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The effect of source material in determining the photoreactivity of DOM in peatland aquatic systems

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Aquatic systems draining peatlands receive a high loading of dissolved organic matter (DOM) from surrounding terrestrial environments. However the fate of aquatic DOM remains poorly constrained, in part due to lack of knowledge regarding the photoreactivity of DOM and how this changes as a function of variability in source material. In this study water samples were collected monthly for a 13-month period from two contrasting aquatic systems in Scotland: a stream draining a peatland with high DOM concentrations (33.3 $\pm$ 14.2 mg DOC L^{-1}) and a reservoir draining a peat catchment with low DOM concentrations (4.16 $\pm$ 0.91 mg DOC L^{-1}). Controlled UV irradiation laboratory experiments were conducted on samples filtered to 0.2 μm in order to assess the photoreactivity of the DOM, measured as the unit mass of DOC lost upon irradiation. Experiments took place over 8h in temperature controlled conditions, with unirradiated samples used as controls. After exposure, a range of analytical techniques were used to characterise the DOM to yield information about its source material and to determine how this was related to the observed photoreactivity. Lignin phenol analyses indicate considerable contribution of *Sphagnum* to DOM at the stream site, particularly during summer, as demonstrated by high P-hydroxy/Vanillyl phenol ratios (P/V). Low P/V ratios were correlated with increased photoreactivity, (Pearson's: -0.410; p = 0.15, n = 13), suggesting that DOM from woody lignin sources within the catchment was more photolabile. Photoreactivity was also negatively correlated with Fluorescence Index (FI) values (Pearson's: -0.555; p = 0.055, n = 13), where low FI values are understood to indicate greater contribution of terrestrially derived material to aquatic DOM. Excitation-emission matrices (EEMs) indicate that DOM at the stream site was primarily comprised of a humic-like peak (Ex/Em = 340, 380/460 nm). However, there was also contribution from a protein-like peak (Ex/Em = 290, 320/350 nm), which was present in samples with lower photoreactivity. DOM at the reservoir site was primarily composed of the same identified protein-like peak, which may account for the lower observed photoreactivity of these samples. Although total DOC concentration is the dominant control on photo-induced DOC losses in peatland aquatic systems, these results show that organic matter characterisation can be used to further comprehend changes to DOM photoreactivity. Increased understanding of DOM processing in aquatic freshwater systems will allow the fate of DOM to be more accurately determined.