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Soil Biology & Biochemistry 40 (2008) 1519–1532

Soil Biology & Biochemistry

www.elsevier.com/locate/soilbio

Summer drought effects upon soil and litter extracellular phenol oxidase activity and soluble carbon release in an upland *Calluna* heathland

Hannah Toberman[a,b,*], Chris D. Evans[b], Christopher Freeman[a], Nathalie Fenner[a], Marie White[a], Bridget A. Emmett[b], Rebekka R.E. Artz[c]

[a]*School of Biological Sciences, University of Bangor, Deiniol Road, Gwynedd LL57 2UW, UK*
[b]*Centre for Ecology and Hydrology Bangor, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd LL57 2UW, UK*
[c]*The Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, Scotland, UK*

Received 3 July 2007; received in revised form 30 November 2007; accepted 7 January 2008
Available online 5 February 2008

Abstract

Extracellular phenol oxidases play an important role in the soil carbon cycle. The effects of a field-scale summer drought manipulation on extracellular litter and soil phenol oxidase activity, soluble phenolic compounds and dissolved organic carbon concentrations were examined for an upland *Calluna* heathland on a peaty podsol in North Wales. Litter and organic soil phenol oxidase activity was found to be positively correlated with moisture content. Thus in shallow organic soils, which are sensitive to drying during periods of low rainfall, drought may inhibit soil phenol oxidase activity as a result of water limitations. The release of soluble phenolic compounds and DOC from the droughted plots was found to be lowered during the drought period and elevated outside of the drought period. It is hypothesized that these changes may be a result of the reduced ability of extracellular phenol oxidases to process recalcitrant polyphenolic material under drought conditions. A drying incubation carried out with litter and soil cores from the same site suggests that extracellular phenol oxidase activity displays an optimal moisture level. This reconciled the observed water limitation of phenol oxidase activity at the heathland experimental site with previously observed stimulation of phenol oxidase activity by water table drawdown in deeper peats.

Keywords: Phenol oxidase; Extracellular enzyme; Drought; Heathland; DOC; Phenolic degradation; Carbon cycling

1. Introduction

Organic matter accumulating soils represent a vast pool of stored carbon (Admundson, 2001; Schulze and Freibauer, 2005). The Intergovernmental Panel on Climate Change (IPCC, 2007) has predicted that global warming may result in a greater frequency and severity of summer droughts at the higher latitudes where extensive areas of organic soils occur. The potential impact of increased drought frequency on carbon storage and release in organic soils is thus of critical concern for the future global carbon balance. It has been estimated that shallow peaty organo-mineral soils (peaty gleys and peaty podsols) cover an area of approximately 3 million hectares in the UK, representing nearly a quarter of the total UK peatland carbon stock (Cannell et al., 1993). This study assesses the effects of repeated summer drought upon litter and soil phenol oxidase activity, phenolics and dissolved organic carbon (DOC) at a peaty podsolic upland heathland site.

Being a crucial component of the cycling of complex organic matter and phenolics in the decompositional environment, extracellular phenol oxidase enzymes may play an important role in the stability of long-term soil carbon stores. Extracellular phenol oxidase pools comprise of an array of different types of phenol oxidase enzymes (Burke and Cairney, 2002), known microbial producers include fungi (Hammel, 1997) and bacteria (Hullo et al., 2001; Endo et al., 2003; Fenner et al., 2005a). Phenol

*Corresponding author at: Centre for Ecology and Hydrology Bangor, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd LL57 2UW, UK. Tel. +44 1248 374525.
E-mail address: htob@ceh.ac.uk (H. Toberman).

0038-0717/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.soilbio.2008.01.004

oxidases act upon complex and simple phenolics, with outcomes ranging from partial oxidation and the release of oxidative intermediates, to complete degradation (Burke and Cairney, 2002; Claus, 2004). Polyphenolics inhibit decomposition by binding to the reactive sites of extracellular enzymes and through the formation of phenolic complexes (Horner et al., 1988; Harborne, 1997). The activity of extracellular phenol oxidases may therefore affect the retention of carbon in the litter and soil environment directly via the breakdown of recalcitrant organic matter, and indirectly by releasing extracellular hydrolase enzymes from phenolic inhibition (Freeman et al., 2001a, 2004).

