Climate-driven shifts in sediment chemistry enhance methane production in northern lakes

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Freshwater ecosystems are a major source of methane (CH4), contributing 0.65 Pg (in CO2 equivalents) yr⁻¹ towards global carbon emissions and offsetting ~25% of the terrestrial carbon sink. Most freshwater CH4 emissions come from littoral sediments, where large quantities of plant material are decomposed. Climate change is predicted to shift plant community composition, and thus change the quality of inputs into detrital food webs, with the potential to affect CH4 production. Here we find that variation in phenol availability from decomposing organic matter underlies large differences in CH4 production in lake sediments. Production is at least 400-times higher from sediments composed of macrophyte litter compared to terrestrial sources because of inhibition of methanogenesis by phenol leachates. Our results now suggest that earth system models and carbon budgets should consider the effects of plant communities on sediment chemistry and ultimately CH4 emissions at a global scale.

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Entific freshwater ecosystems are a major source of methane (CH4), contributing 0.65 Pg (in CO2 equivalents) yr−1 towards global carbon (C) emissions and accounting for an estimated 6–16% of natural CH4 emissions as compared to 1% from the oceans1. Freshwater CH4 emissions are enough to offset an estimated ~25% of the terrestrial carbon sink in CO2 equivalents3. Within individual lakes, up to 77% of CH4 emissions can come from production in littoral sediments, where warm temperatures and accumulated organic matter (OM) promote methanogen activity and ebullition3–5, and shallow waters and wave action facilitate rapid diffusion3,7.

In northern (temperate and boreal) lakes, which account for most of the planet’s ice-free freshwater9,9,10, rates of CH4 emission from littoral sediments are known to vary by at least three orders of magnitude9, leaving considerable uncertainty to be explained in regional and global C budgets. In general, emissions are highest where littoral zones are covered with macrophytes9, and plant-related CH4 fluxes remain one of the least-understood components of the global methane budget10. Emergent aquatic plants can directly transport CH4 to the atmosphere through aerenchyma cells, but this cannot explain all of the variability observed within vegetated littoral zones7,11,12, nor can differences in sediment temperature and OM content13. Another explanation is the activity of sediment microbial communities is inhibited, to varying degrees, by the breakdown of different OM sources14, resulting in variation in the production of CH4 in littoral sediments. Therefore, regional estimates of CH4 emissions may need to consider the aerial coverage of different plant species and functional types if they contribute OM that differentially influences rates of sediment CH4 production.

Water-soluble phenolic compounds from plant litter have specifically been shown to bind to and inactivate extracellular enzymes and exert toxicity in methanogens15,16. These compounds build-up in anaerobic soils and sediments because oxygen limitation restricts phenol oxidase activity and dark conditions prevent photodegradation15,16. In this way, the buildup of phenolic compounds may act similar to a ‘latch’, suppressing CH4 production and holding in place large quantities of C in lake sediments that would otherwise be released as CH4. Oxygen limitation plays a similar role in sequestering CO2 in peatlands by restraining phenol oxidase activity17, and rates of CH4 production have been related to peat chemical composition18–20.

Here we show that the production of CH4 in northern lakes can vary by at least 400-times because of differences in sediment chemistry related to sources of plant litterfall. We predicted that sediments would differ in concentration of methanogenesis-inhibiting phenols according to incoming sources of OM. To test the effects of these differences in sediment chemistry on CH4 production in lakes, we compared natural sediments amended with OM from three widespread sources in north-temperate watersheds that vary in phenol content (Supplementary Table 1): mixed coniferous forest litter (CON), mixed deciduous forest litter (DEC), and litter from a ubiquitous emergent macrophyte, Typha latifolia (TYP). We focused on emergent macrophytes because they contribute disproportionately to CH4 emissions from lakes and wetlands21. We also focused on a single macrophyte species rather than a mixture because they tend to grow in monoculture (e.g., cattail beds), whereas it is more realistic to expect a mix of forest litter inputs (e.g., DEC and CON based on the composition of the littoral forest). The sediments were mixed at 20% OM to approximate the average concentrations found in littoral zones of northern lakes22, and incubated in laboratory conditions to control other effects, such as temperature, light exposure, and differences in ambient water quality, which confound observational studies. As northern watersheds are expected to experience a shift in forest composition23,24 and an increase in emergent macrophyte growth in lakes25,26, these findings present an additional mechanism to increased mineralization and permafrost thaw18,27,28 by which climate change can enhance CH4 emission from northern lakes.

