

## Effects of modified clinoptilolite on phosphorus mobilisation and potassium or ammonium release in Ferrosols

Q. X. Hua<sup>A,B</sup>, J. M. Zhou<sup>A,D</sup>, H. Y. Wang<sup>A</sup>, C. W. Du<sup>A</sup>, X. Q. Chen<sup>A</sup>, and J. Y. Li<sup>C</sup>

<sup>A</sup>State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, 71 East Beijing Road, Nanjing 210008, P.R. China.

<sup>B</sup>Graduate School of Chinese Academy of Science, 19 Yuquan Road, Beijing 100049, P.R. China.

<sup>C</sup>Department of Industrial Engineering, Zhengzhou Institute of Aeronautical Industry Management, 2 Daxue Road, Zhengzhou 450015, P.R. China.

<sup>D</sup>Corresponding author. Email: jmzhou@issas.ac.cn

**Abstract.** An investigation was conducted to study effects of the potassium and ammonium saturated clinoptilolite on P availability in Ferrosols. The adsorption and desorption of phosphorus were determined by shaking 2.5 g soil with 0, 0.5, and 2.5 g clinoptilolite at 0.31 or 1.25 mg P/g soil in 50 mL solution for a total of 72 h (24 h for clinoptilolite and 48 h for phosphate). The nutrient concentrations in supernatants were measured by spectrophotometry. Results showed phosphorus solubility was significantly increased with clinoptilolite addition. Increasing the amount of clinoptilolite enhanced the concentration of P up to 6.85 and 41.29 mg/L at 0.31 and 1.25 mg P/g soil, respectively. Correspondingly, the amount of potassium and ammonium released from the clinoptilolite were up to 63.69 and 12.20 mg/L at 0.31 mg P/g soil, and 107.42 and 29.94 mg/L at 1.25 mg P/g soil. Nutrient concentrations in the treatments in which clinoptilolite was added before P were greater than that in the treatments in which P was added prior to clinoptilolite. The results also suggest that potassium and ammonium saturated clinoptilolite can increase P solubility while providing K and NH<sub>4</sub> to the soil, a concurrent positive effect for plant growth.

**Additional keywords:** clinoptilolite, Ferrosols, phosphate, potassium, ammonium.

### Introduction

Phosphorus (P) is a vital nutrient for plants because of its role in ribonucleic acid and function in energy transfers via ATP. It is often the limiting nutrient in agricultural ecosystems due to its low availability in soils. The low solubility of phosphates with Fe, Al, and Ca in soils is a major cause of the low bioavailability (Ozanne 1980; Du *et al.* 2005; Li *et al.* 2005; Mcbeath *et al.* 2005). Phosphorus use efficiency can be enhanced by increasing its solubility in soil solution or by reducing its sorption to soil particle surfaces.

Zeolite clinoptilolite (Cp), a natural mineral, is composed of pores and corner-sharing aluminosilicate (AlO<sub>4</sub> and SiO<sub>4</sub>) tetrahedrons, joined into 3-dimensional frameworks. The pores are interconnected and form long and wide channels that allow easy movements of resident ions and molecules in and out of the structure. The large vacant spaces resemble honeycomb or cage-like structures (Armbruster 2001; Aleksandrova *et al.* 2004; Polat *et al.* 2004). The presence of aluminium results in a negative charge, which is balanced by positively charged cations.

Much research has been conducted on the effects of Cp on the solubility of phosphate rock (PR). Allen *et al.* (1993) demonstrated that Cp could increase the solubility of PR in Cp-PR systems. They further studied wheat growth on the optimal Cp-PR mixtures as a synthetic soil (Allen *et al.* 1995b). A glasshouse pot trial showed that P uptake from PR by sunflower was greatly enhanced when PR was applied in combination with NH<sub>4</sub>-Cp (Pickering *et al.* 2002). Barbarick *et al.* (1990) showed an increased PR solubility by Cp in nonalkaline soils after measuring the increases in dry matter, nutrient content, and nutrient uptake by sorghum–sudangrass. Another incubation study reported that Cp added to an acid soil decreased the initial rate, and increased the average rate, of PR dissolution (He *et al.* 1999). However, few studies have directly determined the effects of Cp on phosphorus availability after soluble phosphate fertiliser was applied to soils. Ferguson *et al.* (1986) reported that Cp increased P uptake by turfgrass when triple superphosphate was applied to soil. Goh *et al.* (1986) found that the presence of Cp in the silt fractions of 2 Solodized Solonetz soils markedly reduced the adsorption of monopotassium phosphate.

