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Mercury reallocation in thawing subarctic peatlands

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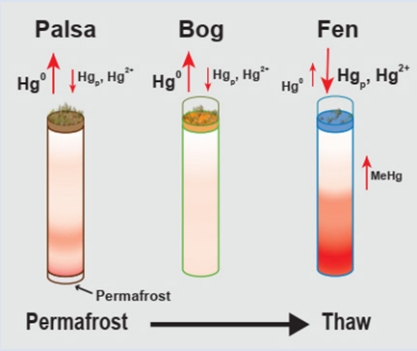
Abstract



Warming Arctic temperatures have led to permafrost thaw that threatens to release previously sequestered mercury (Hg) back into the environment. Mobilisation of Hg in permafrost waters is of concern, as Hg methylation produced under water-saturated conditions results in the neurotoxin, methyl Hg (MeHg). Thawing permafrost may enhance Hg export, but the magnitude and mechanisms of this mobilisation within Arctic ecosystems remain poorly understood. Such uncertainty limits prognostic modelling of Hg mobilisation and impedes a comprehensive assessment of its threat to Arctic ecosystems and peoples. Here, we address this knowledge gap through an assessment of Hg dynamics across a well-studied permafrost thaw sequence at the peak of the growing season in biologically active peat overlying permafrost, quantifying total gaseous mercury (TGM) fluxes, total mercury (Hg_{Tot}) in the active layer peat, porewater MeHg concentrations, and identifying microbes with the potential to methylate Hg. During the initial thaw, TGM is liberated, likely by photoreduction from permafrost where it was previously stored for decades to centuries. As thawing proceeds, TGM is largely driven by hydrologic changes as evidenced by Hg accumulation in water-logged, organic-rich peat sediments in fen sites. MeHg in porewaters increase across the thaw gradient, a pattern coincident with increases in the relative abundance of microbes possibly containing genes allowing for methylation of ionic Hg. Findings suggest that under changing climate, frozen, well-drained habitats will thaw and collapse into saturated landscapes, increasing the production of MeHg and providing a significant source of the toxic, bioaccumulative contaminant.

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Introduction

Anthropogenic Hg emissions have increased Hg deposition to the Arctic three-fold since the Industrial Revolution (Fitzgerald *et al.*, 2005). Terrestrial ecosystems are generally net sinks for atmospheric Hg deposition (Selin, 2009), and Hg sequestration in soil is positively correlated with organic matter content (Grigal, 2003; Smith-Downey *et al.*, 2010). Permafrost constitutes the largest long term reservoir of Hg, containing twice that of all other reservoirs combined (Schuster *et al.*, 2018 and references therein). Changes in the organic carbon (OC) balance from thawing permafrost, coupled with changing redox conditions associated with increases in soil moisture result in the release of labile OC (Hodgkins *et al.*, 2014) that likely drives Hg export (Mu *et al.*, 2019). Reducing conditions favoured in fen environments also influence the bioavailability of Hg *via* binding to thiol functional groups (Skyllberg *et al.*, 2003). Studies of northern peatlands find that Hg export accompanies permafrost thaw associated with climate change (*e.g.*, Rydberg *et al.*, 2010; St. Pierre *et al.* 2018; Mu *et al.*, 2019). Increasing Arctic temperatures also contribute to significant changes in microbial communities and activity which can influence the production of methyl Hg (MeHg), a powerful neurotoxin (Barkay *et al.*, 2011 and references therein; Yang *et al.*, 2016). In this study we present a holistic view of Hg cycling across a permafrost thaw gradient that addresses the interactions of atmospheric, hydrologic and geochemical processes with ecosystem response to changing the distribution and methylating potential of Hg under permafrost thaw (detailed methods descriptions can be found in Supplementary Information).

Stordalen Mire in Abisko, Sweden (68° 22′ N, 19° 03′ E) contains distinct sub-habitats sampled for this study. These representative sub-habitats along a permafrost thaw gradient common to northern peatlands include: i) permafrost-dominated, well-drained palsas occupied by feather mosses and ericaceous and woody plants (ii) intermediate permafrost sites with variable water table depth, dominated by *Sphagnum* spp.

