Biol Fertil Soils (1997) 25:175–181

ORIGINAL PAPER

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Transformation and bioavailability of specifically sorbed phosphate on variable-charge minerals in soils

Received: 29 September 1996

Abstract Crop production on red soils in China is largely limited by the low availability of phosphorus, which is frequently attributed to the adsorption of phosphate by variable-charge minerals including Fe and Al oxides and kaolinite. Isotopic tracing analysis and soil incubation were carried out to investigate the desorption and microbial transformation of applied specifically sorbed P in two pH-contrasting light-textured soils. A rapid release of P from the added mineral-P surface complex in the two tested soils was observed. Most of the released P was recovered in a 0.5 *M* $NaHCO_3$ extract and in soil microbial biomass. Microbial biomass-^{32}P was detected at early stages of incubation and reached up to 10–30% of the added ^{32}P. Approximately 50–70% of the added complex ^{32}P, varying between minerals and soils, was extractable in the 0.5 *M* $NaHCO_3$ at 75 days after incubation for the acid soil but up to 120 days for the neutral soil. Microbial biomass-P plus 0.5 *M* $NaHCO_3$-extractable ^{32}P accounted for more than 60–80% of total added complex-^{32}P, implying high desorption and transformation of the specifically sorbed P in the two soils. There was more inorganic ^{32}P than organic ^{32}P in the $NaHCO_3$ extract, suggesting that chemical release of specifically sorbed P was dominant. Ligand exchange and chemical desorption due to a change in environmental conditions such as pH and ionic strength are likely the major mechanisms responsible for the chemical release of specifically sorbed ^{32}P in the tested soils.

Key words Phosphorus · Specifically sorbed · Soils · Transformation · Microorganism

Introduction

The utilization rate of P fertilizers to plants within the growing season is very low in variable-charge soils (Stevenson 1986; He et al. 1992). The specific adsorption of P on variable-charge minerals such as Fe, Al oxides and kaolinite has been shown to be responsible for the low plant availability of both applied P and indigenous soil P (Barrow 1980; He et al. 1991 a; Parfitt 1978). Laboratory and greenhouse studies indicated that specifically sorbed P was potentially available to plants although it was very difficult to desorb (Parfitt 1979; He et al. 1994 a), which is in agreement with the long-term residual effect of P fertilizers in variable-charge soils (Barrow 1985). The increased availability of soil P to plants in the rhizosphere is usually attributed to root activity, especially higher phosphatase activity in the rhizosphere than in the bulk soil (Marschner et al. 1991; Tarafdar and Jungk 1987). However, it has been shown that the specifically sorbed P can be efficiently used and consequently transformed into organic P fractions by some microorganisms (He and Zhu 1996). Application of organic manures generally considerably enhances the plant availability of soil P, which is likely related to a boom of microbial growth due to the fresh supply of energy materials (Yang et al. 1994). Moreover, the higher phosphatase activity in the rhizosphere could be due to enzyme released or associated with microorganisms whose growth is stimulated by root exudates and/or by enzymes present in plant remains (Tarafdar and Claassen 1988). It is, therefore, hypothesized that microbial transformation plays a crucial role in the increased availability of fertilizer P and indigenous P in rhizosphere and may be responsible for the long-term residual effect of fertilizer P in variable-charge soils. In addition to providing P through mineralization, application of organic manures may also be responsible for the long-term residual effect of fertilizer P in variable-charge soils.

This study was designed to examine the chemical and microbiological transformation of P specifically sorbed by some important variable-charge minerals in soils. Extraction with 0.5 *M* $NaHCO_3$ was used to monitor the flux of

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^{32}P from a specifically sorbed source to the labile P pool. The dynamics of inorganic and organic ^{32}P in the labile P pool and microbial biomass-^{32}P were determined to characterize the desorption and microbial transformation of added specifically sorbed ^{32}P in contrasting pH and fertility soils.

