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## Experimental dissolution of biopolymer-coated phosphorus fertilizers applied to a soil surface: Impact on soil pH and P dynamics

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### ABSTRACT

Biopolymer-coated phosphorus fertilizers have shown promising results in slowing the release of P. However, their dissolution behaviour has been studied mainly in water, and their impacts on soil properties have rarely been addressed. The aim of this study was to compare the dissolution of P from uncoated triple superphosphate (TSP) and biopolymer-coated TSP fertilizers at the surface of cropped Mediterranean soils and to evaluate their impacts on the soil pH and the distributions of several P pools. The experimental treatments were: no fertilizer, uncoated TSP, TSP coated with lignin and TSP coated with lignin and carrageenan. The spatial and temporal variations in the pH of the fertilized soils were investigated using optodes. The concentrations of different pools of P (available P, microbial P), and total P as well as P recovery at different distances from the granules were determined. The coated TSP acidified the soil to a radius of 14 mm around each fertilizer granule, while the acidification spread to 21 mm in the treatment with the uncoated TSP. Moreover, an increase in microbial P was observed in the soil treated with coated TSP, possibly due to the carbon input and the consequent increase in microbial biomass. However, slower P-release was observed from the coated TSP due to the effect of the coating barrier. The P recovery results showed P migration within a 21 mm radius from each granule, and the P recovery from the TSP coated with lignin alone was significantly greater than that from the uncoated TSP treatment.

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### 1. Introduction

Phosphorus (P) is often the most limiting plant nutrient. P deficiency typically occurs not because of a low amount of total P in soil but rather because the soil P is in chemical forms that are not available to plants. Phosphorus fertilizers are applied to soils to increase the supply of bioavailable orthophosphate to plant roots. However, due to the immobilization of P into poorly available P forms, only 10–20 % of P is taken up by the plant in the first year after fertilizer application (Lan and Mingzhu, 2008; Rop et al., 2018; Timilsena et al., 2015), and the remaining P is adsorbed or precipitated. For instance, most orthophosphate ions are adsorbed onto the surface of clay-sized minerals dominated by aluminium and iron oxides (Da Cruz et al., 2017) or precipitated as Calcium phosphates in highly calcareous soils (Bertrand et al., 1999).

Increasing P fertilizer efficiency is a challenge, and “slow-release fertilizers” (SRFs) have been developed for this reason (Fertahi et al., 2021; Giroto et al., 2017). Coating the fertilizer granules with an insoluble material is a common method used in SRF formulations. The coating limits interactions between the soil and the nutrients (i.e., P fixation). Biopolymers are used in formulations coating for granular mineral fertilizers (Ahmad et al., 2015; Noppakundilograt et al., 2015; Wu et al., 2008; Wu and Liu, 2008).

Soil pH affects nutrient availability. A soil pH of 5.5–7 is suitable for nutrients availability to plant roots. The use of biopolymer-coated fertilizers has a buffering effect on soils to an approximate pH of 7 (Wang et al., 2014). Soil microorganisms depend on organic C for energy and to perform cell synthesis (Lupwayi et al., 2010), and the addition of C-rich polymers to soil may stimulate their growth (Xiaoguang et al., 2005) and the immobilization of P. Polymer-coated P fertilizers increase P availability in soil and maintain this increase for longer than uncoated fertilizers (Diez et al., 1992; Garcia et al., 1997). Studies have also shown that the majority of fertilizer P (>80 %) from both uncoated and

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polymer-coated fertilizers remains within the first seven millimetres of the point of application and that <20 % of P migrates farther than a 25.5 mm radius around the fertilizer granule (de Castro et al., 2015; Lawton and Vomocil, 1954; Lombi et al., 2005). However, studies of biopolymer-coated P fertilizers are still scarce; such studies have generally been performed on nitrogen fertilizers; and they generally have not specified the polymer used in the coating.

The purpose of this work was to study the dissolution of P from biopolymer-coated P fertilizers applied to a soil surface and its impact on soil pH and P dynamics. Three different coatings that had been previously prepared and characterized (Fertahi et al., 2020b) were applied: uncoated TSP, coated TSP with lignin (lignin@TSP) and coated TSP with lignin and carrageenan (lignin-carrageenan@TSP). Carrageenan alone was not chosen because of the results reported by Fertahi et al., 2019, showing that TSP coated with only carrageenan had high P-release behaviour in water. The effects of these treatments on soil pH were investigated at different distances from the fertilizer application point over 28 days using optode technology (detailed in the Section 2.3). As the coating materials were highly alkaline (dissolved in NaOH before use), we hypothesized that the coated TSP would acidify the soil less than the uncoated TSP which is known for its low pH. The different pools of P (microbial P, resin P and total P) in soil were measured at different distances from the fertilizer application point at 28 days after application. We hypothesized that i) the P from the coated TSP would spread in a larger radius around the granule due to its slower release rate and that ii) the decomposition of the polymeric coatings and C uptake by microorganisms would lead to microbial growth and greater P immobilization in the treatments with the coated fertilizers.

## 2. Materials and methods

### 2.1. Soil sampling

The soil samples were taken at the Mauguio INRAE experimental station in southern France (3°58'39.898" E, 43°36'45.576" N). The regional climate is a typical Mediterranean climate with a mean annual temperature of 15.6 °C and 650 mm of annual precipitation. Samples were taken from the top 20 cm of four subplots within an agricultural plot in October 2019. The agricultural plot had been cultivated for >20 years with a rotation of durum wheat, chickpea and barley. At the sampling time, the planted crop was chickpea (*Cicer arietinum* L.). The soil samples were air-dried, sieved to 2 mm, homogenized and stored at 4 °C. The main soil physical and chemical characteristics of the soil samples are summarized in Table 1.

### 2.2. Preparation of Petri dishes containing soil and fertilizers

Twenty square Petri dishes (144 cm<sup>2</sup>) were filled with 171.5 g equivalent dry soil that had been adjusted to 60 % water holding capacity

(WHC). Water was added to the soil by carefully spreading 31 mL of distilled water over the soil surface with a pipette. The Petri dishes were closed with lids and pre-incubated for one week at 25 °C in the dark to stabilize soil microbial activity. Every two days, the soil moisture was controlled by weighing, and distilled water was added if necessary. The fertilizer treatments were uncoated granular triple superphosphate (TSP), TSP coated with lignin (lignin@TSP), TSP coated with lignin-carrageenan (lignin-carrageenan@TSP) and an unfertilized soil (control).