The objective of this paper was to study the influence of clinoptilolite saturated by potassium and ammonium solution on the P solubility, Olsen P release, and K and  $\text{NH}_4$  release in an acid soil after monocalcium phosphate was applied to the soil.

## Materials and methods

### Clinoptilolite

Clinoptilolite was collected from a geological deposit in Hei Longjiang Province, north-eastern China. Some properties of the Cp are shown in Table 1. In the experiments, the clinoptilolite was ground to pass a 0.2-mm sieve, and then washed 4 times with  $\text{K}^+$  or  $\text{NH}_4^+$  using 1 M chloride solution. The K- or  $\text{NH}_4$ -saturated samples were repeatedly washed with deionised water to remove interstitial salts until the  $\text{AgNO}_3$  test for  $\text{Cl}^-$  was negative. The samples were then washed 3 times with acetone, oven-dried, and designated as K-Cp and  $\text{NH}_4$ -Cp, respectively. The CEC of K-Cp was 118  $\text{cmol}_c/\text{kg}$  and that of  $\text{NH}_4$ -Cp was 134  $\text{cmol}_c/\text{kg}$ .

### Phosphate

Monocalcium phosphate ( $\text{CaH}_2\text{PO}_4$ , MCP) is main component of superphosphate fertiliser. In this study, we selected analytical reagent MCP as phosphate source. Phosphorus concentrations were applied to give 15.6 mg P/L in 50 mL (or 625 mg P/L in 1.25 mL) and 62.5 mg P/L in 50 mL (or 625 mg P/L in 5 mL). The P added in the systems was approximately equivalent to half (0.31 mg P/g soil) and twice (1.25 mg P/g soil) the maximum sorption capacities of the soil, respectively.

### Soil

The soil used in this study was an Argi-ustic Ferrosols in Chinese Soil Taxonomy (CRGCST 2001) or a Haplic Acrisols in FAO Soil Classification (Chu *et al.* 2003). The soil sample was collected from the Red Soil Ecological Experimental Station of Chinese Academy of Sciences, Yingtan ( $28^\circ 15' 30''\text{N}$ ,  $116^\circ 55' 30''\text{E}$ ), Jiangxi Province, southern China. The clay minerals of this soil were dominated by kaolinite and hydrous mica as well as a small amount of vermiculite. The topsoil (0–0.15 m) was sampled for the experiment. After removing the visible plant residues, stone, and soil fauna, the soil was sieved through 0.4 mm. Some properties of the soil are in Table 2.

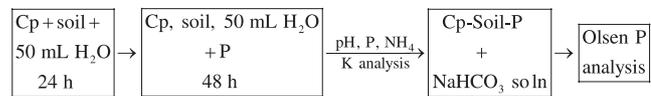
### Adsorption and desorption experiments

Batch-equilibration experiments were conducted to investigate the mobilisation of MCP in soil treated with K- or  $\text{NH}_4$ -Cp. A constant amount of soil (2.5 g) was used, and the amount of K-Cp or  $\text{NH}_4$ -Cp varied depending on the mass ratio of Cp to soil, 0 : 1 (CK), 0.2 : 1, and 1 : 1. Soil and clinoptilolite were mixed with a P solution at a known concentration prepared as described above in 80-mL polypropylene flasks. Suspensions were added 2 drops of toluene to inhibit microbial growth, and then shaken on an end-over-end shaker at  $25 \pm 1^\circ\text{C}$ . The experiments were carried out with 2 subsequent steps. In the preliminary experiment, K- or  $\text{NH}_4$ -Cp was first mixed with soil in 50 mL distilled water and shaken for 24 h and then P was added to the suspension, which was then shaken for another 48 h. The samples

