



## **Geochemical constraints on organic matter decomposition in deep peatlands**

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Decomposition of deep peat deposits controls the long-term carbon balance of peatlands but is poorly understood with respect to rates and controls. To rectify this deficiency, we estimated in situ dissolved inorganic carbon (DIC) and methane ( $\text{CH}_4$ ) production rates from a beaver pond to a central bog dome, and related them to organic matter properties, Gibbs free energies of respiration, and  $\delta^{13}\text{C}$  values of DIC and  $\text{CH}_4$ . DIC and  $\text{CH}_4$  production decreased from maxima of about  $10 \text{ nmol cm}^{-3} \text{ d}^{-1}$  near the water table to values  $< 0.1 \text{ nmol cm}^{-3} \text{ d}^{-1}$  at depths  $> 1 \text{ m}$ , with little differentiation among sites. Deeper into the peat, we measured an accumulation of DIC,  $\text{CH}_4$ , and dissolved organic matter (DOM) enriched in aromatic and phenolic moieties, which resulted from the slowness of diffusive vertical pore water movement. Lack of transport may have slowed decomposition by two factors: (I) Aromatic and phenolic DOM moieties accumulated, while the release of carbohydrate-rich DOM from peat was apparently impeded. (II) The accumulation of DIC and  $\text{CH}_4$  reduced Gibbs free energy of acetoclastic methanogenesis towards a critical threshold value of 25 to  $20 \text{ kJ mol}^{-1} \text{CH}_4$ . Hydrogenotrophic methanogenesis was energetically more favorable and generally dominated according to an isotopic fractionation between  $\text{CO}_2$  and  $\text{CH}_4$  of 1.053 to 1.076; but it was apparently impeded by some other factor. Similar results were obtained at three other peatlands of the Montreal-Ottawa region. We conclude that lateral homogeneity and slowness of decomposition in geologically sealed deep peat deposits is assisted by a lack of solute transport, facilitating the formation of deep peat deposits over millenia.