

Mobilization Characteristics of Indigenous Phosphate by Oxalic Acid and Dilution Factors in Upland Soils

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Phosphorus accumulation in fertilized soils becomes serious problem for agriculture and the environment. In this investigation, we conducted a laboratory scale investigation to find the most desirable displacement methods of the adsorbed phosphate onto the soil particle surfaces. Soil samples which contained high amount of phosphate were collected at two different depths (0-10 cm and 10-20 cm) from four locations at the moderate highland located in Nonsan, Chungnam. To observe the mobilization of solid-phase phosphate, soil samples were equilibrated with oxalic acid solutions ranging from 10^{-5} to 10^{-1} cmol L⁻¹ with the dilution factors of 1:1, 1:2.5, 1:5, 1:10, and 1:20. The mineralized P sharply increased as the concentration of oxalic acid was greater than 5×10^{-4} cmol L⁻¹ under dilution factors of 1:1, 1:2.5, and 1:5. The breaking concentration of oxalic acid was lowered to 10^{-4} cmol L⁻¹ and 5×10^{-5} cmol L⁻¹ for dilution factors of 1:10 and 1:20, respectively. The curve fit obtained from the graph can be described by exponential growth when the dilution factors were 1:1, 1:2.5, and 1:5 while the sigmoidal shape for 1:10 and 1:20, showing the mineralization of P were significantly dependent on the dilution factor.

Key words : Mobilization, Phosphate, Oxalic Acid, Dilution Factors, Upland Soils

Introduction

Most agricultural soils have been fertilized for optimum crop yields. But highly fertilized agricultural soils cause environmental problems such as eutrophication of lakes and rivers through water run-off, soil erosion, and leakage. In application of fertilizer to soil, fertilized nutrients undergo several chemical reactions that influence its availability to plants. Thus, both macro- and micronutrients undergo a complex dynamic equilibrium of mobilization and immobilization that is greatly influenced by the soil pH and microflora and that ultimately affects their accessibility to plant roots for absorption in soil.

Of the major nutrients, phosphorus, commonly deficient in most natural soils, is the most dilute and the least mobile in soil. Phosphorus is also fixed as insoluble iron and aluminum phosphates in acidic soils (especially those with pH lower than 5.0) or calcium phosphates in alkaline soils (pH above 7.0). However, insoluble calcium phosphate can be dissolved and made available to plants by soil and rhizosphere microorganisms via a mechanism

that is thought to involve the release of organic acids (Cunningham and Kuyack, 1992, Goldstein, 1995). Therefore, low P availability in agricultural soils is compensated by a high input of P fertilizer to guarantee high crop productivity and yield.

High sorbing capacity for phosphorus in the soil (e.g. sorption to metal oxides), phosphorus mineralization (e.g. calcium phosphates such as apatite), and/or fixation of P in organic soil matter (conversion of soluble phosphorus into organic phosphorus) result in low availability of this macronutrient for uptake into plants (Marschner, 1995).

Generally, surface adsorption and precipitation processes contribute to its binding to the solid phase from which it may be released subsequently. Anion adsorption on soil mineral surface and its interaction with various organic and inorganic ions and molecules, which has great impact on the bioavailability and mobility of P, has been studied extensively (Parfitt et al., 1977; Lopez-Hernandez et al., 1986; Kafafi et al., 1988; Violante et al., 1991; Violante and Gianfreda, 1993, 1995; Geelhoed et al., 1998).

Anionic sources including inorganic acid and organic acids play a key role in enhancing anion availability to

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plants by participating in ligand exchange reactions on mineral surfaces. Desorption as of mineralization of P, which becomes a critical issue in any attempt to determine the deleterious effect of P accumulation in soils, has received very little attention, especially the effects of amount of oxalic acid as electrolytes on the reversibility of the P adsorption process. Organic acids which provides by plant roots, animal manure, and sewage sludge can compete with P for sorption sites when they are in anionic form, thus enhancing P mobilization. Therefore, this work was to investigate and compare the effect of oxalic acid as an anionic source and dilution factor on the mobilization of adsorbed phosphate in two different soils which had different soil chemical properties.

