



Estimation of total plant available phosphorus in representative soils from Mediterranean areas



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ARTICLE INFO

Article history:

Received 17 August 2016

Received in revised form 15 February 2017

Accepted 17 February 2017

Available online 12 March 2017

Keywords:

Soil P test

Olsen P

Resin extractable

Organic P

Buffer capacity

Fe oxides

ABSTRACT

The sustainable use of P in agriculture, which is a non-renewable and strategic resource, relies on soil P tests. Traditional soil P tests, however, may not accurately assess plant-available P in soils ranging widely in properties. The main objectives of this work were: (i) the study of the accuracy of the widely used Olsen P in assessing available P to plants, and (ii) testing other extraction methods to assess phytoavailable P, in a representative group of soils from Mediterranean areas. To this end, a P depletion experiment was conducted using 18 soils to estimate total available P to plants in soil. In addition to Olsen P, other P extractions were performed to check their accuracy in predicting total available P to plants, including anion exchange resins in Cl^- and HCO_3^- forms. Poor predictions of total available P with Olsen P ($R^2 = 0.53$, $P < 0.001$) were improved when clay and carbonates were taken into account in a predictive model ($R^2 = 0.8$, $P < 0.001$). The best estimations of total available P were obtained with resins, that in HCO_3^- form ($R^2 = 0.87$, $P < 0.001$) performing better than that in Cl^- form ($R^2 = 0.77$, $P < 0.001$). Estimations with resins improved when potential organic P inputs to available P were taken into account. This reveals the role of organic P to the availability of this nutrient to plants. It can be concluded that single models based on Olsen P plus routinely determined soil properties, and single extractions with resins predict total available P in studied soils with sufficient accuracy.

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1. Introduction

Phosphorus is non-renewable and strategic resource inefficiently used in agriculture (Schröder et al., 2011) whose production is expected to peak by middle of the century (Cordell et al., 2009; Keyzer, 2010). Thus, a more efficient use of P in agriculture is mandatory to overcome the consequences of progressive depletion of P rock reserves on agricultural production. This efficient use should rely on more precise prediction of available P to plants in soil (Menzies et al., 2005; Tandy et al., 2011; Jordan-Meille et al., 2012). In addition, environmental implications of imbalanced P applications to agricultural land will be reduced by improving the efficiency in its use (Colomb et al., 2007; Carpenter, 2008; Ryan et al., 2012).

Phosphorus availability to plants is mainly ruled by three factors: (i) the concentration of P in the soil solution ('intensity' factor, I), (ii) the amount of P in the solid phase that can be easily made available to

plants ('quantity' factor, Q), and (iii) the capacity of soil to keep the P concentration in soil solution sufficiently high (P buffer capacity, PBC) (Sánchez Alcalá et al., 2014). Available P to plants is usually assessed by means of P-availability tests or soil P tests (SPTs), which are chemical extractions able to predict when a response to P fertilization can be expected (Tang et al., 2009). Usual SPTs extract amounts of P from soils which are deemed estimates of either I , i.e. P concentration in soil solution or in a low molarity salt soil extracts (Schoenau and Huang, 1991; Van Raij, 1998), or Q , i.e. classical chemical extractions such as Olsen P (Olsen et al., 1954), depending on the particular test (Sánchez Alcalá et al., 2015). However, the usefulness of SPT is limited by the fact that a single measurement cannot encompass all P-related factors potentially affecting plant performance (Ehlert et al., 2003; Sánchez Alcalá et al., 2015). Thus, P-availability estimates based on estimates of PBC and Q (Delgado et al., 2010), or I and Q (van Rotterdam et al., 2012) have proved more effective in assessing available P to plants in soil (Sánchez Alcalá et al., 2015).

