (C) and mercury (Hg) stocks whose cycling feeds back to atmospheric pollution, climate change, and the trophic dynamics of adjacent aquatic ecosystems. At a more local level, patterns of variation in the hydrologic, physical and chemical properties of wetland soils inform the appreciation of these ecosystems in their own right; describing patterns of variation, their potential drivers and consequences is a key step towards placing wetland soils in the context of broader landscape-level processes, such as C and Hg export to aquatic ecosystems. In this case study, we investigated a 10 ha, 3000 year old lake-plain wetland in the Great Lakes region (U.S.A.), located at the interface between a 120 ha, first-order watershed and a 6700 ha inland lake. We monitored water tables, measured soil morphology and physical characteristics, applied interpolation and mapping to model hydrologic flowpaths and spatial variation in soil depth, morphology, total C and Hg stocks, and used chemical analyses (elemental concentrations and isotope signatures, UV–Vis and FTIR spectroscopy) to quantify relationships between soil C and Hg pools, organic matter composition, and C cycling rates. Key findings from this site include: 1) whole-profile soil C and Hg stocks are readily predicted from soil depth; 2) soil saturation is semipermanent but spatially and temporally variable; 3) accumulated organic soil materials are dominated by aromatic moieties, but possess considerable amounts of labile polysaccharides; 4) subtle, topography-mediated hydrologic flowpaths create profiles of interbedded organic and mucky sand horizons with sharp discontinuities in their C and Hg concentrations. Compared to peatlands across the region and North America, soil depths and C stocks are rather low, averaging 84 cm and 394 Mg ha^{−1}, respectively. On the contrary, total Hg concentrations of organic soil materials (137 and 191 ng g^{−1} for fibric vs. sapric, respectively) are at the high end for wetlands of the Great Lakes region, and more representative of those observed in areas of the eastern U.S. with historically elevated atmospheric deposition. Given past and potentially increased future variation in hydrologic regimes due to climate change, the presence of banded (sandy) profiles that may act as preferential flowpaths, and the large quantities of Hg and labile C held in these soils, they may act as significant sources of C and Hg to the atmosphere or adjacent aquatic ecosystems.

1. Introduction

Northern wetlands have higher soil carbon (C) densities than most soils, and because of their vast extent comprise one of the largest C pools on Earth (Bridgman et al., 2006; Post et al., 1982). Furthermore, given the multi-century history of anthropogenic atmospheric deposition, and the capacity of wetland soils to act as sinks for metal cations, these soils also hold much mercury (Hg; Grigal, 2003). The storage and

cycling of these elements in wetland soils impacts atmospheric CO₂ and CH₄ concentrations and associated climate warming (Moore et al., 1998; Updegraff et al., 1995), and also affects the biogeochemistry and trophic dynamics of aquatic ecosystems, where allochthonous inputs of C from wetlands are an important metabolic substrate and Hg is a bioaccumulating toxic metal (Buffam et al., 2011; Kolka et al., 2011).

In a general sense, soil formation in northern wetlands is fairly straightforward- saturation and cold temperatures severely limit aero-

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bic respiration (mineralization of organic matter). Low rates of decomposition are only barely exceeded by rates of primary production in these ecosystems, leading to the gradual accumulation of organic soil materials over time (Aselmann and Crutzen, 1989). Across the northern U.S., Canada, Fennoscandia, and the Russian Federation, most wetland soils consist of 1–3 m of accumulated organic materials with basal deposit ages indicating that accumulation began between 6000 and 11,000 years before present (Gorham, 1991; Kuhry et al., 1993; Miller and Futyma, 1987; Tolonen and Turunen, 1996). However, the straightforward pedogenesis of northern wetland soils belies the very real spatial variability in profile morphology, element stocks and cycling that occurs even within relatively small areas, such as individual landforms, soil map units, or ecosystems (Bartlett and Harriss, 1993; Bridgman et al., 1996; Matthews and Fung, 1987). This variation in soil form and function across spatial levels challenges those who measure and map wetland soils (Chaplot et al., 2000; Lin et al., 2005; Parry et al., 2014; Thompson et al., 1997), calling for case studies that explore spatial variability and its drivers and set the stage for broader questions, such as the role of wetland soils within their larger landscapes or in hydrologic exports of biogeochemically active elements.

Hydrology is the definitive physical factor in wetlands, and as such it impacts the form and function of their soils in a variety of ways (Bridgman et al., 1996; Thormann et al., 1999). First, spatial and long-term temporal variation in groundwater levels influences the composition of organic soil materials; sites with more dynamic or lower water tables support oxidizing conditions that allow decomposition of relatively intact (fibric and hemic) materials to more degraded (sapric) materials (Bockheim et al., 2004; Boelter and Verry, 1977; Heinselman, 1970; Podnieszinski and Leopold, 1998). Second, episodic variation in water table depths drives short-term variation in biogeochemical processes, with saturation-desaturation cycles driving rapid shifts between and high rates of C and Hg transforming processes such as C mineralization, methanogenesis, and Hg volatilization and methylation (Demers et al., 2013; Desrosiers et al., 2006; McClain et al., 2003; Obriest et al., 2010; Wiener et al., 2006; Zhang et al., 2002). Third, in addition to the effects of water table variability on wetland soils, heterogeneity in the lateral movement of water along preferential flowpaths affects soil morphology, C cycling and biogeochemistry. In particular, meandering riparian or alluvial channels support complex, concurrent material additions, removals, transfers and transformations, resulting in spatially and temporally heterogeneous soil forming and biogeochemical processes (Blazewski et al., 2009; Drouin et al., 2011; Jurmu, 2002; Simonson, 1959; Stallard, 1998; Saint-Laurent et al., 2014).

In wetland landscapes, hydrology is more than a direct driver of spatial variability in soil biogeochemistry. Hydrology also imparts spatial patterns through its interactions with the physical and chemical properties of soils and their parent materials. The best-known examples are from ecosystem to landscape-level gradients (or mosaics) of ombrotrophic vs. minerotrophic wetlands. In these settings, elevated concentrations of dissolved ions in minerotrophic wetlands, derived from groundwater interaction with readily weathered parent materials, create ecosystems with very different soil morphologies, pH, and C cycling rates than nutrient-poor, precipitation-fed ombrotrophic wetlands (Keller and Bridgman, 2007; Bridgman et al., 1998; Ye et al., 2012; Zogg and Barnes, 1995). The large swath of wetlands across central North America furnishes similar spatial patterns at a regional level. Across this region of wide-ranging geologic deposits, soils and parent materials, wetlands vary from acidic ombrotrophic systems on Precambrian igneous bedrock, to circumneutral or alkaline (minerotrophic) wetlands on base-rich, Paleozoic sedimentary bedrock and associated glacial drift deposits (Boelter and Verry, 1977; Last and Last, 2012; McLaughlin and Webster, 2010). While C has often been a focus of study for wetlands of different hydrologic sources, soils and parent materials, less attention has been paid to the biogeochemistry of Hg across ombrotrophic-minerotrophic gradients (Tjerngren et al., 2012).

Nonetheless, it is well known that C and Hg cycling in wetland soils are coupled and pH-dependent, as the organic matter that holds C is also a sink for metal cations such as Hg and the metabolic substrate for microbial processes that use N, S, Hg, and Fe as electron acceptors (Hesterberg et al., 2001; Schuster, 1991; Skjellberg et al., 2000, 2006). This highlights the need to view wetland soil C and Hg stocks in the context of variation not only in hydrologic conditions, but in soil and parent material physical and chemical properties.

Because wetlands are the intermediary between terrestrial and aquatic ecosystems, describing the hydrologic, physical and chemical properties of their soils is necessary not only for appreciating these ecosystems in their own right, but also for placing them in the context of broader landscape-level processes, such as C and Hg export to aquatic ecosystems. Furthermore, exploring variation in soil hydrology, physical and chemical properties may reveal predictive relationships that offer insight into processes responsible for spatial patterns. In this study, we characterized depth distributions and spatial patterns in soil C and Hg concentrations and stocks in a lake-plain wetland occupying the interface between a 120 ha, first-order watershed and a large (6700 ha) inland lake, in northern Michigan, U.S.A. To inform this descriptive inventory, we also investigated whether variation in soil C and Hg was predictable from topographic and hydrologic parameters, soil physical or chemical properties, emphasizing organic matter composition and C turnover times that place these soils in a long-term pedogenic context.

2. Methods

2.1. Study site

This research was conducted on the wetlands of the lower Honeysuckle Creek watershed (Fig. 1), a 120 ha, first-order watershed within the 4000 ha University of Michigan Biological Station (UMBS), USA (45. 6°, –84.7°). Landforms of the highly heterogeneous UMBS landscape were deposited at the end of Laurentian glaciation (14,000 to 11,000 years before present) and modified by large, glacially mediated lakes 11,500–10,500 (Algonquin) and 5000–3000 (Nipissing) years before present (Blewett and Winters, 1995; Lapin and Barnes, 1995; Spurr and Zumberge, 1956). Bedrock is Silurian limestone and Devonian shale, but is buried beneath 100–200 m of glacial drift. Glacial till deposited by the wasting ice mass (moraines) forms the highest points on this landscape; one of these moraines (276 m a.s.l.) defines the uppermost reaches of the Honeysuckle Creek watershed, which is ~2.5 km in reach length. From the top of this moraine, the Honeysuckle Creek watershed grades down through lower-lying outwash and lake plains to its confluence at 181 m with present-day Burt Lake, the 4th largest inland lake (~6700 ha) in Michigan. Surface flow never occurs in the uppermost 1 km of the watershed, where glacial drift deposits are deepest and most coarse-textured, and is seasonal (leaf-off periods) and spatially discontinuous in the middle ~1 km, where restrictive, fine-textured till drives periodic episaturation near the surface. Only in the lowermost < 0.5 km of its reach, on the low-relief postglacial Lake Nipissing plain wetland that is the subject of this study, does Honeysuckle Creek exhibit perennial flow, where it originates spontaneously from seeps and appears to be fed by a reasonably consistent supply of unconfined groundwater. Within this wetland, soils are mapped as Terric Haplosaprists of the Tawas series (sandy, mixed, euic, frigid), formed in sapric muck overlying outwash/lake-plain substrates. Soils of successively adjacent upland landforms are Alfic, Lamellic, and Entic Haplorthods of the Cheboygan, Blue Lake, and Rubicon series, respectively (Soil Survey Staff, 1991). The climate of the region is continental, but moderated by the proximity of the Great Lakes (mean annual temperature 5.5°, mean annual precipitation 817 cm including 294 cm snowfall). Current vegetation on the UMBS landscape is similar to the broader upper Great Lakes region and reflects historic clearcutting and uncontrolled wildfires ending in the

