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Long-term changes in organic matter and mercury transport to lakes in the sporadic discontinuous permafrost zone related to peat subsidence

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Abstract

Permafrost-supported peatlands near the southern limit of permafrost are experiencing dramatic landscape changes as a result of recent climate warming, which have the potential to impact aquatic ecosystems through changes in terrestrial run-off. Our objectives were to determine how terrestrial organic matter inputs to aquatic ecosystems in the southern Northwest Territories (Canada) changed as a result of peat subsidence, and whether terrestrial organic matter can be linked to sedimentary mercury. To accomplish this, we analyzed lipid biomarkers, lignin-derived phenols, and other geochemical proxies in sediment cores from two lakes (KAK-1 and TAH-7) affected by recent peat subsidence. Both lakes experienced substantial shifts in organic matter proxies through time, but the trajectory of change differed, reflecting local heterogeneity in hydrological setting and other environmental factors. In KAK-1, recent peat subsidence corresponded to a decrease in lignin-derived phenol yield, increased inferred lignin oxidation, and δ^{15}N depletion. In TAH-7, peat subsidence was likely initiated by a local forest fire, and resulted in an increase in the *n*-alkanol ratio $C_{30}/(C_{30}+C_{28})$ (consistent with a warmer, wetter climate), lignin-derived phenol yield (mainly syringyls), and δ^{13}C depletion. In TAH-7, total mercury inputs were positively correlated to terrestrial carbon inputs, suggesting allochthonous carbon is an important vector for mercury transport to the lake. In both lakes, an increase in the $C_{23}/(C_{23}+C_{29})$ *n*-alkane ratio was observed and suggests increased organic matter input from *Sphagnum* mosses. Our results demonstrate how terrestrial landscape changes occurring as a result of peat subsidence can influence carbon accumulation in aquatic ecosystems in discontinuous permafrost zones.

The thermal insulating properties of peat allow for the persistence of permafrost in areas where average air temperatures are otherwise too warm (Burn and Smith 1988). Consequently, permafrost-supported peatlands near the southern limit of permafrost are highly sensitive to climate warming, as even relatively small changes in mean annual air temperature may cause rapid permafrost degradation. As a result, the area occupied by permafrost features in the sporadic discontinuous permafrost zone is projected to decrease markedly under future climate warming scenarios (Camill 2005).

Permafrost-supported peat plateaus, which are generally elevated ~ 1-3 m above the surrounding landscape, are typically dominated by black spruce (*Picea mariana*) and a ground cover of *Sphagnum* spp. or lichen carpet (Vitt et al. 1994). Thawing of ground ice beneath peat plateaus leads to subsidence and waterlogging of the peat and black spruce stands (Quinton et al. 2010). Saturation conditions in collapsed peat scars can persist for hundreds of years, supporting semiaquatic vegetation communities (with taxa such as *Sphagnum* mosses and *Carex* spp.) that are distinct from the surrounding area (Beilman et al. 2001). Northern peatlands naturally consist of a mosaic of permafrost plateaus, collapse scars, and non-permafrost-derived bogs and fens. Although the process of permafrost aggradation and degradation in sporadic discontinuous permafrost zones can be cyclical

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(e.g., Bauer and Vitt 2011), permafrost degradation is thought to have exceeded aggradation since the mid-1800s (Beilman et al. 2001). The rate of change has increased drastically in the last 30-50 yr in response to recent climate warming (e.g., Quinton et al. 2010).

Aquatic ecosystems are "downhill" from terrestrial ecosystems, and as such may be greatly influenced by permafrost-associated changes occurring in the landscape that alter the quantity and composition of terrestrial run-off into lakes and rivers. Peat plateaus act as barriers to the lateral flow of water across the landscape, and peat subsidence leads to increasing connectivity of drainage channels and changes in the hydrological cycle (Quinton et al. 2009). As well, the production and export of dissolved organic carbon (DOC) has been shown to be higher from collapsed bogs compared to intact permafrost-supported peat plateaus and non-permafrost fens (Olefeldt and Roulet 2014). Related increases in DOC concentrations in lakes can affect many aquatic ecosystem processes, including thermal stratification patterns (Read and Rose 2013), primary production (Carpenter et al. 1998), and bioavailability of metals (French et al. 2014). The submergence of vegetation that occurs as a result of peat subsidence has also been linked to the release of previously stored mercury to aquatic ecosystems (Klaminder et al. 2008), which has significant implications for aquatic biota.

Our understanding of the impacts of permafrost thaw on aquatic ecosystems in the sporadic discontinuous permafrost zone is hindered by a lack of long-term monitoring data in these remote regions. Instead, indirect approaches that make use of natural archives of environmental change, such as lake sediment cores, can be used to reconstruct past ecosystem conditions over timescales of decades to thousands of years (Smol 2008). This includes inferences of aquatic ecosystem changes over time related to permafrost thaw. For example, retrogressive thaw slumps, a spectacular form of permafrost degradation, have been linked to increased lakewater clarity in the western Canadian Arctic based on shifts in subfossil algal diatom assemblages (Thienpont et al. 2013). Retrogressive thaw slump development has also been shown to increase inorganic sedimentation rates in lakes, resulting in diluted sedimentary organic carbon and mercury concentrations (Deison et al. 2012). In permafrost-associated peatlands, recent peat subsidence has been linked to enhanced flux of organic carbon and associated mercury to lakes (Rydberg et al. 2010), as well as increases in inferred lakewater colored DOC (Coleman et al. 2015), based on geochemical and biological sedimentary proxies.