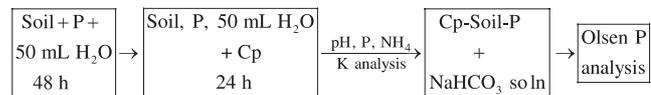
**Table 1.** Some chemical properties of the clinoptilolite

$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$ (g/kg)	CaO	$\text{K}_2\text{O}$	CEC ( $\text{cmol}_c/\text{kg}$ )
113.7	455.4	7.6	39.1	20.5	103.1

were designated as  $\text{Cp}_w$ , and this experiment was denoted in the following diagram:



In a subsequent experiment, P was first adsorbed onto the soil for 48 h, and then Cp was added to the suspension, which was shaken for another 24 h. The samples were designated as  $\text{Cp}_s$  and this experiment was denoted in the next diagram:



The suspensions were then centrifuged (2790G 10 min), and the supernatants were analysed for pH, P, K, and  $\text{NH}_4$ . The residual sample was washed twice with alcohol to remove free P, and extracted with 0.5 M  $\text{NaHCO}_3$  (pH 8.5) in 50 mL for Olsen P. All treatments were prepared in triplicate.

### Analytical methods

The CEC of clinoptilolite was examined by sodium- and ammonium-acetate extraction, and atomic-emission spectrophotometry. The pH was measured with the 2.5 : 1 ratio of water to soil. The particle size of Ferrosols was determined using a LS 230 Laser Diffractionmeter (Beckman Coulter Co., USA), and graded according to American Soil Science Society classification. Iron and aluminum concentrations were measured by ICP-AES after the fusion of  $\text{LiBO}_2$  with the clinoptilolite and after sodium citrate–sodium bicarbonate–sodium hydrosulfite extraction in the soil (Lu 1999). Phosphorus, ammonium, and K concentrations in the solution were determined by molybdophosphate blue method for P (Olsen and Sommers 1982), indophenol blue colourimetric method for  $\text{NH}_4$  (Keeney and Nelson 1982), and atomic-emission spectrophotometry for K.

### Statistic analysis

Analysis of variance and multiple comparisons with Tukey's test were employed for data analysis using SPSS for Windows (Statistical Package for Social Science) and Microsoft office Excel.

## Results and discussion

### Phosphorus in solution

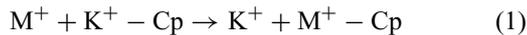
Potassium- and ammonium-Cp addition enhanced the concentrations of P in solution by 44–119% for the soil

**Table 2.** Physical and chemical properties of surface layer (0–0.15 m) of the Argi-ustic Ferrosols

pH ( $\text{H}_2\text{O}$ )	Organic matter (g/kg)	Total P	Olsen P (mg/kg)	Free $\text{Fe}_2\text{O}_3$ (g/kg)	Free $\text{Al}_2\text{O}_3$	Particle size (%)		
						Clay <2 $\mu\text{m}$	Silt 2–50 $\mu\text{m}$	Fine sand 50–100 $\mu\text{m}$
4.57	11.7	0.59	23.08	7.94	1.58	30.2	52.4	8.8

with 0.31 mg P/g and 8–32% for the soil with 1.25 mg P/g, compared with that with no Cp addition (Fig. 1). Further increasing the amount of Cp continually elevated the concentrations of P in solution up to 6.85 mg/L (K-Cp) and 6.66 mg/L (NH<sub>4</sub>-Cp) in the soil with 0.31 mg P/g, and 41.29 mg/L (K-Cp) and 39.29 mg/L (NH<sub>4</sub>-Cp) in the soils with 1.25 mg P/g. In general, adding Cp before P resulted in higher P solution concentrations than addition in the reverse order. When 0.5 g Cp was added in the soil, solution P concentration in the K-Cp treatments was significantly less than that in the NH<sub>4</sub>-Cp treatments, no matter when the Cp was mixed. However, when 2.5 g Cp was added, solution P concentration decreased in the order K-Cp > NH<sub>4</sub>-Cp when Cp was added to soil before P; this order was reversed when P was added to soil before Cp.