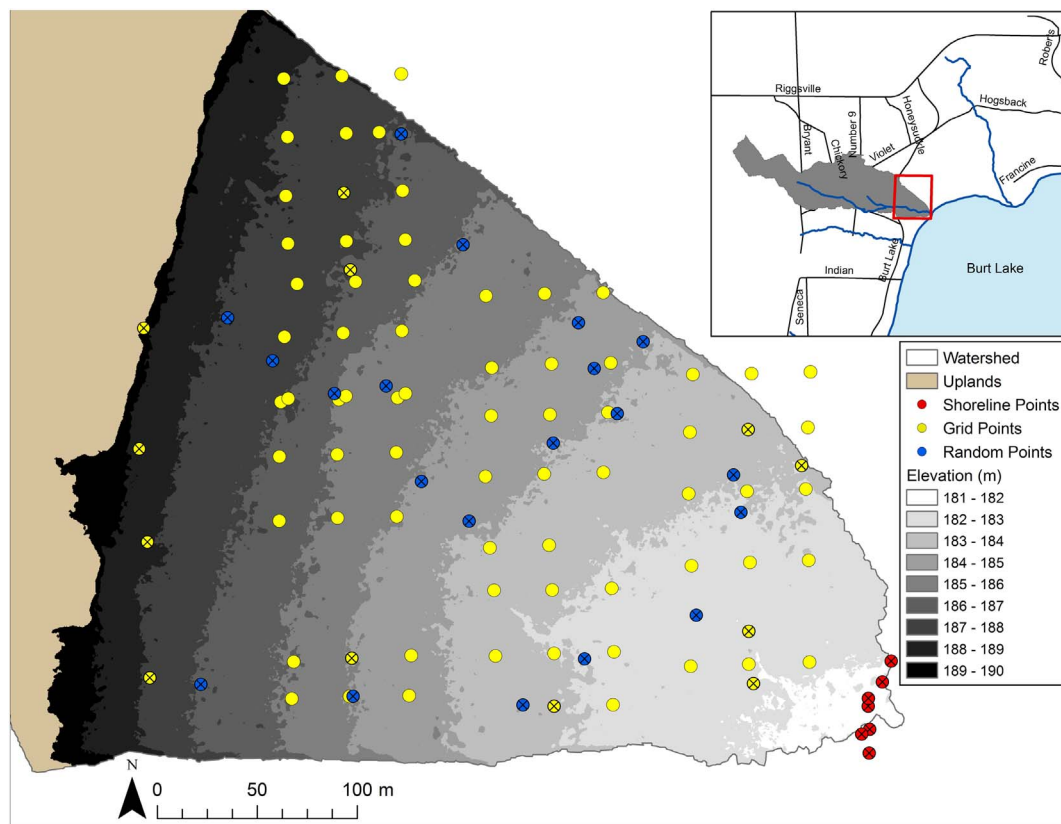


Fig. 1. Maps showing the location of the 10 ha wetland study area and soil sampling activities. The larger map shows the wetland portion of the watershed, which is below 190 m elevation on the postglacial Lake Nipissing plain. One-meter contour intervals are shown in gray shading. Blue points are randomized locations for sampling soil thickness and complete profiles, red points are deliberately selected locations for sampling soil thickness and complete profiles, and yellow points are systematic grid locations where soil thickness was measured. Internal cross-hairs have been added to points where complete soil profiles were collected, in order to aid in visualization. Inset: the larger Honeysuckle Creek watershed (gray shading), draining into Burt Lake, Michigan (45.6°, –84.7°; first order streams and roads are also illustrated). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

early 1920s. Uplands are covered by mixed deciduous and coniferous taxa including *Populus* spp., *Acer* spp., *Quercus rubra*, and *Pinus* spp., while wetlands such as the study area for this work are dominated by *Thuja occidentalis*, *Abies balsamea*, *Tsuga canadensis*, and *Alnus incana*.

2.2. Soil sampling

We collected quantitative, volumetric soil samples during snow-free periods between October 2014 and September 2015, as part of ongoing soil inventory and water table monitoring well installation on the Honeysuckle Creek watershed. For the present study, we focus on the soils of the postglacial Lake Nipissing lake plain (abandoned ca. 3000 years B.P.), with the objective of characterizing complete soil profiles, across the range of elevations, depositional settings, and soil materials present on this wetland landform. To meet this objective in the context of a newly initiated, multi-year study, we report results here from soil sampling at locations determined by several different designs and motivations. Altogether, we collected 39 complete soil profiles throughout the 10 ha study area (Fig. 1). Twenty of these profiles were from random locations, 12 were from a random subset of points from a systematically imposed grid, and 7 were from deliberately selected locations near the shoreline of present-day Burt Lake, which we chose in order to characterize soils in a zone of high microtopographic variation (relict beach and ice-push ridges and beach pools from the recent historic past).

At each sampling location, we first used a 2 m fiberglass push probe (0.7 cm diameter) to measure the depth from the (organic) soil surface to the point of refusal by the dense, sandy, underlying Lake Nipissing floor. We then used a corer to remove intact 30–50 cm increments of

the profile, depending on the depth indicated by the push probe. Each time we removed an increment of the profile, we measured the cumulative depth of the borehole and the depth to water table, using the fiberglass push probe or a wood dowel as a dipstick. Each time we removed an increment of the profile, we differentiated genetic horizons by matrix composition (mucky sand; fibric, hemic, or sapric muck based on the rubbed fiber field test), or rarely by Munsell color, measured their thicknesses with a ruler, and then carefully separated them as complete, volumetric samples for laboratory procedures. Because the soils in this wetland presented a range of different morphologies—most importantly, the occasional presence of interbedded sandy layers—we used different tools to sample them, and describe those differences here. In 32 locations more or less representative of the Tawas series, the solum consisted of partially decomposed organic materials on top of the dense, sandy substrate of the abandoned Lake Nipissing floor. As described for this series, the lowermost horizon (5–10 cm thick) often contained a considerable volume of mineral material. For these profiles, we used a McCauley gate auger (longitudinal half core 5.2 cm in diameter, 50 cm in length, with a 2 m long handle) to sample the full profile, including the organic soil materials and the basal horizon with its noticeable mineral content, before refusal by the dense, sandy substrate of the underlying lake floor. In 7 locations, profiles consisted of discrete, alternating bands of organic materials and mucky sand (3–10 of each). However, the mucky sand horizons in 5 of these banded profiles were poorly consolidated; therefore, as with the more representative profiles described above we were able to drive the McCauley auger down to the point of refusal by the underlying Lake Nipissing floor. In the other two of these locations, ~5 m from the present-day shoreline of Burt Lake, well-consolidated sand horizons interbedded

with the organic soil materials (possibly by ice-push ridging) refused the McCauley auger. For these profiles, we used an AMS slide-hammer sampler (split-wall corer 5.2 cm in diameter, 30 cm in length, with clear polycarbonate liners) to sample the alternating organic/mineral horizons until reaching the recognizable lithologic discontinuity with the underlying Lake Nipissing lake floor.

In autumn 2015, after soil sampling activities were complete in the 10 ha study area, we perceived the need to acquire greater resolution in our density of soil thickness measurements. At that time, we visited points on the systematic grid covering the study area (Fig. 1) and used a high-resolution GPS (Trimble R1 GNSS, ~1 m accuracy) to make soil thickness measurements with fiberglass push probes at 81 locations. In combination with the soil thickness measurements we collected using the same technique at the 39 soil profile sampling locations, these measurements provided 110 locations distributed at a range of densities across the study area for interpolating the soil thickness.

2.3. Soil processing and analysis

In the lab, we air-dried, weighed, homogenized, coarse-ground (mortar and pestle), and sieved (2 mm) each volumetric genetic horizon sample collected in the field. We archived most of the material from each sample after sieving, reserving a 10–30 g split from each for oven drying (105°), ball milling, and analysis. Analyses, which were performed in the UMBS Analytical Chemistry Laboratory, included C and N concentrations and stable isotope signatures (Costech Analytical CHN analyzer [Costech Analytical, Valencia, CA, USA] coupled to a Finnigan Delta Plus XL isotope ratio mass spectrometer [Thermo Scientific, West Palm Beach, FL USA]), and total Hg (THg) concentration by U.S. EPA method 7473 on a Milestone DMA-80 automated mercury analyzer (Milestone Inc., Shelton, CT, USA). We determined pH on 5 g subsamples taken from the air-dried, homogenized archived material using an Accumet AB15 probe and a 2:1 water:soil slurry. As was the case with soil sampling, these processing and analysis procedures took place over several years (2014–2016), with subsets of samples analyzed in batches as time and resources permitted. Therefore, while our methods were consistent throughout, not all parameters reported in the results have the same number of observations. In other words, while these efforts established an extensive and reasonably complete basic characterization dataset, not every soil sample was run for every analyte.

To add greater detail to our soil characterization dataset, we selected individual horizons from three spatially separated, representative Tawas profiles within the 10 ha study area for additional analyses of organic matter composition and radiocarbon. We took these samples from our archive of homogenized samples, and performed analyses on several distinct splits taken from each. To obtain an index of the degree of molecular weight or condensation of soluble organic matter in different horizons (*sensu* Thurman, 1985), we performed pyrophosphate extraction and UV-Vis spectroscopy (Lambda 35 spectrometer, PerkinElmer, Shelton, CT, USA). Our intent for this procedure was to measure absorbances and absorbance ratios that generally approximate the degree of molecular condensation of the soluble phase of these organic soils (Chen et al., 1977). To make inferences related to the relative age and turnover time of C held in different horizons, we prepared archived sample splits for radiocarbon (^{14}C) analysis by graphitization (Vogel et al., 1987), followed by measurement by accelerator mass spectrometry at Lawrence Livermore National Laboratory (Davis et al., 1990). Radiocarbon abundances were normalized to the international radiocarbon standard, oxalic acid 1, and corrected for mass-dependent fractionation according to Stuiver and Polach (1977). Radiocarbon data are provided in Supplementary Table 1; in this manuscript we emphasize soil ^{14}C values according to $\Delta^{14}\text{C}$ notation, as that is the most direct metric of ^{14}C abundance, carries fewer assumptions and has a lower risk of mis-interpretation compared to other notations. We also present and discuss modeled mean residence times and calibrated soil ^{14}C ages, in order to provide long-term

historical context for soil formation. Lastly, we analyzed a split from each of the archived samples used for radiocarbon measurement using Fourier transform infrared spectroscopy (FTIR). For this analysis, we used FTIR data for each sample including overall raw spectra, individual peak areas, and peak area ratios as indices of the functional groups present in the organic matter samples, and also used these indices of composition as correlates in statistical analyses exploring relationships between soil properties. To prepare samples for analysis, we mixed them with KBr in a 1:50 mass ratio, ground them to a fine powder, and pressed them into pellets. We then collected FTIR spectra by transmission through the pressed KBr pellets using a Nicolet iS5 FT-IR spectrometer (Thermo Electron Scientific Instruments LLC, Madison, WI USA) and a pure, pressed KBr pellet for background subtraction. We recorded spectra from 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} and an average of 64 scans. We applied automatic baseline correction to remove distortions, and integrated peaks with Origin 7.5 software (OriginLab Corporation, Northampton, MA USA). We assigned peaks according to Heckman et al. (2011) and Lehmann and Solomon (2010), and interpreted peak areas and peak area ratios as indices of functional group composition.

The final steps of our laboratory and analysis procedures involved computation of oven-dry sample masses, bulk density values, and elemental stocks (mass densities). We used air-dry to oven-dry corrections to convert the every air-dried sample mass recorded at the time of initial processing to an oven-dry basis. We computed the whole soil bulk density as the quotient of the oven dry mass and the volume of the sample as collected in the field. We encountered no rocks in these soils, so corrections for rock volume were not necessary. We used bulk density values to scale C and THg concentrations and horizon thicknesses up to stocks in Mg ha^{-1} and g ha^{-1} , respectively.

2.4. Water table measurements

We measured the depth to water table in 19 shallow monitoring wells distributed along 2 transects running roughly parallel (SW-NE) to the Burt Lake shoreline (Fig. 2). Wells were located roughly evenly along each transect, at a random distance of 5–15 m perpendicular to each transect. We constructed the wells using PVC well points (5.2 or 3.2 cm diameter, 122 or 152 cm length) with fine slotting along their entire lengths. We deployed each well to a depth of contact with the dense, underlying, sandy Lake Nipissing substrate (35–125 cm), and used couplings and non-slotted PVC standpipes where necessary to extend the top of each well above the typical snow line to allow for winter and spring measurements. We measured the depth to the water table using a flat tape water level meter (Model 101B, Solinst Inc., Georgetown, ON, CA) approximately weekly from November 2015 through November 2016, and corrected each reading for the height of the standpipe such that the depth recorded in the field was equal to the depth of the water table below the ground surface. For purposes of broadly contextualizing this yearlong data record, we also report water table depths from 1992 (August), 2014 (October), and 2015 (July–September) in the Results. Importantly, these results are for different locations than areas we sampled with the 2 water table well transects described above. Data for 1992 come from 6 locations in the larger 153 ha area of this wetland ecosystem type, distributed broadly across the 4000 ha UMBS property (Zogg and Barnes, 1995). Data for 2014 and 2015 were taken from our direct observations of water table depths during soil sampling (Section 2.2). Because nearly all of our soil observations (October 2014 to August 2015) were in places where no wells were subsequently deployed or sampled (November 2015 to November 2016), we stress that these supplementary water table observations are strictly for general context and are not appropriate for direct, statistical comparisons.