The analysis of plant biomarkers preserved in lake sediment cores has the potential to provide a powerful tool for investigating the effects of peat subsidence on allochthonous carbon transport to aquatic ecosystems, and for understanding long-term aquatic ecosystem change in northern peatlands in the context of land-water interactions. For example, lignin is a naturally occurring biopolymer that is produced exclusively by vascular terrestrial plants, and the presence of lignin-derived phenols in lakes can be attributed unequivocally to allochthonous sources (Jex et al. 2014). Lignin is an important component of the recalcitrant organic carbon fraction and is resistant to degradation, especially in the cool, dark, anoxic conditions present in lake sediments. Consequently, diagenetic changes to the lignin-derived phenol yield are assumed to be negligible following their burial in the sediment record. As a result, lignin-derived phenols in sediment cores have been used as biomarkers for vegetation changes and TOC cycling throughout the Quaternary (Hu et al. 1999; Ishiwatari et al. 2006), and have also been applied as a biomarker for catchment-derived mercury inputs to lakes (Teisserenc et al. 2011). Long-chain *n*-alkanes, *n*-alkanoic acids, and *n*-alkanols are lipid-derived biomarkers produced by terrestrial plants that, similar to lignin, are resistant to degradation, and can provide additional information on the source of organic matter in lake sediments (Meyers 2003). Their use as paleoenvironmental indicators of past terrestrial ecosystem dynamics and long-term climatic change is becoming increasingly common (e.g., Pautler et al. 2013; Street et al. 2013).

In this study, we analyzed lignin-derived phenols, *n*-alkanes, and *n*-alkanols in dated sediment cores from two small lakes in the Taiga Plain region of the southern Northwest Territories (Canada), in conjunction with total mercury, C/N ratios, $\delta^{13}C$, and $\delta^{15}N$, to better understand how peat subsidence in the sporadic discontinuous permafrost zone alters the transport of allochthonous carbon and catchment-derived mercury to lakes. Our primary objective was to determine how recent increases in the extent of collapsed permafrost scars have affected the quantity, quality, and taxonomic source of terrestrial organic matter delivered to lake sediments in the context of long-term environmental change over the last several 100 yr. Our secondary objective was to assess the role of terrestrial organic matter as a vector for mercury delivery to lakes, and determine whether recent permafrost thaw has led to mercury enrichment. Comparison with a previous study that analyzed subfossil diatom assemblage shifts in the same sediment cores (Coleman et al. 2015) allows us to draw parallels between changes in allochthonous carbon transport and ecological shifts in aquatic biota. The application of organic matter biomarkers preserved in lake sediments will enhance our understanding of how transformative changes occurring in the terrestrial environment as a result of recent climate warming influence aquatic ecosystems in permafrost-supported northern boreal peatlands.

Methods

Study site description

The two study lakes are located southwest of Great Slave Lake (Northwest Territories, Canada) in the Taiga Plains Mid-Boreal Ecozone (Ecosystem Classification Group 2007). Mean annual air temperatures recorded at the nearby Hay River Climate Station (60°48′45″N, 115°47′20″W) have been

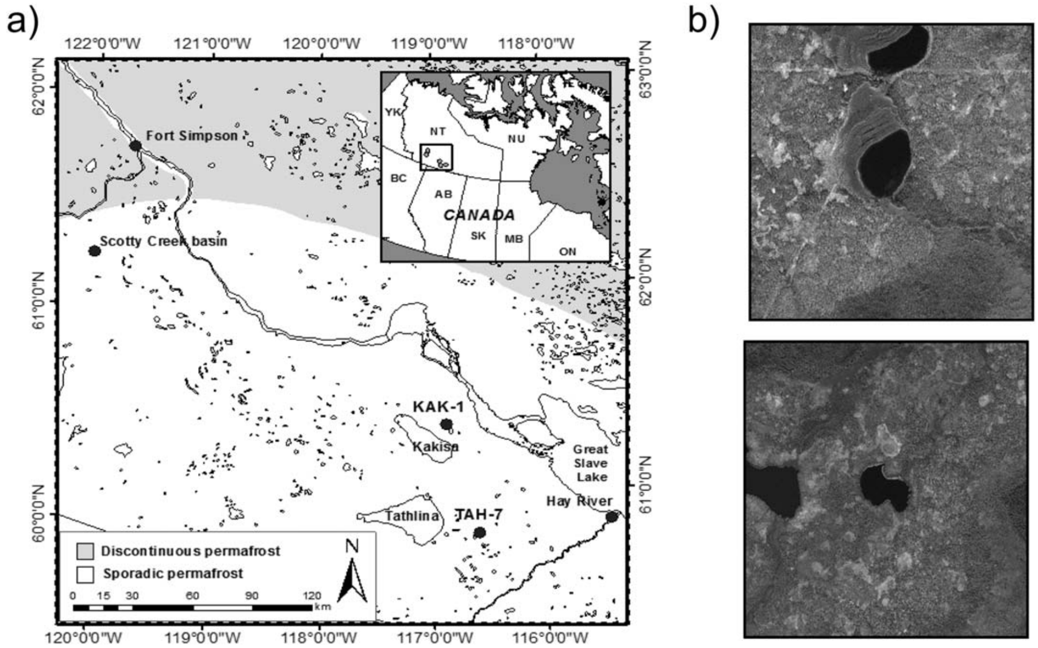

Fig. 1. (a) Map showing the location of our study lakes (KAK-1 and TAH-7) in the sporadic discontinuous permafrost zone of the southern Northwest Territories, (b) high resolution (0.5 m) WorldView satellite imagery of a 1 km^2 area centered around Lake KAK-1 (top) and Lake TAH-7 (bottom).

increasing from −6°C in 1900 to −2°C in 2010. Both lakes are within the sporadic discontinuous permafrost zone where 10-50% of the land surface is underlain by permafrost, which in this region is generally restricted to peat plateaus (Heginbottom and Dubreuil 1995). The landscape is a mosaic of permafrost-supported peat plateaus dominated by black spruce, collapsed peat plateaus, and non-permafrost bogs and fens. Permafrost thaw has been occurring in this region since ~ 1850, and has been accelerating in recent decades (Halsey et al. 1995; Quinton et al. 2010).

KAK-1 (unofficial name) (61°2′4.056″N, 117°33′7.8258″W, altitude 260 m asl) is a small (surface area < 4 hectares), shallow (max. depth < 2 m) lake located north of the small community of Kakisa (Fig. 1). It is an alkaline (pH 8.3), oligotrophic (total unfiltered phosphorus = 7.0 μg/L) lake with high DOC (36.1 mg/L) (Table 1). It is characterized by a large marsh-like area visible on its margin in satellite images (Fig. 1). Because this site was visited in the spring, when it was ice- and snow-covered, the exact composition of this feature has not been verified from the ground. Remote sensing analysis based on aerial images available since 1970 showed a 28% increase in surface area of collapsed peat plateau features in a 1-km^2 area centered on the lake between 1970 and 2012 (Coleman et al. 2015).