Materials and Methods

Soil Sampling and Physico-chemical properties

Soil, grown vegetables for the last ten years, were collected at two different depths (0-10 cm and 10-20 cm) from four locations at the moderate highland located in Nonsan, Chungnam. The soils were air-dried and ground to pass 2 mm sieve using Wiley Mill (AARON Model 3370, USA). The chemical and physical properties were analyzed by soil analysis method (NIAST, 2000) and methods of soil analysis Part II (Table 1). The analytical methods were as follows: Soil texture analysis by hydrometer method, soil pH (Soil : Distilled water=1:5), EC (saturated water extract), organic matter (Walkley-Black method). Total P was measured with a mixture of HCl and NH₄F according to Bray-1 method and water soluble-P as plant available P was extracted with distilled water.

Solution Preparation and P Mineralization Oxalic acid which can compete with P for sorption sites when it is in anionic form was selected for the study because that occur naturally as root exudate in soils. The concentrations of oxalic acids were 1.0, 5×10^{-1} , 10^{-1} , 5×10^{-2} , 10^{-2} , 5×10^{-3} , 10^{-3} M, 5×10^{-4} , and 10^{-4} cmol L⁻¹.

The soil samples were leached with of double-ionized water twice to remove the water soluble phosphate in soil. And the soils were oven-dried to remove the moisture after leaching with water. For mobilization studies of solid-phase phosphate from the soil particles, air-dried soil samples were equilibrated with oxalic acid solutions of known concentration ranging from 10^{-4} cmol L⁻¹ to 1.0 at the rate of 1:1, 1:2.5, 1:5, 1:10, and 1:20. After 8 hours shaking period, the suspension was centrifuged for 15 min. at 1750 rpm. The clear supernatant was decanted for the analysis of phosphate in solution. And the soil samples were washed with double-ionized water twice to remove the oxalic acid and phosphate remained as soil solution phase. After this, the soil samples were centrifuged again to remove the excessive water still remained in soil samples. The soil samples were weighed in order to get the calculation of soil and the correction of concentration of oxalic acid and phosphate. These procedures were repeated until phosphate was not recovered in solution. All treatments were replicated three times.

The concentrations of phosphate in the extract were analyzed using a Dionex 200 Ion Chromatography. Sensitivity of Dionex was changed from 100 to 3 S in order to detect the trace amount of phosphate in the extract from the 3rd extraction. To calculate the only mineralized P by oxalic acid, we subtracted the amount of water-soluble P from the analyzed concentration.

Table 1. Characteristics of soil collected from Nonsan.

Location	Depth (cm)	pH*	EC (dS m ⁻¹)**	OM (%)	P (mg Kg ⁻¹)			Soil Texture
					Total (A)	Water-soluble (B)	(B/A)	
0	0-10	4.41	2.15	3.07	2663.5	1076.3	0.404	Loam
	10-20	5.76	1.77	2.49	2354.7	582.4	0.247	Silt loam
1	0-10	4.42	2.34	2.67	2951.6	820.0	0.278	Loam
	10-20	6.14	1.73	2.47	2674.4	224.3	0.084	Silt loam
2	0-10	6.90	0.99	2.63	2426.1	659.2	0.272	Loam
	10-20	6.48	1.11	2.10	1995.8	503.7	0.252	Silty clay loam
3	0-10	6.24	3.57	2.72	3660.1	982.9	0.269	Loam
	10-20	6.52	1.91	2.75	3120.9	653.5	0.209	Silt loam

Results and Discussion

Mineralization of phosphate by oxalic acid To observe mineralization of phosphate in soils by additions of various concentration of oxalic acid and dilution factors of soil to solution, soil samples were collected at the two different depths from upland. The total and water-extractable P concentrations in soils analyzed by Bray-1 method are given in Table 1. The amount of total and water-soluble P in soil ranged from 1,990 to 3,650 mg kg⁻¹ and 220 to 1,070 mg kg⁻¹, respectively. And the amount of P was greater in the upper 10 cm depth than that in the next 10 cm depth for all soil samples. With this results, we calculated and found that the ratios of total and water-soluble P ranged from 0.269 to 0.404 and 0.084 to 0.252 for upper and lower depth of soil. The ratios were a slightly higher in upper depth (loam soil) than in lower depth (silt loam) although the upper soil had slightly higher amount of organic matter. But the highest ratio occurred from the soil that the soil pH was the lowest among the soil samples investigated. Among the soil samples collected at the upper depth, there were no distinctive correlation depending on soil pH and organic matter which could influence the fate of P. The P distribution in soils could be attributed by fixation of P by the soil where it is applied, allowing for little movement down through the soil.