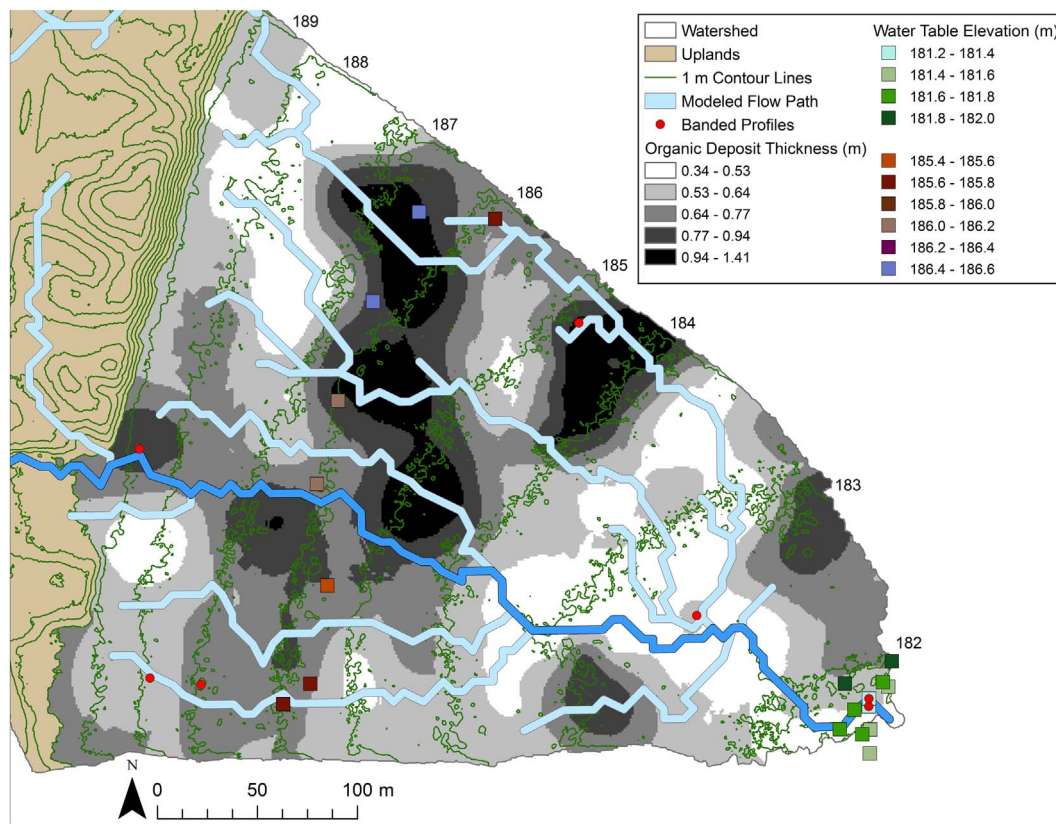


Fig. 2. Map of the 10 ha wetland study area, located between present day Burt Lake (181 m) and the postglacial Lake Nipissing shoreline (190 m). Map shows 1 m elevation contours (green lines and black text), modeled surface flow channels (blue lines), interpolated soil thickness (white to black shading), locations of interbedded sand-organic soil profiles (red points), and mean water table elevations (green to purple squares). Water table elevations are displayed for the locations with permanent water table monitoring wells. The darker blue flow channel highlights the main stem of Honeysuckle Creek, the lowermost ~400 m of which is perennially connected by flowing surface water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.5. Geospatial data derivation

We used a 0.3×0.3 m Digital Elevation Model (DEM) derived from a 2015 aerial LiDAR survey to delineate the Honeysuckle Creek watershed boundary. We also used the DEM to model flow channels based on topography using the Flow Direction and Flow Accumulation Tools in ArcGIS 10.4.1 (ESRI, Inc., Redlands, CA). We set the width of the modeled flow channels to 2 m, which is the width of the Honeysuckle Creek channel where it is observable on the lake plain wetland. We estimated water table elevation from the depth of water below the ground surface (using the wells described in Section 2.3) and the DEM-derived elevation at each well point. To interpolate the soil thickness throughout the wetland between the measurement points, we used variogram and kriging methods. To accomplish this, we first calculated an empirical variogram from the 110 measured soil thicknesses to provide information on the spatial autocorrelation of the data. Next, we fitted a spherical variogram model to the empirical model with a nugget of 0.0079, partial sill of 0.0677, and range of 50.43. We calculated empirical and fitted variograms in R (R Core Team, 2015; Bivand et al., 2013; Pebesma, 2004; Pebesma and Bivand 2005) with the “sp” and “gstat” package, and we used the Kriging Spatial Analyst Tool in ArcGIS 10.4.1 to perform the ordinary kriging using the fitted variogram model to generate a soil depth raster for the portion of the lake plain wetland within the watershed area.

2.6. Data analysis

We performed statistical analyses of soil properties using SigmaPlot (SYSTAT Software, San Jose, CA USA) to conduct parametric tests including ANOVA, *t*-tests, Pearson correlation, and regression (best

subsets and linear). We conducted these tests using an iterative process, intended to first test whether soil samples (i.e., individual horizons) consisting of different matrix materials differed in their properties, and then test for underlying sources of variation in the properties of these individual soil samples (horizons). For the first step, we used one-way ANOVA to test whether key physical and chemical properties differed between litter/fibric, hemic/sapric, and mucky mineral soil materials, noting that response parameters (e.g., C and THg concentrations, pH, C and N isotope signatures) frequently had skewed or bi-modal distributions and non-constant variances. Rather than attempt transformations to fit data from obviously different populations (soil matrix materials) into a single normal distribution, we accepted the ANOVA results from this first set of tests as pedogenically reasonable at face value, and then for the second step of our analyses conducted separate tests for organic (i.e., litter/fibric and hemic/sapric) vs. mucky sand soil materials. In this second step of our analysis, most response parameters for the two types of soil materials (organic vs. mucky sand) had normal distributions, though we used $\ln$ -transformations in the few cases necessary to achieve normal distributions and constant variances. In this step, we also parsed the dataset according to a pedogenic interpretation. Specifically, we questioned whether, relative to the more prevalent non-banded, representative Tawas profiles (32), the 7 profiles consisting of interbedded layers of organic and mucky sand horizons represented a sufficiently different condition or mode of pedogenesis as to be tested separately. Therefore, in this step of our analysis, we performed the same set of tests thrice: once for samples from the representative Tawas profiles, once for samples from the banded organic/mucky sand profiles, and once for samples from both types of profiles collectively. In all cases, we ran best subsets regression to identify models relating soil properties (e.g., depth, pH, or spectral indices of individual samples) to

response parameters of interest (e.g., C, ^{14}C , or THg concentrations of those individual samples). We selected optimal models on the basis of their r^2 , adjusted r^2 (if multi-variate), and C-p statistics, and ran multiple linear regressions to determine model significance in terms of P values. By taking this approach, we intended to determine whether: 1) underlying relationships between soil properties exist and are consistent across samples from both profile types; 2) relationships exist for samples from one profile type but not the other; 3) relationships exist for samples from both profile types but have opposing signs. We found evidence for (1) and (2) but not (3), but in the interest of readability we do not present nor interpret all significant test results that emerged from this portion of the analysis in our [Results](#) and [Discussion](#) sections.

We also used parametric statistics to test for spatial patterns in soil thickness, C and Hg stocks, and water table depth. In these analyses, we were interested in three sets of questions. In the first, we asked whether soil thickness, profile total C or Hg stocks differed according to elevation (one-way ANOVA with three categories: 181–184 m, 184–187 m, 187–190 m) or dominant matrix materials (one-way ANOVA with three profile categories: L/F, H/S, banded organic/mucky sand). In the second, we asked whether the depth to water table differed significantly between the two shallow well transects; because we were not interested in temporal dynamics nor interactions in this study we used a t -test to compare means for wells from the inland transect vs. wells from the shoreline transect. For the third, we asked whether banded organic/mucky sand profiles tended to be more closely associated with the topographically predicted flow channels (t -test with banded vs. representative Tawas as groups, distance to modeled flow channel as response parameter). In these tests, as well as all those described above for individual soil samples (horizons), we accepted results as statistically significant when $P < 0.10$.

3. Results

3.1. Soil hydrologic, physical and chemical properties

Across the lake-plain wetland, water table depths averaged 12 cm below the soil surface throughout the period of observation (Fig. 3; November 2015 to November 2016), though they were significantly closer to the surface in the middle-elevation (interior) portions of the wetland than the lowest elevations near the present-day shoreline of Burt Lake (7 cm vs. 16 cm, t -test, $P < 0.001$). Expressed in terms of absolute elevation (Fig. 2), water table heights approximated the surface topography of the very gently sloping recessional Lake Nipissing plain. Soil samples (horizons) consisting of the three different types of matrix materials differed significantly in most physical and chemical characteristics (Tables 1 and 2). Bulk density was lowest for horizons consisting of litter and fibric (L/F) materials, intermediate for hemic and sapric (H/S) horizons, and highest for mucky sand (AC) soil horizons. Carbon concentrations and C/N ratios showed the opposite pattern, with the highest values in the L/F, intermediate values in the H/S, and lowest values in the AC horizons. Nitrogen and THg concentrations were higher in H/S materials than L/F materials, which were in turn higher than AC horizons. The $\delta^{13}\text{C}$ signature of AC horizons was significantly more enriched than H/S horizons, which were in turn enriched relative to L/F horizons. The $\delta^{15}\text{N}$ signature of bulk soil material was depleted in L/F horizons relative to H/S and AC horizons, which did not differ from one another. Lastly, pH was higher in H/S than L/F and AC horizons, which did not differ from one another.

3.2. Sources of variation in soil C and THg concentrations

Despite having significantly different C and THg concentrations, organic and mucky mineral soil materials had similar sources of variation in their C and THg concentrations, namely, indicators of

depositional setting and other soil chemical and physical properties. Among organic soil materials, horizons containing even traces of sand had significantly lower C and THg concentrations ($P < 0.001$) than those consisting purely of organic matter. Similarly, organic horizons from profiles interbedded with bands of mucky sand had lower mean C concentrations than organic horizons from representative Tawas profiles (35.4 vs. 39.4%, $P = 0.002$), but THg concentrations did not differ significantly for organic horizons from the two types of profiles. Within the banded organic/mucky sand profiles, C concentrations of the field-determined organic horizons ranged from 19.8% to 44.7%, and were positively related to N concentrations ($r^2 = 0.70$, $P = 0.005$) but not to other soil properties. Within the representative Tawas profiles, C concentrations of organic horizons ranged from 31.4% to 45.3%, and this variation was not predictable from any continuously varying soil properties. Total Hg concentrations were lower in L/F than H/S soil materials (140 vs. 196 ng g $^{-1}$, $P = 0.009$) in representative Tawas profiles, but there was no analogous significant difference between organic soil materials in banded organic/mucky sand profiles. Nonetheless, the same three-variable regression model was the best predictor of variation in organic horizon THg concentrations in both profile types. Specifically, the optimal model for organic horizon THg concentration included depth in profile (negative slope, Fig. 4), %C (negative slope), and %N (positive slope), though this predictive relationship was stronger for organic horizons from banded profiles ($r^2 = 0.89$, $P = 0.007$) than from representative Tawas profiles ($r^2 = 0.42$, $P < 0.001$).

Spectral data obtained for organic horizons taken from representative Tawas profiles revealed a number of relationships between soil chemical properties. Specifically, THg and N concentrations of organic soil materials were higher for samples whose pyrophosphate extracts had lower ratios of absorbance at 465 nm to 665 nm (E4:E6 ratios; Fig. 5). Extracts with lower E4:E6 ratios were also associated with solid phase material having significantly lower C concentrations and more enriched $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures (Fig. 6). Organic matter functional group characterization with FTIR analysis revealed no relationships between organic soil THg concentrations and the peak areas or peak area ratios of any specific functional groups. All organic soil horizons measured had similar spectra with prominent peaks for phenolic OH stretching (3380 cm $^{-1}$), carboxyl COO $^{-}$ stretching (1580 cm $^{-1}$), and, to a lesser degree C–O stretching associated with polysaccharides (1270 to 1040 cm $^{-1}$; Fig. 7). Underlying these generally similar spectra, there were significant correlations between functional group composition, $\delta^{15}\text{N}$ signatures, and depths within the profile. Organic horizons from deeper profile positions had significantly lower CH $_2$:aromatic peak area ratios, total polysaccharide:aromatic peak area ratios, and peak areas for a specific polysaccharide C–O stretching band (1081 cm $^{-1}$; Fig. 8). On the same samples, increasingly enriched $\delta^{15}\text{N}$ signatures were associated with decreases in the summed areas of all polysaccharide peaks, and increases in the peak areas of two aromatic functional groups (1270 and 1325 cm $^{-1}$; Fig. 9).