Results and discussion
Methane production in sediments. After 150 days of laboratory incubation, CH4 production was over 400-times higher on average from Typha latifolia (TYP) sediments than from mixed-coniferous (CON) sediments, almost 2,800-times higher than from mixed-deciduous (DEC) sediments, and 1,400-times higher than un-amended controls with 0.3% OM (CTR). In contrast, the CON and DEC treatments did not significantly differ from CTR, suggesting that methanogenesis was inhibited in the sediments amended with forest litter (Fig. 1). Our estimated CH4 production rates for a 150-day growing season ranged from averages of 2.63 mg m−2 to 7.22 × 103 mg m−2 amongst the DEC-, CON-, and TYP-amended sediments. These production rates were comparable on a per-area basis to the range and variability of emissions measured in-situ in littoral zones of northern lakes3, reflecting the close relationship between production and emission in shallow waters7. We also found comparable patterns when repeating the experiment with sediments of 10 and 40% OM (Supplementary Fig. 1). A lack of differences in CO2 production rates amongst the amended sediments further suggested that inhibition of methanogenesis and not microbial activity in general was responsible for variation in CH4 production (Supplementary Fig. 2).

Inhibition of methanogenesis by phenols. We took two approaches to test the hypothesis that inhibition of
methanogenesis was occurring in the lake sediments amended with forest-derived OM (CON- and DEC-treatments). Firstly, we measured the relative abundance of methanogens using qPCR targeting the mcrA gene and found on average $1.72 \times 10^4$ and $1.33 \times 10^4$ fewer mcrA copies in the CON and DEC sediments, respectively, compared to the TYP sediments (Fig. 2). These relative abundances mirrored patterns of CH₄ production in Fig. 1, suggesting that suppression of methanogen growth was related to decreased production of CH₄. Although relative abundance of the mcrA gene that we assayed does not entirely equate with specific activity of methanogen communities, there is strong evidence linking it with CH₄ production both here (i.e., Fig. 1–2) and in previous studies³⁹,⁴⁰. This link arises because methanogenesis is not known to be a facultative process, but rather the only mechanism methanogens use to generate ATP (e.g., versus facultative denitrifiers in sediments and soils). A large methanogen population would typically be sustained only with concomitant rapid methane production rates.

The second approach we took to test for inhibition of methanogenesis was to conduct a parallel set of incubations where we added a small quantity of a methanogen-rich sediment ‘spike’ to our treatments at the start of the experiment. Concurrent with our hypothesis of inhibition by plant-derived compounds, there was no change in CH₄ production in the DEC or CON sediments with the spike added, but CH₄ production doubled in the TYP sediment, and increased most strongly in the un-amended control sediments (Fig. 1). The inhibition of CH₄ production in sediments composed of forest-derived compared to macrophyte-derived OM now offers a new mechanism to explain previously described observations in lakes wherein most of the CH₄ emissions come from littoral zones covered with macrophytes³.

Measurements of the biochemical composition of decomposing OM support our conclusion that the inhibition of methanogenesis was caused by phenols from the forest-derived OM. Fluorescence excitation-emission matrices of OM in sediment porewater across all the treatments revealed the presence of a protein-like fluorescence component that was associated with water-soluble phenolic leaf leachates³¹,³², in addition to the ubiquitous triptophan- and tyrosine-like components (Supplementary Fig. 3). Relative concentration of this water-soluble phenol component was lowest in the porewater of the TYP sediments, highest in the DEC sediments, and undetectable in the un-amended CTR sediments. We further found that CH₄ production decreased with relative phenol concentration across all the amended sediment types and OM concentrations, suggesting that suppressed methanogenesis in CON and DEC sediments was related to water-soluble phenols (Fig. 3). These phenol leaf leachates were likely inhibiting methanogenesis by reducing enzyme and methanogen activity through direct toxicity³³,³⁴, pH depression, and/or other chemical effects³⁵,³⁴. Reduction of methanogenesis can also occur through increased availability of thermodynamically-favorable pathways in sediments (e.g., sulfate reduction), but we did not detect the presence of sulfate reducing bacteria in the sediments (below PCR detection limits; Supplementary Table 2) and so it is likely that sulfate was limiting and/or depleted during the 150-day incubation³³. Our results complement Freeman et al.¹⁷ who demonstrate that anoxic conditions suppress phenol oxidase, resulting in the buildup of phenols that further inhibit overall decomposition rates (measured as CO₂ production). Here we show that the buildup of phenols in anoxic sediments also depends on litter type, and that this has implications to the production of CH₄ specifically. We demonstrate that this inhibition is independent of overall rates of decomposition by showing no differences in CO₂ production between litter types despite dramatic differences in CH₄ production (see Supplementary Fig. 2).