TAH-7 (unofficial name) (60°34′13.785″N, 116°54′14.7846″W, altitude 291 m asl) is located east of Tathlina Lake, approximately 60 km southeast of KAK-1 (Fig. 1). TAH-7 is small (surface area < 4 hectares), shallow (< 2 m), eutrophic (total unfiltered phosphorus = 44.0 μg/L) and slightly alkaline (pH 7.5), with high DOC (46.8 mg/L) and lake color (91 TCU) (Table 1). A 44% increase in collapsed peat plateau features was inferred for a 1-km^2 study area centered on the lake using remotely sensed image analyses between 1970 and 2012 (Coleman et al. 2015).

Table 1. Modern water chemistry and physical characteristics of lakes KAK-1 and TAH-7 in the Great Slave Lowlands region, Northwest Territories, Canada. Water chemistry was sampled in September 2013 and analyzed at the Taiga Environmental Laboratory (Yellowknife, Northwest Territories, Canada).

	KAK-1	TAH-7
Latitude	61°2′4.056″	60°34′13.785″
Longitude	−117°33′7.8258″	−116°54′14.7846″
pH	8.3	7.6
Dissolved organic carbon (mg/L)	36.1	46.8
True colour (TCU)	32.0	91.0
Total phosphorus (μg/L)	7.0	44.0
Total nitrogen (mg/L)	1.1	1.7
Calcium (mg/L)	29.7	18.9
Chloride (mg/L)	0.7	0.7
Surface area (hectares)	3.0	1.8
Maximum depth (m)	1.8	1.9
Extent of collapsed permafrost features (km^2) in 2012 for a 1 km^2 radius of the catchment*	0.25	0.33

*Data from Coleman et al. (2015).

Field and laboratory methods

TAH-7 and KAK-1 were accessed via helicopter in March 2012, and sediment cores (core lengths 55 cm and 27 cm, respectively) were taken from the center of each lake using a Glew (1989) gravity corer with an internal diameter of 7.6 cm. Sediment cores were sectioned at 0.5 cm intervals using a Glew (1988) vertical extruder. Sediment cores were shipped frozen to the University of Ottawa and freeze-dried. Cores were ^{210}Pb dated using an Ortec High Purity Germanium Gamma Spectrometer (Oak Ridge, Tennessee, U.S.A.) following methods in Appleby (2001). Certified Reference Materials obtained from the International Atomic Energy Association (Vienna, Austria) were used for efficiency corrections, and results were analyzed using ScienTissiME (Barry's Bay, Ontario, Canada). A chronology was established using the constant rate of supply model (Appleby and Oldfield 1978). Results for ^{210}Pb dating are presented in the Supporting Information (Fig. S1). These same cores were analyzed for sedimentary diatom assemblages (siliceous algae) in a previous study to reconstruct long-term aquatic ecosystem changes (Coleman et al. 2015).

Freeze-dried sediment samples ($\sim$ 30 mg) were analyzed for total mercury (THg) using an automatic mercury analyzer based on thermal decomposition, dual step gold amalgamation and detection via cold-vapor atomic absorption using an Sp-3D mercury analyzer (Nippon Instrument Corp) (UOP Method 938-00, detection limit of 0.01 ng Hg and range up to 1000 ng Hg; Fox et al. 2005). Select intervals were run in triplicate, and Marine Sediment Certified Reference Materials from the National Research Council of Canada (MESS-3) were used for quality assurance. For organic carbon and δ^{13}C isotopic analyses, freeze-dried sediment was acid-digested in concentrated HCl for 48 h in an acid desiccator to remove inorganic carbon (Harris et al. 2001). Sample vials were then filled with deionized water and centrifuged at 3000 rpm for 10 min and the supernatant discarded. This step was repeated two more times, and then samples were freeze-dried again. For elemental analysis (OC/N), 5-10 mg of sample was weighed into tin capsules containing 20 mg tungsten trioxide and analyzed using a Vario EL III Elemental Analyzer (Elementar, Germany) at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa) following methods described in Brazeau et al. (2013). For δ^{13}C and δ^{15}N analysis, 1 mg and 2.5 mg of sediment, respectively, were weighed into tin capsules and loaded into the Elemental Analyzer interfaced to the DeltaPlus XP Isotope Ratio Mass Spectrometer (Thermo-Finnigan, Germany) at the G.G. Hatch Stable Isotope Laboratory following methods described in Brazeau et al. (2013). The δ^{15}N was analyzed on untreated samples, as inorganic carbon removal can affect δ^{15}N values. δ^{13}C and δ^{15}N were reported using delta (δ) notation in parts per thousand (‰) enrichments or depletions relative to common standards (V-PDB for δ^{13}C and AIR for δ^{15}N). Calibrated internal standards were used for normalization of the data, and precision was better than 0.20‰ (Pella 1990).

Biomarker analysis

Due to limited available sediment, cores were combined into 5-cm intervals for both KAK-1 and TAH-7 to ensure enough material was available for accurate detection of organic matter biomarkers. Solvent extraction (for *n*-alkanes and other lipid biomarkers) followed by cupric oxide (CuO) oxidation (for lignin-derived phenols) was conducted on 0.5 g of freeze-dried sediment in duplicate (for quality assurance) at the University of Toronto Scarborough. Preliminary extractions showed that, because of high percent organic carbon in the samples, 0.5 g was sufficient for accurate quantification of organic matter biomarkers. For solvent extraction, sediments were sonicated sequentially with 30 mL of CH_2Cl_2, $CH_2Cl_2{\cdot}MeOH$ (1 : 1 v/v) and MeOH, and transferred to a flask by gravity filtration through pre-extracted cellulose filters (Fisher Scientific P8). Extracts were then filtered through Whatman GF/A glass fiber filters, concentrated by rotary evaporation, evaporated to dryness in 2 mL glass vials under a stream of N_2, air-dried, and stored at -20°C until they were derivatized for analysis by gas chromatography-mass spectrometry (GC-MS). The remaining air-dried sediment from the solvent extraction was extracted with 1 g CuO, 100 mg ammonium iron (II) sulfate hexahydrate, and 15 mL of 2M NaOH in Teflon-lined bombs at 170°C for 2.5 h. Samples were then acidified to pH 1 with 6M HCl and centrifuged at 2500 rpm for 10 min. The supernatants were liquid-liquid extracted with 30 mL of diethyl ether and dried with anhydrous Na_2SO_4 to remove remaining water. Samples were then concentrated by rotary evaporation, transferred to 2 mL glass vials, and dried under N_2.

