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Investigation of the soil properties that affect Olsen P critical values in different soil types and impact on P fertiliser recommendations

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Running Title: Soil property effects on Olsen P critical values

Abstract

Optimisation of phosphorus (P) fertiliser use is desired to ensure more sustainable use of fertiliser, economic food production and reduction of eutrophication of water bodies. Presently the Olsen P values on which fertilizer recommendations are based to achieve optimum yield are frequently the same for all soils. The aim of this study was to identify the properties of different soils that affect their critical Olsen P values in order to develop better, soil-specific P fertiliser recommendations. A pot experiment using 10 soils with low available P with different P additions was carried out to investigate the impact of wide-ranging soil properties on the relationship between P addition, resultant Olsen P values and yield response of ryegrass to Olsen P values. The relationship between added P and Olsen P varied greatly between the individual soils. These relationships were affected by pH, manganese oxide, crystalline aluminium oxide and amorphous iron oxide contents of the soil. Different soils had widely varying critical Olsen P values for ryegrass. However, these could not be related to the measured soil properties. Fertiliser recommendations and critical values for optimum yield of ryegrass based on the Olsen P test should be soil-specific. The complexity and lack of clarity over which combination of soil properties governs critical Olsen P values calls for further investigation with more soil types and additional soil property measurements to elucidate the different factors controlling critical Olsen P values in different soils.

Keywords

available P; critical P; fertiliser; Olsen P; phosphorus; plant nutrients; soils; soil properties;

Highlights

- Soil-specific P fertiliser recommendations are needed for sustainable fertiliser use
- We investigated soil properties affecting critical Olsen P values and added P fertiliser availability
- Fertiliser P availability was affected by pH and metal (hydr)oxide contents of the soil
- Critical Olsen P values varied with soil, but measured soil properties couldn't explain this variation

Author contributions

Study concept and design; Blackwell**,** Granger, Hawkins, McGrath. Development of protocol; Blackwell, Dunham, Granger, Hawkins, Hernandez-Allica, McGrath. Acquisition of data; Blackwell, Dunham, Granger, Hawkins, Hernandez-Allica, Yuan. Analysis and interpretation of data; Blackwell, Granger, Hawkins, McGrath, Tandy. Drafting of the manuscript; Hawkins, Tandy. Critical revision of the manuscript for intellectual content; Blackwell, Dunham, Granger, Hawkins, Hernandez-Allica, McGrath, Tandy, Yuan.

Introduction

Global food production today is highly dependent on phosphorus (P) fertilisers derived from rock phosphate deposits, which are a finite resource (Blackwell *et al.*, 2019). Thus, there is considerable pressure to optimise the use of P fertilisers, which will have other benefits such as making food production more cost efficient and reducing over fertilisation of agricultural land, which is a source of P pollution to water courses (Macintosh *et al.*, 2018).

Agricultural soils typically contain between 0.01 – 3 mg P L^{-1} in soil solution which is the main source for plants. However, the quantity is insufficient for the requirements of most agricultural crops (Frossard *et al.*, 2000). Resupply of P in solution is dependent on that stored in the soil phase. Availability of P in soil is affected by many soil properties such as the concentrations of iron (Fe) and aluminium (Al) (hydr)oxides (ox), clay, soil organic matter, calcium and pH. Phosphorus is mainly sorbed onto the surfaces of Fe/Alox and clay minerals, which are affected by pH (Blume *et al.*, 2016), and anions that compete for ligand-exchange reactions with these surfaces (Ziadi *et al.*, 2013). Over time P can diffuse into these minerals becoming occluded and thus less available to plants (Blume *et al.*, 2016). It may also react with Fe, Al (acid pH) and calcium (Ca) (alkaline pH) ions in solution to form phosphate minerals with varying levels of solubility (Blume *et al.*, 2016).

Soil extractable P, the fraction of total P (TP) in soil that is readily available for absorption by plant roots, is measured in the laboratory using extracting solutions. The soil P tests rely on a predetermined contact time between the soil and the extracting solution (kinetic reaction) to capture inorganic P from the soil solution and the soil solid phase (Ziadi *et al.*, 2013).

There is no worldwide consensus on which extractant to use for available P; in Europe alone more than 10 are routinely used (Jordan-Meille *et al.*, 2012; Nawara *et al.*, 2017). Substantial variations in soil type and soil pH provide challenges for any single soil P test (Mason *et al.*, 2013). However, in many countries sodium bicarbonate extraction solution i.e. Olsen-P (Olsen *et al.*, 1954) or Colwell-P (Colwell, 1963) is used as a basis for estimating potential soil P availability to crops and to develop P fertilizer recommendations (Tandy *et al.*, 2011; Jordan-Meille *et al.*, 2012).

Critical P concentration is a concept that is commonly applied to formulating crop P requirements and is based on the asymptotic relationship between plant yield and soil extractable P (Olsen & Watanabe, 1957). The critical value (CV) is associated with an arbitrary proportion of the maximum yield but is usually set at between 90 and 98 % (Bolland & Guthridge, 2007; Poulton *et al.*, 2013; Sanchez-Alcala *et al.*, 2015; Nawara *et al.*, 2017), values below this level indicate that there will be a response in yield to fertiliser addition, while above this value little response in yield is expected.

