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Combined use of geophysical and geochemical methods to assess areas of active, degrading and restored blanket bog

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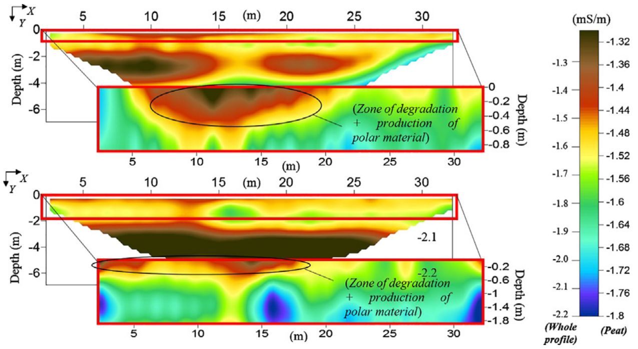
HIGHLIGHTS

- Degradation processes alter the normalized chargeability.
- Degrading and restored locations are dominated by vascular plants.
- Vascular plants permit oxygen diffusion via roots deeper into subsurface.
- Aerated conditions support oxidation of phenols and production of $C{=}O$ double bonds.
- Polar compounds increase normalized chargeability and cation exchange capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Here we combine the use of geo-electrical techniques with geochemical analysis of the solid and liquid phase to determine subsurface properties and general peatland health. Active, degrading and restored peat locations were analysed from the same blanket bog site (ensuring they were under the same environmental conditions, such as rainfall and temperature) at the Garron Plateau, Northern Ireland. A normalized chargeability (ratio of resistivity (inverse of conductivity) and chargeability) profile was compared with organic composition analysis of the solid and liquid phases from active, degrading and restored locations. Results show that the degrading location is undergoing high rates of decomposition and loss of organic matter into the interstitial water, whereas the opposite is true for the active location. The restored peat is showing low rates of decomposition however has a high concentration of organic material in the porewater, primarily composing long chain aliphatic compounds, sourced from vascular plants. The ingression of vascular plants permits the diffusion of oxygen via roots into the subsurface and supports the oxidation of phenols by phenol oxidase, which produces phenoxy radicals and quinones ($C{=}O$ double bonds). This production of conjugated quinones, which are characterized by a $C{=}O$ double bond, in the aerated degrading and restored locations, increase the polarity, cation exchange capacity, and the normalized chargeability of the peat. This higher chargeability is not evident in the active peat due to decreased aerobic decomposition and a domination of sphagnum mosses.

1. Introduction

Ombrotrophic peatlands are valuable yet vulnerable ecosystems whose ecology and degradation status are closely linked to the movement and storage of water (Rezanezhad et al., 2016). Actively

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accumulating bogs form natural organic matter (NOM) by the humification of plants under water saturated and anoxic conditions. Drainage introduces oxygen into the previously anoxic environment, causing rapid aerobic decomposition and loss of organic carbon. In addition, drainage can allow the ingression of oxygen to the subsurface promoting aerobic degradation of organic matter. One of the dominant mechanisms proposed for this aerobic degradation is the 'enzymatic latch hypothesis' (Freeman et al., 2001) where the normally constrained phenol oxidase enzyme is able to freely degrade in aerated conditions. The degradation products created by phenol oxidases are phenoxy radicals and conjugated quinones (Sinsabaugh, 2010), which are characterized by a C═O double bond and are electrophilic and polar. The ingression of vascular plants due to overgrazing can also influence oxygen availability and enzymatic activity by allowing oxygen diffusion to deep roots (Romanowicz et al., 2015).

In the 1960's and 1970's, artificial drainage of blanket bogs was introduced across the UK to lower the water table in an attempt to improve agricultural production of the land and to reduce the risk of flooding downstream by creating a moisture deficit (Wallage et al., 2006). It has recently been recognized that these processes have had several negative environmental impacts, including increased downstream flood risk, increased concentrations of organic material in ground and surface water and increased flux of carbon dioxide (CO_2) to the atmosphere (Holden et al., 2004). In response to these consequences of degradation, many countries are now installing policies that aim to restore a significant portion of peatlands by re-establishing a naturally functioning, actively accumulating system (Emsens et al., 2016). These policies usually involve reducing stocking density for sheep grazing as well as raising the water table by blocking the drains in an attempt to re-create the anoxic conditions necessary for peat accumulation. It is well understood that water table decline within the peat profile, increases rates of decomposition (Wallage et al., 2006), however it is not well-known how rates of humification in drain-blocked areas are affected. Research is now being undertaken to assess the effectiveness of blanket bog restoration (McAnallen et al., 2017). There is a growing recognition that the integration of geophysical measurements into hydrological, process-based watershed studies could significantly advance our understanding of dynamic hydrological processes, especially at intermediate scales, such as in small watersheds to small basins (Robinson et al., 2008). Geophysical studies can be used to improve the understanding of stratigraphy, hydrogeology and hydrochemistry of peatlands (Slater and Reeve, 2002). In particular, near surface geophysics is a strengthening discipline within which hydrogeophysics is emerging, dealing with the application of geophysical methods to investigate subsurface hydrological and microbiological processes (Mendonça et al., 2015a, 2015b).