Dried extracts were derivatized with 100 μL *N*,*O*-bis-(trimethylsilyl)trifluoracetamide and 10 μL anhydrous pyridine for 3 h at 70°C. 400 μL hexane was added to dilute the extracts. Derivatized extracts were analyzed by GC-MS using an Agilent model 6890N chromatograph coupled to an Agilent model 5973N quadrupole mass selective detector with a HP-5MS fused silica column (30 m $\times$ 0.25 m i.d., 0.25 μm film thickness) and helium as a carrier gas. Temperatures were increased from an initial temperature of 65-300°C and held for 20 min. 1 μL of sample was injected in split mode (2 : 1) and the spectrometer operated in the electron ionization mode at 70 eV, and scanned from m/z 50 to 650. Compound identification was based on comparisons to the Wiley 275 MS library, authentic standards, and with published data. Quantification was performed by comparing responses of identified biomarkers to different standard compounds (tetracosane, methyl tricosanoate, ergosterol, behenyl alcohol, and vanillic acid; Otto and Simpson 2006; Pautler et al. 2013).

Statistics

To visualize temporal trends in the biomarker data (lignin-derived phenols and lipid biomarkers), a principal components analysis (PCA) was conducted downcore for KAK-1

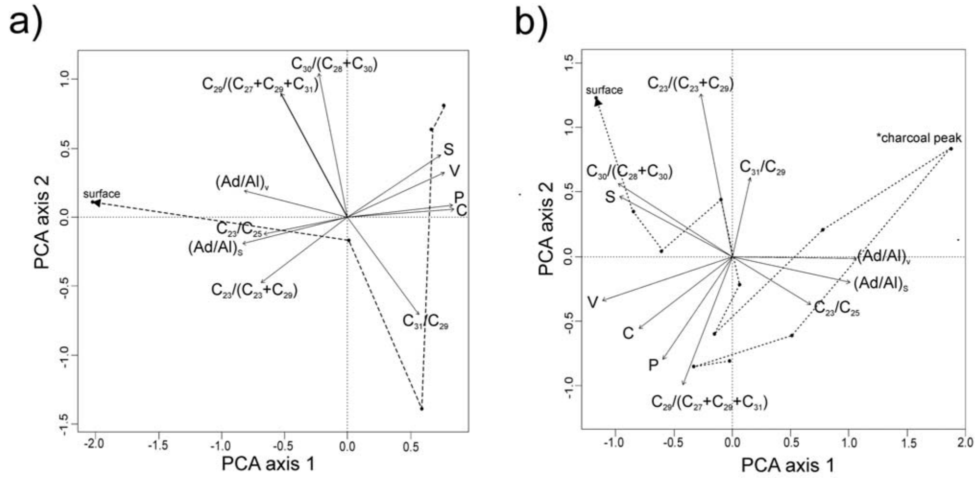

Fig. 2. PCA biplot showing the direction of change in lignin-derived phenols, *n*-alkanes (C_{23}, C_{25}, C_{27}, C_{29}, C_{31}), and *n*-alkanols (C_{28}, C_{30}) toward present day ("surface") in a sediment core from: (a) KAK-1 ($\lambda_1 = 0.6807$, $\lambda_2 = 0.2101$), (b) TAH-7 ($\lambda_1 = 0.4447$, $\lambda_2 = 0.2033$). Abbreviations: V, vanillyls; S, syringyls; C, cinnamyls; P, *p*-hydroxy phenols; $(Ad/Al)_v$, acid : aldehyde ratio of vanillyls; $(Ad/Al)_s$, acid : aldehyde ratio of syringyls.

and TAH-7 using the vegan package (Oksanen et al. 2010) for the R software environment (R Development Core Team 2010). Biomarker variables were normally distributed, and no transformation was required.

A Spearman rank correlation matrix using Bonferonni adjusted *p*-values was generated for total terrestrial lignin-derived phenols (the sum of vanillyls, cinnamyls, and syringyls), $\delta^{13}C$, and THg in TAH-7, to test for significant relationships between mercury and terrestrial carbon inputs. Linkages between terrestrial carbon and THg were compared qualitatively for KAK-1, because a shorter core length for KAK-1 (27 cm vs. 55 cm in TAH-7) reduced the number of preindustrial sediment intervals available for comparison. To compare $\delta^{13}C$ and THg (which were analyzed at 0.5 cm resolution) to VSC (analyzed at 5-cm resolution), these data were pooled and averaged into 5-cm intervals.

Results and discussion

We observed several notable changes in sedimentary plant biomarkers through time in both lakes that can be plausibly linked to peat subsidence, suggesting that recent climate warming has resulted in changes to terrestrial organic matter transport to lakes. Increases in sedimentary mercury concentrations in the sediments of TAH-7 were correlated with increases in lignin-derived phenol yield, although no evidence of mercury enrichment following recent documented (post-1970) peat subsidence was observed for either lake.

Temporal changes in sedimentary organic matter

Overall sources of organic matter to KAK-1 and TAH-7 are broadly similar based on values reported for C/N (12-15) and several biomarker indices such as $C_{23}/(C_{23}+C_{29})$ (0.3-0.5), S/V (0.6-0.8), and C/V (0.1-0.2), indicating a mixture of algal and various terrestrial vascular plant sources (Meyers 2003). However, both lakes show different trajectories of change in organic matter composition through time. In KAK-1, the predominant changes are an increase in the C_{23} *n*-alkane beginning pre-1900, as well as post-1970 decreases in $\delta^{15}N$, lignin-derived phenols, and an increase in inferred lignin oxidation based on increasing acid : aldehyde ratio of syringyls and vanillyls (Figs. 2a, 3). In TAH-7, the main changes observed were an increase in the $C_{30}/(C_{28}+C_{30})$ *n*-alkanol and $C_{23}/(C_{23}+C_{29})$ *n*-alkane ratios, an increase in the concentration of syringyls, and a decrease in $\delta^{13}C$, each beginning pre-1900 (Figs. 2b, 4).