In observing the mineralization of the indigenous P in soils, we extracted P with 9 different concentrations of oxalic acid ranging from 10⁻⁵ to 10⁻¹ cmol L⁻¹. pH of oxalic acid solution ranged from 2.42 to 6.42 as the concentration of oxalic acid decreased from 10⁻¹ to 10⁻⁵ cmol L⁻¹. Fig. 1 shows the phosphate recovered in the soil solution after addition of oxalic acid with the various dilution factors from 1:1 to 1:20 for unit mass of oven dry soil. The concentration of P in solution sharply increased as the concentration of oxalic acid was greater than 5 x 10⁻⁴ cmol L⁻¹ under dilution factors of 1:1, 1:2.5, and 1:5. Under dilution factors of 1:10 and 1:20, the breaking concentration of oxalic acid was lowered to 10⁻⁴ cmol L⁻¹ and 5 x 10⁻⁵ cmol L⁻¹, respectively. This indicated that the dilution factor of soil to solution could play an important role on the mineralization of the indigenous P in soils.

The mineralization of P was greater in upper depth than in lower depth and the maximum amount of mineralized P measured at addition of 10⁻¹ cmol L⁻¹ of oxalic acid for all dilution factors were sharply increased from approximately 18 to 1200 mg kg⁻¹ and 14 to 1000 mg kg⁻¹ for upper and

lower depth as the dilution factors changed from 1:1 to 1:20. The amount of mineralized P corresponded to the amount of indigenous P in soils regardless of dilution factors. From these results, we could conclude that the mineralization of P strongly influenced by amount of indigenous P in addition to the concentration of oxalic acid and dilution factor.

Generally adsorption of P was strongly influenced by soil pH such that adsorption of P increased with decreasing soil pH while adsorption decreased with increasing soil pH (Parfitt, 1978; Violante et al., 1991; Violante and Gianfreda, 1993). And the presence of other anions in soil solution can compete for available sorption site or displace the adsorbed anions on the soil particle surfaces. Therefore, it could be considered that competitive interaction between oxalic acid as anionic adsorbates could occur directly through competition for surface sites and indirectly through effects of anion adsorption on surface charge and protonation as observed by Dynes and Huang (1997) and Geelhoed et al. (1998). Christensen (1984) studied Cd adsorption as a function of the cation species in the presence of competing electrolyte for a given ionic strength. In that experiment he found that Cd adsorption by a soil diminished somewhat when Ca was present at high Cd loadings, but competition from Ca was minimal at low metal loadings, which can be interpreted as effect of ionic strength. Thus, 10th order increment of oxalic acid and dilution factors representing the increase in ionic strength influenced the desorption of adsorbed P in soils.

Numerous comparisons of rate functions for describing soil kinetic data has been done (Sparks and Jardine, 1984). When using multireaction rate functions to describe kinetic data, the simplest model with the best overall fit to the data and with the lowest parameter standard errors is the most desirable. Kinetic of desorption was described by a rate equation previously described by Sparks and Jardine (1984) and expressed as follows (Eq. 1). Eq. 2 is the solution of Eq. 1.

$$dC/dt = -k_{des} \cdot C \quad (\text{Eq. 1})$$

$$C_t = C_o \cdot \exp(-k_{des}t) \quad (\text{Eq. 2})$$

where C_t is the adsorbate concentration in the solid phase (mg kg⁻¹ soil) at time t (min). C_o is the total desorbable concentration in the soil at the beginning (mg kg⁻¹ soil) and k_{des} is the desorption rate constant (min⁻¹). k_{des} can also be said to be the release constant. Based on the above desorption equation, the desorption can be