The carrageenan polymer was a kappa carrageenan sulfated plant polysaccharide (CAS: 11114-20-8). The lignin polymer used in this study was extracted from olive pomace biomass using the alkali method described previously by Fertahi et al., 2019, 2020a, 2020b. The preparation of the biopolymer-coated TSP was also previously described in these references.

Granules with approximately the same mass (39.3 ± 0.1 mg, corresponding to 9.8 mg of P) were selected, and one granule of each fertilizer was placed in the center of each Petri dish. For the coated TSP, the coating mass and moisture were taken into account in the calculations so that the amount of P remained the same among all coated and uncoated granules. Each treatment was replicated four times. The granules were pushed a few millimetres (1–2 mm) into the soil, and a small amount of soil was placed on top of and around each granule in order to achieve a flat soil surface in each Petri dish.

### 2.3. pH measurements

pH mapping of the soil treatments with or without fertilizers was performed using optodes (Fig. S1). An optode is a chemical and optical sensor composed of two parts: a chemical part (dye), which comes into contact with the sample, and an optical part, which records the signal emitted by the chemical sensor (Wencel et al., 2014). Optodes represent a promising technique to obtain information about pH, O<sub>2</sub> and CO<sub>2</sub> gradients in soil systems in a non-invasive, reversible way and to study rhizosphere processes at the microscale (Blossfeld et al., 2013; Blossfeld and Gansert, 2007; Buss et al., 2018; Chen et al., 2021; Larsen et al., 2015). Most pH optodes contain analyte-sensitive and analyte-insensitive dye indicators, and their functions are based on reversible changes in the luminescence properties of a pH-sensitive fluorophore (Blossfeld and Gansert, 2007; Faget et al., 2013). As the phenomenon of fluorescence is reversible, temporal monitoring can be carried out without disturbing the sample. Several types of optodes exist, and they vary depending on the signal-recording mode and the output data format. A distinction can be made between fiber optic measurements, which provide information from a single point, and image measurements, which provide a 2-D data matrix with a spatial dimension. In the present study, we used both systems, i.e., spot optodes to obtain fiber optic measurements and planar optodes for imaging.

For the spot system, the principle of measurement is based on the dual lifetime referencing (DLR) method. This method requires two luminophores, a luminescent standard (analyte-insensitive) and a fluorescent pH indicator, that have different lifetimes, overlapping excitation and emission spectra (Wencel et al., 2014). An optical fiber was used to transfer the excitation light to the spot sensor and to return optical signals to the detector (Fig. S2). The difference between the signals of the indicator fluorophore and the reference luminophore is converted into a phase angle (Blossfeld and Gansert, 2007; Clarke et al., 2015). This angle is then converted into a pH value based on a calibration curve using Eq. (1) (Blossfeld and Gansert, 2007).

$$\text{pH} = \text{pH}_0 + \text{dpH} \cdot \text{Ln} \left( \frac{\phi_{\min} - \phi_{\max}}{\phi - \phi_{\max}} - 1 \right) \quad (1)$$

where  $\phi_{\min}$  and  $\phi_{\max}$  represent the minimum and maximum values of  $\phi$ , respectively.  $\text{dpH}$  and  $\text{pH}_0$  provide the slope and inflection point of the sigmoidal curve, respectively.

**Table 1**  
Soil physical and chemical characteristics.

Soil property	Value
Clay g kg <sup>-1</sup>	210.7 ± 7.6
Fine silt g kg <sup>-1</sup>	121 ± 16.5
Coarse silt g kg <sup>-1</sup>	194.3 ± 14.7
Fine sand g kg <sup>-1</sup>	203.7 ± 17.6
Coarse sand g kg <sup>-1</sup>	270.3 ± 17.9
Total N g kg <sup>-1</sup>	1.09 ± 0.08
Total P g kg <sup>-1</sup>	0.55 ± 0.02
Organic P g kg <sup>-1</sup>	0.14 ± 0.02
Organic carbon g kg <sup>-1</sup>	10.24 ± 1.23
Microbial carbon g kg <sup>-1</sup>	0.45 ± 0.08
CaCO <sub>3</sub> g kg <sup>-1</sup>	<1
CEC cmolc. g kg <sup>-1</sup>	10.25 ± 1.23
pH (water)	7.8 ± 0.2

n = 3, CEC: cation exchange capacity.

For the planar optode system, the measurements are based on the intensity ratiometric method. This method requires a non-pH-sensitive and pH-sensitive fluorophore that have different optical properties (Wencel et al., 2014). The first fluorophore emits in the green part of the spectrum, whereas the second emits in the red part. In the presence of protons, the balance of the protonated/deprotonated forms of the fluorescent probe is altered. This chemical reaction modifies the fluorescence intensity. A camera detects the fluorescence signals from the foil. The digital images were separated into red, green and blue images using image processing software. The pH was calculated based on the Eq. (2) (Faget et al., 2013).

$$\text{pH} = \text{pH}_0 + \text{dpH} \cdot \ln\left(\frac{R_{\min} - R_{\max}}{R - R_{\max}} - 1\right) \quad (2)$$

where  $R_{\min}$  and  $R_{\max}$  represent the minimum and maximum values of  $R$  (the red/green ratio), respectively. The derivation  $\text{dpH}$  gives the slope of the curve, and  $\text{pH}_0$  is the acid dissociation constant of the indicator dye in a specific system.

The planar and spot optodes were purchased from PreSens GmbH®. The planar optode (product code: HP5R – PreSens GmbH, pH range 5.5–7.5) used an imaging system (VisiSens TD), and the spot optode (product code: SP-HP5-SA – PreSens GmbH, pH range 4–7.5) used an optical fiber (pH-1 SMA LG1). Image processing was performed with the open-source software ImageJ (<https://imagej.nih.gov/ij/>).

