

Thermodynamic constrains on the flux of organic matter through a peatland ecosystem

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The transformations and transitions of organic matter into, through and out of a peatland ecosystem must obey the 2nd law of thermodynamics. Beer and Blodau (*Geochimica Cosmochimica Acta*, 2007, 71, 12, 2989-3002) showed that the evolution of CH₄ in peatlands was constrained by equilibrium occurring at depth in the peat as the pore water became a closed system. However, that study did not consider the transition in the solid components of the organic matter flux through the entire ecosystem.

For this study, organic matter samples were taken from each organic matter reservoir and fluvial transfer pathway and analysed the samples by elemental analysis and bomb calorimetry. The samples analysed were: above- and below-ground biomass, heather, mosses, sedges, plant litter layer, peat soil, and monthly samples of particulate and dissolved organic matter. All organic matter samples were taken from a 100% peat catchment within Moor House National Nature Reserve in the North Pennines, UK, and collected samples were compared to standards of lignin, cellulose, and plant protein. It was possible to calculate ΔH_{fOM} , ΔS_{fOM} and ΔG_{fOM} for each of the samples and standards. By assuming that each thermodynamic property can be expressed per g C and that any increase in ΔG_{fOM} can be balanced by the production of CO₂, DOM or CH₄ then it is possible to predict the consequences of the fixation of 1 g of carbon in a peatland soil.

The value of ΔG_{fOM} increases from glucose to components of the biomass: 1g of C fixed as glucose by photosynthesis would result in 0.68 g C as biomass and 0.32 g C as CO₂. The transition from biomass to litter could occur spontaneously but the transition from surface to 1m depth in the peat profile would release 0.18 g C as CO₂ per 1 g of carbon entering the peat profile. Therefore, for every 1 g of carbon fixed from photosynthesis then 0.44g of C would be released as CO₂ and 0.54 g C would be present at 1 m depth. Alternatively, if DOM only were released in transition down the peat profile then for every 1 g of carbon fixed by photosynthesis 0.32 g C would be released as CO₂ and 0.22 g C would be lost as DOM and leaving 0.46 g C as residual peat at 1m depth. If the variation in ΔG_{fOM} of the DOM were considered then for every 1 g of C produced as DOM then between 0 and 0.57g C would be lost as CO₂. At median value of DOM loss then for every 1g of carbon fixed as photosynthesis 0.39 g C would be lost as CO₂ and 0.15 g lost as DOM with 0.46 g C as residual peat. Alternatively, if CH₄ only were released down the soil profile then no organic matter would be left in the peat profile, i.e. CH₄ is not an efficient method of transferring Gibbs free energy. The measured carbon budget for this catchment is that 1 g C fixed as photosynthesis resulted in 0.42 g C as CO₂; 0.29 g C as DOM; 0.04 g C as CH₄ and 0.24 g C as residual peat at 1m depth.