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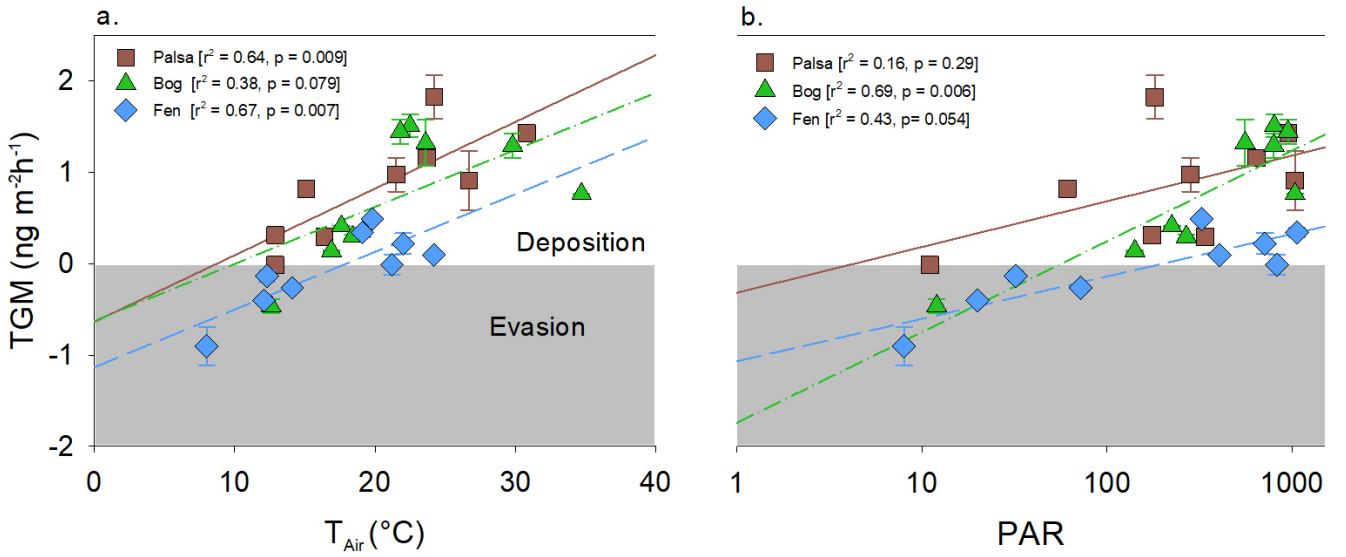

Figure 1 **(a)** Relationships between TGM flux and ambient air temperature (°C) and **(b)** photosynthetically active radiation (PAR). Symbols denote palsa (brown squares), bog (green triangles) and fen (blue diamonds) and include least squares linear regressions and associated r^2 and p values. Evasion of TGM interpreted for values greater than zero and deposition for values less than zero.

(iii) full summer-thaw, fully submerged sites with *Eriophorum angustifolium* (Fig. S-1). Between 1970 and 2000, permafrost thaw and palsa collapse led to the expansion of *Sphagnum* (bog) and *Eriophorum* (fen) by 3 % and 54 %, respectively (Johansson *et al.*, 2006a). Linking thawing permafrost with hydrologic change (Johansson *et al.*, 2006b), vegetation shifts over a 30 year period (Malmer *et al.*, 2005; Johansson *et al.*, 2006a) and carbon dynamics in a mire (*e.g.*, Öquist and Svensson, 2002; Bäckstrand *et al.*, 2010) provide essential context to develop a predictive framework for Hg cycling in the future thawed permafrost.