Similar to organic soil materials, depositional setting and other soil properties were significant sources of variation in soil C and THg concentrations in mucky mineral soil materials (AC horizons). In particular, AC horizons had lower C (8.7 vs. 18.8%, $P = 0.035$), and higher THg concentrations (27.8 vs. 4.9 ng g $^{-1}$, $P = 0.032$) when they were present as bands interbedded with organic horizons than when they were sampled as basal horizons at the bottom of representative Tawas profiles. Among all AC horizons, increasing C concentrations were correlated with increasing N concentrations ($r^2 = 0.70$, $P = 0.002$) and decreasing pH ($r^2 = 0.88$, $P = 0.063$). Total Hg concentrations increased with increasing $\delta^{15}\text{N}$ enrichment ($r^2 = 0.60$, $P = 0.022$), but, unlike organic horizons, there was no relationship with depth below the surface.

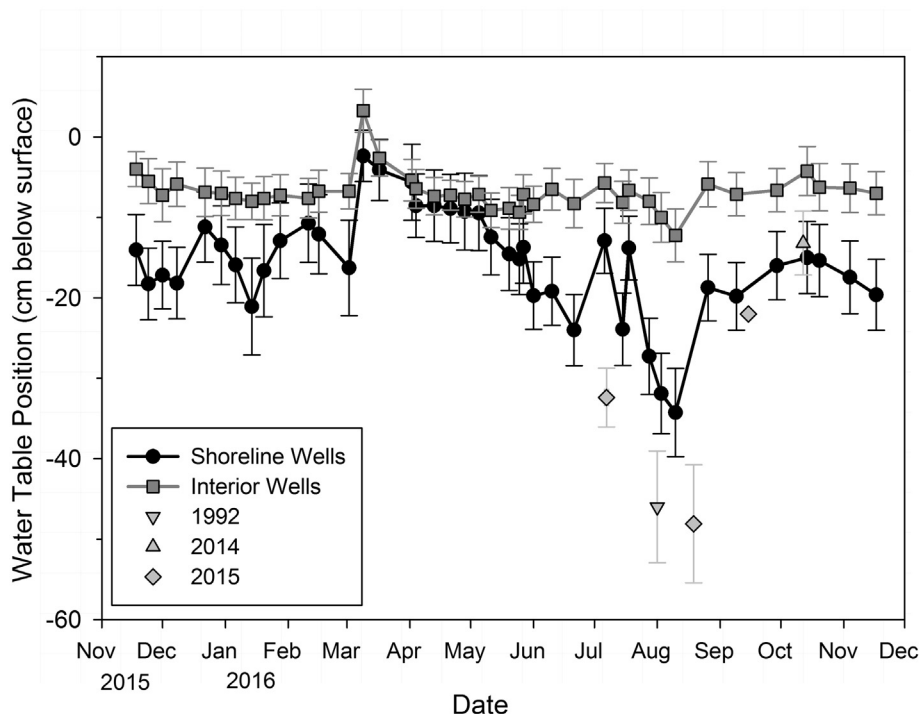


Fig. 3. Water table depths for the 10 ha study area. Time series data show the mean ($\pm$ SE) for 8 wells along the Burt Lake shoreline transect (black circles) and 8 wells along the interior transect (gray squares), observed every 1–3 weeks from November 2015 through November 2016. The mean water table differed significantly between these two transects across the overall period of observation ($P < 0.001$; 16 vs. 7 cm below the surface, respectively). To provide general context for this one year of observation, data collected by other methods in 1992, 2014, and 2015 are shown with individual gray points (mean $\pm$ SE). Contextualization data are from 6 water table wells across the larger area (153 ha) of this wetland ecosystem type on UMBS property, observed in August 1992 (Zogg and Barnes, 1995), as well as direct measurements taken during soil profile collection in October 2014 (10), July 2015 (19), August 2015 (7), and September 2015 (1).

3.3. Spatial patterns in profile C and Hg stocks; C turnover times in soil profiles

Profile total C storage averaged 394 Mg ha^{-1} , ranging from 119 to 961 Mg ha^{-1} . Most of the variation in profile total C storage was predictable from soil depth ($r^2 = 0.86$, $P < 0.001$), which ranged from 35 to 162 cm where observed at profile sampling locations (mean = 84 cm). Profiles consisting of different matrix materials (H/S, L/F, or banded) did not differ in their thickness nor total C storage (ANOVA, $P = 0.29$). The abundance of ^{14}C in organic soil horizons declined with increasing depth, driving increases in the modeled mean residence times of C with increasing depth (Fig. 10). Profile total THg storage averaged 167 g ha^{-1} , ranging from 74 to 318 g ha^{-1} and increasing significantly with soil depth ($r^2 = 0.57$, $P < 0.001$) and total C storage ($r^2 = 0.49$, $P < 0.001$). Similar to the profile total C storage, however, the types of matrix materials present did not influence profile total Hg storage. Soil depth and thus C and Hg stocks were greatest in areas in the intermediate elevations of this lake plain wetland (184–187 m), while profiles that were slightly higher in elevation ($> 187 \text{ m}$) or closer to Burt Lake ($< 184 \text{ m}$) had lesser amounts of accumulated soil material, C and Hg (Fig. 3, $P < 0.001$ for thickness, $P = 0.048$ for C, $P = 0.098$ for THg). Soils in the

Table 2

Carbon: nitrogen mass ratios and natural abundance stable isotope signatures (‰) by soil matrix material. Values for each parameter are the mean, standard deviation, and sample size; see Section 2.3 for information about sample analysis and number of observations for each parameter. Superscripts identify significantly different means at $P < 0.10$.

Matrix	C/N	σ	n	$\delta^{13}\text{C}$	σ	n	$\delta^{15}\text{N}$	σ	n
L/F	36 ^a	8	14	−27.00 ^a	1.44	17	−1.8 ^a	1.6	16
H/S	25 ^b	4	54	−26.26 ^b	0.77	62	−0.1 ^b	1.1	54
A/C	20 ^c	6	10	−24.90 ^c	3.26	16	−0.04 ^b	1.6	10

intermediate elevations averaged 83 cm deep, held 495 Mg C ha^{-1} , and $196 \text{ g THg ha}^{-1}$; in the higher and lower elevations of the wetland, soil depths averaged 53 and 56 cm, C stocks averaged 241 and 292 Mg ha^{-1} , and THg stocks averaged 126 and 132 g ha^{-1} , respectively. Soil profiles consisting of interbedded organic materials and mucky sand were found throughout the wetland across the range of elevations, but were significantly closer to modeled preferential flow channels than were the representative Tawas profiles (1.3 vs. 10.0 m, $P = 0.026$), indicating that the topographic flow routing model effectively captured the spatial distribution of the banded soils.

Table 1

Bulk density (g cm^{-3}), pH, total C and N concentrations (%), and total Hg concentration (ng g^{-1}) by soil matrix material. Matrix material categories are L/F (litter and fibric materials field designated as Oi horizons), H/S (hemic and sapric materials field designated as Oe and Oa horizons), and A/C (mucky sand and sandy muck materials present either as bands interbedded with organic soil materials or as basal horizons in representative Tawas profiles). Values for each parameter are the mean, standard deviation, and sample size; see Section 2.3 for information about sample analysis and number of observations for each parameter. Superscripts identify significantly different means at $P < 0.10$.

Matrix	Db	σ	n	pH	σ	n	%C	σ	n	%N	σ	n	THg	σ	n
L/F	0.08 ^a	0.08	18	6.1 ^a	0.59	5	40.6 ^a	2.8	16	1.2 ^a	0.23	14	137 ^a	43	15
H/S	0.16 ^b	0.12	90	6.5 ^b	0.19	44	38.3 ^b	4.1	54	1.5 ^b	0.28	54	191 ^b	68	62
A/C	0.79 ^c	0.39	21	6.0 ^a	0.87	4	11.9 ^c	7.7	10	0.58 ^c	0.29	10	29 ^c	34	9

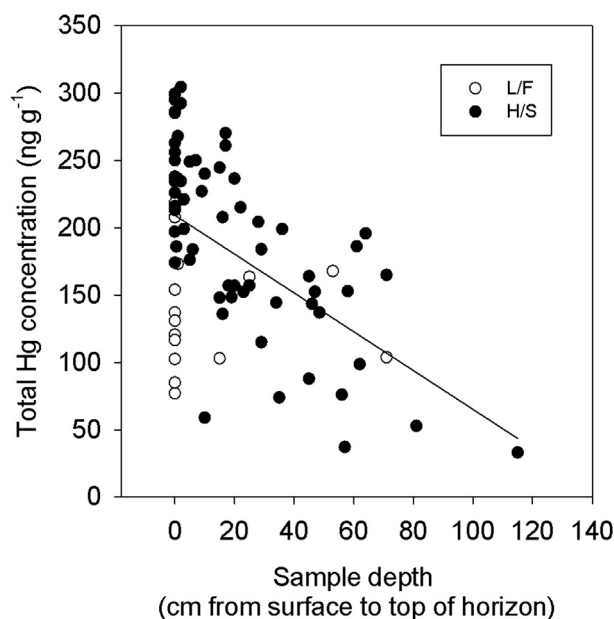


Fig. 4. Organic soil THg concentrations decline with depth. Points represent individual organic soil horizons (open circles are litter and fibric horizons; filled circles are hemic and sapric horizons) from representative Tawas and banded organic/mucky sand profile types. Depth is expressed as the depth of the horizon's upper boundary beneath the soil surface. In either profile type, a three-parameter linear regression model including depth, %C and %N was the optimal model (Section 3.2).

4. Discussion

The soils in the 10 ha area of lake plain wetland in the Honeysuckle Creek watershed hold organic matter stocks that are quite variable in space, and much larger than upland forest soils on this landscape (Gough et al., 2007; Pregitzer et al., 2008), or across the Great Lakes region (Grigal and Ohmann, 1992). Compared other wetland soils in the Great Lakes region, the C densities we report here are rather low, reflecting the relatively shallow deposits of accumulated organic matter at our site. Weishampel et al. (2009) reported mean stocks of 600 and 1500 Mg C ha⁻¹ in spruce bogs and peatlands of northern Minnesota, respectively, where mean peat depths were ~2.5 m. In a statewide survey of peat resources in Michigan (LeMasters et al., 1984), organic soil depths ranged from 1.3 to 2.1 m across the northern part of the state. The same survey showed that C concentrations fell within a fairly narrow range (43–56% C); thus, the principal source of variation in total C stocks in Michigan is the depth of the deposits. Compared more broadly to peatlands across North America, the soils we describe here also have a relatively low C density, compared to the median estimate of 1500 Mg C ha⁻¹ in Bridgman et al. (2006). However, while the C stocks of the soils we describe here are low, their composition is broadly representative. In our study, 87 of 108 organic horizons encountered consisted of sapric materials, and across the conterminous U.S., the well-decomposed Saprists represent 80% of peatlands (Bridgman et al., 2006).