The fertiliser recommendations for England and Wales are based on the Olsen-P soil test and currently recommend a value (critical value) of 16 - 25 mg L^{-1} (index 2) for optimisation of crop yields (AHDB, 2019). However, the same critical value is given for most crops (except vegetables) despite it being known that different crops require different amounts of soil available P (Nawara *et al.*, 2017; Sandaña *et al.*, 2018). One reason different crops may have different critical values is faster growing species such as maize require P more quickly than slower growing species (Smolders *et al.*, 2020). If the desorption rate of P from soil is too slow to keep up with plant demand, it will manifest as a higher critical value, because P desorption from soil in extraction tests are unlikely to be affected in the same way. The critical value is also the same for all soil types even though bicarbonate soil extracts do not show a good correlation between extracted P and relative yield when a range of different soil types are considered (Nawara *et al.*, 2017; Zehetner *et al.*, 2018; Conyers *et al.*, 2020). Similarly, the fertiliser application recommendations are not soil-specific, despite the fact that soils have different abilities to bind P, and are therefore likely to show dissimilar P availability within a short time of fertiliser addition (Brennan *et al.*, 1994).

Some national fertiliser guidelines have used soil properties to tailor their recommendations. For example, the Scottish P guidelines, based on the Modified Morgan soil test (ammonium acetate), use P sorption capacity to modify the target soil test value as well as recommended fertiliser additions (Sinclair *et al.*, 2015). In Australia, where the bicarbonate Colwell-P test is used, the phosphorus buffering index (PBI) is used to modify critical soil test values (Simpson *et al.*, 2009). However, the Colwell-P test is known to extract more non-labile P than the Olsen-P test (Six *et al.*, 2012) and some authors found that inclusion of the PBI did not improve the response of pasture to Olsen-P test results (Gourley *et al.*, 2007; Gourley *et al.*, 2019).

Critical P values have been largely determined from field experiments. However, the relationship between the response to P and crop yield can be influenced by factors such as rainfall, temperature, seedbed preparation, soil structure, agronomic management and pests and diseases (Poulton *et al.*, 2013; Conyers *et al.*, 2020).

The use of pot experiments allows variation in some of the confounding factors affecting field-based trials to be either minimised or eliminated. The pot experiment reported here looks at the fate of fertiliser shortly after addition in a grazing/silage scenario and investigates the relationship between added soil P, resultant Olsen-P and yield of ryegrass using 10 soils from the UK with very different properties. It also establishes critical Olsen-P values for ryegrass under controlled conditions. Ryegrass is an important crop in the UK, but little work has been carried out on establishing critical values for it under UK conditions, compared with other crops. We hypothesize that Olsen-P critical values are different for different soils and this is related to soil properties.

Materials and Methods

Soil Sampling and Selection

Thirty-three soils (25 kg of each) were initially collected, from various sites in the south of the UK, to 10 cm depth, by scraping off the vegetation and using a spade. The selection of sites for sampling was based on the likelihood of having a very low Olsen-P status (P index of 0) and contrasting soil types. The soils were homogenised, air dried and sieved to ≤4 mm. Sub-samples were sieved to ≤2 mm for analysis of Olsen-P concentration and pH. Organic carbon (OC) and oxide content (see below for details) were measured on finely ground soil (PM400 Planetary ball mill using agate bowls and balls, Retsch GMBH, Germany). Soils of low P status, (≤ 9 mg P L^{-1}, soil Index 0, (AHDB, 2019)) and the widest range of pH, OC and oxide contents were selected as candidates (10 soils) for the pot experiment. Location coordinates, land use, soil texture and soil classification for each soil are shown in Table S1.

Experiment 1

A portion of each soil for each treatment was placed in a plastic bag and each bag had P as $Ca(H_2PO_4)_2.H_2O$ solution added between 0 and 200 mg P kg^{-1} (N = 20, Table S2) and a basal nutrient solution (400 mg N kg^{-1} (NH_4NO_3), 100 mg K kg^{-1} (KCl), 32 mg Mg kg^{-1} ($MgSO_4.7H_2O$), 43 mg S kg^{-1} ($MgSO_4.7H_2O$), 3 mg Mn kg^{-1} ($MnCl_2.4H_2O$), 0.7 mg B kg^{-1} (H_3BO_3), 0.1 mg Co kg^{-1} ($CoSO_4.7H_2O$) 2.3 mg Cu kg^{-1} ($CuSO_4$), 2 mg Zn kg^{-1} ($ZnSO_4$), and 0.3 mg Mo kg^{-1} ($Na_2MoO_4.2H_2O$)). Deionised water was added to each bag to wet the soils to 50 % of their water holding capacity (WHC) taking into account their air-dry moisture content. They were gently mixed so as not to damage the soil structure. The soils were kept open to the air (to maintain aerobic respiration) in the dark at 20 °C for 7 days to stabilize the P. After incubation 300 g of soil was thoroughly mixed with 100 g of acid washed quartz chips (6 mm) to improve the soils structure and placed into a pot with very fine mesh at the bottom to prevent soil loss. Ryegrass (L. *perenne*, cv Abermagic) was sown at the rate of 0.25 g seeds pot^{-1} and the soil was adjusted to 70 % WHC with deionised water. For the low potassium (K) soils i.e. (Barnfield and Tadham) an additional 200 mg K kg^{-1} pot^{-1} as KCl solution, was added to the soils. In addition, 1333 mg kg^{-1} N and K were added to each pot every two weeks as NH_4NO_3 and KNO_3 solutions. The plants were grown under controlled environmental conditions with a day/night light regime of 16/8 h (500 - 550 µmol m^2 sec^{-1}) and temperature of 20/16 ºC respectively. Pots were watered daily to maintain 70 % WHC by weighing. One pot per treatment per soil was established.