For each treatment, three Petri dishes were subjected to pH measurement with spots, and one Petri dish was subjected to planar optode measurements. A total of 156 self-adhesive spots (7 mm) were placed in a line onto clean glass slides (13 spots were used for one Petri dish \* 3 Petri dishes \* 4 treatments). The spots were soaked for at least 3 h in 100 mM phosphate-buffered saline for equilibration and rinsed prior to being placed on glass slides. Each glass slide was then placed onto the soil surface by placing the central spot above the fertilizer granules; this location corresponded to section S0 (S0 = 0–7 mm = spot 1). The other spots were placed at different distances from the granule (Fig. 1A), i.e., 7–14 mm, 14–21 mm, 21–28 mm, 28–35 mm, 42–49 mm and 56–63 mm.

The planar optodes were cut into small (2 cm \* 1.5 cm) and large rectangles (6 cm \* 1.5 cm). They were attached to glass slides and equilibrated in a buffer solution as described previously for the spot optodes. The glass slide with the large rectangular foil sensor was placed at the center of the Petri dish above the fertilizer granule, and the two small pieces of the planar optodes were placed at the edges of the Petri dish (Fig. 1B).

The Petri dishes were then sealed with parafilm to prevent moisture loss and covered with aluminium foil to protect the optodes from ambient light. After that, the Petri dishes were incubated for 28 days at 25 °C in darkness. pH measurements were made in a custom-made dark chamber after 6 h, 1, 2, 3, 6, 7, 10, 15, 20, 24 and 28 days of incubation. After each measurement, the Petri dish was closed again until the following measurement, and the moisture was controlled and readjusted to 60 % WHC. To this end, water was homogeneously added evenly through holes on all four sides of the Petri dish, thus preventing interference with the sensors or with P diffusion.

The spot and planar optodes were calibrated in a phosphate ( $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ ) buffer solution. As fluorescent pH probes are sensitive to ionic strength (Weidgans et al., 2004), the ionic strength of the buffer solution was adjusted to 20 mM with NaCl. This ionic strength was chosen based on the electrical conductivity of the soil sampled at a radius of 20 mm around the TSP fertilizer granules (Table S1).

#### 2.4. Measurements of P pools

After the last pH measurement, i.e., after 28 days of incubation, the soil was collected for P pool measurements. Small cylinders ( $d = 7$

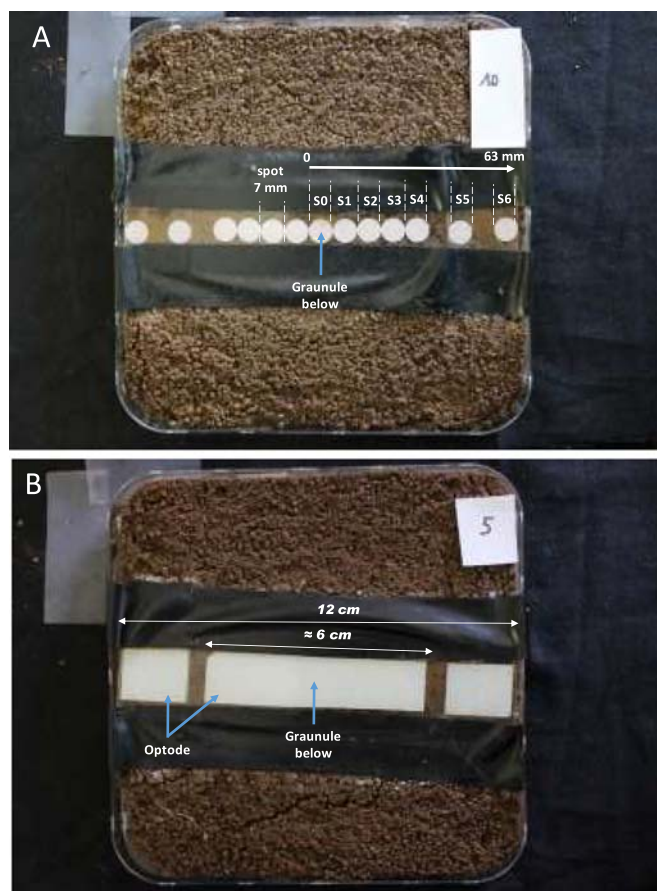


Fig. 1. Petri dishes with soil and TSP granules in the middle, with A) spot optodes ( $n = 3$ ) and B) planar optodes ( $n = 1$ ) placed on glass slides and fixed above the soil surface.

mm,  $h = 2$  cm) were used to collect the soil at distances of 0–7, 7–14, 14–21, 42–49, and 56–63 mm from each TSP granule, as described in Fig. 2. Soil samples were taken in four directions (north, south, west and east) from the center of each dish. One soil subsample was used for resin-P measurements, while another subsample was used for microbial P measurements. Resin-P targets phosphate ions in solution and loosely sorbs onto soil surfaces; therefore, it represents plant-available P. Microbial P targets the P contained in soil microorganism cells. Both were extracted with anion exchange resin membranes (AERs) according to the protocol proposed by Bünemann et al., 2012.

Briefly, AER membranes (6 cm \* 2 cm, VWR 551642S) were shaken for 1 h in 0.5 M  $\text{NaHCO}_3$  to bring them into the bicarbonate form. For resin-P, approximately 1 g of dried soil (0.5 g for S0) was weighed out, and 30 mL of distilled water and a resin strip were added to the soil. The samples were shaken horizontally on an end-over-end shaker (60  $\text{rev} \cdot \text{min}^{-1}$ ) for 16 h. For microbial P, we followed the same procedure as for resin-P, with the addition of 1 mL of hexanol to the soil:water suspension before the shaking step. The microbial P was then calculated as the difference between the measured P from fumigated and unfumigated splits. The adsorbed P was eluted by shaking the AER membranes in 30 mL of 0.1 M NaCl+HCl for 2 h, and the concentration of P was determined colorimetrically using the malachite green method (Ohno and Zibilske, 1991).

