Soil Biology & Biochemistry xxx (2015) 1–10

Contents lists available at ScienceDirect

Soil Biology & Biochemistry

journal homepage: www.elsevier.com/locate/soilbio

A novel biologically-based approach to evaluating soil phosphorus availability across complex landscapes

Thomas H. DeLuca [a, *], Helen C. Glanville [b], Matthew Harris [b], Bridget A. Emmett [c], Melissa R.A. Pingree [a], Laura L. de Sosa [b], Cristina Morenà [b], Davey L. Jones [b]

[a] School of Environmental and Forest Sciences, University of Washington, 102 Anderson Hall, Box 352100, Seattle, WA 98195-2100, USA
[b] School of Environment, Natural Resources & Geography, Bangor University, Deiniol Road, Bangor, LL57 2UW, UK
[c] Centre for Ecology and Hydrology, Environment Centre Wales, Deiniol Road, Bangor, Gwynedd, LL57 2UW, UK

ARTICLE INFO

Article history:
Received 22 December 2014
Received in revised form
29 April 2015
Accepted 16 May 2015
Available online xxx

Keywords:
Bioavailability
Ecosystem assessment
Nutrient index
Phosphate
Soil quality indicator

ABSTRACT

Plants employ a range of strategies to increase phosphorus (P) availability in soil. Current soil P extraction methods (e.g. Olsen P), however, often fail to capture the potential importance of rhizosphere processes in supplying P to the plant. This has led to criticism of these standard approaches, especially in non-agricultural soils of low P status and when comparing soil types across diverse landscapes. Similarly, more complex soil P extraction protocols (e.g. Hedley sequential fractionation) lack functional significance from a plant ecology perspective. In response to this, we present a novel procedure using a suite of established extraction protocols to explore the concept of a protocol that characterizes P pools available via plant and microbial P acquisition mechanisms. The biologically based P (BBP) extraction was conducted by using four extractions in parallel: (1) 10 mM $CaCl_2$ (soluble P); (2) 10 mM citric acid (chelate extractable P); (3) phytase and phosphatase solution (enzyme extractable organic P); (4) 1 M HCl (mineral occluded P). To test the protocol, we conducted the analyses on a total of 204 soil samples collected as part of a UK national ecosystem survey (Countryside Survey) in 1998 and repeated again in 2007. In the survey, Olsen P showed a net decline in national soil P levels during this 10 year period. In agreement with these results, soluble P, citrate extractable P and mineral occluded P were all found to decrease over the 10 year study period. In contrast, enzyme extractable organic P increased over the same period likely due to the accumulation of organic P in the mineral soil. The method illustrates a noted shift in P pools over the 10 year period, but no net loss of P from the system. This new method is simple and inexpensive and therefore has the potential to greatly improve our ability to characterise and understand changes in soil P status across complex landscapes.

1. Introduction

Increasing food security concerns and decreasing mineable phosphorus (P) supplies necessitate efficient use of soil P resources; however, current methods used to assess plant available P are often ineffective when used on landscapes with a great degree of plant and soil heterogeneity. Soil P exists in a variety of forms including soluble inorganic, insoluble inorganic (P_i), organic, and surface adsorbed with the amounts present in each fraction varying greatly between soil types (Bieleski, 1973).

The ability to effectively assess soil P status and phytoavailability is extremely important in terms of environmental protection and agricultural productivity; however, phytoavailable P is not a distinct value for any given soil (Withers et al., 2014). Importantly, plants express unique mechanisms for releasing P from different pools of differing recalcitrance, each contributing to P availability to varying extents depending upon several plant and soil parameters (Neumann and Römheld, 1999; Lambers et al., 2006). Current efforts to monitor soil P status are based on methods specifically developed for agricultural purposes with the specific objective of estimating the phytoavailability of soil P and enabling fertiliser rate recommendations (e.g. Mehlich, 1978; Menon et al., 1989; Saggar et al., 1992; Sims et al., 2000). Commonly, these are single solution extractions (e.g. $NaHCO_3$ or acid NH_4F) which correlate with plant inorganic P uptake in a controlled environment (e.g. Bray and

* Corresponding author. Tel.: +1 206 685 1928.
E-mail address: deluca@uw.edu (T.H. DeLuca).

http://dx.doi.org/10.1016/j.soilbio.2015.05.016
0038-0717/

Kurtz, 1945; Olsen et al., 1954; Mehlich, 1984). These extractions have proved very useful for agriculture as they offer a straightforward index of P fertility. However, single extraction methods do not adequately characterise the bioavailability of P across complex landscapes (e.g. multiple land uses or natural vegetative communities) in which P availability is directly influenced by plant community and shifts in soil biophysical conditions. Phosphorus fractionation schemes were developed in an attempt to better characterize the P status of soils (e.g. Hedley et al., 1982). Such fractionation approaches expose a single soil sample to a sequence of extractants to quantify pools of progressively occluded P. These approaches offer a more detailed picture of soil P status, are more suited to use over complex landscapes, offer some sense of how P might become available over time and they can provide an indication of the mechanisms controlling P solubility in a given soil (Cross and Schlesinger, 1995; Levy and Schlesinger, 1999; Negassa and Leinwieber, 2009). Examples of fractionation methods include the widely adopted Hedley procedure (Hedley et al., 1982) or the Chang and Jackson method (Chang and Jackson, 1957). Unfortunately, fractionation methods are time consuming and require careful preparation and processing making them inappropriate for routine use, especially in agriculture. Furthermore, these fractionations do not adequately reflect rhizosphere processes (Johnson et al., 2003; Yang and Post, 2011). Phosphorus solubilised by rhizosphere processes (in particular organic acid, proton and ectoenzyme excretion) are not individually characterised in these schemes. Instead, chemical analogues are used which, while they may correlate well with plant availability or P accumulation with soil development, they do not offer insight into the potential P uptake mechanisms or rhizosphere P transformations that drive ecosystem P dynamics.