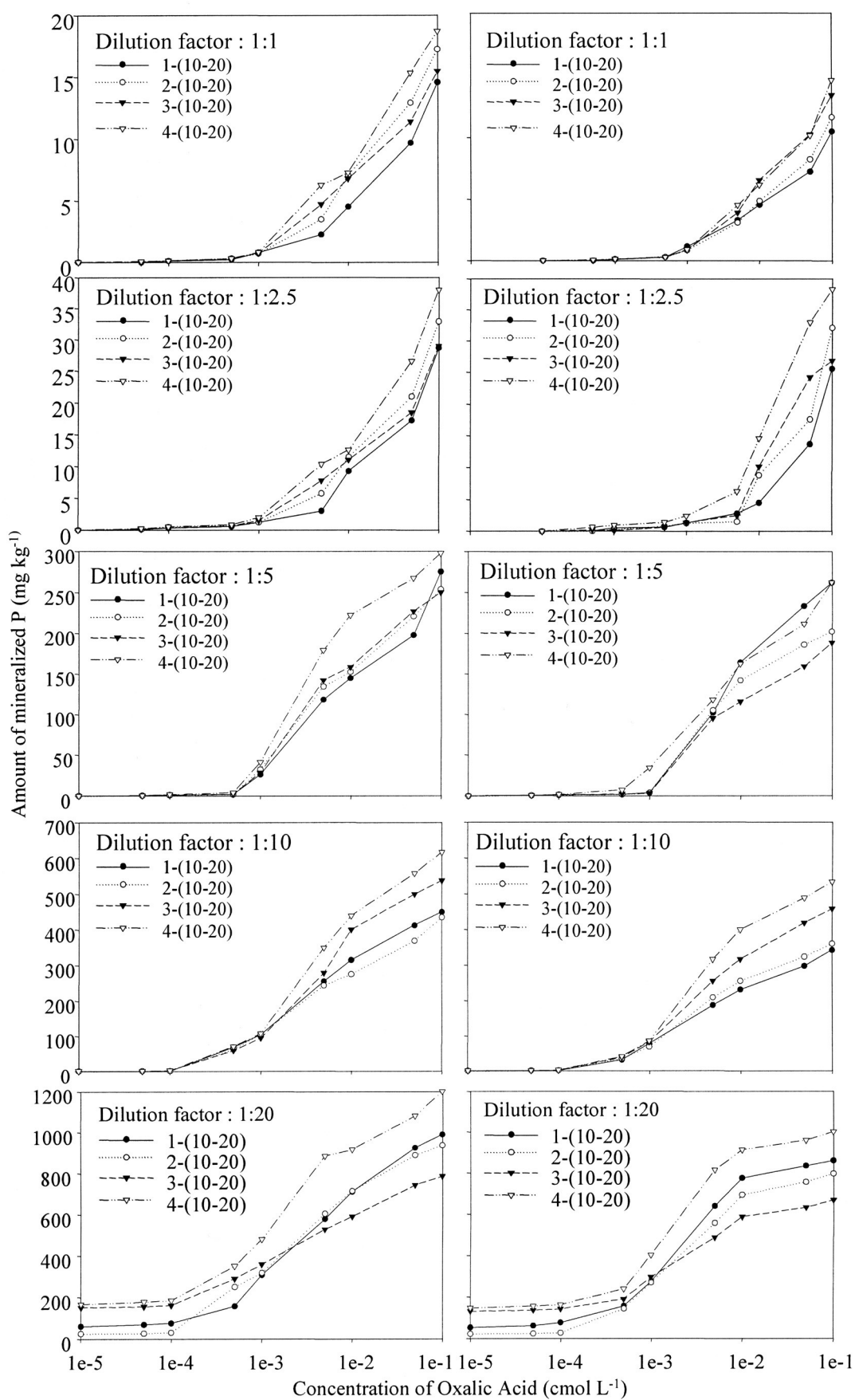


Fig. 1. Amount of mineralized P by various concentrations of oxalic acid under 5 different dilution factors for soils collected from sequential two depths. Inside the parenthesis indicates the depth of soil samples for 4 different locations.

described by shape of exponential decay.

The shapes of mineralized P for the different dilution factors can be described as following two equations. The best curve fit can be exponential decay equation 3 when the dilution factors were 1:1, 1:2.5, and 1:5 while the sigmoidal type of equation 4 for 1:10 and 1:20

$$C = a \exp(b \times x) \quad b > 0 \quad (\text{Eq. 3})$$

$$C = a / (1 + \exp(-\frac{(x - x_0)}{b})) \quad b > 0 \quad (\text{Eq. 4})$$

The regressions obtained from both equation were greater than 0.915, that indicate these equations can better describe the mineralization of P by oxalic acid in a given conditions.