The soil used to determine the resin-P concentration was recovered by centrifugation to determine the remaining total P. To do so, the soil (50 mg dry basis) was digested by microwave at 220 °C using 1 mL of 15.6 M nitric acid, and the P concentration was determined using malachite green (Ohno and Zibilske, 1991). To determine the total P content at each distance from the granule, the resin-P and total remaining P

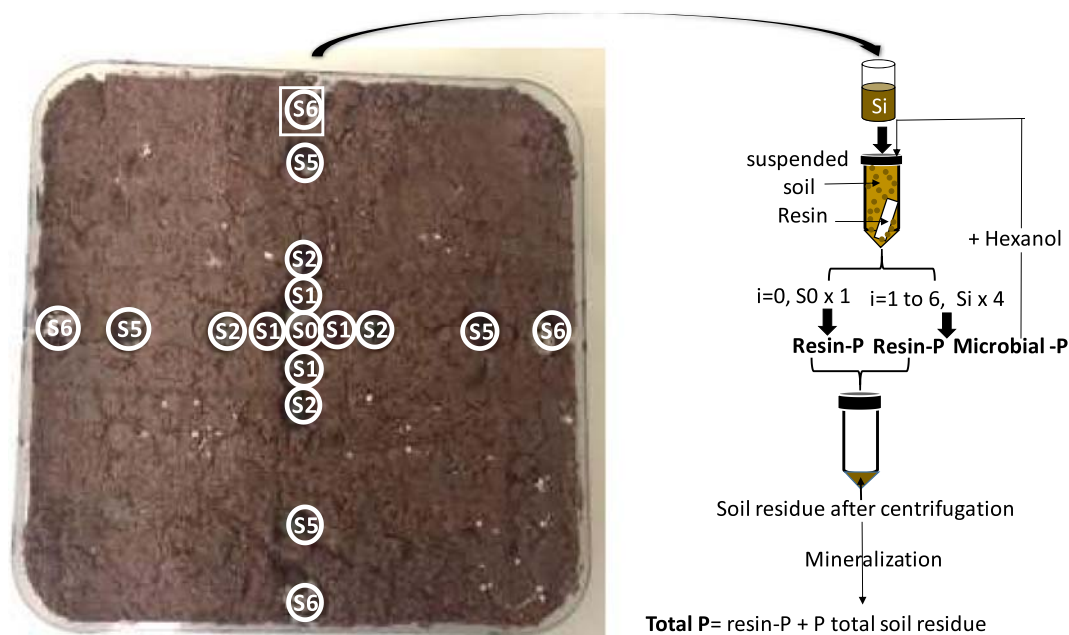


Fig. 2. Sampling methodology of soil from the Petri dish at different distances from the granule after 28 days of incubation.  $S_i$  represents the sections of soil at different distances from the granule ( $i = 0, 1, 2, 5, 6$ ).

were summed. The total P was then used to calculate the recovery of P from fertilizer using Eq. (3) (de Castro et al., 2015).

$$Pfs_i = \frac{([Pf]Si * Wi)}{\sum_{i=0} ([Pf]Si * Wi)} \quad (3)$$

where  $i$  represents the soil sections at different distances from the granule ( $i=0, 1, 2, 3, 5, 6$ ) and  $[Pf]Si$  and  $Wi$  represent the concentration of total P at  $S_i$  (mg/kg) and the soil weight at each distance (kg), respectively.  $[Pf]Si$  was calculated by subtracting the P concentration of the unfertilized soil from the P concentration of the fertilized soil.

2.5. Data analyses

Analysis of variance (ANOVA) and mixed modeling were performed using R version 3.4.2. A Two-way ANOVA was performed to study the effect of the fertilizer treatment and the distance from the fertilizer granule on resin-P, microbial P and P recovery. Mixed models (package:

lme4) were developed to study the effect of the fertilizer treatments, the distance from the fertilizer granule and time (fixed effects) on the soil pH, with the Petri dishes as the random effect. If significant differences were found, Tukey's (for ANOVA) and Emmeans (for mixed models) post hoc tests were used to perform pairwise multiple comparisons ( $p < 0.05$ ).

3. Results and discussions

3.1. The dynamics of soil pH with uncoated and coated TSP fertilizers

The control soil had a pH of  $7.8 \pm 0.2$  that did not change significantly throughout the 28 days of incubation or at the different positions within the Petri dish (Fig. 3A). With the addition of TSP fertilizers, strong acidification in the soil located directly around the granule was observed, i.e., a decrease of  $>4$  pH units compared to that in the unfertilized soil (Fig. 3B-D). The decrease in soil pH was probably caused by

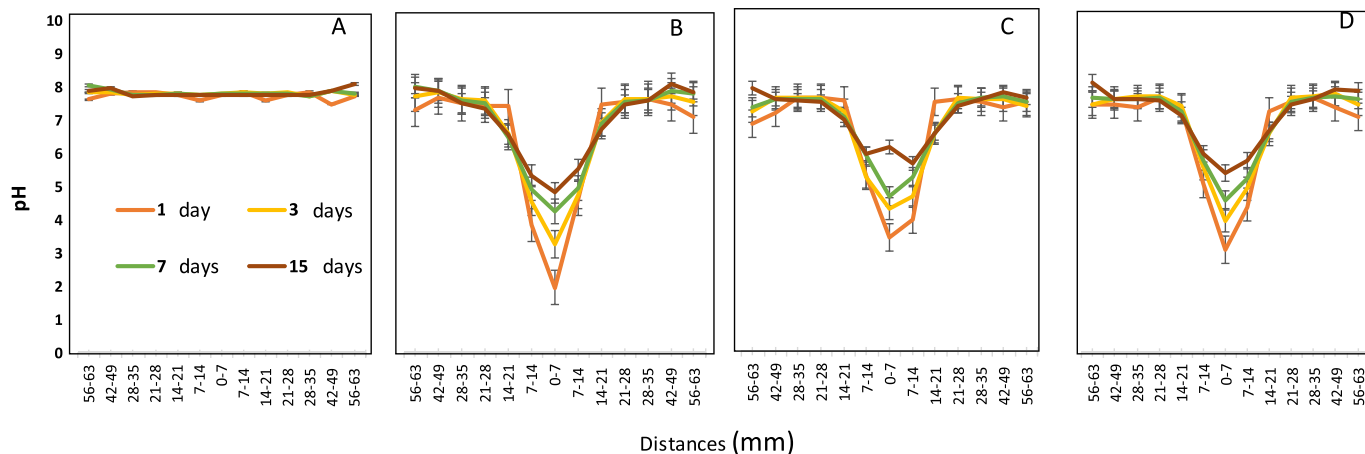


Fig. 3. Spot measurements of soil pH as a function of time (measurements at days 1, 3, 7 and 15) and distance from the added granule for A) no TSP fertilizer (control), B) uncoated TSP, C) lignin@TSP and D) lignin-carrageenan@TSP,  $n = 3$ .