Materials and methods

Phosphorus-mineral surface complexes including kaolinite-P, goethite-P and Al oxide P were prepared by equilibrating a known amount of the mineral with ^{32}P-labeled ^{31}P solution (55.8 dpm μg^{-1} P). The amount of ^{31}P added was equivalent to 90% of sorption saturation, based on a previously determined P sorption isotherm. After removal of loosely bound P by washing with deionized water, the mineral-P complex was resuspended prior to use in soil incubation. The source and properties of the tested minerals have been described elsewhere (He et al. 1991a). Two light-textured soils with contrasting pH and fertility were selected for the incubation study. The neutral silty soil was more fertile and productive than the acid sandy soil. Some chemical properties of the tested soils are described in Table 1. Organic carbon was determined by the chromate-oxidation method (Nelson and Sommers 1982), soil texture by a pipette method (Day 1965) and clay mineral composition analyzed by X-ray diffraction techniques (Whittig 1965). Fresh soil samples from the 0–15 cm depth were collected from the field and passed through a 2-mm sieve prior to incubation.

Incubation study

Fresh soil samples (equivalent to 300 g oven-dried soil) were weighed and thoroughly mixed with the mineral-P complex. The amount of complex P added was 100 mg P kg^{-1} soil. A proper amount of glucose was added to bring the C/P (initial soil-labile P extractable to 0.5 *M* $NaHCO_3$ plus the complex-P added) ratio to 60. Nitrogen (150 mg kg^{-1}, as NH_4NO_3) and potassium (100 mg kg^{-1}, as K_2SO_4) were also applied to ensure that the nutrient requirement of microorganisms was met. The moisture of the soil was adjusted to 0.3 bar according to a prior determined tension-moisture relationship curve. The soil container was weighed every other day and the lost moisture was supplemented. The soil samples were incubated at 23 °C in a temperature-controlled chamber. At intervals of 10, 15, 25, 50, 75 and 120 days, subsamples were analyzed for 0.5 *M* $NaHCO_3$-extractable inorganic and organic ^{32}P, and microbial biomass-^{32}P. The specific activity of ^{32}P was measured with a liquid scintillation counter. The decay of ^{32}P and the quenching effect of the extractant were automatically corrected for by a computer program with input of time data and a previously determined quench curve. Fractionation of organic and inorganic ^{32}P in the 0.5 *M* $NaHCO_3$ extract was done by using activated charcoal to remove organic materials from the extract and measuring the specific radioactivity of ^{32}P in both the original extract (total ^{32}P) and the charcoal-treated solution (inorganic ^{32}P) (He et al. 1994b). Organic ^{32}P was obtained by the difference between the total ^{32}P and the inorganic ^{32}P in the extract. Microbial biomass-^{32}P was measured by a fumigation extraction procedure (Brookes et al. 1982).

Results

In the acid sandy soil 0.5 *M* $NaHCO_3$-extractable ^{32}P increased with incubation time to a peak at 75 days and decreased thereafter for all the tested mineral-P complexes (Fig. 1), indicating that the specifically sorbed ^{32}P was released into the soil-labile P pool. The 0.5 *M* $NaHCO_3$-extractable ^{32}P in the neutral silty soil as a function of incubation time (Fig. 2) was different from that in the acid sandy soil. The labile ^{32}P in the neutral silty soil increased with incubation time up to 120 days for montmorillonite-P and Al oxide-P complexes, but increased up to 75 days and then remained constant for kaolinite-P. As for the goethite-P complex, the pattern of $NaHCO_3$-extractable ^{32}P with time was similar to that in the acid sandy soil.

