



Phosphate stable oxygen isotope variability within a temperate agricultural soil



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ARTICLE INFO

Article history:

Received 23 July 2015

Received in revised form 13 September 2016

Accepted 21 September 2016

Available online 28 September 2016

Keywords:

Phosphorus

Grassland

Spatial analysis

GW model

North Wyke farm platform

ABSTRACT

In this study, we conduct a spatial analysis of soil total phosphorus (TP), acid extractable phosphate (PO_4) and the stable oxygen (O) isotope ratio within the PO_4 molecule ($\delta^{18}\text{O}_{\text{PO}_4}$) from an intensively managed agricultural grassland site. Total P in the soil was found to range from 736 to 1952 mg P kg⁻¹, of which between 12 and 48% was extractable using a 1 M HCl (HCl_{PO_4}) solution with the two variables exhibiting a strong positive correlation. The $\delta^{18}\text{O}_{\text{PO}_4}$ of the extracted PO_4 ranged from 17.0 to 21.6‰ with a mean of 18.8‰ (± 0.8). While the spatial variability of Total P has been researched at various scales, this is the first study to assess the variability of soil $\delta^{18}\text{O}_{\text{PO}_4}$ at a field-scale resolution. We investigate whether or not $\delta^{18}\text{O}_{\text{PO}_4}$ variability has any significant relationship with: (i) itself with respect to spatial autocorrelation effects; and (ii) HCl_{PO_4} , elevation and slope - both globally and locally. Results indicate that $\delta^{18}\text{O}_{\text{PO}_4}$ was not spatially autocorrelated; and that $\delta^{18}\text{O}_{\text{PO}_4}$ was only weakly related to HCl_{PO_4} , elevation and slope, when considering the study field as a whole. Interestingly, the latter relationships appear to vary in strength locally. In particular, the $\delta^{18}\text{O}_{\text{PO}_4}$ to HCl_{PO_4} relationship may depend on the underlying soil class and/or on different field managements that had operated across an historical north-south field division of the study field, a division that had been removed four years prior to this study.

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1. Introduction

Phosphorus (P) is an essential element for plant growth and is applied to agricultural systems, often in large quantities, to underpin intensive levels of agricultural production (Haygarth et al., 2014). It can be applied as either inorganic mineral fertilizers, or via the spreading of animal wastes or other organic materials. Such wastes can occur either directly voided by the animal in the field or applied in bulk after storage while animals are housed. However, P can have significant detrimental effects when they move from land into water bodies. These effects range from direct toxicity (Lewis and Morris, 1986) through to indirect consequences such as eutrophication (Smith et al., 1999). Surface waters are particularly sensitive to P because critical concentrations of only a few tens of µg of phosphate (PO_4) can cause eutrophication, but are an order of magnitude lower than soil PO_4 concentrations required for crop growth (Heathwaite and Dils, 2000). Identifying the different pollutant sources that are impacting on a water body is critical to

understand its ecosystem health. However apportioning a pollutant to any given source or sources is fraught with difficulty and in recent years techniques have been developed to try to elucidate pollutant origins (e.g. Baker et al., 2002; Collins et al., 1997; Old et al., 2012) and these include the use of natural abundance stable isotope ratios (e.g. Amberger et al., 1987; Granger et al., 2008). More recently still the stable isotope approach has been applied to P and although P only has one stable isotope, the technique uses the stable oxygen (O) isotope ratio within the PO_4 molecule ($\delta^{18}\text{O}_{\text{PO}_4}$) to isotopically characterise PO_4 sources and transformations. However, data on the $\delta^{18}\text{O}_{\text{PO}_4}$ of different PO_4 sources remains limited (Tamburini et al., 2014; Young et al., 2009).