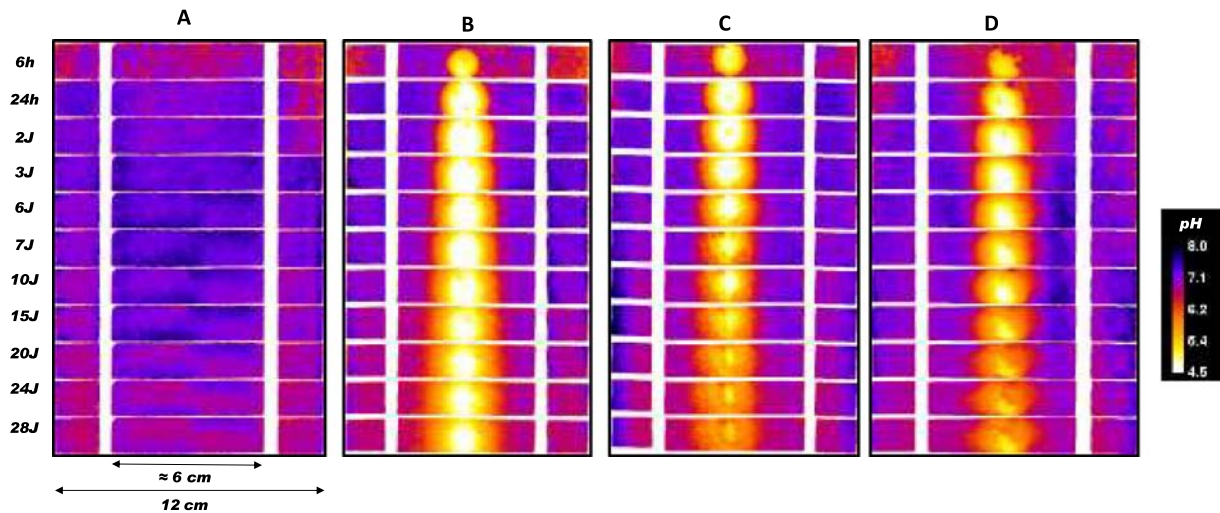


Fig. 4. Planar pH optode measurements of soil pH dynamics taken over 28 days in soils treated with A) no TSP fertilizer (control), B) uncoated TSP, C) lignin@TSP and D) lignin-carrageenan@TSP,  $n = 1$ .

the low pH of the TSP (the pH of the saturated TSP solution  $< 2$ ). When the control was excluded from the statistical analysis, the interaction between the fertilizer treatment, distance from the granule and time was significant (Table S2).

The soil acidification caused by the coated TSP was significantly weaker than that caused by the uncoated TSPs, while no significant difference in acidification was observed between the two coated treatments (lignin@TSP and lignin-carrageenan@TSP; Table S3). In the uncoated TSP treatment, the pH above the granule (distance 0–7 mm) decreased strongly (by 5.2 pH units) after 1 day, while the coated TSP decreased the pH by 4 units. The acidification caused by the fertilizer treatments reached a radius of 14 mm for the coated TSP and 21 mm for the uncoated TSP (Fig. S3). In all fertilizer treatments, the pH beyond 21 mm from the granule was similar to that in the control soil. The area affected by fertilization remained acidic, exhibiting only a slight increase in pH over time; this increase was pronounced in the treatments with the coated fertilizers, as shown in Fig. S3. The increase in pH in the soils treated with coated fertilizers could be related to the basic nature of the coating. In fact, the lignin used in the coating formulations was extracted from olive pomace residue (Fertahi et al., 2020b) using sodium hydroxide, which is strongly alkaline.

The planar optode 2-D representation (Fig. 4) highlighted the same phenomenon observed by the spot optodes but provided a spatial representation of the pH changes that confirmed the previously discussed results.

The control soil had a homogeneous spatio-temporal pH distribution and a pH of approximately 7.7; this result is in good agreement with the spot measurements. The soils treated with TSP granules showed circular, isotropic soil acidification to a radius of 21 mm around the granule after 28 days. In the soils with coated TSPs, the soil acidification area reached only 14 mm after 28 days. The soil pH just above the granule increased gradually after 3 days, reaching values in the range of 6–6.5 after 28 days, compared to 4–4.5 in the uncoated TSP treatment. The pH range obtained using the biopolymer-coated TSP is much more favourable for soil P availability (Wang et al., 2014) than that produced by the uncoated TSP.

Lombi et al., 2005 reported that in calcareous and non-calcareous alkaline soils, the pH of soils treated with TSP and monoammonium phosphate (MAP) granules decreased by 0.8–0.9 pH units at a distance of 13.5 mm from the fertilizer and by  $< 0.2$  pH units at a distance of 25.5 mm; no significant change was observed beyond 25.5 mm. Those authors argued that the decrease in soil pH was probably caused by the low pH of TSP and MAP (the pH values of saturated TSP and MAP solutions are  $< 2$  and 3.5, respectively) and the nitrification of the  $\text{NH}_4$

present in the MAP fertilizer (Nascimento et al., 2018; Saunders, 1958). The initial soil pH partly drives the change in soil pH in response to fertilizer addition (Nascimento et al., 2018) due to proton exchange. In the study of Lombi et al., 2005, acidification was limited due to the high buffering capacity of the carbonates in the alkaline calcareous soil (pH = 8.6). Moreover, differences in the methods of pH measurement may also have contributed to the observed discrepancies. However, although their absolute values differed, both studies presented similar patterns of soil pH variation under the influence of TSP granules.