The grass biomass was harvested monthly by cutting 2 cm above the soil surface. Biomass was dried at 105 ºC until constant weight. The grass was grown for 16 weeks in total.

Experiment 2

Ryegrass grown on soils from Peldon, Tadham, Thornby and Woodah did not appear to reach their maximum yield potential at the P treatments included in Experiment 1. This was seen by the fact there was no decline in the monthly yield unlike the other soils. For these soils the experiment was repeated with P treatments between 0 and 600 mg P kg^{-1} (N = 11, Table S2). The same procedure was followed as for experiment 1 but 300 g of soil with added P was mixed with 300 g acid washed quartz chips (6 mm) after 7 days of incubation before potting.

Soil Characterisation Analysis

Soil was air-dried for 48 h before passing through a 2 mm stainless steel sieve prior to analysis. Soil clay, silt and sand fractions were determined by the pipette method by an external laboratory (NRM Laboratories, UK) and textural classification followed the WRB soil taxonomy (FAO, 2015). Water holding capacity was measured gravimetrically by saturating 50 g ≤ 2 mm sieved soil in a filter paper and funnel and allowing to drain for 2 nights. Soil pH was measured in water at a ratio of 1:2.5. Total carbon (C) and nitrogen (N) were determined on finely ground soil by dry combustion (Tiessen & Moir, 1993) (TruMac Combustion Analyser, LECO, St Joseph, Michigan, USA). Inorganic C (IC) was measured on addition of phosphoric acid to the sample (Primacs Inorganic C Analyser, Skalar Analytical BV, Breda, Netherlands). Organic C (OC) was calculated from the difference between the total and inorganic C. For the PBI a single addition of P solution (KH_2PO_4 in 0.1 M $CaCl_2$) at 1000 mg P kg^{-1} was added to the ≤ 2 mm soil at a 1:10 soil to solution ratio. The mixture was shaken for 17 h on an orbital shaker (120 rpm, room temperature), filtered through Whatman 5 filter paper and the clear solution was acidified to 5 % HNO_3 before P was determined by Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES, Perkin Elmer optima 7500 DV, Waltham, MA, USA). The PBI index was calculated using equation 1:

$$\mathrm{PBI} = \frac{(Ps+(4.59\ OlsenP))}{c^{0.41}} \qquad (1)$$

where Ps is the P sorbed (mg P kg^{-1} soil) and c is the final solution P concentration (mg P L^{-1}) (Burkitt *et al.*, 2002).

Dithionite extractable Fe, Al and Mn were extracted using 1g finely ground soil and a citrate-dithionite-bicarbonate extractant at a soil:solution ratio of 1:50 (Mehra &

Jackson, 1960). Samples were preheated at 40 °C for 2h and then shaken for 16 h at 25 °C using a reciprocal shaker. The solutions were then centrifuged at 4000 rpm (15 min, 20 °C) and filtered through 0.45 µm disposable membrane filters (Sartorius Ministart 16555K). The samples were analysed by ICP-OES. These were deemed to be the total (hydr)oxides (Barberis *et al.*, 1996; Loeppert & Inskeep, 1996).

Acid oxalate extractable Fe, Al and Mn were extracted with a mixed solution of ammonium oxalate and oxalic acid at a soil:solution ratio of 1:100 (Schwertman, 1964). Finely ground soil samples were shaken in the dark (4 h, 20 °C) using a reciprocal shaker and then filtered through Whatman 42 filter paper. The samples were acidified to 5% HNO_3 and analysed by ICP-OES. These were deemed to be amorphous (hydr)oxides (Barberis *et al.*, 1996; Loeppert & Inskeep, 1996). Fe, Al and Mn from crystalline (hydr)oxides were calculated by subtracting the amorphous (hydr)oxide concentrations from the total (hydr)oxide concentrations.

Total P and other macro and micro-nutrients were determined by digesting finely ground soil with an HCl/HNO_3 mixture (Aqua Regia) on a temperature-controlled heating block (Carbolite). Soils were digested at a soil:acid ratio of 1:20 (McGrath & Cunliffe, 1985) and analysed by ICP-OES.