This study involved comparison between: a drained and over grazed (*degrading*) peat; an actively accumulating (*active*) peat; and a previously drained and overgrazed peat which has undergone drain blocking and reduced grazing (*restored*) from an upland blanket bog catchment in Northern Ireland. The electrical resistivity of the peat subsurface, which is a physical property related to soil type, porosity and the ionic strength of the pore fluid, was measured at each of the three locations (Robinson et al., 2008). Eq. (1) can be used to describe this process which involves placing an array of conductive electrodes into the peat and injecting a current (I) into the ground and then measuring the resulting voltage ($V\rho$) via potential electrodes (Reynolds, 2011). This response ($V\rho/I$) is termed the transfer resistance (through Ohm's law), and is multiplied by a geometric factor (K) which accounts for distances and layout of electrodes to calculate the apparent resistivity (ρ_a) (Mendonça et al., 2015c).

Apparent resistivity calculation (Reynolds, 2011):

$$\rho_a = \frac{Vp}{I}\mathrm{K}(\Omega\mathrm{m}) \tag{1}$$

The bulk conductivity is the inverse of resistivity and is also therefore dependent upon soil type, porosity and the ionic strength of the pore fluid. As resistivity surveys are particularly sensitive to the effects of the fluid conductivity and saturation, Induced Polarization (IP) methods were used as they are more sensitive to the surface chemical properties of the soil (Lesmes and Frye, 2001). Recent research advances in IP (Kemna et al., 2012; Binley et al., 2015; Robinson et al., 2008) have made the technology more attractive for hydrogeophysical research. IP measures the charge loss (chargeability (M)) of the subsurface material over a given time (Robinson et al., 2008). The response is highly dependent on surface chemistry, which is controlled by charge density, surface area and fluid chemistry (Slater and Reeve, 2002). A measure of the magnitude of the IP effect in the time domain is the chargeability (M) (Eq. (2)), where Vs is the residual voltage recorded within a given time window ($dt = t_2 - t_1$) after which the injection of current was stopped (t_1).

Chargeability calculation (Mendonça et al., 2015a, 2015b, 2015c):

$$M = \frac{1}{Vp}\int_{t_1}^{t_2} Vs\, dt \tag{2}$$

As the resistivity of peat is principally a function of the electrical properties of fluids in the pore space, and chargeability is a function of both the pore fluid electrical properties and those of the interface between the solid matrix and the fluid-bearing pore space, Keller (1959) proposed a normalization of chargeability by calculating the ratio of chargeability to resistivity (Eq. (3)), which Keller termed "specific capacity".

Normalized chargeability calculation (Reynolds, 2011):

$$M_N = {}^{M}/_{\rho} \tag{3}$$

This normalized chargeability (M_N) helps to isolate information about surface chemical processes (Doherty et al., 2010), especially where fluid conductivity (σ_w) is high (Lesmes and Frye, 2001) and is a better lithologic discriminator than chargeability as it is less influenced by fluid conductivity (Slater and Lesmes, 2002). In the case of peat which has undergone significant aerobic degradation normalized chargeability may be related to the cation exchange capacity of the soils (Revil et al., 2017), in the case of peats it is the negatively charged functional groups that sorb metals (Vile et al., 1999).

Fourier Transform Infrared (FTIR) spectroscopy is a technique which has been widely used to characterise organic matter quality of bulk peat (Holmgren and Norden, 1988) and is capable of distinguishing the principal chemical classes in soil organic matter, such as carbohydrates, lignins, cellulose and proteinaceous compounds, through the vibrational characteristics of their structural chemical bonds (Artz et al., 2008). In particular, FTIR can also identify the presence of C═O compounds such as quinones. Comprehensive Two-Dimensional Gas Chromatography with Flame Ionization Detector (GCxGC-FID) is one of the most powerful tools for environmental analysis of organic compounds in complex matrices and involves splitting a sample injection to two independent gas chromatography columns one of which measures polarity. When the information from the two columns is combined it provides more information about sample constituents than can be observed from a single injection, greatly reducing analysis time (Welke and Zini, 2011).

2. Material and methods

2.1. The study site

The Garron Plateau (Fig. 1) (latitude 55.003, longitude −6.061) contains the most extensive area of intact blanket bog in Northern Ireland, with an area of over 4650 ha (Joint Nature Conservation Committee, 2016). The peatland complex holds Dungonell reservoir, which is owned by Northern Ireland Water and provides drinking water to the surrounding area. The Garron Plateau peatland is a designated Area of Special Scientific Interest (ASSI), Special Area of conservation (SAC), Special Protection Area (SPA) and a Ramsar site. Although highly protected, previous sampling and analysis undertaken by the Department of