Results and Discussion

Mechanisms driving Hg cycling in Arctic ecosystems

1. Evasion. Full quantification of Hg mobilisation requires an assessment of the dynamics of Hg exchange at the atmosphere-land interface. During three days of dynamic chamber flux measurements (in the peak of the growing season) all three sites exhibited a diel pattern in TGM fluxes, as shown in previous studies (Carpi and Lindberg, 1997; Poissant *et al.*, 2004; chamber flux measurement approach described in Supplementary Information). Evasion of TGM occurred during warmer, peak daytime PAR while TGM deposition occurred during cooler, low PAR (<400) periods (Fig. 1). The palsa site yielded the highest TGM evasion coupled with the least amount of Hg deposition during the low PAR hours. The bog exhibited the most variability of the three sites. The strong correlation between TGM flux and PAR in the bog site is consistent with earlier interpretations (Klaminder *et al.*, 2008) of increased photoreduction reactions in water-saturated soils, resulting from permafrost thaw, leading to lower peat Hg concentrations (Gustin *et al.*, 2006). The bog TGM flux, together with lower Hg_{Tot} concentrations deeper in the peat, suggest significant Hg loss (Klaminder *et al.*, 2008), with the semi-wet or intermediate stage of the thaw resulting in less Hg retention in soils and vegetation (Fig. 2). The fen site experienced both the lowest TGM evasion and the highest TGM deposition (most negative fluxes). Some studies have found that biotic demethylation of Hg can be a significant source of evasion (Pannu *et al.*, 2014 and references therein). Both the fen and the palsa sites showed stronger relationships between air temperature and TGM flux and this may influence both biotic and abiotic reactions (Fig. 1).

2. Soil carbon labileness and sulphur redox. The three habitat types representing a permafrost thaw gradient were also characterised by markedly different peat Hg_{Tot} concentrations. The palsa site had the highest overall Hg_{Tot} with concentrations ranging from 257 µg kg^{-1} near the surface and decreasing to 15 µg kg^{-1} with depth to the active layer boundary (44 cm from surface) (Fig. S-4). The bog site had the lowest overall Hg_{Tot} (concentrations from 10-75 µg kg^{-1}). The fully thawed fen habitat had intermediate Hg_{Tot} concentrations (10-165 µg kg^{-1}), with values decreasing gradually with depth as in the palsa. Relative Hg_{Tot} pools estimated by combining bulk density at each site (profiled at ~5 cm increments) with the Hg_{Tot} measurements (details in Supplementary Information) followed the same pattern, with; palsa (2.7 mg m^{-2}), bog (1.4 mg m^{-2}) and fen (4.7 mg m^{-2}) (Fig. 2). These findings suggest that the Hg liberated from thawing palsa has two potential pathways of reallocation; palsa may thaw directly to a bog and from there result in Hg export, or alternatively palsa may transition directly to a fen where Hg accumulation is enhanced.

Total peat sulphur (S) concentrations (Fig. S-4) provide additional evidence pointing to Hg_{Tot} accumulation. The surface of the fen sites (~0-1 cm depths) contain almost double the amount of S relative to both the palsa and the bog sites. At the fen, total Hg shows a strong relationship with C, N and S (r^2 = 0.73, 0.77, 0.82), whereas in the bog and palsa the correlations are weak or insignificant (Fig. S-5). In reducing environments, S in peat forms organo-sulphides, especially in the presence of hydrogen sulphide (Schartup *et al.*, 2014) which enhances storage of Hg.

The degree to which these dynamic landscapes might serve as sources of the biologically available and toxic MeHg was evaluated through the analysis of porewater chemistry. In addition to enhanced peat Hg accumulation in the fen, we also found elevated concentrations of MeHg in fen porewater that were similar to those reported in other wetland studies (*e.g.*, Tjerngren *et al.*, 2012). This pattern was in contrast to the notably lower porewater MeHg concentrations in the bog site (Table S-1). The methylation of Hg in the mire may be

a function of bioavailable Hg and/or linked with the ability of the microbial community to methylate Hg. Differences in redox conditions, organic matter structure and composition, and microbial communities between bog and fen sites may explain the observed differences in MeHg. The presence of higher total S in the fen site may also enhance the bioavailability of ionic Hg leading to methylation (Skyllberg *et al.*, 2003). Additionally, the Hg bound to more labile OC may be more easily methylated by microbes than Hg bound to more recalcitrant C. Hodgkins *et al.* (2014) compared the same bog and fen sites in this study, drawing clear distinctions between the compositions of the organic matter. They highlight the ability of *Sphagnum* to control the rate of decomposition in the bog by producing phenolic compounds. This pattern is in stark contrast to the fen, where decomposition rates highly correspond to microbially derived organic matter (Hodgkins *et al.*, 2016).