Many studies have demonstrated that Cp can adsorb cations from solution (Allen *et al.* 1993; Inglezakis *et al.* 2002, 2004; Opena and Williams 2003;). Thus, the decrease in P adsorption is most likely the result from the reaction between Ca<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> or other cations in soil suspension with the additional Cp through the following simplified equations as described by Allen *et al.* (1995a):



where M<sup>+</sup> indicates 1/2Ca<sup>2+</sup>, 1/3Fe<sup>3+</sup>, 1/3Al<sup>3+</sup> or other cations in soil suspension. Calcium was the dominant cation exchanging with K and NH<sub>4</sub>. The concentrations of Fe and Al in solution were only 1.22 and 2.63 mg/L at 0.31 mg P/g soil, and 0.01 and 0.23 mg/L at 1.25 mg P/g soil, respectively, which were much lower than Ca concentration due to MCP addition. The affiliation of Ca<sup>2+</sup> on Cp releases K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> from Cp to solution, which forces the equilibrium towards a higher solubility of phosphate; thereby, the more cations that

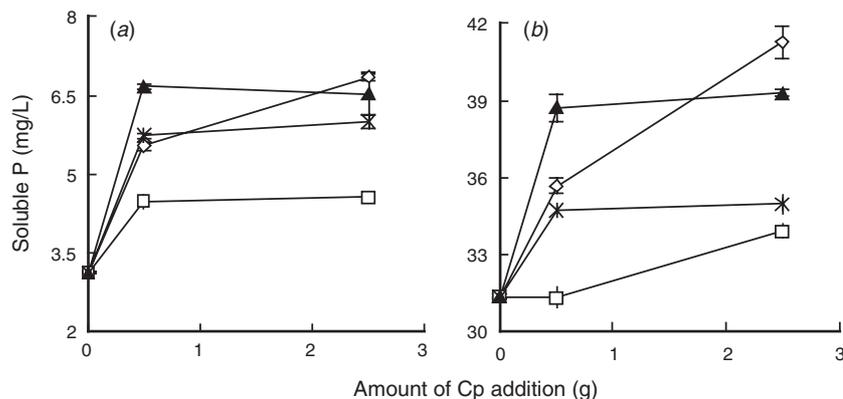
were adsorbed onto Cp as the Cp amount increased, the more P remained in solution.

The pH values (Fig. 2) varied similarly to P in solution. As the amount of Cp increased, pH increased up to 6.79 and 6.34 at 0.31 and 1.25 mg P/g soil, respectively. Possibly, H<sup>+</sup> in solution can replace K<sup>+</sup> or NH<sub>4</sub><sup>+</sup> from Cp. This process enhanced the solution pH. This hypothesis can be confirmed in that the greater amount of Cp resulted in a higher pH because more Cp provided more sites to adsorb H<sup>+</sup>. Another explanation is that adsorption of Ca, Fe, and Al on Cp reduces adsorption of phosphate on soil surfaces, which can also increase solution pH because increasing phosphate adsorption on soil Fe and Al oxides generally decreases pH. The result confirmed the influences of the modified Cp on P because the increase in pH reduced the adsorption of P on the soil surface.

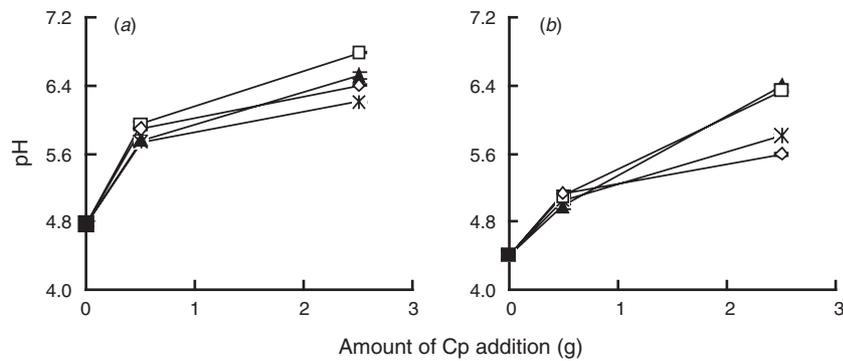
Differences in solution P between K-Cp and NH<sub>4</sub>-Cp systems (Fig. 1) may be attributed to the cation affinity of Cp. NH<sub>4</sub> was held less tightly than K on the Cp exchange sites because NH<sub>4</sub> is much larger than K; therefore, Ca, Fe, and Al were adsorbed more readily by the NH<sub>4</sub>-Cp than K-Cp. The affiliation of Ca, Fe, and Al on Cp created a larger Ca, Fe, Al concentration gradient, and increased P in solution. Allen *et al.* (1996) reported similar results using K- and NH<sub>4</sub>-Cp and phosphate rocks. However, the concentration of P in solution was the opposite in the treatments in which Cp was added to soil before P at the 2.5 g Cp addition. This is possibly because the P maximum sorption capacity (Q<sub>max</sub>) of K-Cp (27.3 mg P/kg) is greater than that of NH<sub>4</sub>-Cp (about 0 mg P/kg).