One potential source of PO_4 in water is from soil, which often receives P inputs in excess of requirements resulting in P accumulation within the soil (Haygarth et al., 1998a). Therefore, as with many other soil properties, an understanding of soil P variability is essential for designing sampling strategies or the evaluation of the effectiveness of diffuse water pollution mitigation measures (Goovaerts, 1998; Rivero et al., 2007). Despite this, few studies describe spatial variability of soil properties and their inter-relationships at a landscape scale (i.e. Marriott et al., 1997; Page et al., 2005). The spatial variability of a given soil property may be related to the combined action of several physical, chemical or biological processes that act at different spatial

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scales depending on the soil property and process of interest (Goovaerts, 1998). Soil spatial variability is present in both natural and agricultural systems, even if the latter have a long-term uniform management history (Goovaerts, 1998; Marriott et al., 1997). Understanding soil spatial variability is essential to land-based experiments at all scales and its omission is detrimental to the conclusions drawn from such experimental data.

In this study, we conduct a spatial analysis of soil $\delta^{18}\text{O}_{\text{PO}_4}$ from an intensively managed agricultural grassland site. While the spatial variability of total P has been described at different scales by other researchers (e.g. Glendell et al., 2014; Page et al., 2005; Penn et al., 2007), this is the first study to assess the variability of soil $\delta^{18}\text{O}_{\text{PO}_4}$ at a field-scale. We investigate whether or not $\delta^{18}\text{O}_{\text{PO}_4}$ variability has any significant relationship with: (i) itself with respect to spatial autocorrelation effects; and (ii) soil P (extracted using 1 M HCl (HCl_{PO_4})), elevation and slope – both globally and locally within the study field. In particular, the following four null hypotheses are tested:

- A. $\delta^{18}\text{O}_{\text{PO}_4}$ does not strongly co-vary with HCl_{PO_4} , with elevation and with slope across the field as a whole.
- B. $\delta^{18}\text{O}_{\text{PO}_4}$ is not a spatially-autocorrelated process.
- C. The relationships of (A) do not significantly change in different areas of the field.
- D. The relationship between $\delta^{18}\text{O}_{\text{PO}_4}$ and HCl_{PO_4} is not conditional on the the under-lying soil class or different management histories.

Furthermore, in order to efficiently test the given set of null hypotheses, all statistical analyses are conducted in a manner that accounts for a certain sub-optimality in the study sample design. In particular, statistical methods are chosen to cater for significant areas of under- and over-sampling.

2. Methods

2.1. Study site

To characterise soil P spatial variability, a series of soil samples were collected from one field of the Rothamsted Research ‘North Wyke Farm Platform’, in south-west England (50.8°N, 3.0°W). The field sampled, referred to as ‘Great Field’, was located on a north-west facing hillslope and comprises clay loam soil overlying the shales and thin subsidiary sandstone bands of the Crackington formation (Harrod and Hogan, 2008). The soils can be further divided in three main types; Hallsworth (USDA Aeric haplaquept, FAO Stagni-vertic cambisol), Halstow (USDA typichaplaquepts, FAO dystic gleysol), and Denbigh (USDA Dysticeutrochrept, FAO Stagni-eutric cambisol) (Harrod and Hogan, 2008). The long-term annual temperature and rainfall are 9.6 °C and 1056 mm, respectively, with a high proportion of rainfall occurring between October and March resulting in waterlogged soils.

Records of the historic farm management show that prior to 2010 the field comprised two separate areas (north 1.5 ha and south 5.6 ha) with contrasting management histories. The northern part had been managed as permanent grassland for at least 25 years, whereas the southern part has been ploughed three times in the last 25 years, most recently in September 2007 when it was re-seeded with a ryegrass/clover mixture following a previous winter barley crop. At the time of the study, both areas of the field had the same vegetation cover being classified under the National Vegetation Classification (NVC) category: “MG7 *Lolium perenne* *Poa trivialis* and related grasslands”. The southern region, however, had a higher clover content (*Trifolium repens*), less dense vegetation cover and approximately double the sward height compared to the northern part. These management histories are representative of normal management cycles of intensive grassland management (Bilotta et al., 2007).

2.2. Sample design, collection and analysis

To quantify spatial variability in $\delta^{18}\text{O}_{\text{PO}_4}$, a sampling pattern was chosen with the view of a geostatistical analysis not only to $\delta^{18}\text{O}_{\text{PO}_4}$, but to other soil variables, as presented in Peukert et al. (2012). In order to assess spatial variability across three different spatial scales, 78 soil samples were taken in total with samples at: (i) a broad scale (75 × 75 m grid); (ii) an intermediate scale (25 × 25 m grid); and (iii) a small scale (10 × 10 m grid). A hand-held GPS (Nomad Trimble, Sunnyvale, USA) was used to map and mark the sampling points.