Fractionation of $NaHCO_3$-extractable ^{32}P indicated that inorganic ^{32}P was greater than organic ^{32}P for all mineral-P complexes at all incubation stages except that the inorganic and organic ^{32}P were nearly equal for montmorillonite-P and Al oxide-P complexes during the 10–25 days incubation period in the acid sandy soil (Fig. 1). These results show that chemical release of specifically sorbed P was dominant. Exchange of ^{32}P by soil ^{31}P and chemical desorption of ^{32}P because of a change in environmental conditions such as pH and ionic strength are likely the mechanisms involved in the chemical release of specifically sorbed P into labile soil P pool. Chemical release of ^{32}P from any mineral-P complex was more obvious in the neutral silty soil than in the acid sandy soil (Figs. 1, 2). Organic ^{32}P was detected at an early stage (day 10) but the dynamic pattern of organic ^{32}P in the labile P pool varied between soils and mineral-P complexes. In the acid sandy soil, organic ^{32}P reached a maximum at days 25 and 50, respectively, for montmorillonite-P and kaolinite-P complex and at day 75 for goethite-P and Al oxide-P complex (Fig. 1). In the neutral silty soil, organic ^{32}P increased steadily up to the end of incubation (day 120) but there was a weak peak at days 25 and 75, respectively, for goethite-P and Al oxide-P complex (Fig. 2).

Microbial transformation of specifically sorbed P was affected by both soil properties and mineral-P complex characteristics. In the neutral silty soil, a high percentage of ^{32}P was detected by $NaHCO_3$ extraction at an early stage of incubation (in 10 days) and more than 70% of the $NaHCO_3$-extractable ^{32}P was in the inorganic form from all the added mineral-P complexes (Fig. 2). These results indicate that P desorption from mineral-P complex dominated at the initial stage (within 50 days), and microbial transformation of specifically sorbed ^{32}P increased at later

Table 1 Selected physical and chemical properties of soils

Soils	Texture	pH		Organic C (g kg^{-1})	Olsen-P (mg kg^{-1})	Clay mineral composition[a]
		H_2O	KCl			
Acid sandy loam	65% sand, 18% silt, 17% clay	4.6	3.9	6.5	2.7	K (0.5), Chl (0.4), oxides (0.1)
Neutral silty loam	30% sand, 60% silt, 16% clay	7.8	7.2	18.0	35.7	Ill (0.4), Verm (0.3), mica (0.3)

[a] *K* kaolinite, *Chl* chlorite, *Ill* illite, *Verm* vermiculite; values inside the parentheses are relative amounts of each mineral in the clay