Experimental Soil Analysis

Soils were sampled at two time points; 1 week after P addition (at the end of the 7 days incubation), and at the end of the growth experiment. They were air dried for 48 h and passed through a 2 mm sieve. Olsen-P was extracted using 0.5 M $NaHCO_3$ (pH 8.5) at a soil solution ratio of 1:20 (Olsen *et al.*, 1954). Samples were shaken for 30 min on an orbital shaker (130 rpm, 20 °C) and filtered through Whatman 2 filter papers. Activated charcoal (1 g) was added to the filtrates and mixed to decolour the samples which were then re-filtered through fresh Whatman 2 filter papers. Phosphorus in the filtrates was determined by the phospho-molybdenum blue method (Aquakem 250 discrete photometric analyser, Thermo Scientific, Hemel Hempstead, Hertfordshire, UK) after sample neutralisation using 1.5 M sulphuric acid (Murphy & Riley, 1962). Total P was analysed as above.

Plant Analysis

Oven dry grass samples were milled using a hammer mill and digested with high purity $HNO_3/HClO_4$ (85/15, v/v) in a heating block (Zhao *et al.*, 1994). Total concentrations of P and other macro and micro-nutrients in digested solutions were determined by ICP-OES.

Statistics

For all statistical analysis, results were considered significant at $p < 0.05$. Soil characteristics measured prior to P addition to the soil were tested for correlation using Pearson correlation coefficients.

The relationship between soil PBI and soil characteristics was assessed using stepwise multiple linear regression (MLR) using $\log_{10}$ transformed PBI values to satisfy the assumption of homogeneity of variance (soil characteristics were also $\log_{10}$ transformed when necessary). to select the best combination of soil characteristics to explain the variability in soil PBI values (see supplementary information for more details).

The relationship between initial Olsen-P and added P was assessed for each soil using polynomial regression (see supplementary information for more details). Inverting the fitted quadratic model to express added P as a function of Olsen-P allows the estimation of the amount of P (fertilizer) to be added to increase the Olsen-P value from a starting level (Olsen-P_1) to a target level (Olsen-P_2):

$$Added\ P = \frac{1}{2q}\left[\sqrt{l^2 - 4q(c - OlsenP_1)} - \sqrt{l^2 - 4q(c - OlsenP_2)}\right] \qquad (2)$$

where *c*, *l* and *q* are the fitted intercept, linear and quadratic parameters, respectively, of the Olsen-P quadratic models. The relationship between the fitted quadratic equation parameters for these Olsen-P models and soil characteristics was assessed using MLR (see supplementary information).

Two different approaches were applied to model total grass yield as a function of soil Olsen-P, and the results compared. The first fitted, the non-linear Mitscherlich asymptotic regression model:

$$Yield = a - \left(b\, r^{Olsen-P}\right) \qquad (3)$$

where *a* is the asymptotic yield in grams and *b* and r are the range and rate parameters, respectively, estimated by maximum likelihood (Poulton *et al.*, 2013). This form of model was chosen because the parameters have a single interpretation for yield responses to nutrient inputs. Inverting this relationship allows calculation of the critical Olsen-P (CV90) to obtain 90% of the asymptotic yield:

$$CV90 = \frac{In(-0.1a/b)}{In\, r} \qquad (4)$$

Standard errors for the fitted curve were obtained from the maximum-likelihood fit, and approximate standard errors for CV90 obtained using the RFUNCTION procedure in Genstat, and 95% confidence intervals constructed both for the fitted curve and for CV90 using these standard errors.

The second approach used the modified arsine-log method (Correndo *et al.*, 2017), considered to be more appropriate than fitting the Mitscherlich model as it takes account of the uncertainty associated with the measured Olsen-P values as well as with the measured yields (the Mitscherlich model considers the Olsen-P values to be measured without error). The fitted parameters and CV90 values were estimated using the Excel macro provided by Correndo et al (2017), with 95% confidence intervals for the estimated CV90.

The relationship between the CV90 values from the Mitscherlich fitting and soil characteristics was investigated using MLR as for the Olsen P model parameters above.

GenStat v.19 (2018) was used for all statistics unless stated otherwise.

Results

The soils used in the growth trials had highly variable soil characteristics (Table 1). For example, pH ranged from acid to alkaline (4.5 to 7.88) and PBI ranged from 70 to 767. Concentrations of amorphous and crystalline Al, Fe and Mn (hydr)oxides also varied greatly, while OC ranged from 1.5 to 28.6 %. There were significant correlations between some of the soil characteristics which partially may have been pseudo-correlations based on the same extractant being used for several characteristics (Table S3). Crystalline aluminium (hydr)oxides (CAlox) and crystalline iron (hydr)oxides (CFeox) correlated positively with each other (p <0.05), amorphous iron (hydr)oxides (AFeox) correlated with amorphous aluminium (hydr)oxides (AAlox) (p <0.05), PBI (p <0.05) and pH (p <0.05) positively while AAlox correlated with AFeox (p <0.05), amorphous manganese (hydr)oxides (AMnox) (p <0.01) positively and pH negatively (p <0.05). Clay, OC and TP also correlated positively ((p <0.05).