All samples were collected in May 2011 to a soil depth of 7.5 cm and were oven dried at 105 °C for 24 h. Dried soils were then sieved through a 2 mm mesh. Total P (TP) was determined at an external laboratory (Natural Resource Management, Berkshire, U.K.) through digestion of the soils ground to 0.5 mm in aqua-regia followed by subsequent analysis on an ICP-AES. The $\delta^{18}\text{O}_{\text{PO}_4}$ of the soil was determined on the 1 M HCl extractant described by Tamburini et al. (2010) but with a few modifications. Briefly, between 10 and 20 g dry soil was added to 100 ml 1 M HCl and shaken overnight. The supernatants were collected after separation from the residual solids by centrifugation and filtration. Phosphate concentrations were determined colourimetrically on an Aquachem 250 analyser using a molybdenum blue reaction (Murphy and Riley, 1962) after they were diluted by at least 1/10 to avoid acid interference with the molybdenum chemistry. The extracted PO_4 is precipitated and dissolved as firstly ammonium phospho-molybdate and then magnesium ammonium phosphate before excess magnesium and chloride is removed through the addition of a cation resin and a small dose of silver nitrate crystals respectively. The resultant PO_4 in solution is then converted to silver phosphate (Ag_3PO_4) though the addition of an Ag-ammine solution and subsequent adjustment of the pH to between 7 and 8 with 0.5 M HNO_3 before incubation for two days at 50 °C in an oven.

Soil PO_4 extracted using 1 M HCl (HCl_{PO_4}) represents an integration of several potential PO_4 pools (Zohar et al., 2010): (i) the most labile, water-extractable soil PO_4 , including intracellular microbial PO_4 typically released through processes such as soil drying and re-wetting and cell lysis (ii) weakly adsorbed bicarbonate-extractable soil PO_4 , and (iii) strongly fixed, calcium and iron bound P. The weak acid extraction does not include the strongly adsorbed aluminium oxide bound PO_4 , which requires a NaOH-based extraction (Tiessen and Moir, 1993), nor does it include P in organic matter, the hydrolysis of which with 1 M HCl has been shown to be negligible during the development of the extraction protocol by Tamburini et al. (2010). To confirm that organic P forms were not being hydrolysed, duplicate soil samples were extracted using ^{18}O -labeled and unlabelled 1 M HCl. If the extracted HCl_{PO_4} was to contain large amounts of hydrolysed organic P or condensed PO_4 species (e.g. polyphosphates, pyrophosphates, etc.) then the $\delta^{18}\text{O}_{\text{PO}_4}$ of the sample duplicates would be markedly different. For all tested samples, the ^{18}O of the sample extracted with unlabelled and ^{18}O -labeled acid was no > 1%. The contribution of calcium-bound P is also considered to be negligible as both the soil parent material was neither igneous nor calcareous, and the soil pH is generally < 6. Therefore HCl_{PO_4} is assumed to extract PO_4 from the same soil pool as is released by water, anion resins, and NaHCO_3 extraction, namely extracellular labile PO_4 and metabolic intracellular microbial PO_4 and also some iron bound PO_4 . Using the 1 M HCl as an extractant enables far greater quantities PO_4 to become available, quantities that are required to allow the successful precipitation of Ag_3PO_4 from small amount of soil.

Oxygen isotope analysis was carried out ETH Zurich on a Vario Pyro Cube (Elementar GmbH, Hanau, Germany) coupled in continuous flow to an Isoprime 100 isotopic ratio mass spectrometer IRMS (Isoprime, Manchester, UK). Triplicate samples of ~0.3 mg of Ag_3PO_4 were weighted into silver capsules together with a small amount of fine carbon black powder to promote the reaction between the Ag_3PO_4 and carbon to produce CO. The produced reaction gases are carried through a

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