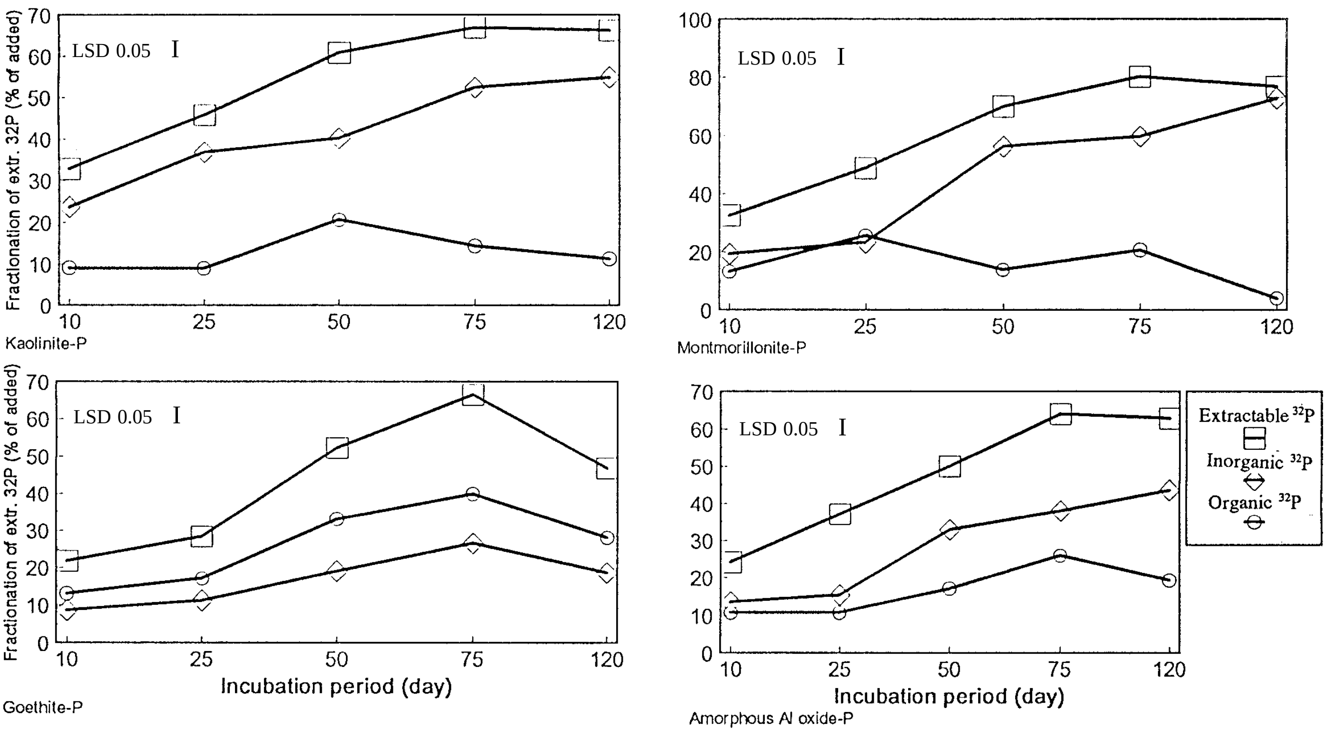

Fig. 1 Dynamics of $NaHCO_3$-extractable ^{32}P from added mineral-^{32}P in acid sandy soil