### 3.2. Dynamics of phosphorus pools

The resin-P at 28 days after fertilizer application was significantly greater in the first 21 mm from the granules than that in the untreated soil, but no significant effect of fertilization on resin-P was observed beyond 21 mm (Fig. 5). No significant differences were observed among fertilizer treatments, except that a higher resin-P concentration was detected at 14–21 mm in the lignin@TSP soil (+66%) than in the uncoated

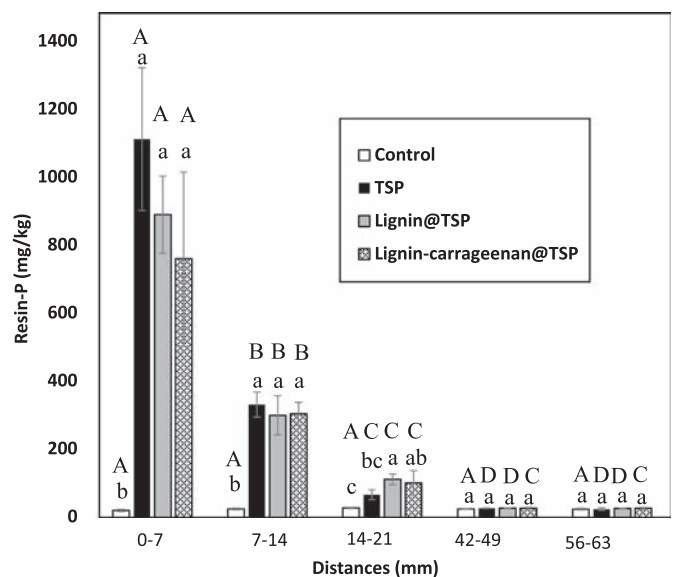


Fig. 5. Resin-P (mg/kg) as a function of the treatment and distance from the granule after 28 days of incubation. Lowercase letters indicate significant differences ( $p < 0.05$ ) among treatments at the same distance. Capital letters indicate significant differences ( $p < 0.05$ ) among distances in the same treatment. Error bars represent the standard error.

TSP soil. The coated TSP resulted in a larger P diffusion range than the uncoated fertilizer, which could be related to its slower P-release kinetics in water (Fertahi et al., 2020b).

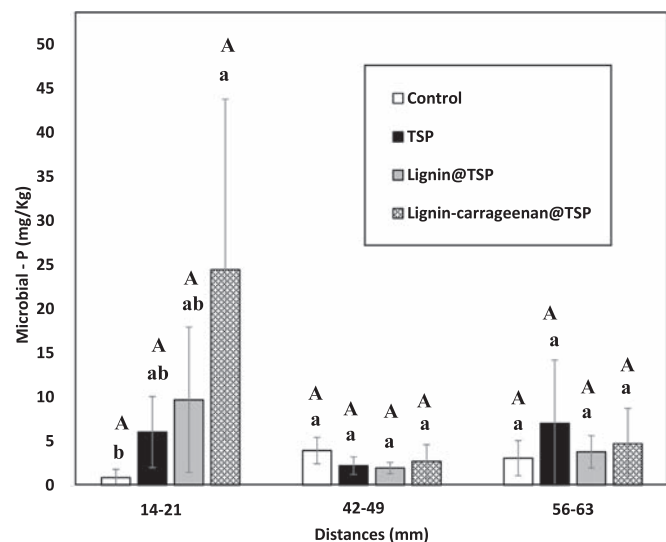
The short range of the effect of the fertilizers is likely linked to precipitation reactions between the P from the TSP and soil ions. In calcareous soils, the dominant reaction of P is precipitation with Ca and Mg (Nascimento et al., 2018; Yang et al., 2012). In non-calcareous soils, P adsorption onto the surface of Fe and Al hydroxides prevails (McLaughlin et al., 2011). In the case of this study, the biopolymer-based coatings did not improve the availability of resin-P from TSP after 28 days, except at a specific distance around the granule (14–21 mm). Although the soil in our study was not highly calcareous, our results are in agreement with those reported by Nascimento et al., 2018.

In this study, the coated fertilizers showed slow P-release behaviour in the first few days, and the concentrations of P around the granules were relatively low. The lower P concentration may have led to less P adsorption by soil colloids or fixation by minerals due to the shorter contact time between P and soil and the relatively low P saturation in the granule environment; these conditions may have allowed P to migrate away from the granules.

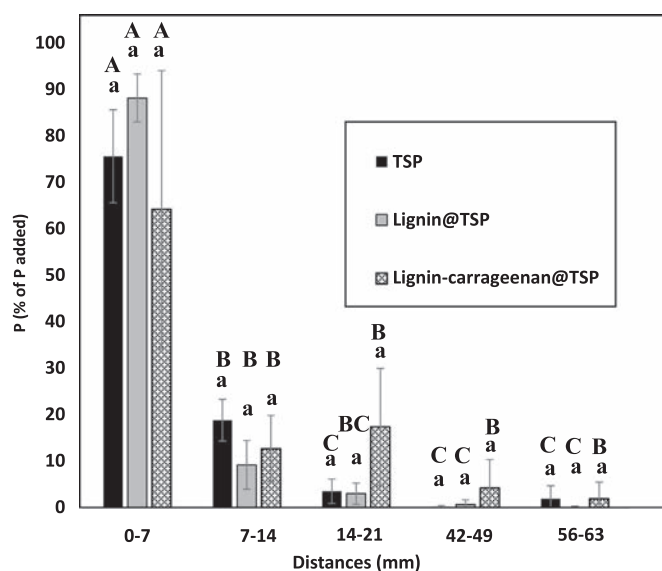
The microbial P concentration ranged from 6 to 25 mg P/kg dry soil in the fertilized soils; in the control, it was approximately 1 mg P/kg (Fig. 6). The application of P fertilizers increased the microbial P concentration at a distance of 21 mm by +500% in the uncoated TSP treatment, by 900% in the lignin@TSP treatment and by 2400% in the lignin-carrageenan@TSP treatment compared to the control. However, this increase was significant only for the lignin-carrageenan treatment due to the high variability of the results. Farther than 42 mm from the granule, the effects of the fertilizer treatments were not significant.

The increase in microbial biomass P may have enhanced P availability in soil, as this pool acts as both a sink for and a source of P (Singh and Singh, 1993). The highest concentrations of microbial P were generated by the coated TSPs, which confirms the hypothesis that the decomposition of carbon-rich polymeric coatings by microorganisms would result in phosphorus immobilization by the soil microorganisms as a result of their increased activity or growth. The quantity of C provided by the coating to the soil was 26.5 mg/kg dry soil, which constitutes a considerably larger amount than the total microbial C (450 mg/kg).

P recovery did not vary significantly among treatments, but it varied significantly with the distance from the granule (Fig. 7). Most fertilizer P (>64%) remained within the first 7 mm from the central granule, and



**Fig. 6.** Microbial P as a function of the treatment and distance from the granule after 28 days of incubation. Lowercase letters indicate significant differences ( $p < 0.05$ ) among treatments at the same distance. Capital letters indicate significant differences ( $p < 0.05$ ) among distances in the same treatment. Error bars represent the standard error.