#### Olsen P release

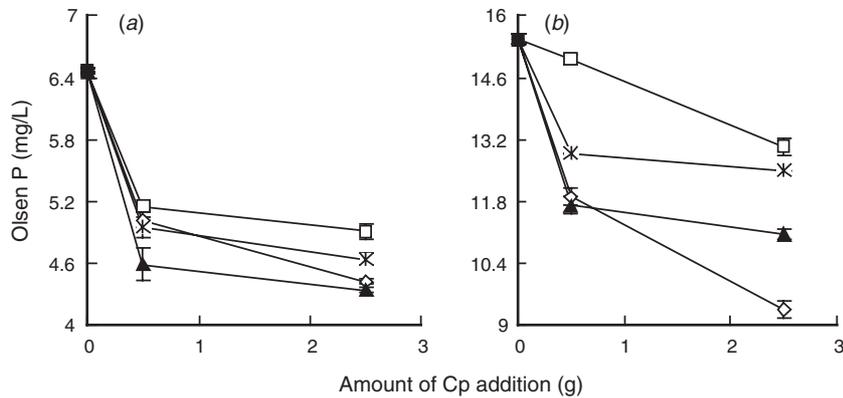
As shown in Fig. 3, the addition of Cp resulted in a significant decrease in Olsen P. Because K- or NH<sub>4</sub>-Cp led to an increase in soluble P, Olsen P reduced in comparison with no Cp



**Fig. 1.** Influence of Cp on P adsorption on acid soil at (a) 0.31 mg P/g soil and (b) 1.25 mg P/g soil. ▲ NH<sub>4</sub>-Cp<sub>w</sub>; \* NH<sub>4</sub>-Cp<sub>s</sub>; ◇ K-Cp<sub>w</sub>; □ K-Cp<sub>s</sub>; ■ soil only, no Cp addition. Cp<sub>w</sub>, NH<sub>4</sub>- and K-Cp were dispersed into soil with deionised water prior to P adsorbed; Cp<sub>s</sub>, P was adsorbed onto soil before NH<sub>4</sub>- or K-Cp was added into the suspension. Each point is the mean of triplication samples; error bars show the standard deviation.



**Fig. 2.** Influence of Cp on pH at (a) 0.31 mg P/g soil and (b) 1.25 mg P/g soil. ▲ NH<sub>4</sub>-Cp<sub>w</sub>; \* NH<sub>4</sub>-Cp<sub>s</sub>; ◇ K-Cp<sub>w</sub>; □ K-Cp<sub>s</sub>; ■ soil only, no Cp additions. Cp<sub>w</sub>, NH<sub>4</sub><sup>-</sup>, and K-Cp were dispersed into soil with deionised water prior to P adsorbed; Cp<sub>s</sub>, P was adsorbed onto soil before NH<sub>4</sub><sup>-</sup> or K-Cp was added into the suspension. Each point is the mean of triplication samples; error bars show the standard deviation.