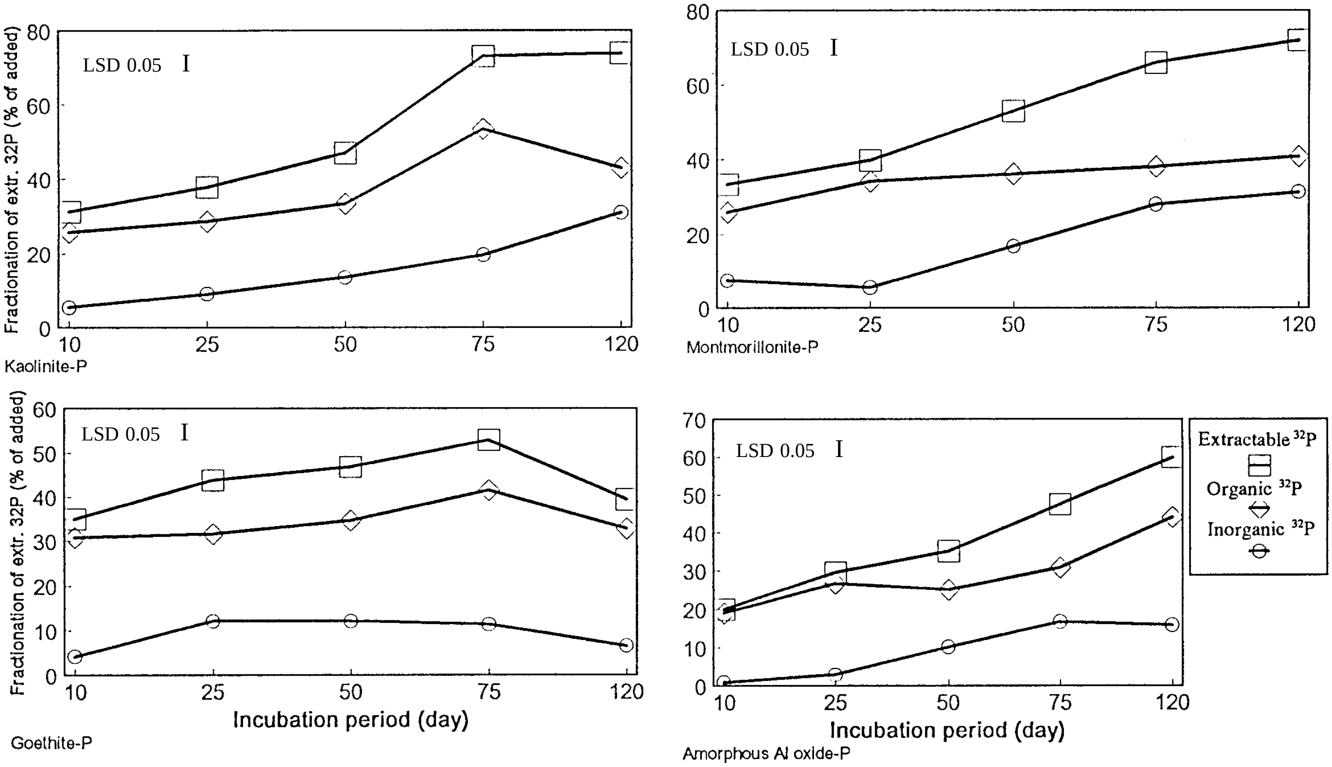

Fig. 2 Dynamics of $NaHCO_3$-extractable ^{32}P from added mineral-^{32}P in neutral silty soil

times (50–120 days) in the neutral silty soil. In the acid sandy soil, organic ^{32}P was similar in amount to the inorganic P at an early stage for all mineral-P complexes except for kaolinite-P, for which inorganic ^{32}P was much greater than the organic ^{32}P in the $NaHCO_3$ extract at this stage (Fig. 1), implying that microbial transformation plays

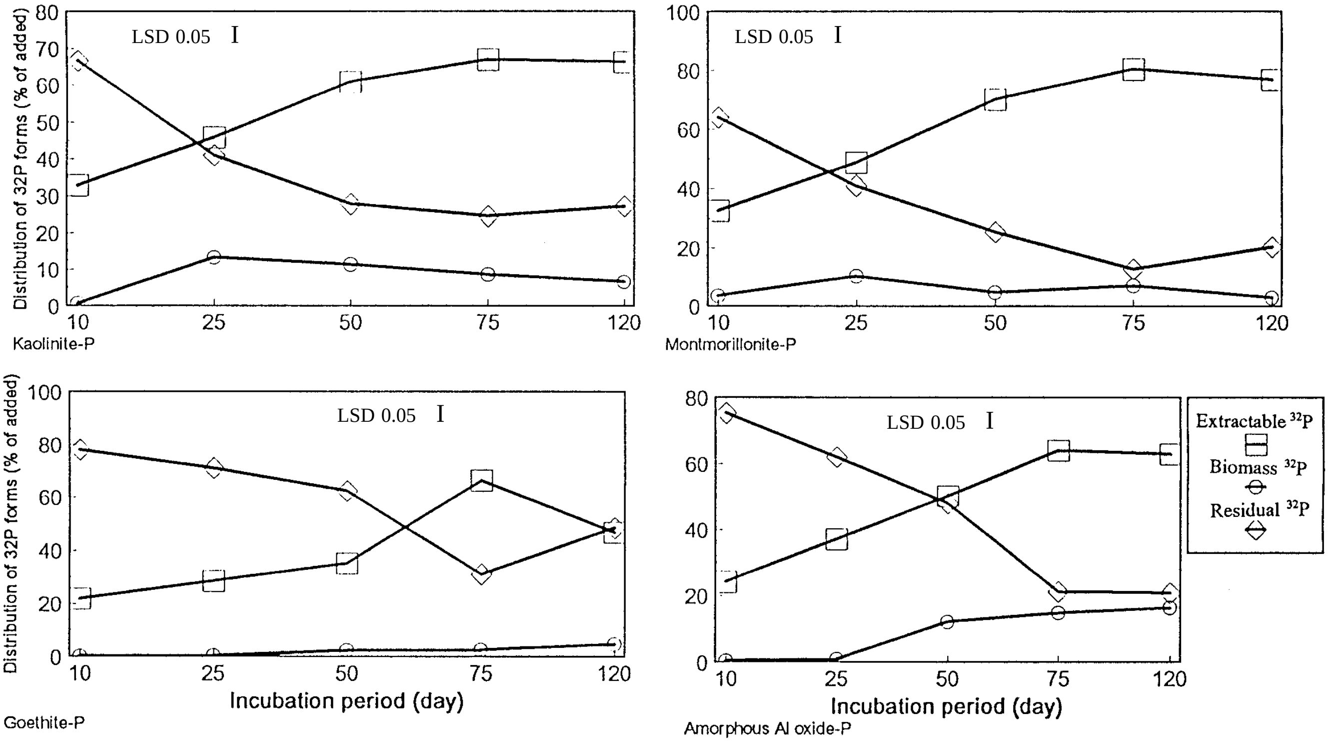

Fig. 3 Transformation dynamics of added specifically sorbed ^{32}P in acid sandy soil