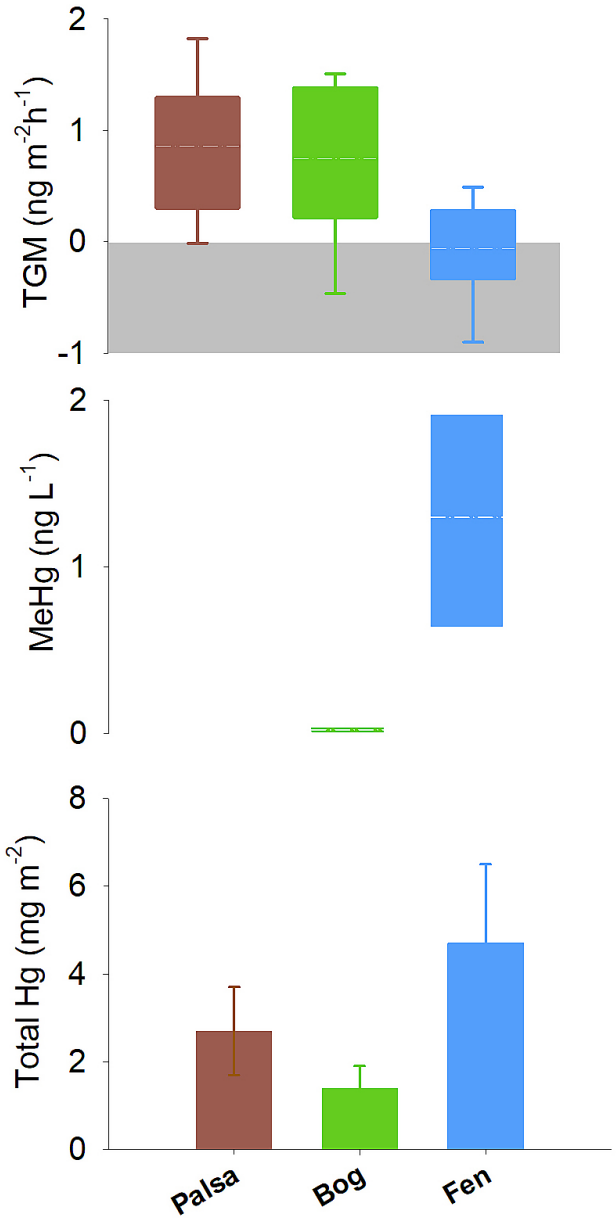

Figure 2 Summarised Hg in the three sub-habitats (from top to bottom): TGM, porewater methyl Hg (MeHg), and total peat Hg (corrected for dry bulk density).

3. Methylation potential of peatland sub-habitats. The microbial communities are markedly different across the palsa, bog and fen as attested by 16S rRNA gene analyses (Mondav *et al.*, 2014; 2017). We examined observed lineages for potential Hg methylators (*i.e.* microbial genera either experimentally demonstrated to methylate Hg or inferred to do so by the presence of the *hgcA* and *hgcB* genes required for Hg methylation (Parks *et al.*, 2013; Table S-2; detailed methods in Supplementary Information). These potential Hg-methylating microbes increased across the thaw gradient from low relative abundance in the palsa and bog (~0.5 % and ~0.7 % of the community, respectively) to markedly higher abundance in the fen (~7.8 %) (Fig. 3 and Table S-2). The identified potential Hg-methylators include sulphate- and iron-reducing lineages from the *Deltaproteobacteria* and *Clostridia*, as well as methanogens of *Methanomicrobia* (Table S-2). *Methanoregula*, an important methanogen at the site (Mondav *et al.*, 2017) and one of the potential Hg-methylators present, was both relatively more abundant and more diverse (more lineages recovered) in the fen. Overall, the presence of a larger and more diverse community of potential Hg-methylators in the fen supports the role of microbes in driving elevated MeHg in fen porewaters and the presence of potential Hg-methylating methanogens highlights the interacting impacts of permafrost thaw on the production of both methane and MeHg.

