

## Transport, anoxia and energy control on anaerobic respiration and methanogenesis in anoxic peat soils

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In deep and permanently water saturated peat deposits, extremely low diffusive transport and concomitant build-up of metabolic end-products, i.e. of dissolved inorganic carbon (DIC) and methane ( $\text{CH}_4$ ), have been found to slow-down anaerobic respiration and methanogenesis. Such accumulation of DIC and  $\text{CH}_4$  lowers the Gibbs free energy yield of terminal respiration and methanogenesis, which can inhibit the course of anaerobic metabolic processes. In particular, this affects terminal steps of the breakdown of organic carbon (C), such as methanogenesis, acetogenesis and fermentation processes, which occur near thermodynamic minimum energy thresholds. This effect is thus of critical importance for the long-term C sequestration, as the slow-down of decomposition ultimately regulates the long-term fate of C in deep peat deposits. The exact controls of this observed slow-down of organic matter mineralization are not yet fully understood. Moreover, altered patterns of water or gas transport due to predicted changes in climate may affect these controls in peat soils.

Therefore, the aim of this study was to investigate how burial of peat leads to an inactivation of anaerobic decomposition and to investigate the effects of advective water transport and persistently anoxic conditions on anaerobic decomposition, temporal evolution of thermodynamic energy yields to methanogenesis and methanogenic pathways. To this end, we conducted a column experiment with homogenized, ombrotrophic peat over a period of 300 days at 20°C. We tested i) a control treatment under diffusive transport only, ii) an advective flow treatment with a flow of 10 mm d<sup>-1</sup>, and iv) an anoxic treatment to evaluate changes in decomposition in absence of oxygen in the unsaturated zone of the cores.

A slow-down of anaerobic respiration and methanogenesis generally set in at larger depths after 150 days at  $\text{CH}_4$  concentrations of 0.6-0.9 mmol L<sup>-1</sup> and DIC concentrations of 6-12 mmol L<sup>-1</sup>. This effect occurred at higher concentration levels and faster than previously observed. Advective water transport effectively extended the zone of methanogenesis down to 40 cm depth until inhibiting conditions were reached, although net turnover at greater depths was not affected. Strictly anoxic conditions in the unsaturated zone, where diffusive transport is high, had little effect on accelerating anaerobic decomposition. The slow-down of net production rates of  $\text{CO}_2$  and  $\text{CH}_4$  agreed well with the decline over time of Gibbs free energies available to methanogenesis, supporting a thermodynamic constraint on decomposition in deeper peat deposits.

**Keywords:** Peatlands; Anaerobic decomposition; Methanogenesis; Production rates; Advection; Anoxia; Thermodynamic calculations.