In contrast to their C stocks, soils in our study wetland hold considerably more THg than forest and wetland soils from the broader Great Lakes region. In an intensively studied watershed in northern Minnesota, Grigal et al. (2000) reported mean THg concentrations of 18 and 45 ng g⁻¹ for upland mineral and bog organic soils, respectively, constituting stocks of 52 and 39 g ha⁻¹. In a west-to-east survey of soil THg from Minnesota to Michigan, Nater and Grigal (1992) reported soil organic horizon THg concentrations ranging from ~120 to 190 ng g⁻¹, which increased along the eastward transect and were highest in Michigan. Mineral soil THg concentrations were in the 20–30 ng g⁻¹ range throughout, and based upon deep mineral soil samples there appeared to be no substantial geologic sources of Hg in the region. This

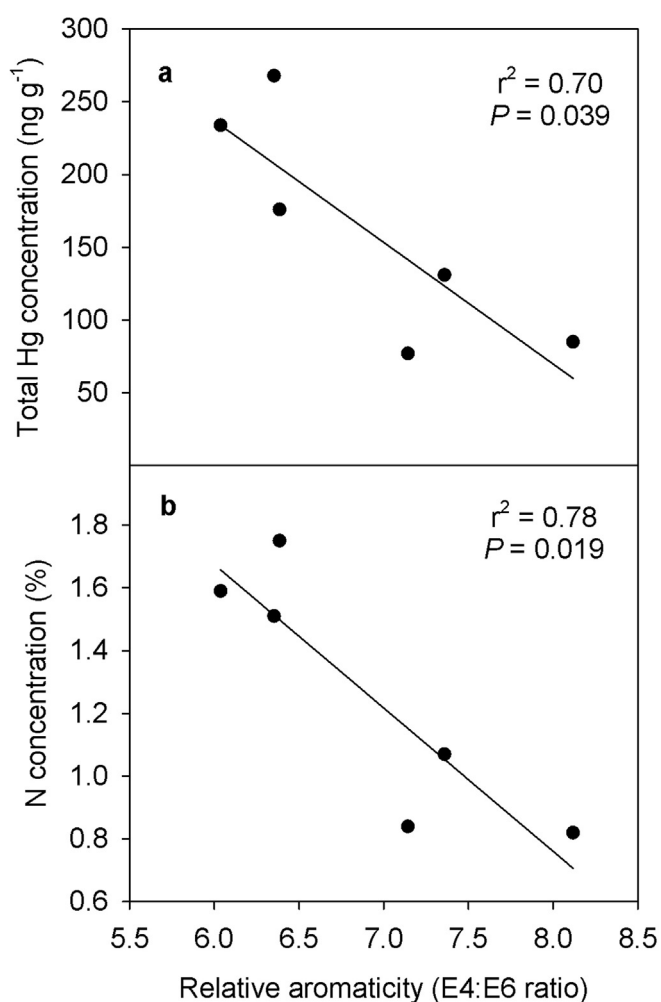


Fig. 5. Organic soil materials having lower E4:E6 ratios in their pyrophosphate extracts have higher THg (panel a) and N (panel b) concentrations. Points represent 8 individual horizons from three representative, organic soil profiles collected throughout the 10 ha study area. Best-fit lines and statistics are from linear regression.

fits the broader pattern across the U.S. and Canada, where (mineral) topsoils have THg concentrations ranging mostly between 20 and 50 ng g⁻¹, geologic sources of Hg are essentially restricted to the west, and atmospheric deposition dominates in the east (Woodruff et al., 2009). Thus, wetlands located in areas of even higher atmospheric deposition, such as the Adirondacks of northern New York, have higher THg concentrations than our study site. Demers et al. (2013) and Selvendiran et al. (2008) studied a range of wetland soils in that region, varying in depths, organic materials, and locations (headwaters, riparian flats, beaver meadow). At those sites, organic soils had THg concentrations between 100 and 300 ng g⁻¹ in the upper 50 cm and 20–50 ng g⁻¹ in deeper depths. Given these higher concentrations, as well as deeper organic deposits, profile total THg stocks were also higher than we report for our site in Michigan, with values in the 170–240 g ha⁻¹ range for riparian deep peat profiles (5–6 m deep) and 100–200 g ha⁻¹ for headwater peatlands (7 m deep). Across all of these studies, Hg concentrations are closely linked with C concentrations, especially in the top ~1 m of the soil profile, where organic materials have accumulated during the era of atmospheric Hg deposition.

At our study site and many others with organic soils, soil depth is a good predictor of spatial variation in organic matter and C stocks (Chimner et al., 2014; Parsekian et al., 2012). Given the widespread applicability and straightforward technique of measuring soil depth and the relationship between C and Hg concentrations, empirical estimates of C and Hg stocks are possible for wetlands with generally similar soil

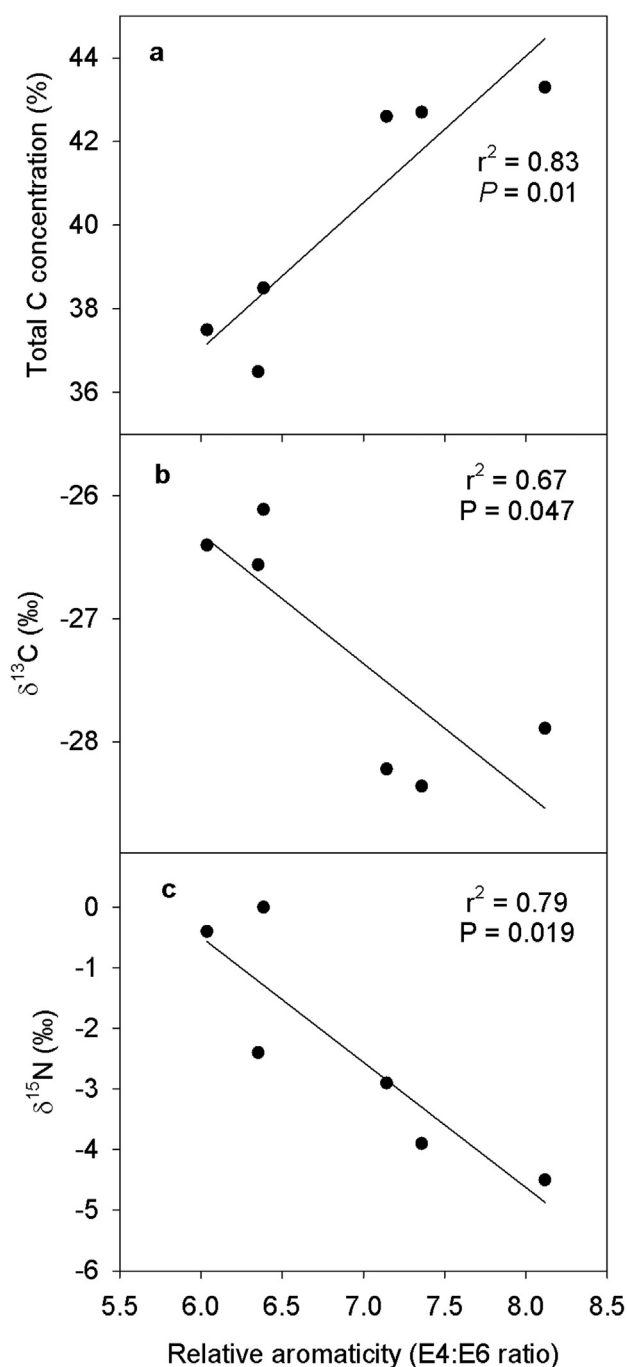


Fig. 6. Organic soil materials having lower E4:E6 ratios in their pyrophosphate extracts have lower C concentrations (panel a), and more depleted $\delta^{13}\text{C}$ (panel b) and $\delta^{15}\text{N}$ (panel c) signatures. Points represent 8 individual horizons from three representative, organic soil profiles collected throughout the 10 ha study area. Best-fit lines and statistics are from linear regression.

physical and chemical characteristics. However, while this general approach is transferrable across sites, site-to-site differences in factors such as the type of organic soil materials, historic Hg deposition rates, or geologic Hg sources exclude the direct application of our results to other sites. The need for caution is compounded by the lack of any mechanistic factor for predicting spatial variation in soil depth at our site. Given that soils are deeper in the middle elevations of the wetland, where the water table was higher and more consistent during the year of continuous observation, it is possible that the elevated water table in this part of the wetland is a long-term feature that has driven greater organic matter accumulation. It is also possible that water table depths

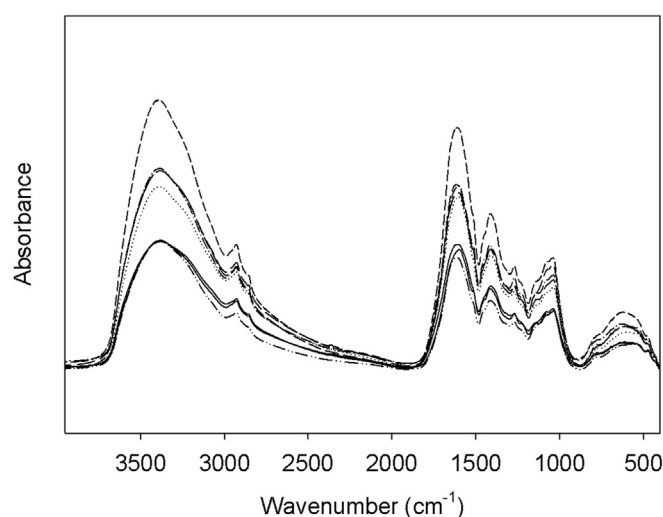


Fig. 7. FTIR spectra (absorbance) for 8 individual horizons from three representative, organic soil profiles collected throughout the 10 ha study area. Individual horizons are differentiated by their unique line styles, but owing to their overall similarity in functional composition are not identified individually. Best-fit lines and statistics are from linear regression.

overall, or the difference in water table depths between the interior and shoreline portions of the wetland are not representative of the long time period during which these soils have formed. The Tawas series concept, revised in 2006, indicates water tables from 0 to 30 cm of the soil surface throughout the year. In this regard, our year of water table observations fits well within representative hydrologic conditions. Likewise, recent observations from UMBS support a similar seasonal pattern (low in summer months, increasing in autumn), and point observations of low water tables (July and August 2015, August 1992) are from known multi-month dry periods (precipitation data from UMBS extend back to 1912). On the other hand, if fairly short (multi-month) dry periods are sufficient to lower water tables by 20 cm or more, this suggests that saturation in our study area is maintained by fairly recent groundwater, and indicates that C and Hg cycling processes within them may respond abruptly to climate variability and change. Given the well-known dependence of processes such as C mineralization, methanogenesis, and Hg methylation on moisture content and redox potential in organic soils (Bridgman et al., 1998; Taggart et al., 2012; Updegraff et al., 1995), climate-driven changes in hydrology may have substantial impacts on the C and Hg stocks held in these soils.

Whether or not water table data from the recent past are representative of long-term hydrology or have any predictive value in assessing spatial patterns in total C and Hg stocks, variation in the depth distribution of these elements is important. In this study, preferential flowpaths modeled from topographic inputs—presumably stable over time—indicate that hydrologic forces create distinct soil morphologies and depth distributions of C and Hg. Specifically, the presence of flowing water at some time, indicated by banded profiles in locations predicted by the topographic model, creates sharp discontinuities in the depth distribution of C and Hg. It is unclear whether these banded profiles represent abandoned surface water flowpaths that developed concurrently with upward accumulation of organic materials during soil formation, if their genesis is reinforced in situ by water table flow, or both. Regardless, the different particle densities of mucky sand vs. organic horizons suggest intermittent changes in depositional velocity, and the difference in hydraulic conductivity between the two soil materials suggests potential for preferential flow in the mucky sand horizons. Where these flowpaths are laterally continuous, preferential flow could allow for loss of C via hydrologic export to Burt Lake in dissolved phase, e.g., during “flushing” events triggered by precipita-