To better understand and predict the effect of dilution factor for the mineralization of P depending on the oxalic acid concentration, we plotted the amount of mineralized P vs. dilution factor as shown in Fig. 2. The slope gradient indicating the changes of the mineralized P can represent the effect of dilution factor on the P mineralization by oxalic acid. Dilution factor for mineralization of P was very distinctive at the dilution factor greater than 1:2.5. Also there was drastic increase of mineralized P as oxalic acid concentration changed from 10^{-3} to 5×10^{-3} cmol L⁻¹. From these results, we could conclude that the dilution factor was most effective at high concentration of oxalic acid. Therefore, we should consider the dilution factor in enhancing the availability of solid-type of P whatever the existence of P fraction is in soil.

Conclusions

In most soils, the P content of surface horizons is

greater than subsoil because added P tends to be fixed by the soil where it is applied, allowing for little movement down through the soil. Phosphate that adsorb strongly on the surface of naturally occurring solids are generally far less mobile in the environment than ions that do not adsorb strongly. However, the displacement can be significantly increased by increased concentration of counter competing anions carrying higher valence as well as dilution factors. And the displacement of phosphate was significantly improved in the presence of multi-species of the counter ions. Therefore, these results may be helpful in designing displacement treatment in lowering the phosphate levels in the field.

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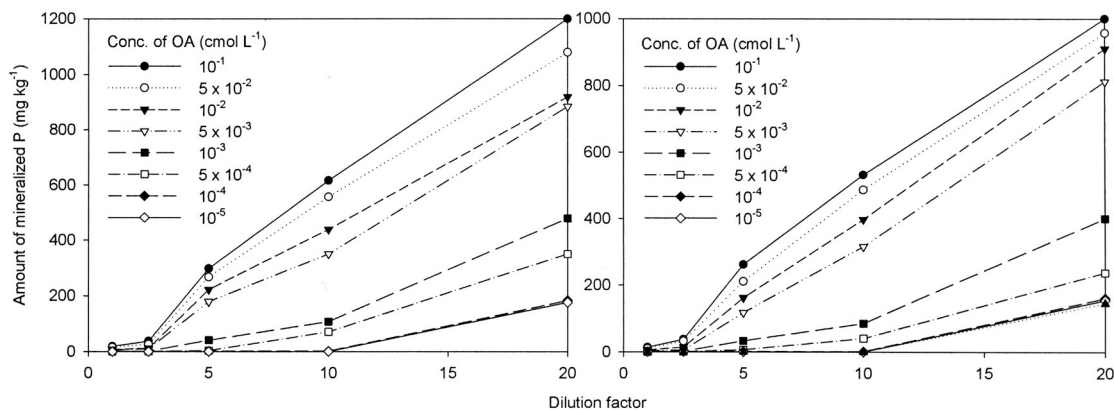


Fig. 2. Amount of mineralized P in soil depending on the ratio of soil to solution.

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밭토양에서 옥살릭산과 희석요인에 의한 자체 인산의 이동 특성

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토양내에서 인의 축적은 농업과 환경에 심각한 문제로 대두되고 있다. 본 연구에서는 토양입자표면에 흡착된 인산이온의 치환방법을 조사하기 위하여 실험실 규모의 연구를 수행하였다. 토양시료는 충남 논산에 위치한 구릉지 밭토양 4개 지점에서 0-10 cm와 10-20 cm 깊이의 토양시료를 채취하였다. 인의 가용화를 조사하기 위하여 10^{-5} to 10^{-1} cmol L⁻¹의 옥살릭산을 1:1, 1:2.5, 1:5, 1:10 및 1:20의 희석비율로 처리하여 조사하였다. 인 가용화는 희석비율이 1:5 이하의 경우 옥살릭산의 농도가 5×10^{-4} cmol L⁻¹ 이상으로 처리될 때 증가가 시작되었다. 그리고 희석비율이 1:10과 1:20 일 때 인가용화 시작점은 1:5 이하와 비교 시 10^{-4} cmol L⁻¹에서 5×10^{-5} cmol L⁻¹로 낮아짐을 알 수 있었다. 본 연구에서 얻는 그래프의 곡선적정 결과 희석배수가 1:5 이하에서는 지수증가의 형태이나 1:10 이상의 경우 S자 만곡형으로 인의 가용화는 희석배수에 의해 많은 영향을 받는 것으로 조사되었다.