**Fig. 7.** P recovery (%) as a function of the treatment and distance from the granule after 28 days of incubation. Lowercase letters indicate significant differences ( $p < 0.05$ ) between treatments at the same distance. Capital letters indicate significant differences ( $p < 0.05$ ) between distances in the same treatment. Error bars represent the standard error.

<19% diffused to a 7–21 mm distance. Almost no fertilizer P was found beyond 21 mm from the granule. There was no significant difference in P recovery between the uncoated and coated TSPs; this result is in agreement with de Castro et al., 2015, who published similar results regarding P recovery with MAP and polymer-coated MAP. The authors reported that approximately 80% of fertilizer P was recovered within the first 0–7.5 mm from the fertilizer application site, while 10% and 6% were recovered at 7.5–13.5 mm and 13.5–25.5 mm from the application site, respectively. Similarly, Fink et al., 2016 and Lombi et al., 2005 reported that the recovery of P from P fertilizers applied at the center of a Petri dish was concentrated within a 13 mm radius from the fertilizer application site.

#### 4. Conclusion

This study uses innovative optode technology to study the effect of biopolymer-coated fertilizers on soil acidity. In addition, it sheds light on the effect of coated fertilizers on soil microbial P, which has rarely been studied in this context in the literature. Our study showed that biopolymer-coated TSPs dissolve differently from uncoated TSPs in cropped calcareous soil and observed similar dissolution patterns between TSP coated with lignin alone or and lignin blended with carrageenan. Both uncoated and coated TSPs acidified the soil near the fertilizer granule. However, the acidification effect was weaker and less persistent in the coated TSP treatments than in the uncoated TSP treatments. The available P concentration was high in the first 21 mm from the granule after 28 days. The coated TSP had a larger P diffusion range than the uncoated fertilizer. This result confirmed our initial hypothesis and is in agreement with the results of Nascimento et al., 2018. The application of coated P fertilizers increased the microbial P concentration in the immediate vicinity of the granules compared to that under uncoated TSP. Most fertilizer P (P recovery %) remained within the first 7 mm of the granule, and the TSP coated with lignin alone resulted in significantly higher P recovery at 14 mm than the TSP treatment. The results of the uncoated P fertilizer were in agreement with Fink et al., 2016, Lombi et al., 2005 and de Castro et al., 2015.

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## Declaration of competing interest

The authors declare no conflict of interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aos.2022.12.004>.