KAK-1

An increase in the C_{23}/C_{25} *n*-alkane ratio was observed above the 10-15 cm interval ($\sim$ 1935), increasing from values of 0.5-0.6 to $\sim$ 0.75 (Fig. 5). The increase in this ratio was driven by increases in C_{23}, as the concentration of C_{25} remained fairly constant. Both the C_{23} and C_{25} *n*-alkanes are produced by semiaquatic vegetation like emergent aquatic macrophytes and *Sphagnum* mosses (Ficken et al. 2000; Bingham et al. 2010). Present-day aquatic macrophyte abundances are low in these highly colored lakes, and therefore increases in the C_{23} *n*-alkane are likely tracking organic matter inputs from mosses. In particular, *Sphagnum* taxa that occupy wetter habitats have been shown to produce higher abundances of the C_{23} *n*-alkane compared to *Sphagnum* that colonize relatively drier habitats, which are enriched in the C_{25} *n*-alkane (Bingham et al. 2010).

An increase in the $C_{23}/(C_{23}+C_{29})$ ratio was observed slightly earlier, above the 15-20 cm interval (pre-1900), increasing from 0.4-0.45 to $\sim$ 0.5 (Fig. 5). This increase was driven both by increases in C_{23} and decreases in C_{29} concentrations, and likely tracks an increase in the contribution of organic matter to the lake from *Sphagnum* mosses relative to

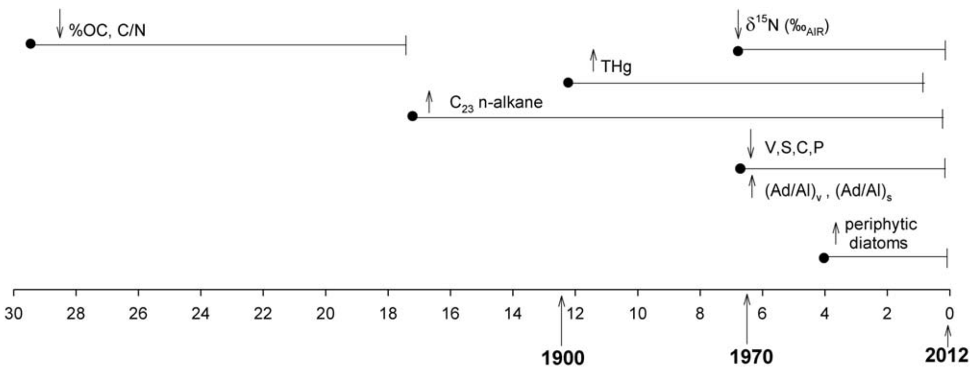

Fig. 3. A visual representation of the main changes in organic matter proxies through time in KAK-1. The timing and nature of diatom changes, added for comparison with organic matter proxies, were originally reported in Coleman et al. (2015). Abbreviations: %OC, percent organic carbon; C/N, organic carbon : nitrogen; THg, total mercury; V, vanillyls; S, syringyls; C, cinnamyls; P, *p*-hydroxy phenols; $(Ad/Al)_v$, acid : aldehyde ratio of vanillyls; $(Ad/Al)_s$, acid : aldehyde ratio of syringyls.

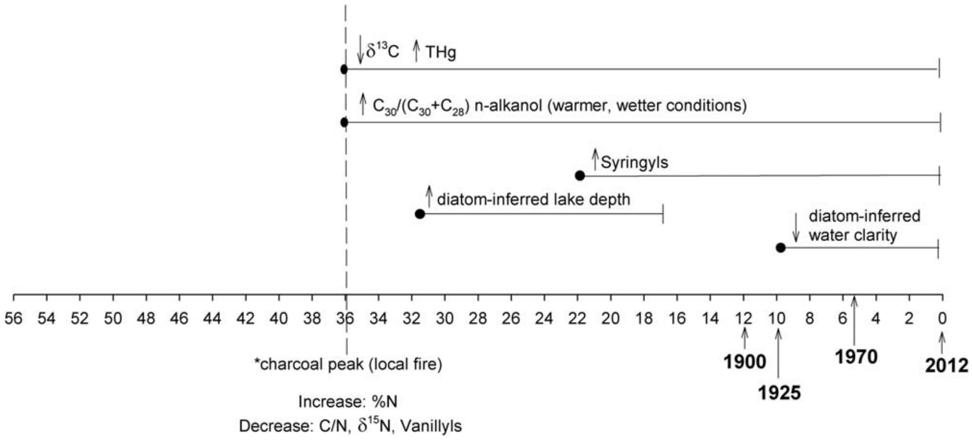

Fig. 4. A visual representation of the main changes in organic matter proxies through time in TAH-7. The timing and nature of diatom changes, added for comparison with organic matter proxies, were originally reported in Coleman et al. (2015). Abbreviations: %N, percent nitrogen; C/N, organic carbon : nitrogen; THg, total mercury.

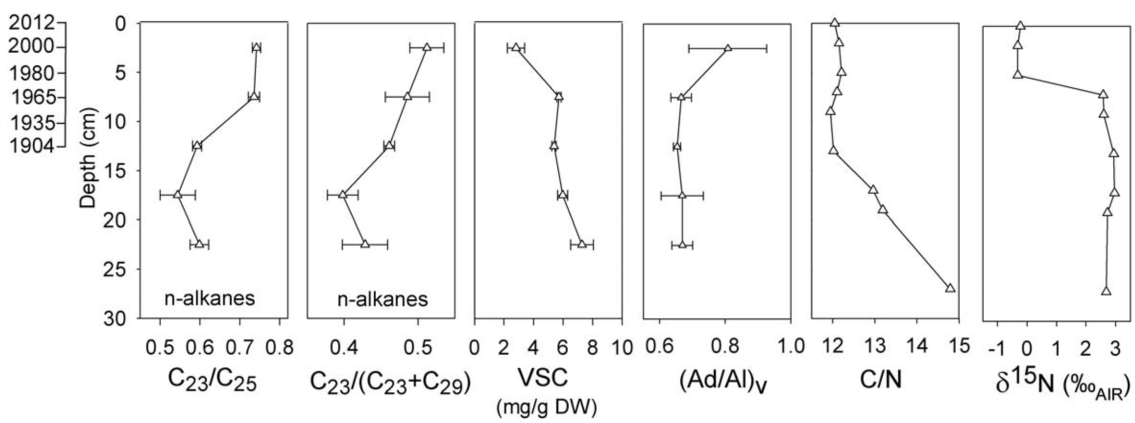

Fig. 5. Stratigraphies showing temporal changes in select geochemical proxies and biomarkers in a sediment core from KAK-1. ^{210}Pb dates are shown on the left. Abbreviations: C/N, organic carbon : nitrogen; VSC, vanillyls + syringyls + cinnamyls; $(Ad/Al)_v$, acid : aldehyde ratio of vanillyls.