**Fig. 3.** Olsen P release from the residual mixtures of modified Cp and soil at (a) 0.31 mg P/g soil and (b) 1.25 mg P/g soil. ▲ NH<sub>4</sub>-Cp<sub>w</sub>; \* NH<sub>4</sub>-Cp<sub>s</sub>; ◇ K-Cp<sub>w</sub>; □ K-Cp<sub>s</sub>; ■ soil only, no Cp additions. Cp<sub>w</sub>, NH<sub>4</sub><sup>-</sup>, and K-Cp were dispersed into soil with deionised water prior to P adsorbed; Cp<sub>s</sub>, P was adsorbed onto soil before NH<sub>4</sub><sup>-</sup> or K-Cp was added into the suspension. Each point is the mean of triplication samples; error bars show the standard deviation.

addition. The factors that affected P solubility in soil and Cp mixture correspondingly influenced Olsen P release. The treatment of the highest concentration of Olsen P contained lowest soluble P concentration (Fig. 1).

The more Cp was added, the less P was extracted by bicarbonate, which is the reverse of soluble P. At the low P level, Olsen P released in the treatments with 0.5 and 2.5 g Cp was 71.0–79.7% and 67.2–76.0% of that with no Cp addition, respectively. A similar phenomenon occurred at the high P level, in which the P release was 75.7–97.1% and 60.4–84.3% of that with no Cp addition.

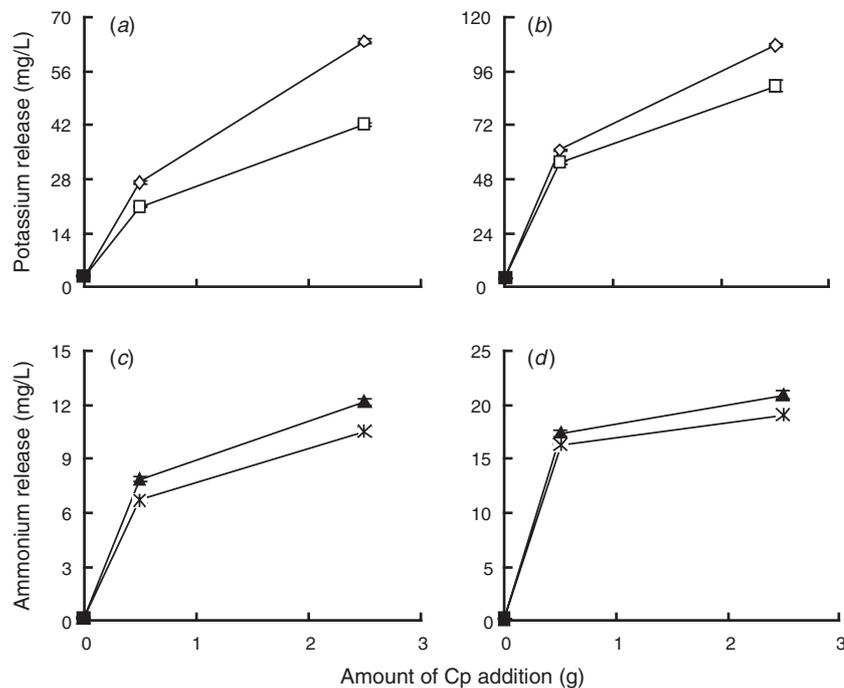
When the same amount of Cp was added, Olsen P release in the treatments in which P was added first was much higher than that in the treatments in which Cp was added first. This indicates that, when P was added first, P was adsorbed on soil surfaces, probably on Fe or Al oxides. The adsorbed P was then released by bicarbonate in Olsen P extraction. However,

when Cp was added first, the adsorption of P on soil surfaces was depressed due to the strong association of Cp and Ca, Fe, or Al, resulting in a high P in solution. This left less P on soil Fe and Al oxides to be extracted by bicarbonate. Shaking time might have affected Olsen P release. The shaking time is longer in the treatments with P addition before Cp than the treatments with Cp addition before P.

#### Potassium and ammonium release

The release of K and NH<sub>4</sub> from Cp, soil, and MCP was the overall result of ion exchange reactions as shown in the Eqns 1 and 2; thereby, the factors affecting P adsorption also influenced K and NH<sub>4</sub> release.