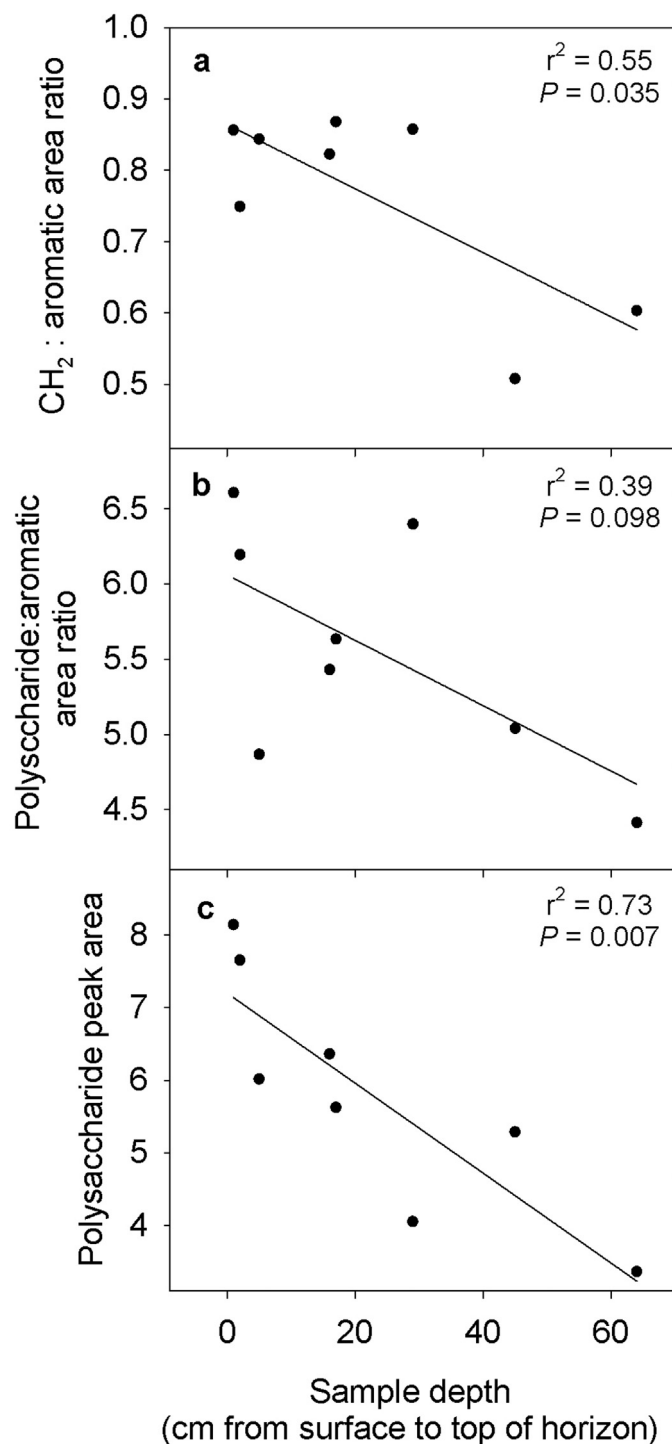


Fig. 8. Deeper horizons have lower CH_2 :aromatic (panel a) and total polysaccharide:aromatic (panel b) ratios, and smaller polysaccharide peak areas (panel c). These FTIR data are for 8 individual horizons from three representative, organic soil profiles collected throughout the 10 ha study area, and depth is expressed as the depth of the horizon's upper boundary beneath the soil surface. Best-fit lines and statistics are from linear regression.

tion following dry periods (Inamdar et al., 2004; Schiff et al., 1998). Particulate phase exports, whether via surface water flow channels or through the highly conductive sandy matrix, could also drive exports of C from these banded profiles (Kolka et al., 1999, 2001; Schuster et al., 2008). Indeed, we found that organic and mucky sand horizons both had lower C concentrations when present in banded profiles than in representative Tawas profiles, suggesting possible loss of C. In contrast,

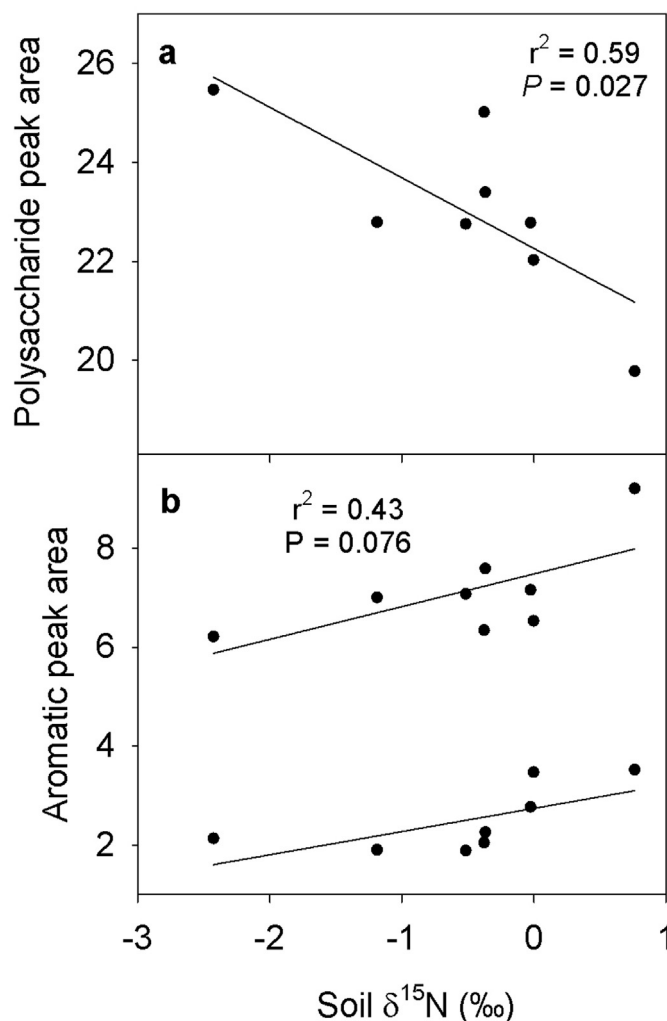


Fig. 9. Total area of all polysaccharide peaks decreases (panel a), and areas of two aromatic peaks increase (panel b), with increasingly enriched $\delta^{15}\text{N}$ signatures in organic soil horizons. These FTIR data are for 8 individual horizons from three representative, organic soil profiles collected throughout the 10 ha study area. Best-fit lines and statistics are from linear regression.

THg concentrations of mucky sand horizons were higher when interbedded with organic horizons, and did not vary with depth, suggesting that they may be accumulating Hg as they act as conduits for preferential flow. In terms of the potential for hydrologic export of C and Hg into adjacent Burt Lake, preferential flowpaths are all the more important, because the largest C and Hg stocks are not located directly adjacent to the lake, but rather in the intermediate elevations of the wetland. This corresponds to a 200–300 m buffer distance in this low-relief landform, where disturbances or management activities that mix organic and mineral soil materials could establish new flowpaths for transporting C and Hg stocks from soils to surface waters (Kolka et al., 2001; McLaughlin et al., 2011; Trettin et al., 2011). Future studies from this watershed will address management activities, hydrologic C and Hg concentrations and fluxes, in order to identify the magnitude, timing, and route of C and Hg exports to Burt Lake.

Despite their semi-quantitative, relatively coarse insights into organic matter composition, the spectroscopic assays we applied to this analysis offer several important considerations about the organic soil materials in this wetland. First, UV–Vis spectra from pyrophosphate extracts support the notion more energetically favorable, plant litter-like substrates are preferentially degraded during the gradual accumulation of organic matter in these soils. Evidence for this comes from the results that organic soil materials having more condensed soluble

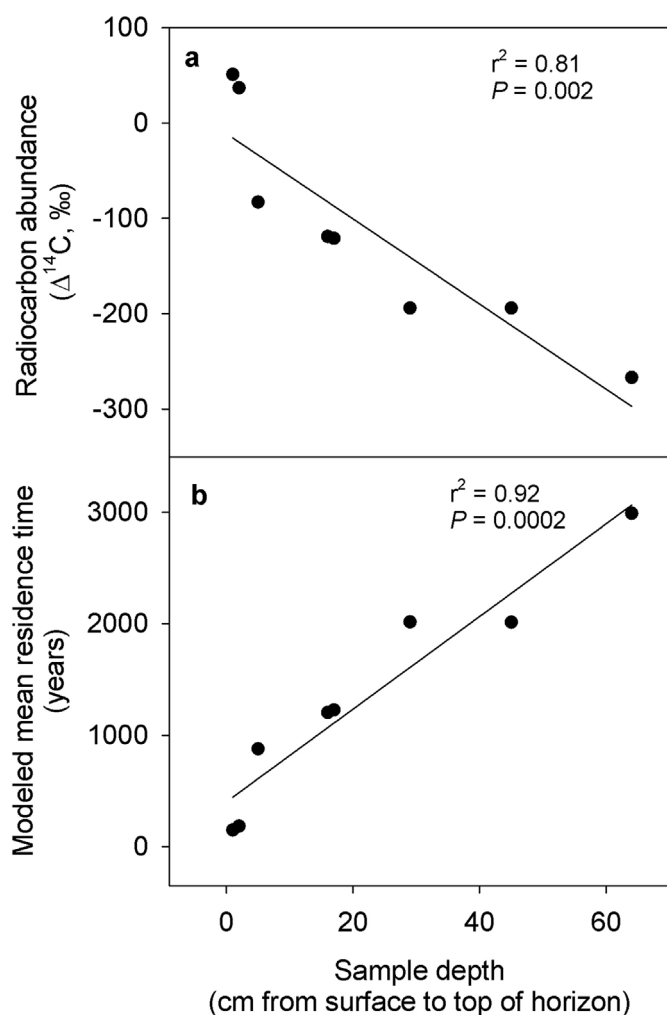


Fig. 10. Radiocarbon abundance decreases (panel a), and modeled mean residence time of C increases (panel b) with depth in organic soil horizons. Points represent 8 individual horizons collected from three representative soil profiles throughout the 10 ha study area. Depth is expressed as the depth of the horizon's upper boundary beneath the soil surface. Best-fit lines and statistics are from linear regression.

organic matter (i.e., lower E4:E6 ratios) had lower C concentrations, more enriched ^{13}C and ^{15}N signatures, and higher N and THg concentrations, contextualized by studies that generally correlate the E4:E6 ratio with organic matter molecular weight, condensation, or aromaticity (Carter and Gregorich, 2006; Chen et al., 1977; Thurman, 1985). Importantly, this method by itself has no direct, molecular-scale insight, and the lack of similar relationships between soil chemical properties and FTIR spectra indicates the need for caution in overgeneralizing this interpretation. In fact, FTIR spectra reveal that while these organic materials are high in aromatic moieties, which may be less energetically favorable substrates for microbial metabolism, they also contain considerable quantities of less condensed (presumably more labile) polysaccharides. This is especially true for horizons nearer the surface, which based on their radiocarbon results consist of more recently-deposited materials (enriched ^{14}C signatures) with faster turnover times (modeled mean residence times). The key inference of these insights into functional group composition is that overall, the organic materials in these soils are not themselves inherently recalcitrant, and absent any chemical stabilization mechanisms, lowering of water tables exposes readily oxidizable substrates to C mineralization. This exposes the climate vulnerability of these soils, both in hindsight across warm, dry periods millennia in the past (Booth et al., 2006; Booth and Jackson, 2003), and looking to the future, with recent and anticipated increases in temperature and evaporation in this region

(Kim et al., 2016; Magnuson et al., 1997).

The soils in this wetland ecosystem are best appreciated in their historic, landscape-level context, and ^{14}C data are a key ingredient in establishing this context. Although the oldest calibrated ^{14}C age observed in the dataset (2431 yr for the deepest sample) cannot be interpreted as an absolute date for the initiation of soil development, it does suggest that organic matter accumulation on this lake-plain landform began not long after the lowering of the postglacial Lake Nipissing. The principal reason why calibrated ^{14}C ages may not be accurate at face value pertains to atmospheric nuclear weapons testing (i.e., the “bomb spike”), which has led to a globally elevated ^{14}C signature of the atmosphere since the 1950s. As a result, C that has been fixed via photosynthesis and subsequently input to soil since 1950 has a highly enriched ^{14}C signature, and even small amounts of downward movement of this material can substantially “modernize” the apparent ^{14}C age of bulk soil materials at greater depth (Stuiver et al., 1998; Torn et al., 2009). Thus, the oldest C held within the deepest soils of this lake plain wetland are likely older than 2431 years. Taking a regional physiographic view of the setting in which these soils formed, Lake Nipissing was a high lake stage initiated ~5000 years B.P. when post-glacial crustal rebound closed the North Bay outlet in Lake Huron, raising lake levels in the Michigan-Huron basin. In the vicinity of our study site, the maximum water plane of Lake Nipissing was located at a (modern-day) elevation of 189–190 m, where it remained until ~4000 years B.P. (Spurr and Zumberge, 1956). During the subsequent 500 years, downcutting of the modern-day Port Huron outlet at the southern end of Lake Huron gradually lowered the regional water plane, which stabilized at contemporary levels by about 3000 years B.P. (Hough, 1958; Lewis, 1970). Thus, with about 3 millennia available for soil formation on the sandy Lake Nipissing plain at our study site, the range of observed profile thicknesses suggests median net organic matter accumulation rates of 4.3 cm vertical per century (range = 1–7 cm) or $0.13 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$ (range = $0.04\text{--}0.32 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$). These rates are in the middle of the range reported for peatlands in the boreal zone, but as with their total C stocks, at the low end of the range for peatlands in the conterminous U.S. and Mexico (Gorham, 1991; Bridgman et al., 2006).