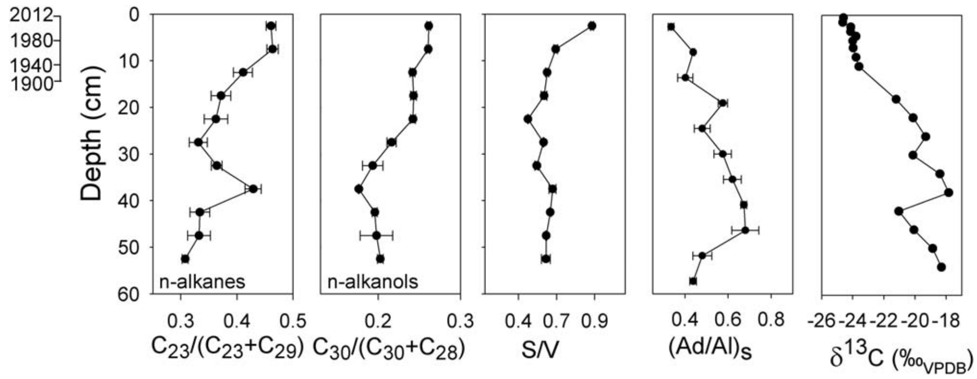

Fig. 6. Stratigraphies showing temporal changes in select geochemical proxies and biomarkers in a sediment core from TAH-7. ^{210}Pb dates are shown on the left. Abbreviations: S/V, ratio of syringyls : vanillyls; $(Ad/Al)_s$, acid : aldehyde ratio of syringyls.

higher plants (Bush and McInerney 2013). This may be a response to the collapse of well-drained peat plateaus, which is known to have been occurring in this region since ~ 1850 (Thie 1974; Halsey et al. 1995). The collapse of peat plateaus results in the waterlogging of spruce trees and other vegetation, and subsequent colonization by sedges and *Sphagnum* mosses (Vitt et al. 1994). The *p*-hydroxy phenols, which are common copper oxide oxidation products of *Sphagnum* tissues (Williams et al. 1998), did not increase with the C_{23} *n*-alkane (Fig. 2a). This may be because the *p*-hydroxy phenols come from diverse sources, including both lignin and non-lignin derived (e.g., Goñi et al. 2000), reducing their usefulness as biomarkers of *Sphagnum* inputs.

Analysis of remotely sensed images available for KAK-1 since 1970 showed a 28% increase in the area of collapsed peat scars between 1970 and 2012 (Coleman et al. 2015). In the sediment record, this corresponded to post-1970 δ^{15}N depletion from a value of ~ 2.5‰ to −0.5‰, and in the surface 0-5 cm interval, decreases in the concentrations of all major lignin-derived phenol groups (V, S, C, and P) and increases in the degree of lignin oxidation inferred from higher $(Ad/Al)_v$ and $(Ad/Al)_s$ (Figs. 2a, 5). Reductions in lignin yield and increased acid : aldehyde ratio has been observed with progressing lignin degradation in soils (Otto and Simpson 2006), possibly indicating the transport of more degraded carbon to KAK-1 lake sediments after 1970. Warming temperatures and permafrost thaw may have led to enhanced microbial degradation of organic matter in the catchment, or alternatively, these changes may reflect the mobilization of older, more degraded carbon to the lake following peat subsidence.

The complexity of the nitrogen cycle can make it challenging to interpret changes in δ^{15}N in lake sediment cores. Organic matter derived from peat is generally depleted in δ^{15}N (Bragazza et al. 2005), and decreasing δ^{15}N in KAK-1 may be further evidence of increasing inputs of *Sphagnum*-derived organic matter relative to higher plants, as was inferred from increasing $C_{23}/(C_{23}+C_{29})$. Decreasing δ^{15}N in recently deposited KAK-1 sediments may also be a direct result of thawing of near-surface permafrost soils in northern peatlands, which has the potential to release significant amounts of biologically available nitrogen for plant growth (Keuper et al. 2012). Depletion of δ^{15}N after 1970 may also be related to isotopic effects occurring during organic matter degradation, which increasing $(Ad/Al)_v$ and $(Ad/Al)_s$ ratios indicate was enhanced at this time. Depletion of δ^{15}N tends to occur under anoxic conditions, whereas aerobic degradation of nitrogen tends to lead to δ^{15}N enrichment (Galman et al. 2009). No change in δ^{15}N was observed in nearby TAH-7, indicating that increased atmospheric nitrogen deposition was not the predominant driver of δ^{15}N depletion in KAK-1.

Changes in organic matter quantity and composition has the potential to impact aquatic biota through changes in lake color, nutrient cycling, and food web interactions (Pace et al. 2004; Benoy et al. 2007). A previous diatom-based paleoecological assessment of limnological changes in KAK-1 on the same sediment core used in this study observed an increase in the diversity of periphytic diatom taxa after ~ 1990, but no other notable changes in diatom assemblages through time (Coleman et al. 2015). An increase in periphytic diatom species diversity and abundance is a common response to the longer ice-free growing season that has been observed in shallow lakes across the Northern Hemisphere as a result of climate warming (Rühland et al. 2008, 2015). The relatively complacent diatom profile suggests that the substantial changes in terrestrial organic matter inputs we infer for KAK-1 have not resulted in ecological shifts within the diatom assemblage.