As shown in Fig. 4, K and ammonium release significantly increased with the increasing amount of K- and NH<sub>4</sub>-Cp. The concentrations of K and NH<sub>4</sub> were only 3.01 and 0.19 mg/L at 0.31 mg P/g soil and 3.9 and 0.22 mg/L at 1.25 mg P/g



**Fig. 4.** Potassium and ammonium release from the mixtures of modified Cp and soil at (a, c) 0.31 mg P/g soil and (b, d) 1.25 mg P/g soil. ▲ NH<sub>4</sub>-Cp<sub>w</sub>; \* NH<sub>4</sub>-Cp<sub>s</sub>; ◇ K-Cp<sub>w</sub>; □ K-Cp<sub>s</sub>; ■ soil only, no Cp additions. Cp<sub>w</sub>, NH<sub>4</sub><sup>-</sup>, and K-Cp were dispersed into soil with deionised water prior to P adsorbed; Cp<sub>s</sub>, P was adsorbed onto soil before NH<sub>4</sub><sup>-</sup> or K-Cp was added into the suspension. Each point is the mean of triplication samples; error bars show the standard deviation.

soil in the treatments with no Cp addition. With 2.5 g Cp addition, the concentrations were 63.69 mg/L (K) and 12.20 mg/L (NH<sub>4</sub>) at 0.31 mg P/g soil, and 107.42 mg/L (K) and 20.94 mg/L (NH<sub>4</sub>) at 1.25 mg P/g soil. More K and NH<sub>4</sub> were released at the high P level. When 0.5 g Cp was added, the concentrations of K and NH<sub>4</sub> at the low P level were 37.4–44.6% and 41.0–45.2% of that at high P level, while the percentages were 47.2–59.3% and 55.2–58.3% when 2.5 g Cp was added. As expected, the most K and NH<sub>4</sub> were released in the treatment with 2.5 g Cp addition at high P level. Therefore, K- and NH<sub>4</sub>-Cp can be a source of K and NH<sub>4</sub> for plant growth.

### Conclusions

Potassium- and ammonium-Cp can increase P solubility in Ferrosols. As the amount of Cp relative to soil increased, P concentration in the solution significantly increased. Correspondingly, K and ammonium were released from K- and NH<sub>4</sub>-Cp into the soil solution. However, the release of Olsen P from residual mixtures of soil and Cp decreased. The concentrations of P, K, and NH<sub>4</sub> in the solutions were up to 6.85, 63.69, and 12.20 mg/L at 0.31 mg P/g soil, and 41.28, 107.42, and 20.94 mg/L at 1.25 mg P/g soil, respectively. Differences of nutrient release pattern occurred depending on whether the K- and NH<sub>4</sub>-Cp were added

before or after the P addition. Concentrations of P, K, and NH<sub>4</sub> in the equilibrium solution were higher when Cp was added before P. These results suggest that positive effects on plant nutrition can be achieved concurrently in Ferrosols by adjusting the ratios of Cp and soil and the rates of P application.

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### References

- Aleksandrova VS, Zykova OP, Markiv EY (2004) Ion-exchange properties and IR spectra of natural clinoptilolite modified with titanium hydroxophosphates. *Russian Journal of Applied Chemistry* **77**, 30–33. doi: 10.1023/B:RJAC.0000024571.34058.6e
- Allen ER, Hossner LR, Ming DW, Henninger DL (1993) Solubility and cation exchange in phosphate rock and saturated clinoptilolite mixtures. *Soil Science Society of America Journal* **57**, 1368–1374.
- Allen ER, Hossner LR, Ming DW, Henninger DL (1996) Release rates of phosphorus, ammonium, and potassium in clinoptilolite-phosphate rock systems. *Soil Science Society of America Journal* **60**, 1467–1472.