Relationship between added P and Olsen-P

The relationship between added P and extractable P values (initial Olsen-P) varied greatly between the individual soils (Figure 1, Table S4). In general, a quadratic equation best described this relationship for all soils, meaning that as the added concentrations increased, a larger proportion of this P was available. Only three soils had quadratic parameters, q, that were non-significant (Rough, Tadham, Thornby, Table 2). Some soils bound the added P strongly, allowing only a small proportion to be extracted by the Olsen-P procedure (e.g. Barnfield), while others bound it less strongly resulting in higher Olsen-P values (e.g. Sleaford). However, even in the soils where P was bound less strongly, less than 50% of the added P was found in the Olsen extract one week after addition.

Soil characteristics affecting Olsen-P values

It is known that PBI affects the binding capacity a soil has for P (Burkitt *et al.*, 2002), and thus should, in theory, affect the Olsen-P value of soil with added P. Therefore, MLR was carried out to elucidate which soil characteristics affected PBI in the soils used. The PBI was significantly affected by pH and crystalline manganese (hydr)oxides (CMnox) which together accounted for 85 % of its variation ($F_{2,7}$ = 26.58, p = <0.001, pH p <0.001, $\log_{10}$ (CMnox +1) p <0.001) and is represented by equation 6;

$$log_{10}\, PBI = 3.086 - 0.1683\, pH + 0.2784\, log_{10}\, (CMnox\ + 1) \quad (6)$$

For each of the three parameters (*c, l, q*) (Table 2) describing the relationship between added P and Olsen-P for the ten soils, MLR was carried out to investigate which soil characteristics affected the initial Olsen-P values 1 week after P addition. Parameter *c* (equation 7) was affected by CAlox, AMnox, initial TP and CMnox (which together accounted for 37.4 % of variance, although this was not significant due to the small number of samples ($F_{4,5}$ = 2.35, p = 0.187)).

$$log_{10}(c+1) = 0.1360\,log_{10}\ (CAlox\ +1) - 0.464\,log_{10}\,AMnox + 1.623\,log_{10}\,TP - 0.193\,log_{10}\,(CMnox+1) - 2.75 \quad (7)$$

(log_{10} (CAlox + 1) p = 0.087, log_{10} AMnox p = 0.080, log_{10} TP p = 0.055, log_{10} (CMnox +1) p = 0.261)

Parameter l was only significantly affected by PBI (equation 8) and accounted for 55.2 % of its variance ($F_{1,8}$ = 12.09, p = 0.008, log_{10} PBI p = 0.008).

$$l = -0.3044\,log_{10}\,PBI + 0.845 \quad (8)$$

Parameter q was affected by AFeox and PBI which together accounted for 38 % of the variance, although the overall relationship was not significant ($F_{2,7}$ = 3.76, p = 0.078), individual parameters were (log10 AFeox p = 0.046, PBI p = 0.049) (equation 9).

$$q = 0.00426 - 0.001137\,log_{10}\ AFeox + 0.000001246\,PBI \qquad (9)$$

Although not all analyses proved to be significant, probably as a result of the relatively small number of samples, it gives an indication of which soil characteristics are affecting Olsen-P values following addition of inorganic P fertiliser to this group of soils. We cannot rule out that this may prove to be different if soils with other predominant soil characteristics were used and we suggest a much larger experiment of this type with a greatly increased number of soils be carried out to provide more insight.

Growth curves and calculation of critical P values

Different soils had very different relationships between grass yield and soil Olsen-P concentrations (Figures 2 and 3). Values for CV90 varied between 7.3 - 194 mg kg^{-1} Olsen-P for the Mitscherlich method and between 12.3 – 186 mg kg^{-1} for the modified

Arcsine-log method. Although the two methods produced slightly different results and 95 % confidence intervals, neither method showed overall lower or higher values or smaller confidence intervals for all soils. After converting the values to mg L^{-1} (using the values in Table S7) and then to the P index used in the fertilizer recommendations for England and Wales (AHDB, 2019), the target values were found to range from index 0 – 8 for the Mitscherlich method (Table 3). However, MLR analysis of the CV90 values and soil characteristics, to investigate the cause of the soil specific CV90 values, showed no significant results. This was backed up by correlation analysis (Table S3) which found no significant correlations between CV90’s and soil characteristics.

Supplementary tables S5 and S6 give final soil Olsen-P values and total P removed by grass per pot.