**Implications.** As sediments amended with TYP produced so much more CH₄ than forest litter (CON and DEC), our findings

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**Fig. 2** Relative abundance of mcrA gene copies in amended sediments. Relative abundance is orders of magnitude higher in sediments amended with emergent macrophyte (Typha latifolia; TYP) litter than deciduous (DEC) or coniferous (CON) forest litter and mirrors CH₄ production in Fig. 1. DNA was pooled across replicates ($n = 4$ per %OM treatment) and expressed as relative abundance per gram dry-weight (g₉₉₉₉) of sediment normalized for extraction yield determined by qPCR. Samples were run in triplicate and compared to a standard curve generated from eDNA PCR product to capture the environmental variability in sequences. Error bars for amendments represent standard error across %OM treatments (10, 20, 40%).

**Fig. 3** CH₄ production in sediments declines with phenols. The relationship is shown across OM amendment type (DEC, CON, and TYP) and concentrations (10, 20, 40%), with 95% CI shaded. Concentrations of phenols are relative and determined from fluorescence excitation-emission spectroscopy.
may have far-reaching implications for global carbon cycling. For example, species distribution models (SDMs) predict more favorable climatic conditions for the growth of *Typha latifolia*—and other emergent macrophytes with similar phenolic foliage content (Supplementary Table 1)—in the Boreal Shield in the coming decades (Supplementary Fig. 4)26,35. To consider the implications for CH$_4$ emissions, we overlaid published24 SDMs produced by Natural Resources Canada for *Typha latifolia* onto lakes in the Boreal Shield, an ecoregion with relatively homogenous underlying geology and plant communities similar to those in our incubations. By then relating projected occurrence to colonization of suitable lake habitat, we found that the number of Boreal Shield lakes likely to be colonized by *T. latifolia* could double (1.7–2.5 times increase) between 2041 and 2070 (Supplementary Table 3). Assuming no changes other than predicted emergent macrophyte spread, we estimated that the increase in *T. latifolia* alone could elevate CH$_4$ production across Boreal Shield lakes by at least 73% during a 150-year-old growing season (Supplementary Table 3, Fig. 4). Of course, these estimates are heavily caved by several assumptions and uncertainties. For example, climate-driven changes in other factors, such as temperature, oxygenation potential, and increased forest litterfall production, will certainly influence CH$_4$ production from lake sediments, and all production may not necessarily result in emissions1. We have also not accounted for the gas dynamics of living plants, such as rhizosphere processes and aerenchymal transfer that may further enhance emissions where TYP is present31. Similarly we have not accounted for the differential mixing of forest-derived OM in sediments resulting from expected shifts in forest composition36. However our rough calculation is intended to emphasize that lake sediment chemistry is sufficiently important that it should be considered in earth system models, or at the very least in lake carbon budgets37.

Methane production in freshwater ecosystems has recently been recognized as an important component of global C cycles38. Here we have discovered a new mechanism by which plant-related shifts in sediment chemistry under a changing climate can increase methane production in lakes. This mechanism can account for the observed variability in CH$_4$ emission that has been reported both across and within lakes23,39, and should enable more precise models and C budgets in northern watersheds.

**Methods**

**Experimental design.** We amended natural sediments with three different sources: senescent coniferous (CON) and deciduous (DEC) litterfall from a transitional/mixed forest stand (Central Ontario: 44°27.23’N, 79°30.23 ’W), and senescent *Typha latifolia* (TYP) from Ramsey Lake (in Sudbury, Canada: 46°28.98’N, 80°58’19.8 ’W). TYP is one of several common emergent macrophytes in Boreal Shield lakes, all with similar distribution and phenolic content of foliage (Supplementary Table 2, Supplementary Table 3). The CON mix consisted primarily of *Acer rubrum*, *Acer saccharum*, *Betula spp.*, *Populus tremuloides*, *Ulmus americana*, *Quercus rubra*, and *Quercus alba*. All OM was oven-dried for 12 h at 60 °C, ground, and sieved to retain only the fine particulate organic matter (FPOM) fraction (<1 mm).