A revised framework for Hg cycling in Arctic ecosystems

Contrary to earlier conceptual models of Hg export from Arctic ecosystems (*e.g.*, Klaminder *et al.*, 2008), we found that while Hg is liberated from peat during the intermediate thaw stage it is subsequently accumulated in a later thaw stage represented in the fen site. Recent studies from Alaska (Obrist *et al.*, 2017; Douglas and Blum, 2019) found TGM uptake by vegetation to be a significant pathway of Hg accumulation. Increasingly longer growing seasons associated with changing climate (Callaghan *et al.*, 2010 and references therein), coupled with the expansion of fen sites throughout the mire (Johansson *et al.*, 2006a), suggest this mechanism is likely relevant in Stordalen Mire. A second potential fate, depending on the pace of climate change, may be catastrophic collapse of permafrost as observed in the western Canadian Arctic (St. Pierre *et al.*, 2018). This second pathway bypasses the peat or fen storage and flushes large quantities of both total and methyl Hg from the ecosystem (St. Pierre *et al.*, 2018).

Conclusions

Examination of Hg_{Tot} pools in thawing peat, combined with mechanisms of gaseous Hg flux and MeHg production, lead to a revised conceptual model of pathways of Hg loss and retention in thawing permafrost peatlands (Fig. 4). Taken together, these results suggest a more complex set of processes amongst permafrost thaw regions. During initial stages of permafrost thaw, when the active layer in the palsa deepens, export of gas-phase TGM is a primary pathway of Hg loss. As the thaw continues vegetation changes to a *Sphagnum*-dominated semi-thawed ecosystem, where Hg export into the atmosphere limits accumulation of Hg in peat and the peat bound Hg_{Tot} pool is depleted. The final stage of thaw, characterised by fully thawed fens, results in a more biologically mobile Hg pool. This transition is facilitated *via* favourable redox conditions, more labile organic matter and a diverse microbial community capable of methylation, resulting in greater Hg retention in fen peat and also higher levels of porewater MeHg that may be exported to nearby lakes and streams. Given the prediction

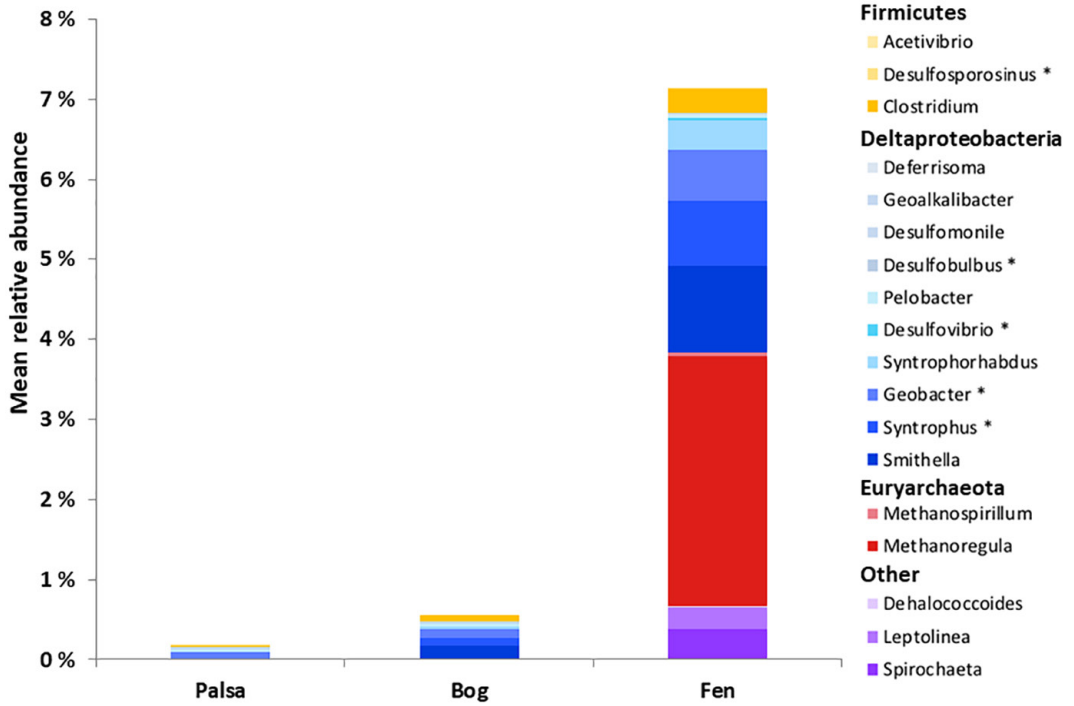

Figure 3 Mean relative abundance of potential Hg methylators at Stordalen Mire (n = 38 for palsa, 47 for bog, and 42 for fen), using microbial community data from 2010-2012 reanalysed from Mondav *et al.* (2017). * indicates genera with members experimentally confirmed to methylate Hg.