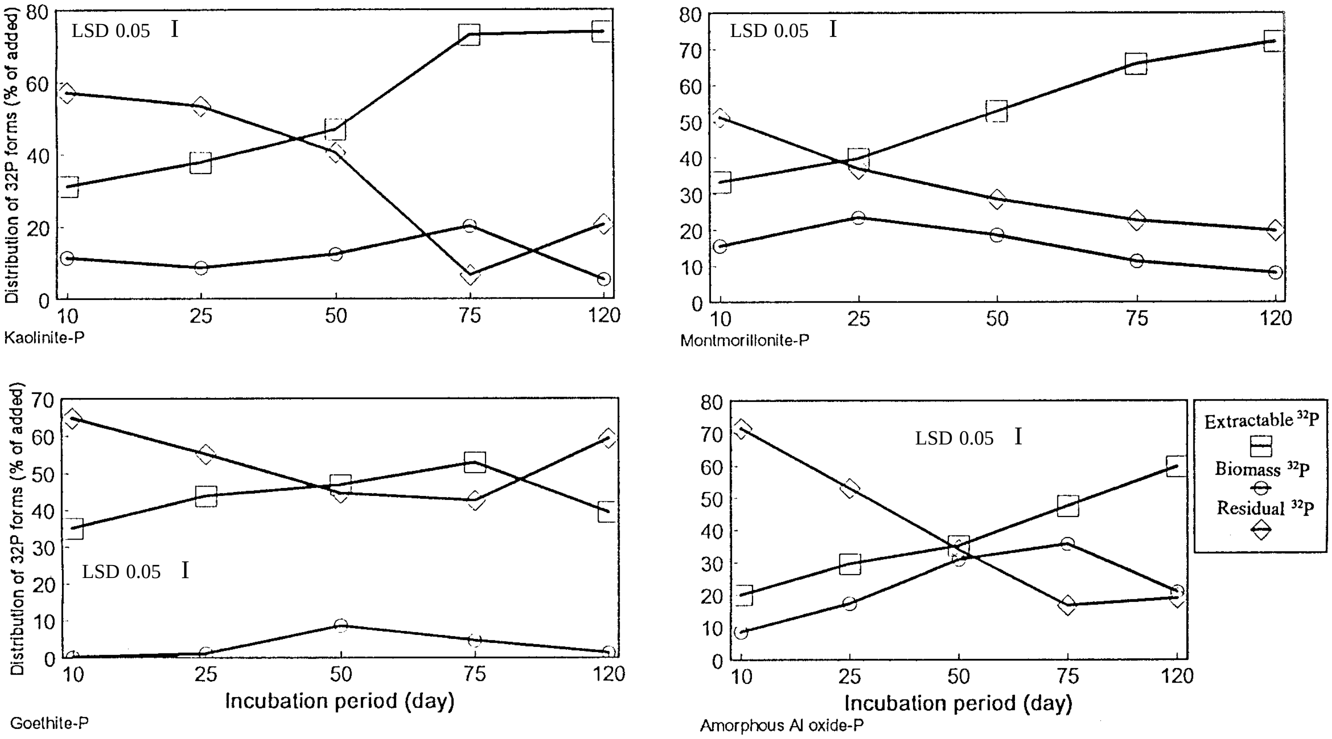

Fig. 4 Transformation dynamics of added specifically sorbed ^{32}P in neutral silty soil

a more important role in the transformation of specifically sorbed P for the acid sandy soil than for the neutral silty soil.