We diluted the FPOM with a base inorganic sediments with a “base inorganic sediment” mix, denoted by loss-on-ignition at 500 °C for 2 h to create final OM concentrations (by dry-weight) of 20% across the three amendments (CON, DEC, TYP). We used 20% to approximate typical OM concentrations found in littoral zones of northern lakes25 (and confirmed in a nearby lake23) but we also measured CH$_4$ production with 10 and 40% OM to confirm similarity of patterns across conditions. The base sediment was collected from the shoreline of Geneva Lake (near Sudbury, Canada: 46°45’27.2’N, 81°33’19.8’W) away from *T. latifolia* beds and direct inputs of forest-derived OM and was sieved to exclude particles larger than 2 mm. We distributed the mixed sediments into 230 mL mason jars equipped with rubber septa, with four replicate jars per each %OM and amendment type combination. An estimated 70% of methane production occurs in the top 5 cm of saturated soils30, so we filled the jars to a depth of 4.5 cm (allowing room for expansion), before saturating them with TOC-scrubbed A10 MilliQ water (EMD Millipore Corp., Darmstadt, Germany). We also created replicated control jars (CTR) containing only base sediment, otherwise constructed and treated in the same manner.

We duplicated the 20% OM experimental setup with a “methane-rich spike”. The spike consisted of replacing 5% of the base sediment with sediment from the top 5 cm of a littoral site in Ramsey Lake previously known to have high rates of methane production. Amendments of CON, DEC, TYP were adjusted for the 2.8% methane production. Amendments of CON, DEC, TYP were adjusted for the 2.8% methane production. We incubated the sediments and periodically collected headspace samples to measure CH$_4$ and CO$_2$ production after 150 days, representative of the length of a growing season in the Boreal Shield. The sediments were incubated in a BioChambers SPC-56 growth chamber in the dark at 20.5 °C. At the start of the incubations, headspace air in each jar was replaced four times with N$_2$ using a vacuum manifold to ensure anaerobic conditions and removal of atmospheric CO$_2$ and CH$_4$. We collected headspace gas by homogenizing 10 mL of N$_2$ into headspace prior to extracting a 10 mL gas sample by syringe, repeating this periodically over the 150-day incubation to ensure we reach a plateau CO$_2$ and CH$_4$ production in all sediments (Supplementary Fig. 5). The total volume removed was quantified and used to correct headspace volume throughout the incubation. Both CH$_4$ and CO$_2$ were detected as CH$_4$ using a SRI 8610C gas chromatograph (0.5 mL sample loop, 105 °C column temperature), and production was calculated at the end of 150 days, adding back the portions that were removed and expressing totals as mg m$^{-2}$ of dry sediment given an area of 28.3 cm$^2$ for each jar.

**Relative phenol concentration.** To measure relative phenol concentration, we collected porewater from each jar after the 150-day incubations and filtered the samples through 0.5 μm glass fiber filters. Samples were acidified to pH <2 with HCl, and stored in airtight vials at −4 °C. Fluorescence EEMs (excitation–emission matrices) were generated using an Agilent Cary Eclipse Fluorescence Spectrophotometer with a 1 cm path-length cuvette. EEMs were generated from excitation and emission intensities (EX: 250–450 nm in 5 nm steps, EM: 300–600 nm in 2 nm steps) that were adjusted for inner-filter effects with absorbance as measured with an Agilent Cary 60 UV-Vis Spectrophotometer. All EEM sample correction and PARAFAC modeling was done in Matlab R2015b according to the methods outlined in ref. 48. Five PARAFAC components were validated by a split-half method49, explaining 98.7% of the variance in the EEM. Components C1 and C2 were comparable to common humic-like components, with maximum excitation/emission intensities of (310/414 nm) and (345/462 nm) respectively. C3 was similar to the common tryptophan protein-like component (280/354 nm), and C4 the common tyrosine protein-like component (270/306 nm). Component C5 (275/318 nm) was identified as a protein-like component that is associated with leaf litter phenol leachates30,31,32 (Supplementary Fig. 3).

We further confirmed the association between C5 and litter-derived phenol leachates using ultra-high resolution mass spectrometry data collected on a subset of samples in our PARAFAC model from an accompanying field-scale incubation study broadly described in ref. 38 (Supplementary Fig. 6). We extracted DOM from 5.5 mL of filtered and acidified (HCl, pH 2) porewater from sediment in each of 39 field-deployed mesocosms using styrene divinyl benzene polymer solid phase extraction (SPE) cartridges (Agilent Bond Elut PPL, 100 mg)51. The methanol extract was stored at −20 °C in the dark until further analysis. SPE-DOM concentration was determined by an aliquot of the SPE-DOM extract (at 40 °C) and re-dissolving it in ultrapure water. The methanol extracts were diluted to yield a DOC concentration of 5 mg L$^{-1}$ in ultrapure water and MS grade methanol.
and analyzed with Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) on a 15 Tesla solariX (Bruker Daltonik, Bremen, Germany) at the University of Oldenburg using electrospray ionization in negative mode with 4 kV capillary voltage. Data were acquired in broadband mode using 8 megaword data sets and a range of 92–2000 Da with 125 scans accumulated per mass spectrum. Mass spectra were calibrated internally with a list of known compounds in the target range of 0–1 kDa. Peaks were then assigned with the following restrictions: 

\[ C_{n}H_{m}O_{p}N_{q}S_{r}P_{t} \rightarrow \text{masses above the method detection limit} \] 

Additionally, masses detected in less than two samples were removed prior to further analysis. Signal intensities of assigned peaks were normalized to the sum of all peak intensities with identified molecular formulae in each sample.