Phenol oxidases are inhibited by low temperatures (Freeman et al., 2001b), low oxygen availability (Pind et al., 1994; Freeman et al., 2001a) and low pH (Ruggiero and Radogna, 1984; Pind et al., 1994), and it was expected that levels of phenol oxidase activity would be naturally constrained by the cold, wet, acidic conditions at the heathland study site. However, phenol oxidases have been found to be produced by bacteria in wetland peat (Fenner et al., 2005a) and by ericoid mycorrhizal fungi in heathland soils (Bending and Read, 1997), and the abundance of woody matter with a high phenolic content suggests that phenol oxidases may play an important role in the microbial conditioning of the *Calluna* dominated organic matter at the site.

Moisture limitations during natural dry periods inhibit extracellular phenol oxidase activity in forest litter and dry Californian annual grassland soil (Criquet et al., 2000; Nardo et al., 2004; Henry et al., 2005), and it was hypothesized that low litter moisture levels during the summer drought manipulation at the heathland study site would inhibit litter phenol oxidase activity. Stimulatory and neutral responses to drought conditions, however, have been reported in peatland soils (Freeman et al., 1996; Williams et al., 2000; Fenner et al., 2005a), the stimulatory response having been suggested to be driven by increased peat aeration under drought conditions (Fenner et al., 2005a). Therefore two possible scenarios were hypothesized for the effect upon phenol oxidase activity in the organic soil horizon: (i) by increasing soil aeration summer drought would stimulate phenol oxidase activity, or (ii) low soil moisture levels during the summer drought would inhibit phenol oxidase activity.

Recent concerns surrounding the release of carbon from soil stores (Bellamy et al., 2005) has included the observation of long-term increases in DOC concentrations in upland waters (Evans et al., 2005; Skjelkvåle et al., 2005), and intensified summer droughting has been suggested as a potential contributor to this trend (e.g. Worrall et al., 2004). It was expected that changes in phenol oxidase activity at the heathland study site would drive changes in soluble phenolics in the water draining the organic soil horizon and contribute to changes in total DOC draining from the site.

2. Methods

2.1. Site characteristics and climate manipulation

The Clocaenog CLIMOOR experiment is situated at 490 m a.s.l. on a hilltop (53°03′N, 30°28′W). Mean annual air temperature and rainfall at the site are 8.2 °C and 1700 mm yr^{-1}. Vegetation at the site is predominantly *Calluna vulgaris* L., with *Vaccinium myrtilus* L. and *Empetrum nigrum* L. The soil is a peaty podsol with ~4–10 cm of organic soil (organic matter 89%, pH 3.9) overlaying ~18–20 cm organic-rich mineral soil (organic matter 37%, pH 4.0). Nine experimental plots (5 m × 4 m) have been established at the site, with a light frame structure of steel tubes constructed around each plot, covered by thin plastic sleeves to prevent contaminants from leaching into the plots. These have been utilised to create three plots each of two non-intrusive climate manipulation treatments: night-time warming and summer drought, alongside three control plots (see Beier et al., 2004 for further details). The drought and control plots have been used for this study. The frame of each drought plot supports a retractable transparent polyethylene plastic roof and during a dictated summer drought period (~June to late August/early September) rain sensors activate the motor to extend the roof over the plot when it rains and retract it again when the rain stops. A wind sensor retracts the roofs if winds exceed 10 m s^{-1}. The control plots have a frame but no roof. A trench around each plot prevents surface and shallow soil water flow downslope between plots. The drought manipulations have been running annually since 1999. The summer drought manipulations have had no effect on litter and organic soil horizon pH (data not shown). The dates of the summer drought periods included in this study were 28 June 2005 to 21 September 2005 and 13 June 2006 to 17 October 2006.

2.2. Sample collection

Soil and litter samples were collected monthly from November 2004 to November 2005 (excluding February and March 2005), monthly March 2006 to June 2006, fortnightly over the 2006 summer drought period, and monthly following the 2006 summer drought period until November 2006. At each sampling date, four cores were taken from the total depth of the organic soil horizon at random locations within the top left-hand region of each plot using a 2.5 cm diameter half-moon hand-held auger and mixed as a bulk sample for each plot. Small quantities of mixed litter were collected at similar locations to the soil cores and pooled for each plot. Samples were manually mixed, stored at 5 °C and measurements of phenol oxidase activity, water extractable phenolics (June–November 2005, May–November 2006), and moisture content carried out within 72 h of collection. In order to thoroughly mix the litter samples and ease the process of the enzyme assays, the 2004–2005 litter samples were blended for two