Microbial-biomass-^{32}P increased with increasing incubation time, and reached a maximum at 25 days for kaolinite-P and montmorillonite-P, but increased steadily up to

Table 2 Transformations (% of total added ^{32}P) of added specifically sorbed ^{32}P in soils at the end of incubation (120 days)

Soils	Mineral-P complexes	0.5 *M* $NaHCO_3$-extractable ^{32}P (extr-^{32}P)			Biomass-^{32}P (bio-^{32}P)	Extr-^{32}P+ bio-^{32}P	Residual-^{32}P
		Organic	Inorganic	Total			
Acid sandy loam	Kaolinite-P	11.3	54.9	66.2	6.6	72.8	27.2
	Montmorillonite-P	4.0	72.8	76.8	2.9	79.7	20.3
	Goethite-P	28.1	18.7	46.8	4.7	51.5	48.5
	Al oxide-P	19.3	43.6	62.9	16.3	79.2	20.8
Neutral silty loam	Kaolinite-P	31.0	42.9	73.9	5.4	79.3	20.7
	Montmorillonite-P	31.3	40.8	72.1	8.1	80.2	19.8
	Goethite-P	6.6	32.8	39.4	1.3	40.7	59.3
	Al oxide-P	15.8	44.1	59.9	21.0	80.9	19.1

the end of the incubation (120 days) for goethite-P and Al oxide-P in the acid sandy soil (Fig. 3). In the neutral silty soil, microbial biomass-^{32}P reached a maximum within the incubation time for all the tested mineral-P complexes, but in the time when the peak appeared varied greatly between complexes: 25 days for montmorillonite-P, 50 days for goethite-P and 75 days for both kaolinite and Al oxide-P (Fig. 4). It appeared that the incorporation of ^{32}P from the mineral-^{32}P complex into soil microbial biomass lagged far behind that of soluble ^{32}P, for which soil microbial biomass-^{32}P reached a peak in a week (unpublished data). Such a delay in ^{32}P incorporation into soil microbial biomass indicates that ^{32}P must be desorbed into solution before it is absorbed by microorganisms. As a whole, microbial biomass-^{32}P accounted for a small fraction of total added ^{32}P, 5–10% for the acid soil and 10–20% for the neutral soil. However, as shown in Figs. 1 and 2, the contribution of microbial biomass to the labile P pool was quantitatively more important because from 25 to 40% of the $NaHCO_3$-extractable-^{32}P was found in the organic form.

It is commonly accepted that $NaHCO_3$-extractable P and microbial biomass-P could be the most important P pools readily or potentially available to plants (Smith and Paul 1991). The results from this study showed that the specifically sorbed P, added to the soil, was potentially available to plants. Up to the end of incubation, the sum of $NaHCO_3$-extractable ^{32}P and microbial biomass-^{32}P accounted for 70–80% of total ^{32}P added in the form of mineral-P complex except for goethite-P in the two soils tested (Table 2). The potential availability of specifically sorbed P for the four tested mineral-P complexes increased in the order of geothite P<<<kaolinite-P<<<montmorillonite-P=amorphous Al oxide-P in the acid sandy soil whilst the order was geothite-P<<<kaolinite-P=montmorillonite-P=amorphous Al oxide-P in the neutral silty soil (Table 2).