In many northern wetland ecosystems, fire is a leading cause of C and Hg export from organic soils (Frolking et al., 2011; Turetsky et al., 2006, 2011; Kolka et al., 2014), highlighting a key distinction of our study site. In our study wetland, the absence of charred stumps from the early 20th century (common on adjacent uplands) from all but the extreme southern boundary, and the presence of only a single fragment of macroscopic charcoal in the entire sample set suggests that fires may not have substantially impacted these soils, nor their accumulation of C and Hg stocks. Thus, it is likely that the chief mechanisms of C export from this soil are via hydrologic transport or oxidative respiration. Ruling out catastrophic losses due to fire, it becomes likely that hydrologic transport and oxidative respiration are the main mechanisms for C loss from these soils, and long-term rates of forest biomass production (C inputs) can be used to constrain their net C balance. On the UMBS landscape, median aboveground biomass production rates on lake-plain wetlands and outwash plains are 0.5 and $0.8 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$, respectively (Nave et al., 2017). Compared to net rates of soil C accumulation ($0.04\text{--}0.32 \text{ Mg C ha}^{-1} \text{ yr}^{-1}$, calculated by dividing the profile total C stocks by a landform age of 3000 years), annual biomass production rates are quite large. Assuming that all biomass is eventually input to soil as detritus over the time frame recorded by these organic soils, this approximation suggests that most of the organic matter produced in this ecosystem does not persist in the soil. While this exercise is predicated on significant assumptions about the past, its inferences are supported by our overall results and the context provided by other studies. Namely, organic soils in this wetland are shallower than most across the region and the conterminous U.S., consist of well-decomposed organic materials, and are located in a setting where variable water table depths can expose significant

quantities of fairly labile C to aerobic decomposition. Thus, even though this wetland holds the some of the oldest, largest C pools on its landscape, these stores are not static.

5. Conclusion

Soils of this lake-plain wetland exhibit wide variation in their C and Hg stocks, which is tied to variation in soil depth. Semipermanent saturation drives accumulation of these predominantly organic soils, and although they consist mostly of well-decomposed sapric organic matter high in aromatic functional groups, substantial quantities of polysaccharides are present and presumably available as a labile substrate for C mineralization during occasional dry periods. Subtle, topographically-mediated hydrologic flowpaths, on the surface and within soil profiles consisting of interbedded organic and mucky sand horizons, produce sharp discontinuities in C and Hg concentrations, and have the potential to act as preferential flowpaths linking wetland soils with the adjacent inland lake. Compared to other peatlands of the Great Lakes region and North America, the soils here are shallower and hold less C; however, Hg concentrations are similar to northeastern U.S. wetlands, where atmospheric Hg deposition rates are greater.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.geoderma.2017.05.035>.

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References

- Aselmann, I., Crutzen, P.J., 1989. Global distribution of natural fresh-water wetlands and Rice paddies, their net primary productivity, seasonality and possible methane emissions. *J. Atmos. Chem.* 8 (4), 307–358.
- Bartlett, K.B., Harriss, R.C., 1993. Review and assessment of methane emissions from wetlands. *Chemosphere* 26 (1–4), 261–320.
- Bivand, R.S., Pebesma, E., Gomez-Rubio, V., 2013. *Applied spatial data analysis with R*, Second edition. Springer, NY.
- Blazewski, G.A., Stolt, M.H., Gold, A.J., Gurwick, N., Groffman, P.M., 2009. Spatial distribution of carbon in the subsurface of riparian zones. *Soil Sci. Soc. Am. J.* 73 (5), 1733–1740.
- Blewett, W.L., Winters, H.A., 1995. The importance of glaciofluvial features within Michigan's Port Huron moraine. *Ann. Assoc. Am. Geogr.* 85, 306–319.
- Bockheim, J.G., Hinkel, K.M., Eisner, W.R., Dai, X.Y., 2004. Carbon pools and accumulation rates in an age-series of soils in drained thaw-lake basins, Arctic Alaska. *Soil Sci. Soc. Am. J.* 68 (2), 697–704.
- Boelter, D.H., Verry, E.S., 1977. Peatland and water in the northern lake states. In: USDA-Forest Service General Technical Report NC-31, (26pp).
- Booth, R.K., Jackson, S.T., 2003. A high-resolution record of late-Holocene moisture variability from a Michigan raised bog, USA. *The Holocene* 13, 863–876.
- Booth, R.K., Notaro, M., Jackson, S.T., Kutzbach, J.E., 2006. Widespread drought episodes in the western Great Lakes region during the past 2000 years: geographic extent and potential mechanisms. *Earth Planet. Sci. Lett.* 242, 415–427.
- Bridgman, S.D., Pastor, J., Janssens, J., Chapin, C., Malterer, T., 1996. Multiple limiting gradients in peatlands: a call for a new paradigm. *Wetlands* 16, 45–65.
- Bridgman, S.D., Updegraff, K., Pastor, J., 1998. Carbon, nitrogen, and phosphorus mineralization in northern wetlands. *Ecology* 79 (5), 1545–1561.
- Bridgman, S.D., Megonigal, J.P., Keller, J.K., Bliss, N.B., Trettin, C., 2006. The carbon balance of North American wetlands. *Wetlands* 26 (4), 889–916.
- Buffam, I., Turner, M.G., Desai, A.R., Hanson, P.C., Rusak, J.A., Lottig, N.R., Stanley, E.H., Carpenter, S.R., 2011. Integrating aquatic and terrestrial components to construct a complete carbon budget for a north temperate lake district. *Glob. Chang. Biol.* 17, 1193–1211.
- Carter, M.R., Gregorich, E.G., 2006. *Soil Sampling and Methods of Analysis*, second ed. Taylor and Francis Publishers, Boca Raton, FL, USA (198pp).
- Chaplot, V., Walter, C., Curmi, P., 2000. Improving soil hydromorphy prediction according to DEM resolution and available pedological data. *Geoderma* 97 (3–4), 405–422.
- Chen, Y., Senesi, N., Schnitzer, M., 1977. Information provided on humic substances by E4/E6 ratios. *Soil Sci. Soc. Am. J.* 41, 352–358.
- Chimner, R.A., Ott, C.A., Perry, C.H., Kolka, R.K., 2014. Developing and Evaluating Rapid Field Methods to Estimate Peat Carbon. *Wetlands* 34, 1241–1246.
- Davis, J.C., Proctor, I.D., Southon, J.R., Caffee, M.W., Heikinen, D.W., Roberts, M.L., Moore, T.L., Turteltaub, K.W., Nelson, D.E., Loyd, D.H., Vogel, J.S., 1990. LLNL/US AMS facility and research program. *Nuc. Inst. Meth. Phys. B* 269–272.
- Demers, J.D., Yavitt, J.B., Driscoll, C.T., Montesdeoca, M.R., 2013. Legacy mercury and stoichiometry with C, N, and S in soil, pore water, and stream water across the upland-wetland interface: the influence of hydrogeologic setting. *J. Geophys. Res.* B 118 (2), 825–841.
- Desrosiers, M., Planas, D., Mucci, A., 2006. Mercury methylation in the epilithon of boreal shield aquatic ecosystems. *Environ. Sci. Technol.* 40, 1540–1546.
- Drouin, A., Saint-Laurent, D., Lavoie, L., Ouellet, C., 2011. High-precision elevation model to evaluate the spatial distribution of soil organic carbon in active floodplains. *Wetlands* 31 (6), 1151–1164.
- Frolking, S., et al., 2011. Peatlands in the Earth's 21st century climate system. *Environ. Rev.* 19, 371–396.
- Gorham, E., 1991. Northern Peatlands - role in the carbon-cycle and probable responses to climatic warming. *Ecol. Appl.* 1 (2), 182–195.
- Gough, C.M., Vogel, C.S., Harrold, K., George, K., Curtis, P.S., 2007. The legacy of harvest and fire on ecosystem carbon storage in a north temperate forest. *Glob. Chang. Biol.* 13, 1935–1949.
- Grigal, D.F., 2003. Mercury sequestration in forests and peatlands: a review. *J. Environ. Qual.* 32 (2), 393–405.
- Grigal, D.F., Ohmann, L.F., 1992. Carbon storage in upland forests of the Lake States. *Soil Sci. Soc. Am. J.* 56, 935–943.
- Grigal, D.F., Kolka, R.K., Fleck, J.A., Nater, E.A., 2000. Mercury budget of an upland-peatland watershed. *Biogeochemistry* 50, 95–109.
- Heckman, K.A., Vazquez-Ortega, A., Gao, X., Chorover, J., Rasmussen, C., 2011. Changes in water extractable organic matter during incubation of forest floor material in the presence of quartz, goethite, and gibbsite surfaces. *Geochim. Cosmochim. Acta* 75, 4295–4309.
- Heinselman, M.L., 1970. Landscape evolution, peatland types, and the environment in the Agassiz Peatlands Natural Area, Minnesota. *Ecol. Monogr.* 40, 235–261.
- Hesterberg, D., Chou, J.W., Hutchison, K.J., Sayers, D.E., 2001. Bonding of Hg(II) to reduced organic, sulfur in humic acid as affected by S/Hg ratio. *Environ. Sci. Technol.* 35 (13), 2741–2745.
- Hough, J.L., 1958. Revision of the Nipissing Stage of the Great Lakes. 46. Illinois State Academy of Science Transactionspp. 133–141.
- Inamdar, S.P., Christopher, S.F., Mitchell, M.J., 2004. Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrol. Process.* 18, 2651–2661.
- Jurmu, M.C., 2002. A morphological comparison of narrow, low-gradient streams traversing wetland environments to alluvial streams. *Environ. Manag.* 30 (6), 831–856.
- Keller, J.K., Bridgman, S.D., 2007. Pathways of anaerobic carbon cycling across an ombrotrophic-minerotrophic peatland gradient. *Limnol. Oceanogr.* 52 (1), 96–107.
- Kim, J., Ivanov, V.Y., Fatichi, S., 2016. Climate change and uncertainty assessment over a hydroclimatic transect of Michigan. *Stoch. Env. Res. Risk A.* 30, 923–944.
- Kolka, R.K., Grigal, D.F., Verry, E.S., Nater, E.A., 1999. Mercury and organic carbon relationships in streams draining forested upland peatland watersheds. *J. Environ. Qual.* 28, 766–775.
- Kolka, R.K., Grigal, D.F., Nater, E.A., Verry, E.S., 2001. Hydrologic cycling of mercury and organic carbon in a forested upland-bog watershed. *Soil Sci. Soc. Am. J.* 65 (3), 897–905.
- Kolka, R.K., Mitchell, C.P.J., Jeremiason, J.D., Hines, N.A., Grigal, D.F., Engstrom, D.R., Coleman-Wasik, J.K., Nater, E.A., Swain, E.B., Monson, B.A., Fleck, J.A., Johnson, B., Almendinger, J.E., Branfireun, B.A., Brezonik, B.L., Cotner, J.B., 2011. Mercury Cycling in Peatland Watersheds. In: Kolka, R.K., Sebestyen, S.D., Verry, E.S., Brooks, K.N. (Eds.), *Peatland Biogeochemistry and Watershed Hydrology at the Marcell Experimental Forest* CRC Press, Taylor and Francis Group, Boca Raton, FL, USA, pp. 349–370.
- Kolka, R., Sturtevant, B., Townsend, P., Miesel, J., Wolter, P., Fraver, S., DeSutter, T., 2014. Post-fire comparisons of forest floor and soil carbon, nitrogen, and mercury pools with fire severity indices. *Soil Sci. Soc. Am. J.* 78, S58–S65.
- Kuhry, P., Nicholson, B.J., Gignac, L.D., Vitt, D.H., Bayley, S.E., 1993. Development of sphagnum-dominated peatlands in boreal continental Canada. *Can. J. Bot.* 71 (1), 10–22.
- Lapin, M., Barnes, B.V., 1995. Using the landscape ecosystem approach to assess species and ecosystem diversity. *Conserv. Biol.* 9 (5), 1148–1158.