TAH-7

We observed a long-term increase in the *n*-alkanol index $C_{30}/(C_{30}+C_{28})$ above the 35-40 cm interval, from ~ 0.2 to 0.26 toward the surface of the core (Figs. 2b, 6). This index has been used as a climate proxy in previous studies, where deposition of C_{30} is predicted to be more predominant than C_{28} in warmer, wetter conditions (Zhang et al. 2006; Pautler et al. 2013). The increase in $C_{30}/(C_{30}+C_{28})$ directly corresponds to diatom-inferred increases in lake depth previously reported for TAH-7 (Coleman et al. 2015), an independent confirmation of an increase in wetness. A long-term trend of decreasing $\delta^{13}C$ also began at this time, from $\sim -18‰$ to $-24‰$ (Fig. 6), which may potentially indicate changes in carbon cycling or terrestrial carbon transport. Bulk sediment $\delta^{13}C$ depletion to $-26‰$ has previously been observed associated with high lignin-derived phenol yields in a sediment core from Nepal (Glaser and Zech 2005).

The beginning of the long-term increase in $C_{30}/(C_{30}+C_{28})$ and decrease in $\delta^{13}C$ occurred immediately following a local forest fire inferred from the sedimentary macroscopic charcoal record (Coleman et al. 2015). We noted several anomalies in our biomarker and elemental/isotopic proxies in the sediment interval corresponding to the macroscopic charcoal peak (38 cm), including an increase in %N and a decrease in C/N and $\delta^{15}N$ (Figs. 2b, S2). Anomalies in %N and $\delta^{15}N$ may be tracking a short-term pulse of nutrients into the lake (and a subsequent increase in algal production) that often occurs following a forest fire. Over the longer-term, forest fires can stimulate rapid permafrost degradation (Vitt et al. 1994; Mackay 1995), and the inferred increase in wetness may be the result of extensive peat plateau collapse. Inferred increases in $C_{23}/(C_{23}+C_{29})$ above a core depth of 30 cm (from 0.33 to 0.46) and an increase in S/V above 25 cm (Fig. 6) may be reflecting the long-term trajectory of change in drainage patterns and catchment vegetation originally stimulated by peat subsidence following the fire event. Similar to observed changes in KAK-1, the increase in the C_{23} *n*-alkane relative to C_{29} may be an indication of an increase in organic matter contribution from *Sphagnum* mosses, which often colonize collapsed peat scars. Syringyls are produced exclusively by angiosperms (Hedges and Mann 1979), and may be tracking a change in drainage patterns and terrestrial run-off to the lake following the collapse of peat plateaus.

After ~ 1925, diatom assemblage shifts indicative of an increase in colored DOC were observed (Coleman et al. 2015), which corresponded to the lowest $\delta^{13}C$ values recorded in this sediment core (Fig. 6). This suggests that the long-term trajectory of changing terrestrial organic matter transport has led to the crossing of a significant ecological threshold for DOC. Similarly, lower $\delta^{13}C$ values were recorded during periods of higher inferred TOC concentrations in sub-Arctic lakes in Scandinavia (Rosén et al. 2009; Vonk et al. 2012). The link between $\delta^{13}C$ and inferences of increased DOC does not necessarily imply a direct causal link, as multiple limnological parameters may influence bulk sediment $\delta^{13}C$. Remotely sensed images available since 1950 showed a 44% increase in collapsed peat plateau scars around TAH-7 between 1970 and 2012 (Coleman et al. 2015), but most changes in organic matter proxies occurred much earlier, with the possible exception of a further increase in syringyl yield in the uppermost sediment interval (Fig. 6).

Terrestrial organic matter as a vector for mercury transport

Increases in total mercury (THg) concentrations toward present day were observed in both KAK-1 and TAH-7. In KAK-1, THg increased from ~ 50 ng/g OC to ~ 115 ng/g OC after ~ 1900, between core depths 14-2 cm (Fig. 7a). In TAH-7, a steady increase in THg concentrations was observed between 38 cm and 10 cm (~ 1940), from an average of ~ 68 ng/g OC between 55 cm and 38 cm to an average of ~ 200 ng/g OC between 0 cm and 10 cm (Fig. 7a). Increases in THg in lake sediment cores are often attributed to post-industrial atmospheric mercury emissions

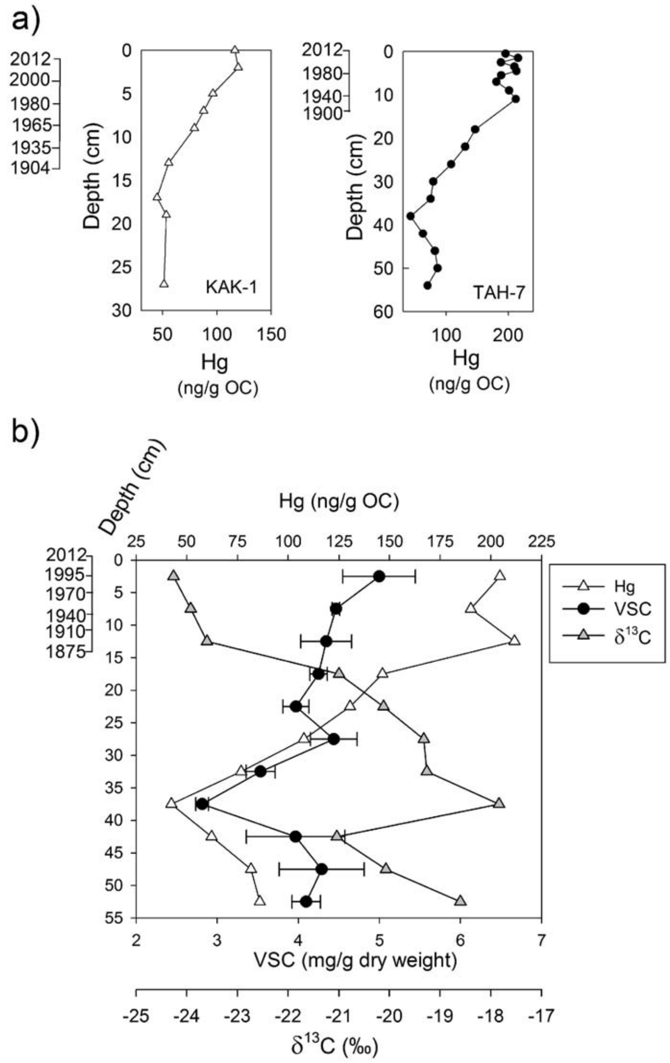

Fig. 7. (a) Sedimentary mercury profiles for KAK-1 (left) and TAH-7 (right); (b) TOC-normalized total mercury concentrations (THg) vs. total concentration (mg/g dry weight) of vanillyls + syringyls + cinnamyls (VSC) and $\partial^{13}C$ in TAH-7 by depth. ^{210}Pb dates are shown on the left.