Discussion

Kaolinite and Fe, Al oxides have long been recognized as major soil components responsible for P fixation in variable-charge soil (Parfitt 1978; Barrow 1985). This conclusion is based on findings that phosphate is specifically sorbed on these variable-charge minerals, and the desorption of the sorbed P is very difficult and slow in aqueous solutions such as 0.01 *M* $CaCl_2$ and 0.02 *M* KCl (Hingston et al. 1974; Ryden et al. 1977; McLaughlin et al. 1981; Goldberg and Sposito 1985). However, the model liquid may be very different from the soil solution. The soil solution, particularly in the rhizosphere, contains not only indifferent inorganic ions such as Ca^{2+}, Cl^-, K^+ and Na^+ but also organic and inorganic ligands which can desorb the specifically sorbed P through ligand exchange or competitive adsorption (Lopez-Hernandez et al. 1986; Marschner et al. 1990; Nagarajah et al. 1970; He et al. 1990a; 1990b; 1992). Results from this study provided evidence showing that considerable desorption of specifically sorbed P did occur even in bulk soil under both acid and neutral conditions (Figs. 1, 2). The transformation of specifically sorbed ^{32}P was 70–80% of total added ^{32}P for kaolinite-P, Al oxide-P and montmorillonite-P and was around 50% for goethite-P in the two soils (Table 2). This showed that release of ^{32}P from the complex was both rapid and considerable. Many factors could affect P release in soil, but chemical desorption appeared to be one of the dominant processes involved. The isotopic exchange of the specifically sorbed ^{32}P by soil ^{31}P could not be excluded from possible desorption. But the results indicate that the added specifically sorbed ^{32}P is in equilibrium with the soil solution P, and is readily or potentially available to plants.

A laboratory culture study demonstrated a high utilization and transformation of the specifically sorbed P by inoculated soil microorganisms (He and Zhu 1996), implying that soil microorganisms have great potential for use and transformation of specifically sorbed P. But under soil conditions, the growth of microorganisms is largely limited by other factors such as the availability of organic C, nutrients, moisture, inhibiting substances and soil fauna grazing them. Thus, the microbial utilization efficiency of specifically sorbed P was much lower in soil than in culture media. Results obtained from this study show that microorganisms play an important role in the transformation of specifically sorbed P in soils as evident in the high percentage of organic ^{32}P in the $NaHCO_3$ extract. Moreover, microorganisms can release low molecular weight organic acids, such as citric and oxalic acid (Kucey et al. 1989), thus enhancing the desorption of specifically sorbed P through ligand exchange by these organic anions (He et al. 1992). The role of microbial transformation in the availability of soil P was also evident from the field observation that application of organic manure generally increases soil P availability and improves crop growth (Yang et al. 1994). One of the mechanisms responsible for the increase in available P is likely related to the beneficial effect of organic manure on microorganisms which, in turn, speed up the turnover of soil P.

Much work has been done on the adsorption and desorption of P by variable-charge minerals (Hingston et al. 1974; Ryden et al. 1977; McLaughlin et al. 1980; Goldberg and Sposito 1985). However, the bioavailability of phosphate sorbed by individual variable-charge minerals is not well defined. In our previous study, using an isotopic exchange method to assess the fixation and availability of sorbed P, it was found that a high percentage of P sorbed by kaolinite and Al oxide was isotopically exchangeable, especially at high sorption saturation. Phosphorus sorbed on goethite was less exchangeable but its exchangeability was much higher than that predicted by desorption in aqueous solution (He et al. 1991 a). Pot experiments with rice plants indicated that P uptake by plants from the mineral-P complexes was quantitatively comparable to the isotopically exchangeable P but much more than the desorbed P (He et al. 1994 a). Results from this study demonstrated that kaolinite-P and Al oxide-P were relatively ready to desorb or subject to microbial transformation, and retain P from leaching while acting as important sources of available P. Therefore, kaolinite and Al oxides may serve more as an important carrier of than a sink for available P in soils, and mineral-P complexes, such as kaolinite-P and Al oxide-P, could be potentially used as P fertilizer for light-textured soils where P leaching is often a problem (Vlahos et al. 1989; Ward and Summers 1993; Weaver et al. 1988 a; 1988 b). Goethite-P was relatively stable to desorption and microbial transformation in soils. But the goethite-P was found to be as available as kaolinite-P or Al oxide-P to microorganisms with a laboratory culture study (He and Zhu 1996). Obviously, more research is needed to understand the chemical fixation of P in variable-charge soils.

Acknowledgements The financial support of the International Foundation of Science and the Zhejiang provincial Natural Science foundation is gratefully acknowledged. The authors wish to thank Dr. V.C. Baligar, USDA-ARS Lab, Beaver, for his help in reading the first draft of the paper, and to thank the reviewers for their excellent comments on the manuscript.

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