Discussion

The added P became bound in the soils to various degrees during the week after addition, resulting in very different relationships between added P and Olsen-P for each soil. This affects the amount of fertilizer needed by each soil to increase the Olsen-P by a given amount. For example, if 10 mg kg^{-1} is the initial Olsen-P value and 20 mg kg^{-1} is the target value, it can be seen (Table 4) that the amount of P needed to increase Olsen-P to the target value would range between 24.6 mg kg^{-1} soil (Peldon) to 78.4 mg kg^{-1} soil (Tadham), a threefold variation, although this might be subtly different when dealing with soil that has been stabilised at a higher P index for a long time compared to a short time. Given that the fertiliser recommendations for England and Wales (AHDB, 2019) recommend the same addition of P fertilizer whatever the soil type, it should be questioned if these recommendations need to be amended to be more soil-specific. The fertiliser recommendations in Scotland have recently been changed to classify Scottish soil types into three groups depending on their P sorption capacity and recommend different P target soil indices and fertiliser additions based on this (Sinclair *et al.*, 2015). The same is true for Australian recommendations for pasture which take into account PBI when calculating P fertiliser additions (Simpson *et al.*, 2009). While most national fertiliser recommendations don't take into account any soil characteristics or soil types in Europe (Jordan-Meille *et al.*, 2012) a few do, to include soil type, soil texture and soil pH (Csatho *et al.*, 2007; Fotyma *et al.*, 2008; COMIFER, 2009). Adding too little fertilizer may result in reduced yields while adding to much may not only be wasteful of a critical resource and result in an unnecessary cost but could also result in environmental problems.

Different soil characteristics affected the relationship between added P and Olsen-P. The untreated soil Olsen-P (*c*) was positively influenced by TP and CAlox prior to P addition, and negatively influenced by A/CMnox, suggesting that the Olsen extraction method can more efficiently extract P from CAlox than A/CMnox (Braun *et al.*, 2019). It has been shown that phosphate binding to C/AAlox consists mainly of surface complexes that are readily extracted by weak extraction solutions (Gypser *et al.*, 2018; Gypser *et al.*, 2019). However, it is not clear how phosphate is adsorbed to Mnox, as although some authors suggest binding to MnO_2 is by outer-sphere surface complexes (Mustafa *et al.*, 2006), it has been suggested that binding to hydrous manganese oxide maybe by stronger inner sphere complexes (Pan *et al.*, 2014). The slope (*l*) was negatively influenced by PBI, therefore indirectly influenced positively by pH and negatively by CMnox. This is in contrast to other studies where Olsen-P showed a negative relationship with pH, however, these soils included some with high carbonate contents (Wuenscher *et al.*, 2015). Therefore, this difference could be related to the formation of calcium phosphates at high pH and carbonate content, leading to a decrease in Olsen-P (Brady, 1990). There is little information in the literature about the relationship between Mnox and Olsen-P, and it seems that Mnoxs are largely not considered when looking at P binding in soil. Turner and Blackwell (2013) did find that there was a negative relationship between readily exchangeable inorganic P and AMnox as well as with the readily exchangeable + chemisorbed to oxides fraction. Phosphate has also been shown to adsorb onto MnO_2 and Hausmannite under experimental conditions (Mustafa *et al.*, 2006; Li & Jaisi, 2015).

In our work we used two methods (Mitschelich, Arcsine-log) to calculate CV90 values (Olsen-P) based on grass yield curves and Olsen-P measurements 1 week after P addition. Despite the modified Arcsine-log method considering the uncertainty associated with Olsen-P measurements, it wasn't possible to say that one method gave an overall better prediction of the CV90 values or the 95 % confidence intervals. Neither method showed smaller confidence intervals for most of the soils. Therefore, in this study it seems that the error associated with Olsen-P measurements are not significant in the calculations.

It is well known that different crops have different critical P values (Nawara *et al.*, 2017; Sandaña *et al.*, 2018) so we should not compare the critical P values of ryegrass with other crops. Sanchez-Alcala et al (2015) report critical P values of 10.7 – 45.9 mg kg^{-1} Olsen-P in micropots for CV95 for ryegrass using 49 different Mediterranean soils compared to our 7.3 – 194 mg kg^{-1} CV90. However, their study was only carried out for 30 days so the CV would only reflect the initial growth rather than yield over the longer term like our study (16 weeks growth) which is more relevant for agronomic purposes and the grazing/silage scenario. The soils in our study also had a lower pH range but higher range of OC and AFe/Alox which could explain the discrepancy between the breadth of the range of CV values. Considering field based pasture experiments, Gourley et al (2019) report a CV95 Olsen P value of 15 mg kg^{-1} for improved pasture averaged over the whole of Australia, with soil texture class having no significant effect on the value. Edmeades et al (2006) found CV97 values of 10 – 45 mg L^{-1} Olsen-P for pasture, compared to our 8.5 – 153 mg L^{-1}. Again, our range of values is wider than Edmeades et al. (2006) but they calculated values based on soil class rather than for each soil and in doing so may have averaged out the values and made the range smaller. They also did not include peat soils which in our study showed the highest CV.

At present, fertiliser recommendations for England and Wales (AHDB, 2019) advise that agricultural soils be maintained at P index 2 in order to achieve optimum yields. This is based on the principle of diminished returns where, after a certain point, addition of fertiliser will not produce an economically worthwhile increase in yield. However, from our results it can clearly be seen that soils with different characteristics show 90 % yield at very different Olsen-P values. Of course, the actual values may change if measured after a longer time period from fertiliser addition, because available P becomes increasingly more strongly fixed over time, unless the soil is P saturated. The indices range from index 0 to 8 (using the Mitscherlich method) with only 3 out of 10 soils having CV90 in index 2 as suggested by the fertiliser recommendations, 2 out of 10 having lower indices and 5 out of ten having higher indices. There is no trend between the original land use of where the soil was collected and CV90 i.e. grassland soils requiring higher or lower indices than soils used for arable crops. Consequently, this leads to several questions: 1) is Olsen-P a suitable soil test for informing fertiliser recommendations?; 2) should different recommendations be given for different soil types?; 3) what is affecting the Olsen-P

CV90 values that has not being taken into account?; 4) can other soil factors be combined with Olsen-P to give a better measure of a critical P value?