(e.g., Lockhart et al. 1995; Deison et al. 2012). However, terrestrial organic matter is a potentially important vector for the delivery of mercury to aquatic ecosystems (Ouellet et al. 2009; Teisserenc et al. 2011), and consequently climate warming and permafrost thaw may influence mercury transport through changes in terrestrial carbon inputs. In TAH-7, the increase in THg began in the preindustrial period, suggesting that increased anthropogenic mercury emissions are not responsible for this trend. Instead, we hypothesized that changes in terrestrial organic matter transport may be the predominant driver of increases in sedimentary mercury concentrations in TAH-7.

Teasing apart the influence of terrestrial organic carbon on mercury accumulation in sediment cores is challenging, and can potentially be obscured by diagenetic alterations of organic matter downcore. Sobek et al. (2014) suggested that post-depositional diagenesis of organic matter proxies can be significant, and they attributed sedimentary declines in organic carbon concentrations, increases in C/N, and $\delta^{13}C$ enrichment to organic matter degradation occurring 25-50 yr following sediment deposition and burial in Arctic lakes. The integration of organic matter biomarkers with elemental and isotopic proxies can provide multiple lines of evidence for an association between sedimentary mercury and terrestrial organic matter, especially since lignin-derived phenols and aliphatic compounds are highly resistant to degradation upon burial.

In TAH-7, the total concentration of the terrestrially sourced lignin-derived phenol groups (VSC) was positively correlated to THg ($r = 0.8$, $p = 0.003$) and both VSC and THg were negatively correlated to $\delta^{13}C$ ($r = -0.71$, $p = 0.014$ and $r = -0.79$, $p = 0.004$, respectively) (Fig. 7b). No changes in %OC or C/N were observed coincident with $\delta^{13}C$ depletion that would indicate downcore trends in $\delta^{13}C$ are the result of diagenetic processes. Furthermore, the significant correlation between $\delta^{13}C$ and VSC provides further evidence that downcore trends in $\delta^{13}C$ are tracking a change in carbon source. Collectively, this suggests that the major source of mercury to TAH-7 is associated with terrestrial runoff. This is consistent with the findings of Hermanns et al. (2013), who reported covariance between mercury and soil-derived elements like copper over a 4000 yr preindustrial sediment record from Lake Hambre in Patagonia, indicating that mercury in Lake Hambre was strongly controlled by terrestrial runoff.

A possible signal of post-industrial THg enrichment was evident in KAK-1, where THg increased between 1900 and 2000 (Fig. 7a). However, KAK-1 has also experienced permafrost thaw and changes in organic matter inputs over time (although mainly in the C_{23} *n*-alkanes, and not lignin-derived phenols), which may also affect mercury inputs. Thus, in northern regions experiencing changes in organic matter inputs under a warming climate, the relationship between THg and terrestrial carbon flux obscures potential Hg enrichment resulting from anthropogenic mercury emissions. In TAH-7, sedimentary THg concentrations stabilized by ~ 1940, which may indicate that contributions from atmospheric mercury emissions are relatively minimal in the lake.

Remote sensing analysis revealed increases in collapsed peat scars at both KAK-1 and TAH-7 since 1970 (Coleman et al. 2015). Previous investigations in northern Sweden demonstrated that a thawing palsa mire released significant amounts of terrestrial carbon and associated mercury to surface waters (Klaminder et al. 2008; Rydberg et al. 2010). Therefore, we hypothesized that a similar increase in sedimentary mercury concentration would occur in TAH-7 and KAK-1 after 1970 in response to peat subsidence. However, neither lake showed clear evidence of post-1970 enrichment in THg (Fig. 7a), although the correlation between VSC and THg in TAH-7 suggests that future changes in terrestrial carbon transport in sporadic discontinuous permafrost zones under a warming climate can potentially increase the flux of mercury from the catchment to aquatic ecosystems. It is important to note that we only measured total mercury, not methyl mercury, and that methyl mercury is the form of mercury of most ecotoxicological concern. Peat subsidence may potentially increase mercury bioaccumulation in the food web without increasing total mercury export if subsequent environmental changes (e.g., increasing wetness) facilitated increases in mercury methylation rates (Kelly et al. 1995). As methyl mercury does not preserve over time in sediment cores, paleolimnological techniques are not well suited to answer this question (Brazeau et al. 2013).

Conclusions

Peatlands in the sporadic discontinuous permafrost zone are highly heterogeneous, and as a result can be expected to exhibit localized variability in response to regional stressors like climate warming and peat subsidence. This was evident in our comparison of long-term changes in organic matter composition in TAH-7 and KAK-1 in the southern Northwest Territories (Canada). In TAH-7, lignin-derived phenols (particularly syringyls) increased associated with peat subsidence, likely reflecting altered drainage patterns following collapse of peat plateaus. In KAK-1, post-1970 decreases in lignin-derived phenol yield and increased lignin oxidation (Al/Ad ratios) was observed, potentially reflecting the impacts of peat subsidence on organic matter transport to lakes under a different hydrological setting. In both lakes, however, we observed a general trend of increasing $C_{23}/(C_{23} + C_{29})$, suggesting that this *n*-alkane index may be useful for tracking ecosystem change in permafrost-associated peatlands. In TAH-7, the onset of shifts in organic matter proxies corresponded to a peak in macroscopic charcoal, demonstrating the importance of forest fire regimes on permafrost dynamics in the sporadic discontinuous permafrost zone. Significant correlations between THg, δ^{13}C, and lignin-derived phenol yield in TAH-7 demonstrate the potential importance of terrestrial carbon as a vector for mercury delivery to aquatic ecosystems under future climate warming scenarios.

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