- Last, F.M., Last, W.M., 2012. Lacustrine carbonates of the northern Great Plains of Canada. *Sediment. Geol.* 277, 1–31.
- Lehmann, J., Solomon, D., 2010. Organic carbon chemistry in soils observed by synchrotron-based spectroscopy. In: Singh, B., Gräfe, M. (Eds.), *Developments in Soil Science*. 34. Elsevier B.V., The Netherlands, pp. 289–312.
- LeMasters, G.S., Jones, E.A., Mogk, J.G., Bartelli, L.J., Kennedy, E.J., Shetron, S.J., Trettin, C.C., Smith, M.R., Bourdo, E.A., 1984. State of Michigan: Peat resource estimation. In: Final Report. 1 Michigan Technological University, Ford Forestry Center Technical Bulletin 84-1 (157pp).
- Lewis, C.F., 1970. Recent uplift of Manitoulin Island, Ontario. *Can. J. Earth Sci.* 7, 665–675.
- Lin, H.S., Wheeler, D., Bell, J., Wilding, L., 2005. Assessment of soil spatial variability at multiple scales. *Ecol. Model.* 182 (3–4), 271–290.
- Magnuson, J.J., Webster, K.E., Assel, R.A., Bowser, C.J., Dillon, P.J., Eaton, J.G., Evans, H.E., Fee, E.J., Hall, R.I., Mortsch, L.R., Schindler, D.W., Quinn, F.H., 1997. Potential effects of climate changes on aquatic systems: Laurentian Great Lakes and Precambrian Shield Region. *Hydrol. Process.* 11, 825–871.
- Matthews, E., Fung, I., 1987. Methan emission from natural wetlands: global distribution, area, and environmental characteristics of sources. *Glob. Biogeochem. Cycles* 1, 61–86.
- McClain, M.E., et al., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems* 6 (4), 301–312.
- McLaughlin, J.W., Webster, K.L., 2010. Alkalinity and acidity cycling and fluxes in an intermediate fen peatland in northern Ontario. *Biogeochemistry* 99 (1–3), 143–155.
- McLaughlin, J.W., Calhoun, E.B.W., Gale, M.R., Jurgensen, M.F., Trettin, C.C., 2011. Biogeochemical cycling and chemical fluxes in a managed northern forested wetland, Michigan, USA. *For. Ecol. Manag.* 261 (3), 649–661.
- Miller, N.G., Futyma, R.P., 1987. Paleohydrological implications of holocene peatland development in Northern Michigan. *Quat. Res.* 27 (3), 297–311.
- Moore, T.R., Roulet, N.T., Waddington, J.M., 1998. Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands. *Clim. Chang.* 40 (2), 229–245.
- Nater, E.A., Grigal, D.F., 1992. Regional trends in mercury distribution across the Great-Lakes States, North Central USA. *Nature* 358, 139–141.
- Nave, L.E., Gough, C.M., Le Moine, J., Nadelhoffer, K.J., 2017. Physiographic factors underlie rates of biomass production during succession in Great Lakes forest landscapes. *For. Ecol. Manag.* 397, 157–173.
- Obrist, D., Fain, X., Berger, C., 2010. Gaseous elemental mercury emissions and CO₂ respiration rates in terrestrial soils under controlled aerobic and anaerobic laboratory conditions. *Sci. Total Environ.* 408 (7), 1691–1700.
- Parry, L.E., West, L.J., Holden, J., Chapman, P.J., 2014. Evaluating approaches for estimating peat depth. *J. Geophys. Res.* B 119 (4), 567–576.
- Parsekian, A.D., Slater, L., Ntarlagiannis, D., Nolan, J., Sebesteyen, S.D., Kolka, R.K., Hanson, P.J., 2012. Uncertainty in peat volume and soil carbon estimated using ground-penetrating radar and probing. *Soil Sci. Soc. Am. J.* 76, 1911–1918.
- Pebesma, E.J., 2004. Multivariable geostatistics in S: the gstat package. *Comput. Geosci.* 30, 683–691.
- Pebesma, E.J., Bivand, R.S., 2005. Classes and methods for spatial data in R. *R News* 5. < <https://cran.r-project.org/doc/Rnews/> > .
- Podniesinski, G.S., Leopold, D.J., 1998. Plant community development and peat strategy in forested fens in response to ground-water flow systems. *Wetlands* 18 (3), 409–430.
- Post, W.M., Emanuel, W.R., Zinke, P.J., Stangenberger, A.G., 1982. Soil carbon pools and world life zones. *Nature* 298 (5870), 156–159.
- Pregitzer, K.S., Burton, A.J., Zak, D.R., Talhelm, A.F., 2008. Simulated chronic nitrogen deposition increases carbon storage in Northern Temperate Forests. *Glob. Chang. Biol.* 14, 142–153.
- R Core Team, 2015. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. < <https://www.R-project.org/> > .
- Saint-Laurent, D., Gervais-Beaulac, V., Berthelot, J.S., 2014. Variability of soil properties in different flood-risk zones and link with hydroclimatic changes (Southern Quebec, Canada). *Geoderma* 214, 80–90.
- Schiff, S., Aravena, R., Mewhinney, E., Elgood, R., Warner, B., Dillon, P., Trumbore, S., 1998. Precambrian shield wetlands: hydrologic control of the sources and export of dissolved organic matter. *Clim. Chang.* 40, 167–188.
- Schuster, E., 1991. The behavior of mercury in the soil with special emphasis on complexation and adsorption processes - a review of the literature. *Water Air Soil Pollut.* 56, 667–680.
- Schuster, P.F., Shanley, J.B., Reddy, M.M., Aiken, G.R., Marvin-DiPasquale, M., Roth, D.A., Taylor, H.E., Krabbenhoft, D.P., DeWilde, J.F., 2008. Mercury and organic carbon dynamics during runoff episodes from a Northeastern USA watershed. *Water Air Soil Pollut.* 187, 89–108.
- Selvendiran, P., Driscoll, C.T., Montesdeoca, M.R., Bushey, J.T., 2008. Inputs, storage, and transport of total and methyl mercury in two temperate forest wetlands. *J. Geophys. Res. Biogeosci.* 113.
- Simonson, R.W., 1959. Outline of a generalized theory of soil genesis. *Soil Sci. Soc. Am. J.* 23, 152–156.
- Skyllberg, U., Xia, K., Bloom, P.R., Nater, E.A., Bleam, W.F., 2000. Binding of mercury(II) to reduced sulfur in soil organic matter along upland-peat soil transects. *J. Environ. Qual.* 29, 855–865.
- Skyllberg, U., Bloom, P.R., Qian, J., Lin, C.M., Bleam, W.F., 2006. Complexation of mercury(II) in soil organic matter: EXAFS evidence for linear two-coordination with reduced sulfur groups. *Environ. Sci. Technol.* 40 (13), 4174–4180.
- Soil Survey Staff, 1991. Natural Resources Conservation Service, United States Department of Agriculture. Soil Survey of Cheboygan County, Michigan.
- Spurr, S.H., Zumberge, J.H., 1956. Late Pleistocene features of Cheboygan and Emmet counties, Michigan. *Am. J. Sci.* 254, 96–109.
- Stallard, R.F., 1998. Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. *Glob. Biogeochem. Cycles* 12 (2), 231–257.
- Stuiver, M., Polach, H.A., 1977. Discussion: reporting of ¹⁴C data. *Radiocarbon* 19, 355–363.
- Stuiver, M., Reimer, P.J., Braziuns, T.F., 1998. High-precision radiocarbon age calibration for terrestrial and marine samples. *Radiocarbon* 40(3), 1127–1151.
- Taggart, M., Heitman, J.L., Shi, W., Vepraskas, M., 2012. Temperature and water content effects on carbon mineralization for sapric soil material. *Wetlands* 32, 939–944.
- Thompson, J.A., Bell, J.C., Butler, C.A., 1997. Quantitative soil-landscape modeling for estimating the areal extent of hydromorphic soils. *Soil Sci. Soc. Am. J.* 61 (3), 971–980.
- Thormann, M.N., Szumigalski, A.R., Bayley, S.E., 1999. Aboveground peat and carbon accumulation potentials along a bog-fen-marsh wetland gradient in southern boreal Alberta, Canada. *Wetlands* 19 (2), 305–317.
- Thurman, E.M., 1985. Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht (ISBN 90-247-3143-7).
- Thurman, E.M., 1985. Organic Geochemistry of Natural Waters. Martinus Nijhoff/DR W. Junk Publishers, Kluwer Academic Publishers Group, Dordrecht, The Netherlands, pp. 497.
- Tjerngren, U., Karlsson, T., Björn, E., Skjellberg, U., 2012. Potential Hg methylation and MeHg demethylation rates related to the nutrient status of different boreal wetlands. *Biogeochemistry* 108 (1–3), 335–350.
- Tolonen, K., Turunen, J., 1996. Accumulation rates of carbon in mires in Finland and implications for climate change. *The Holocene* 6 (2), 171–178.
- Torn, M.S., Swanston, C.W., Castanha, C., Trumbore, S.E., 2009. Storage and turnover of organic matter in soil. In: Senesi, N., Xing, B., Huang, P.M. (Eds.), *Biophysico-chemical Processes Involving Natural Nonliving Organic Matter in Environmental Systems*. John Wiley and Sons Publishers, Inc.
- Trettin, C.C., Jurgensen, M.F., Gale, M.R., McLaughlin, J.W., 2011. Recovery of carbon and nutrient pools in a northern forested wetland 11 years after harvesting and site preparation. *For. Ecol. Manag.* 262 (9), 1826–1833.
- Turetsky, M.R., et al., 2006. Wildfires threaten mercury stocks in northern soils. *Geophys. Res. Lett.* 33 (16).
- Turetsky, M.R., et al., 2011. Recent acceleration of biomass burning and carbon losses in Alaskan forests and peatlands. *Nat. Geosci.* 4 (1), 27–31.
- Updegraff, K., Pastor, J., Bridgman, S.D., Johnston, C.A., 1995. Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. *Ecol. Appl.* 5 (1), 151–163.
- Vogel, J.S., Southon, J.R., Nelson, D.E., 1987. Catalyst and binder effects in the use of filamentous graphite for AMS. *Nucl. Inst. Meth. Phys. B.* 29, 50–56.
- Weishampel, P., Kolka, R., King, J.Y., 2009. Carbon pools and productivity in a 1-km(2) heterogeneous forest and peatland mosaic in Minnesota, USA. *For. Ecol. Manag.* 257, 747–754.
- Wiener, J.G., Knights, B.C., Sandheinrich, M.B., Jeremiason, J.D., Brigham, M.E., Engstrom, D.R., Woodruff, L.G., Cannon, W.F., Balogh, S.J., 2006. Mercury in soils, lakes, and fish in Voyageurs National Park (Minnesota): Importance of atmospheric deposition and ecosystem factors. *Environ. Sci. Technol.* 40, 6261–6268.
- Woodruff, L.G., Cannon, W.F., Eberl, D.D., Smith, D.B., Kilburn, J.E., Horton, J.D., Garrett, R.G., Klassen, R.A., 2009. Continental-scale patterns in soil geochemistry and mineralogy: results from two transects across the United States and Canada. *Appl. Geochem.* 24, 1369–1381.
- Ye, R.Z., et al., 2012. pH controls over anaerobic carbon mineralization, the efficiency of methane production, and methanogenic pathways in peatlands across an ombrotrophic-minerotrophic gradient. *Soil Biol. Biochem.* 54, 36–47.
- Zhang, Y., Li, C.S., Trettin, C.C., Li, H., Sun, G., 2002. An integrated model of soil, hydrology, and vegetation for carbon dynamics in wetland ecosystems. *Glob. Biogeochem. Cycles* 16 (4).
- Zogg, G.P., Barnes, B.V., 1995. Ecological classification and analysis of wetland ecosystems, Northern Lower Michigan, USA. *Can. J. For. Res.* 25 (11), 1865–1875.