- Allen ER, Ming DW, Hossner LR, Henninger DL (1995a) Modeling transport kinetics in clinoptilolite-phosphate rock system. *Soil Science Society of America Journal* **59**, 248–255.
- Allen ER, Ming DW, Hossner LR, Henninger DL, Galindo C (1995b) Growth and nutrient uptake of wheat in clinoptilolite-phosphate rock substrates. *Agronomy Journal* **87**, 1052–1059.
- Armbruster T (2001) Clinoptilolite-heulandite: applications and basic research. In 'Studies in surface science and catalysis 135. Zeolite and mesoporous materials at the dawn of the 21st Century'. (Eds A Galarnau, FD Renzo, F Faujula, J Vadrine) pp. 13–27. (Elsevier: New York)
- Barbarick KA, Lai TM, Eberl DD (1990) Exchange fertilizer (phosphate rock plus ammonium-zeolite) effects on sorghum-sudangrass. *Soil Science Society of America Journal* **54**, 911–916.
- Chu HY, Zhu JG, Xie ZB, Zeng Q, Li ZG, Cao ZH (2003) Availability and toxicity of exogenous lanthanum in a haplic Acrisols. *Geoderma* **115**, 121–128.
- CRGCST (2001) 'Chinese Soil Taxonomy.' (Science Press: Beijing)
- Du ZY, Zhou JM, Wang HY, Du CW, Chen XQ (2005) Effect of nitrogen fertilizers on movement and transformation of phosphorus in an acid soil. *Pedosphere* **15**, 424–431.
- Ferguson GA, Pepper IL, Kneebone WR (1986) Growth of creeping bentgrass on a new medium for turfgrass growth: clinoptilolite zeolite-amended sand. *Agronomy Journal* **78**, 1095–1098.
- Goh TB, Pawluk S, Dudas MJ (1986) Adsorption and release of phosphate in chernozemic and solodized solonchic soils. *Canadian Journal of Soil Science* **66**, 521–529.
- He ZL, Baligar VC, Martens DC, Ritchey KD, Elrashidi M (1999) Effect of byproduct, nitrogen fertilizer, and zeolite on phosphate rock dissolution and extractable phosphorus in acid soil. *Plant and Soil* **208**, 199–207. doi: 10.1023/A:1004545115290
- Inglezakis VJ, Loizidou MM, Grigoropoulou HP (2002) Equilibrium and kinetic ion exchange studies of Pb, Cr, Fe and Cu on natural clinoptilolite. *Water Research* **36**, 2784–2792. doi: 10.1016/S0043-1354(01)00504-8
- Inglezakis VJ, Loizidou MM, Grigoropoulou HP (2004) Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility. *Journal of Colloid and Interface Science* **275**, 570–576. doi: 10.1016/j.jcis.2004.02.070
- Keeney DR, Nelson DW (1982) Nitrogen-inorganic forms. In 'Methods of soil analysis. Part 2. Chemical and microbiological properties'. (Eds AL Page, RH Miller, DR Keeney) pp. 643–698. (ASA and SSSA Publishing: Madison, WI)
- Li ST, Zhou JM, Wang HY, Du CW, Chen XQ (2005) Kinetics of phosphate release from three phosphate-treated soils. *Pedosphere* **15**, 518–525.
- Lu RK (1999) 'Methods of soil and agrochemistry analysis.' (Publishing House of Agricultural Science and Technology in China: Beijing)
- Mcbeath TM, Armstrong RD, Lombi E, McLaughlin MJ, Holloway RE (2005) Responsiveness of wheat (*Triticum aestivum*) to liquid and granular phosphorus fertilisers in southern Australian soils. *Australian Journal of Soil Research* **43**, 203–212. doi: 10.1071/SR04066
- Olsen SR, Sommers LE (1982) Phosphorus. In 'Methods of soil analysis. Part 2. Chemical and microbiological properties'. (Eds AL Page, RH Miller, DR Keeney) pp. 403–430. (ASA and SSSA Publishing: Madison, WI)
- Opena GB, Williams KA (2003) Use of precharged zeolite to provide aluminum during blue hydrangea production. *Journal of Plant Nutrition* **26**, 1825–1840. doi: 10.1081/PLN-120023286
- Ozanne PG (1980) Phosphate nutrition of plants—a general treatise. In 'The role of phosphorus in agriculture'. (Eds FE Khasawneh, EC Sample, EJ Kamprath) pp. 559–590. (ASA, CSSA and SSSA Publishing: Madison, WI)
- Pickering HW, Menzies NW, Hunter MN (2002) Zeolite/rock phosphate—a novel slow release phosphorus fertilizer for potted plant production. *Scientia Horticulturae* **94**, 333–343. doi: 10.1016/S0304-4238(02)00006-7
- Polat E, Karaca M, Demir H, Onus AN (2004) Use of natural zeolite (clinoptilolite) in agriculture. *Journal of Fruit and Ornamental Plant Research* **12**, 183–189.

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