Several authors report that individual soil characteristics or soil classes affect critical P values. For example Bell et al (2013) found that different classes of soil had different Colwell-P CV90 values and Gourley et al (2007; 2019) and Moody (2007) both found that PBI could be used to adjust Colwell-P critical P values. However, it is known that Colwell-P extracts more non-labile P than Olsen-P (Six *et al.*, 2012), and Gourley et al (2007; 2019) found that for the same soils there was no significant difference between Olsen-P critical values with different texture, PBI or regional origin. In field trials Johnston et al (2013) found that soil organic matter and texture affected the Olsen-P CV but not in pot trials, leading to the conclusion that this was actually due to their effects on soil structure. However, Nawara et al. (2017) also found that Olsen-P CV varied between soils in field experiments although they did not look at soil type or characteristics, and Edmeades et al (2006) found Olsen-P CV values varied between soil groups. Other researchers report similar variation in CV for pot experiments where differences in soil structure and other field based heterogeneity would have been eliminated (Sanchez-Alcala *et al.*, 2015; Recena *et al.*, 2016).

Despite our CV90 values varying for different soils, MLR of these values with soil characteristics did not show any significant relationships, meaning the reason for this variation in CV90 values remains unclear. Sanchez-Alcala et al (2015) reported that although there was no correlation between Olsen-P CV's for ryegrass and soil characteristics for non-calcareous soils (as we found), for calcareous soils there was a relationship between CV's and pH or calcium carbonate equivalent. This is consistent with the ability of bicarbonate solution to dissolve substantial amounts of calcium phosphates in calcareous soils which would not supply a large amount of P to soil solution, therefore overestimating plant availability (Sanchez-Alcala *et al.*, 2015). However, as our soils did not contain a substantial amount of carbonate then this was not a contributing factor to the differences in our CV90 values. Recena et al (2016) reported that CVs were correlated to clay, pH, iron (hydr)oxides (Feox), phosphorus buffering capacity, OC, phosphatase activity or phytase hydrolysable P. While Sanchez-Alcala (2014) found different Olsen-P concentrations are needed to supply plant relevant concentrations of P in soil solution for different soils. For non-calcareous soils, total Feox, AAlox and clay increased the Olsen-P needed to supply a plant with relevant soil solution P concentrations, and for calcareous soils, total Feox, clay and calcium carbonate equivalent increased it, while AFeox decreased it (Sanchez-Alcala *et al.*, 2014). Phosphatase activity and phytase hydrolysable P are both a measure of organic P; this ties in with later work that shows total P extracted by Olsen solution which includes both inorganic and organic P, increases the accuracy of predicting plant uptake of P from Olsen-P extractions (Recena *et al.*, 2019). This also indicates that organic P plays an important role in P supply to plants in some soils but has previously received relatively little consideration.

This raises some questions about the efficiency of inorganic Olsen-P as a method for measuring CV90's. If Olsen-P is used as the standard soil test method, then different recommendations for different soil types should be given. As it seems that multiple soil characteristics including measures of organic P, which were not analysed in this study, may be needed to take into account the differences in CV90 values among soils. It is likely that this is a reason why we cannot find a relationship between CV90's and soil characteristics in our study and maybe that depending on the soil, different characteristics take precedence in controlling P supply to plants.

Therefore, it is recommended that a wider study be carried out on a larger set of soils with multiple replicates, for these relationships between Olsen-P CV90 and soil characteristics to be clarified, as well as the characteristics affecting the relationship between added P and Olsen-P to be confirmed. It may also be prudent to measure the total P in Olsen-P extracts, so organic P is also considered. A standard approach to such studies would also allow meta-analysis of data from a range of studies and allow further conclusions to be drawn.

Conclusions

The relationship between added P and Olsen-P in soil was affected by pH, Mnox, CAlox and AFeox in our soils. Therefore, we suggest that fertiliser recommendations based on Olsen-P values should be made more soil-specific. Critical P values for optimum yield of ryegrass based on the Olsen-P test were also shown to vary greatly with soil type as hypothesized, although the measured soil properties showed no relationships with this. Therefore, we suggest further investigation should be carried out to establish what additional factors can explain the difference in critical Olsen-P values between soils, in order that more efficient P fertiliser recommendations can be developed.