Relative phenol leachate concentration was estimated as the product of proportional C5 fluorescence and total dissolved organic carbon (DOC) concentration in sediment porewater, as measured in a Shimadzu TOC-5000A in FPOC mode.

**Methanogen suppression.** To compare the relative abundance of methanogens between samples, DNA was first extracted in duplicate using the MoBio PowerSoil kit (MegaBiolog, Carlsbad, CA, USA). qPCR was then carried out in triplicate on pooled DNA extractions to better characterize the communities from the four sediment replicates of the CTR and each OM type mixed at 10, 20 and 40% concentration.

The mcrA replicates of the CTR and each OM type were mixed at 10, 20 and 40% concentration. DNA extractions to better characterize the communities from the 4 sediment types (DEC, CON, TYP). Samples were sequenced on an Illumina MiSeq (ThermoFisher Scientific). Resulting sequences were merged using Pandaseq and further quality filtered and purity was checked (260/280 nm ratio) using a Take3 spectrophotometry system on a Synergy H1 microplate reader (BioTek, Winooski VT, USA). Dissociation curves indicated a pure product, which was confirmed on a 1.5% agarose gel. DNA was then pooled to provide six replicates of the control (CTR) and two replicates per %OM treatment (10, 20, 40%) for a total of 6 samples for each sediment type (DEC, CON, TYP). Samples were sequenced on an Illumina MiSeq using the prokaryote primers Pro 341 F (5′-CCTACGGGNGGCWGCAG-3′) and Pro 805R (5′-GACTACNVGGGTATCTAATCC-3′) by Metagenome Bio Inc. Resulting sequences were merged using Pandaseq and further quality filtered and taxonomy was assigned using the Green Genes database using Usearch v8.1.861 and QIME v1.94-44. Data were plotted with the R package package, and abundance data were corrected using the DeSeq2 package in R.48,49 PC was used to represent samples using the drsA primers DSR-F (5′-ASACGACTTGAGACCAGACCAG-3′) and DSR-R (5′-GTGCMCCTGCGGAC-3′)40. The PC was running Phire Hot Start II PCR Mastermix (Thermal Fisher Scientific). Conditions were an initial denaturation at 98°C for 2 min and 30 cycles of 98°C for 20 s, 59°C for 20 s, 72°C for 40 s and a final extension for 2 min at 72°C.

**Ecosystem-scale emissions.** We estimated the impact of increased T. latifolia occurrence on CH₄ production during the growing season by applying our estimated production rates (mg m⁻² day⁻¹) to current and projected areal coverages for boreal Shield lakes. Surface areas were obtained from the Global Lakes and Wetlands Database (GLWD) for emergent macrophytes between 1000 km² in size, which were divided into the boreal Shield (spatially delineated by the National Ecological Framework for Canada) as an area of 1.8 million km² located between ca. 45°N and 60°N characterized by underlying Precambrian bedrock). For each lake, we extracted current and projected probability of occurrence of T. latifolia from Natural Resources Canada. We used a distribution model raster of the rate of production of CH₄ in our incubation study and coverage by TYP (m², current and projected), propagating uncertainty from climate models and scenarios along with variation in our CH₄ production estimates. Estimates were scaled up to 100% of the sediment profile assuming our 5 cm surficial sediments represented 70% of total production and presented in CO₂ equivalents (1 kg of CH₄ = 25 kg CO₂) to maintain consistency with global emission estimates in ref. 2.

**Statistical analysis.** To compare production rates across OM type, we performed a one-way ANOVA. The ANOVA included the effect of type and its interaction with the methanogen spike with the baseline (intercept) group adjusted to compare significance among groups. The ANOVA was repeated for 10, 20, and 40% OM separately. We then fitted a log-log model to test for an effect of relative phenol concentrations on CH₄ production. All analyses were done in R v. 3.3.0.69

**Data availability.** All sequence data have been deposited in the NCBI Sequence Read Archive under BioProject accession code PRJNA347436. Other datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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