Soil P tests related to the Q factor may not extract rapidly all the available P compounds in soil (Menon et al., 1989; Six et al., 2012). In addition, the amounts extracted by SPTs depend on the chemical nature of the extractant, the dominant P forms, and soil properties such as pH or nature of sorbent surfaces (Delgado and Torrent, 1997; Delgado and Scalenghe, 2008). This latter point constrains the use of one given

Abbreviations: AER, Anion exchange resin; ca, Citrate-ascorbate; cb, Citrate-bicarbonate; cbd, Citrate-bicarbonate-dithionite; SOM, Soil organic matter; CCE, Calcium carbonate equivalent; PBC, P buffer capacity of soil; SPT, Soil P test; DGT, Diffusive gradients in thin films.

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SPT in different types of soils and explains the wide variety of official SPTs used for assessing P fertilization in different countries (Neyroud and Lischer, 2003; Delgado and Scalenghe, 2008; Jordan-Meille et al., 2012). Only the use of near-infinite sinks, such as Fe oxides or anion-exchange resins (AER), has proved to estimate total available P to plants in soils ranging widely in soil properties (Delgado and Torrent, 1997). This may be explained because sinks mimic the functioning of plant roots (Abdu, 2006; Jordan-Meille et al., 2012) because they adsorb P from the soil solution enhancing its release from the soil solid phase without solubilisation reactions by chemical extractants (Fernandes and Coutinho, 1997; Menzies et al., 2005). In addition, these extractions have proved to be sensitive not only to Q, but also to PBC, which is crucial affecting P availability to plants (Ehlert et al., 2003; Celardin, 2003). This contributes to explain the better results obtained with P sinks when compared with classical test such as Olsen P in soils with similar properties (Delgado et al., 2010).

Although widely used in many areas of the World, such as in Mediterranean countries, Olsen P has limited usefulness in precise assessment of plant available P (Delgado et al., 2010; Tandy et al., 2011; Sánchez Alcalá et al., 2014). Relationship between Olsen P and plant available P is affected by nature of P sorbent surfaces (Martin et al., 2002; Rahnamaie et al., 2007), by pH, carbonates (Delgado and Torrent, 1997; Sánchez Alcalá et al., 2015), and by the contribution of organic P to plant uptake (Recena et al., 2015). Although organic P has been described as the dominant forms in many soils (Saavedra and Delgado, 2005; Delgado and Scalenghe, 2008), its contribution to plant available P remains unclear. Recently, Recena et al. (2016) revealed that specific organic P fractions and phosphatase activity in rhizosphere affected the accuracy of Olsen P as SPT. In spite of these evidences, deeper knowledge on the reasons for the low accuracy of this SPT is necessary for its use in efficient P fertilization practices. In particular, it is necessary to have precise information on the contribution of organic P to plant available P and to the accuracy of Olsen P as SPT. All this is expected to allow for the proposal of models based on this STP to accurately estimate plant available P. Alternatively, more accurate single P extractions methods for assessing available P in soils could contribute to a more efficient P use in agriculture (Recena et al., 2015). However, according to Ehlert et al. (2003), single SPTs, most of them estimates of the Q factor, are not sufficient for fertilizer recommendations, and PBC should be taken into account. Since P extractions with sinks, particularly anion exchange resins, may be related to PBC, their utility in assessing TAP in soils should be better explored. This work is thus aimed at: (i) the study of the accuracy of Olsen P to estimate available P to plants, and (ii) testing other single and easily performable extraction methods to assess phytoavailable P in a representative group of soils from Mediterranean areas. The research is expected to provide new insight on soil properties governing P uptake by plants and the accuracy of tested P extractions to estimate plant available P. This will be useful not only in the study of the limits of studied P extractions as soil P test, but also in the performance of models based on these extractions to accurately assess available P to plants. In addition, it will be also useful to know the requirements that should meet by new P extraction methods to accurately estimate available P to plants in soil.