Supporting Information

The following supporting information is available in the online version of this article:

Table S1. Soil location and description

Table S2. Experimental Treatments

Table S3. Correlation matrix of soil parameters

Table S4. Initial soil Olsen-P concentrations 1 week after P addition

Table S5. Final soil Olsen P concentrations

Table S6. Total P removed by the grass during the experimental time (P concentration in grass * biomass) mg P per pot

Table S7. Weight per volume of soil conversion (<2 mm)

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Table 1. Initial soil characterisation parameters

Soil	pH	TP mg kg^{-1}	PBI	OC %	Clay %	AAlox mg kg^{-1}	AFeox mg kg^{-1}	AMnox mg kg^{-1}	AP mg kg^{-1}	CAlox mg kg^{-1}	CFeox mg kg^{-1}	CMnox mg kg^{-1}	CP mg kg^{-1}
Barnfield	5.70	418	124	1.53	34	1347	4437	1332	75	1250	19380	0	144
Halstead	7.84	654	154	1.69	37	845	1799	510	218	521	12276	42	0
Knowstone	4.50	546	767	9.58	39	2350	10040	79	209	701	7634	36	93
Peldon	6.61	343	70	1.87	31	886	4485	377	113	0	8091	0	42
Rough	5.46	492	152	4.24	24	900	4815	175	190	0	954	0	16
Sleaford	7.88	521	105	1.85	39	938	3304	193	211	0	9769	1	0
Stowford	5.02	368	237	6.07	22	2209	6272	76	140	178	4446	8	33
Tadham	5.85	1026	271	28.6	58	1954	7970	423	312	0	0	22	0
Thornby	6.42	757	94	2.65	33	1178	7638	428	294	634	18938	0	136
Woodah	4.95	952	229	6.94	33	4103	8712	6322	439	204	15867	0	111

TP = Total Phosphorus; PBI = Phosphorus Buffering Index; OC = Organic Carbon; AAlox = Amorphous Aluminium (hyr)oxides; AFeox = Amorphous Iron (hyr)oxides; AMnox = Amorphous Manganese (hyr)oxides; AP = Phosphorus on amorphous (hyr)oxides; CAlox = Crystalline Aluminium (hyr)oxides; CFeox = Crystalline Iron (hyr)oxides; CMnox = Crystalline Manganese (hyr)oxides; CP = Phosphorus on crystalline (hyr)oxides;

Table 2. Quadratic regression parameters for the relationship between added P and Olsen-P

Soil	*c*	*l*	*q*
Barnfield	2.619***	0.0549***	3.277×10^{-4}***
Halstead	5.958**	0.1637***	6.250×10^{-4}**
Knowstone	3.945***	0.0002	6.680×10^{-4}***
Peldon	-0.210	0.4204***	-1.782×10^{-4}*
Rough	5.224***	0.2134***	2.51×10^{-5}
Sleaford	4.147***	0.1731***	9.017×10^{-4}***
Stowford	3.298***	0.1368***	3.595×10^{-4}***
Tadham	2.670	0.1079*	9.47×10^{-5}
Thornby	9.300	0.2570*	8.90×10^{-5}
Woodah	2.523***	0.1229***	4.67×10^{-5}***

*** significant at the $P < 0.001$ level, ** significant at the $P < 0.01$ level, *significant at the $P < 0.05$ level

Table 3. Critical P values (CV90) calculated by the Mitscherlich and modified Arcsine-log methods as measured (mg kg^{-1}) and converted to mg l^{-1} values (using measured soil weight to volume conversion values, Table S6) and indexes as in the UK Nutrient management guide (AHDB, 2019).

	Mitscherlich			Modified Arcsine-log		
Soil	CV90 mg kg^{-1}	CV90 mg l^{-1}	index	CV90 mg kg^{-1}	CV90 mg l^{-1}	index
Barnfield	7.3	8.5	0	12.3	14.4	1
Halstead	22.2	27.1	3	26.4	32.3	3
Knowstone	10.5	8.31	0	10.4	8.22	0
Peldon	194	241	8	137	171	7
Rough	17.3	18.4	2	25.5	27.2	3
Sleaford	19.8	25.7	2	28.7	37.3	3
Stowford	21.0	20.0	2	22.1	21.0	2
Tadham	169	153	7	186	168	7
Thornby	72.3	77.9	5	128	138	6
Woodah	36.1	32.2	3	55.3	49.4	4

Table 4. Addition of P needed to increase soil from 10 to 20 mg kg^{-1} Olsen-P one week after addition

Soil	mg P kg soil
Barnfield	73.2
Halstead	45.4
Knowstone	59.8
Peldon	24.6
Rough	46.4
Sleaford	38.4
Stowford	53.3
Tadham	78.4
Thornby	38.3
Woodah	75.8

Figure 1. Relationship between added P and initial Olsen-P in ten soils with widely varying characteristics.

Figure 2. Grass yields with increasing initial Olsen-P values using the Mitscherlich method. The cross represents the calculated Critical Olsen-P values at 90 % of the maximum yield (CV90) and the shaded red area is the 95 % confidence intervals for this.

Figure 3. Grass yields (as relative yield) with increasing initial Olsen-P values using the modified arcsine-log method. The cross represents the calculated Critical Olsen-P values at 90 % of the maximum yield (CV90) and the shaded red area is the 95 % confidence intervals for this.