In this paper we introduce an alternative biologically inspired P extraction approach to evaluate soil P status. Here we combine together four established approaches to assessing different pools of bioavailable P thereby simultaneously assessing soil P as influenced by plant rhizosphere mediated processes across a diverse array of soils. The extractants were chosen to emulate four common and significant plant rhizosphere mediated P acquisition mechanisms: (1) root interception, (2) organic acid complexation, (3) enzyme hydrolysis and (4) proton excretion induced acidification. In this study, we should note that we did not include microbial biomass P, which is another biologically significant soil P pool, but not one that is accessed by a specific enzyme or exudate. Rather than sequentially extracting these P pools as in the Hedley fractionation, we run the extractions in parallel to measure the total amount of P mobilised by each individual test. The purpose of this effort was to create a simple P assessment regime that reflects biologically mediated shifts in P availability and is sensitive to landscape scale variation in soil P status. The combined analyses are collectively referred to as the Biologically Based P (BBP) extraction regime. The BBP method is compared with the standard Olsen P method across a variety of soils that were collected in 1998 and again in 2007 as part of a UK natural survey. The method was then compared with Olsen P on field moist and air dried soils collected from a catchment in North Wales.

2. Materials and methods

2.1. Soils

For the main study, soil samples were collected throughout the UK as part of the Centre for Ecology and Hydrology Countryside Survey (CS) in 1998 (CS98) and 2007 (CS07) with sites representing all the dominant landscape types and soil groups in the UK (Emmett et al., 2010; Reynolds et al., 2013). To encompass all the major soil and land use types, a total of 2614 soil samples were collected throughout the UK, based on a stratified random sample of 1 km squares at gridpoints on a 15 km grid using the Institute of Terrestrial Ecology (ITE) Land Classification as the basis of the stratification (Wood et al., 2012). At each grid intersection, a 1 km^2 sample area was selected. Within the 1 km^2 sample area, 3 plots (5×5 m^2) were randomly located and a single 15 cm long $\times$ 4 cm diameter soil sample was collected from each of the plots. Additional information about vegetation and soils were also collected from the same plots. To facilitate comparison of P pool concentrations during the two sample dates, we used the vegetation and soil categories provided in the CS (Emmett et al., 2010). For plant communities we used the 'aggregate vegetation' class (AVC) which includes eight categories: 1) lowland wooded; 2) upland wooded; 3) crops and weeds; 4) tall grass and herbs; 5) fertile grassland; 6) infertile grassland; 7) moorland; 8) heath and bog. For soil types, we use the loss-on-ignition categories of: 1) mineral; 2) humus-mineral; 3) organo-mineral; 4) organic. The 1 km^2 areas were stratified within the 45 major Land Classes of the UK. All the sites were characterised by a temperate climate with a North-South mean annual temperature range of 7.5–10.6 °C and East-West mean annual rainfall range from 650 to 1700 mm.

Samples were stored at 4 °C prior to analysis for key characteristics including pH, total C and N, mineralisable C and N, Olsen-P (0.5 M $NaHCO_3$, pH 8.5), bulk density and soil biota as described in Emmett et al. (2008, 2010), Simfukwe et al. (2011) and Reynolds et al. (2013). All remaining sample was then air-dried and sieved prior to long term storage and use in this study.

To assess the changes in soil P seen between the 1998 and 2007 Countryside Survey, a subset of 102 spatially paired soils (204 samples in total) from the CS98 and CS07 archived soils was selected randomly from the larger set. In order to represent the archive's spatial diversity, the samples were stratified according to their "Environmental Zone" – nine classifications derived from Institute of Terrestrial Ecology Land Classes which reflect an array of geographically distinct regions of Britain (Bunce et al., 1996). Across all land use and vegetation classes the dominant soil types (% of total) were brown soils (33%), surface water gley soils (19%), podzolic soils (14%), peat soils (12%), groundwater gley soils (11%), lithomorphic soils (8%) and pelosol soils (3%) (Avery, 1990; Simfukwe et al., 2011). These soils were assessed using the novel BBP extraction regime described below and for total C based on loss-on-ignition (Nelson and Sommers, 1982; Reynolds et al., 2012).

2.2. Principles behind the proposed BBP method

We employed four existing soil P analysis methods to provide a clear picture of soil P status as influenced by plant rhizosphere mediated processes. Phosphorus phytoavailability in soil is limited by its low solubility and potential for surface sorption resulting in a small pool of readily available P, a larger pool of more recalcitrant "active P" forms (including microbial biomass P, weakly sorbed P, and some soluble P complexes and precipitates) and a 'fixed P' pool which may remain unchanged in soil for many years. The BBP method uses a combination of established extraction procedures to represent the P solubilised by mechanisms employed by plants or microorganisms to access P: (1) soluble/root interception, (2) chelate extractable, organic acid complexation/dissolution, (3) enzyme hydrolysis and (4) proton excretion induced acidification (see Table 1 for clarification). The procedures were adapted in order to correspond to the maximum level of each extractant reported in the literature.

Each P pool was measured in parallel by shaking 0.5 g of soil with each extractant (10 ml; described below) in separate 15 ml centrifuge tubes for 3 h on a reciprocal shaker at 200 rev min^{-1}.

Please cite this article in press as: DeLuca, T.H., et al., A novel biologically-based approach to evaluating soil phosphorus availability across complex landscapes, Soil Biology & Biochemistry (2015), http://dx.doi.org/10.1016/j.soilbio.2015.05.016