2. Materials and methods

2.1. Materials

The group of 18 soils selected for the present study was the same as that used by Recena et al. (2016). The soils came from different agricultural areas of Spain, encompassing the most representative orders under Mediterranean climate according to Soil Taxonomy (Soil Survey Staff, 2010): Mollisols, Entisols, Inceptisols, Alfisols, and Vertisols. Most of these soils were used for olive orchards or for wheat-sunflower rotation. Location, taxonomy, parent material, rainfall, and agricultural use are described in Table S1. In each selected location,

where a homogeneous soil was identified, samples were taken at 20 cm depth, obtaining a collection of soil samples (from 5 to 33 depending on the site; Table S1) ranging widely in Olsen P values. From this collection, those soil samples with the two extreme Olsen P values from each site were selected and named “low-P” and “high-P” samples according to their Olsen P values. Olsen P for low-P samples ranged from 5 to 16 mg kg⁻¹, for high-P samples from 9 to 49 mg kg⁻¹, and the difference between high-P and low-P samples for the same soil between 3 and 33 mg kg⁻¹ (Recena et al., 2015). For the P starvation experiment described below, soil was ground to <6 mm, and for soil analysis, a subsample of the soil was ground to <2 mm. The “high P” and “low P” samples were examined in order to check that they differed by <5% in the basic soil properties (soil organic matter, clay, carbonates, pH, and Fe bound to oxides).

2.2. Methods

2.2.1. Soil analysis

Soils were analyzed for particle size distribution according to Gee and Bauder (1986), organic matter (SOM) by the oxidation method of Walkley and Black (1934), total CaCO₃ equivalent (CCE) by the calcimeter method, and pH in water at a soil:extractant ratio of 1:2.5. The sequential chemical fractionation of de Santiago and Delgado (2006) was used to measure the Fe present in Fe oxides: citrate-ascorbate to release Fe in poorly crystalline Fe oxides (Fe_{ca}), and citrate-bicarbonate-dithionite to release Fe in crystalline oxides (Fe_{cbd}). In these extracts, Fe was determined by atomic absorption spectrometry.

Total inorganic P (Pi) was determined as that extractable with 0.5 M H₂SO₄ (Kuo, 1996). Total P (TP) was determined following dry combustion at 550 °C for 2 h and extraction with 0.5 M H₂SO₄ (Kuo, 1996). In both acid extracts for Pi and TP determination, P was determined using the molybdenum blue colorimetric method of Murphy and Riley (1962). Total organic P (OP) was estimated as the difference between TP and Pi (Kuo, 1996).

Sorption curves at 6 d in 0.01 M CaCl₂ were performed according to the method of Fox and Kamprath (1970). Sorption curves were fitted to the Freundlich equation:

$$\text{Sorbed P} = AX^{1/b} + Q_0 \quad (1)$$

where the sorbed P by soil is expressed as a multiplicative function of the remaining P concentration in solution (X), and b can be considered the affinity factor, in such a way that P affinity for soil increases with increasing b values. Q₀ can be deemed the initially amount of adsorbed P. The P buffer capacity (PBC) was estimated as the slope of the sorption curve at equilibrium concentration, and at 0.01, 0.02, 0.2 and 1 mg L⁻¹ (PBC₁). The Langmuir model was used to estimate the maximum P sorption capacity (X_m).

2.2.2. P extractions from soil

Different P extraction methods were used to assess their ability to estimate total available P to plants (TAP). Olsen P was determined according to Olsen et al. (1954). An extraction with 0.27 M Na citrate + 0.11 M NaHCO₃ (CB) was performed using 1 g of soil in 40 mL of extractant at 1, 3 and 24 h in polyethylene centrifuge tubes. The two first sequential extractions in the Ruiz et al. (1997) fractionation scheme were performed involving first 0.1 M NaOH + 1 M NaCl, and second citrate-bicarbonate, as described above, as second step, both during 17 h. In both steps, the phytase hydrolysable P was determined as described by Recena et al. (2016). In all these chemical extractions, P was determined by the colorimetric method of Murphy and Riley (1962).

Extraction by near-infinite sinks was performed by using two types of anion exchange resins (AER) which has been widely described in the literature. Extraction with AER in Cl⁻ form (P_{Cl-AER}) was performed

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