## References

- Ahmad, N.N.R., Fernando, W.J.N., Uzir, M.H., 2015. Parametric evaluation using mechanistic model for release rate of phosphate ions from chitosan-coated phosphorus fertilizer pellets. *Biosyst. Eng.* 129, 78–86.
- Bertrand, I., Hinsinger, P., Jaillard, B., 1999. Dynamics of phosphorus in the rhizosphere of maize and rape grown on synthetic, phosphated calcite and goethite dynamics of phosphorus in the rhizosphere of maize and rape grown on synthetic, phosphated calcite and goethite. *Plant Soil* 211, 111–119.
- Blossfeld, S., Gansert, D., 2007. A novel non-invasive optical method for quantitative visualization of pH dynamics in the rhizosphere of plants. *Plant Cell Environ.* 30, 176–186.
- Blossfeld, S., Schreiber, C.M., Liebsch, G., Kuhn, A.J., Hinsinger, P., 2013. Quantitative imaging of rhizosphere pH and CO<sub>2</sub> dynamics with planar optodes. *Ann. Bot.* 112, 267–276.
- Bünemann, E.K., Oberson, A., Liebsch, F., Keller, F., Annaheim, K.E., Huguenin-Elie, O., Frossard, E., 2012. Rapid microbial phosphorus immobilization dominates gross phosphorus fluxes in a grassland soil with low inorganic phosphorus availability. *Soil Biol. Biochem.* 51, 84–95.
- Buss, W., Shepherd, J.G., Heal, K.V., Mašek, O., 2018. Spatial and temporal microscale pH change at the soil-biochar interface. *Geoderma* 331, 50–52.
- de Castro, R.C., de Melo Benites, V., César Teixeira, P., dos Anjos, M.J., de Oliveira, L.F., 2015. Phosphorus migration analysis using synchrotron radiation in soil treated with brazilian granular fertilizers. *Appl. Radiat. Isot.* 105, 233–237.
- Chen, X., Lewis, S., Heal, K.V., Lin, Q., Sohi, S.P., 2021. Biochar engineering and ageing influence the spatiotemporal dynamics of soil pH in the rhizosphere. *Geoderma* 386, 114919. <https://doi.org/10.1016/j.geoderma.2020.114919>.
- Clarke, J.S., Achterberg, E.P., Rérolle, V.M.C., Abi Kaed Bey, S., Floquet, C.F.A., Mowlem, M.C., 2015. Characterisation and deployment of an immobilised pH sensor spot towards surface ocean pH measurements. *Anal. Chim. Acta* 897, 69–80.
- Da Cruz, D.F., Bortoletto-Santos, R., Guimarães, G.G.F., Polito, W.L., Ribeiro, C., 2017. Role of polymeric coating on the phosphate availability as a fertilizer: insight from phosphate release by castor polyurethane coatings. *J. Agric. Food Chem.* 65, 5890–5895.
- Diez, J.A., Cartagena, M.C., Vallejo, A., 1992. Controlling phosphorus fixation in calcareous soils by using coated diammonium phosphate. *Fertil. Res.* 31, 269–274.
- Faget, M., Blossfeldt, S., Von Gillhausen, P., Schurr, U., Temperton, V.M., 2013. Disentangling who is who during rhizosphere acidification in root interactions: combining fluorescence with optode techniques. *Front. Plant Sci.* 4, 392. <https://doi.org/10.3389/fpls.2013.00392>.
- Fertahi, S., Bertrand, I., Amjoud, M., Oukarroum, A., Arji, M., Barakat, A., 2019. Properties of coated slow-release triple superphosphate (TSP) fertilizers based on lignin and carrageenan formulations. *ACS Sustain. Chem. Eng.* 7, 10371–10382.
- Fertahi, S., Bertrand, I., Ilouk, M., Oukarroum, A., Amjoud, M., Zeroual, Y., Barakat, A., 2020a. Impact of plasticizers on lignin-carrageenan formulation properties and on phosphorus release from a coated triple superphosphate fertilizer. *Ind. Eng. Chem. Res.* 59, 14172–14179.
- Fertahi, S., Bertrand, I., Ilouk, M., Oukarroum, A., Amjoud, M.B., Zeroual, Y., Barakat, A., 2020b. New generation of controlled release phosphorus fertilizers based on biological macromolecules : effect of formulation properties on phosphorus release. *Int. J. Biol. Macromol.* 143, 153–162.
- Fertahi, S., Ilouk, M., Zeroual, Y., Oukarroum, A., 2021. Recent trends in organic coating based on biopolymers and biomass for controlled and slow release fertilizers. *J. Control. Release* 330, 341–361.
- Fink, J.R., Inda, A.V., Bavaresco, J., Sánchez-rodríguez, A.R., Barrón, V., Torrent, J., Bayer, C., 2016. Diffusion and uptake of phosphorus, and root development of corn seedlings, in three contrasting subtropical soils under conventional tillage or no-tillage. *Biol. Fertil. Soils* 52, 203–210.
- García, M.C., Díez, J.A., Vallejo, A., García, L., Cartagena, M.C., 1997. Effect of applying soluble and coated phosphate fertilizers on phosphate availability in calcareous soils and on P absorption by a rye-grass crop. *J. Agric. Food Chem.* 45, 1931–1936.
- Giroto, A.S., Guimarães, G.G.F., Foschini, M., Ribeiro, C., 2017. Role of slow-release nano-composite fertilizers on nitrogen and phosphate availability in soil. *Sci. Rep.* 7, 46032. <https://doi.org/10.1038/srep46032>.
- Lan, W., Mingzhu, L., 2008. Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention. *Polym. Adv. Technol.* 19, 785–792.
- Larsen, M., Santner, J., Oburger, E., Wenzel, W.W., Glud, R.N., 2015. O<sub>2</sub> dynamics in the rhizosphere of young rice plants (*Oryza sativa* L.) as studied by planar optodes. *Plant Soil* 390, 279–292.
- Lawton, K., Vomocil, J.A., 1954. The dissolution and migration of phosphorus from granular superphosphate in some Michigan soils. *Soil Sci. Soc. Am. J.* 18, 26–32.
- Lombi, E., McLaughlin, M.J., Johnston, C., Armstrong, R.D., Holloway, R.E., 2005. Mobility, solubility and lability of fluid and granular forms of P fertilizer in calcareous and non-calcareous soils under laboratory conditions. *Plant Soil* 269, 25–34.
- Lupwayi, N.Z., Grant, C.A., Soon, Y.K., Clayton, G.W., Bittman, S., Malhi, S.S., Zebbarth, B.J., 2010. Soil microbial community response to controlled-release urea fertilizer under zero tillage and conventional tillage. *Appl. Soil Ecol.* 45, 254–261.
- McLaughlin, M.J., McBeath, T.M., Smernik, R., Stacey, S.P., Ajiboye, B., Guppy, C., 2011. The chemical nature of P accumulation in agricultural soils-implications for fertilizer management and design: an Australian perspective. *Plant Soil* 349, 69–87.
- Nascimento, C.A.C., Pagliari, P.H., Faria, Lde A., Vitti, G.C., 2018. Phosphorus mobility and behavior in soils treated with calcium, ammonium, and magnesium phosphates. *Soil Sci. Soc. Am. J.* 82, 622–631.
- Noppakundilongrat, S., Pheatcharat, N., Kiatkamjornwong, S., 2015. Multilayer-coated NPK compound fertilizer hydrogel with controlled nutrient release and water absorbency. *J. Appl. Polym. Sci.* 132, 41249. <https://doi.org/10.1002/app.41249>.
- Ohno, T., Zibilske, L.M., 1991. Determination of low concentrations of phosphorus in soil extracts using malachite green. *Soil Sci. Soc. Am. J.* 55, 892–895.
- Rop, K., Karuku, G.N., Mbui, D., Michira, I., Njomo, N., 2018. Formulation of slow release NPK fertilizer (cellulose-graft-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer) composite and evaluating its N mineralization potential. *Ann. Agric. Sci.* 63, 163–172.
- Saunders, W.M.H., 1958. The effect of different phosphate fertilizers on soil pH and the consequent effect on phosphate retention. *N. Z. J. Agric. Res.* 1, 675–682.
- Singh, H., Singh, K.P., 1993. Effect of residue placement and chemical fertilizer on soil microbial biomass under tropical dryland cultivation. *Biol. Fertil. Soils* 16, 275–281.
- Timilsena, Y.P., Adhikari, R., Casey, P., Muster, T., Gill, H., Adhikari, B., 2015. Enhanced efficiency fertilizers: a review of formulation and nutrient release patterns. *J. Sci. Food Agric.* 95, 1131–1142.
- Wang, X., Lu, S., Gao, C., Xu, X., Wei, Y., Bai, X., Feng, C., Gao, N., Liu, M., Wu, L., 2014. Biomass-based multifunctional fertilizer system featuring controlled-release nutrient, water-retention and amelioration of soil. *RSC Adv.* 4, 18382–18390.
- Weidgans, B.M., Krause, C., Klimant, I., Wolfbeis, O.S., 2004. Fluorescent pH sensors with negligible sensitivity to ionic strength. *Analyst* 129, 645–650.
- Wencel, D., Abel, T., McDonagh, C., 2014. Optical chemical pH sensors. *Anal. Chem.* 86, 15–29.
- Wu, L., Liu, M., 2008. Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention. *Carbohydr. Polym.* 72, 240–247.
- Wu, L., Liu, M., Liang, Rui, 2008. Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention. *Bioresour. Technol.* 99, 547–554.
- Xiaoguang, J., Wenju, L., Lijun, C., Haijun, Z., Qi, L., Peng, W., Dazhong, W., 2005. Effect of slow-release urea fertilizers on urease activity, microbial biomass, and nematode communities in an aquic brown soil. *Sci. China Ser. C* 48, 26–32.
- Yang, J.C., Wang, Z.G., Zhou, J., Jiang, H.M., Zhang, J.F., Pan, P., Han, Z., Lu, C., Li, L.L., Ge, C.L., 2012. Inorganic phosphorus fractionation and its translocation dynamics in a low-P soil. *J. Environ. Radioact.* 112, 64–69.