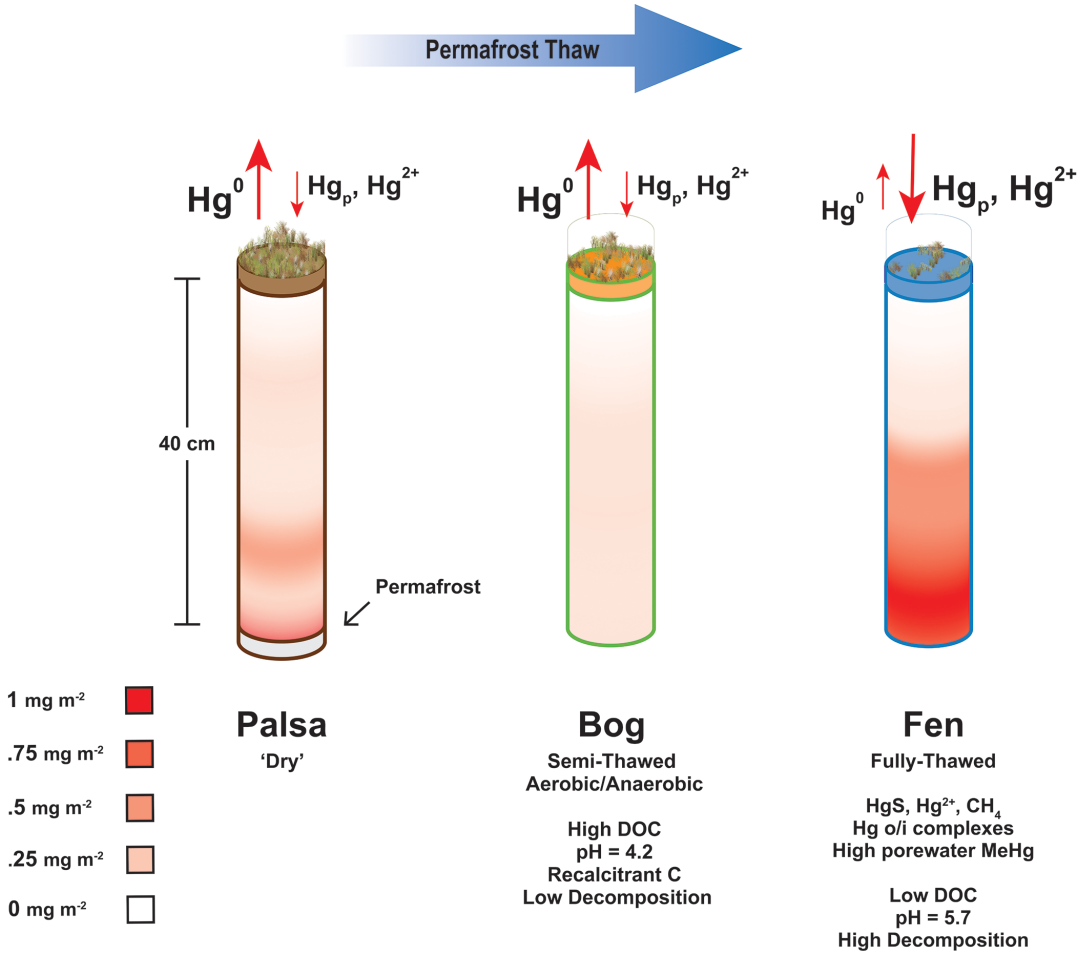

Figure 4 Schematic of biogeochemical Hg cycling across permafrost thaw with emphasis on Hg pools and major pathways. Red arrows denote gaseous (Hg^0) flux for each stage of the thaw sequence. Peat inventories are for total Hg for the top 40 cm of the mire surface (cf. legend for corresponding range).

of loss of discontinuous zone permafrost by 2100 (Slater and Lawrence, 2013), it is imperative that long term studies coupling Hg cycling, microbial community composition and mechanisms driving gene expression of Hg methylation as well as varying environmental conditions are carried out to improve predictions of the fate of Hg stored in permafrost within these dynamically changing ecosystems.

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Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1922.

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