# ORIGINAL PAPER

Y.S. Zhang · W. Werner · H.W. Scherer · X. Sun

# Effect of organic manure on organic phosphorus fractions in two paddy soils

Received: 17 March 1993

Abstract We investigated the transformation of the organic P fractions from organic manure in two paddy soils (Ultisol, Entisol) and the influence of organic manure or cellulose on organic P under anaerobic conditions. The results obtained from the P fractionation experiment indicated that during the incubation labile and moderately labile organic P fractions increased in the Ultisol and decreased in the Entisol, which might be related to the difference in the organic matter content of both soils. Immediately after the application of organic manure, a large part of labile and moderately labile organic P supplied with the manure was transformed into moderately resistant organic P, possibly Ca- or Mg-inositol P were transformed into Fe-inositol P. During anaerobic incubation, the labile forms of organic P in the soils treated with organic manure were increased along with the incubation period in the first 4 weeks. The change in the moderately labile fraction was dramatic. It increased sharply in the first 2 weeks, then decreased, which was more pronounced in the soils treated with pig faeces. The moderately resistant fraction decreased during the whole incubation period. This indicated that under anaerobic conditions, the moderately resistant fraction can be transformed into labile and moderately labile organic P fractions, perhaps as  $Fe^{3+}$ -inositol P is reduced to Fe<sup>+2</sup>-inositol P. Cellulose as an organic substrate had an increasing effect on organic P, especially when it was combined with inorganic P. Therefore, it is suggested that the application of inorganic P fertilizer combined with organic manure may be an effective way of protecting inorganic P against intensive sorption in soils.

Y.S. Zhang · X. Sun

Department of Soil Science and Agrochemistry,

Zhejiang Agricultural University, Hangzhou 310029, P.R. China W. Werner (⊠) · H.W. Scherer

Agrikulturchemisches Institut

der Rheinischen Friedrich-Wilhelms-Universität Bonn, Meckenheimer Allee 176, D-53115 Bonn, Germany **Key words** Paddy soils · Anaerobic conditions · Organic P fractions · Organic manure · Cellulose

## Introduction

The effects of organic manure on P mobilization, P adsorption and desorption (Sah and Mikkelsen 1986a, b; Zhang et al. 1993), P movement in soils (Hannapel et al. 1964a, b), and the availability of P supplied in farmyard manure applied to soils (Meek et al. 1979; Azar et al. 1980; Mo et al. 1991) have been investigated intensively. But most of this research has been mainly focused on the importance of inorganic P for plant nutrition. However, organically bound P comprises about 50-70% of total P in most mineral soils and up to 90% in organic soils. For this reason Bowman and Cole (1978a) indicated that the sum of both inorganic P and organic P extractable with 0.5 mol NaHCO<sub>3</sub> is a better indicator of plant response than inorganic P alone. According to Zhang et al. (1988) the content of labile and moderately labile organic P determined by Bowman and Cole's method is a useful index of whether the soil is rich in P and organic matter. A highly fertile soil is characterized by a higher content of these organic P fractions. He and Li (1987), after verifying the reliability of the Bowman-Cole method for organic P fractionation in relation to its availability to plants, showed that labile organic P was statistically closely related to RNA, lecithin, G-6-P, and glycerophosphate and could be extracted almost completely by 0.5 mol NaHCO<sub>3</sub>. This organic P fraction is easily available to plants (Mo et al. 1991). In a solution culture experiment under aseptic conditions with clover seedlings supplied with G-6-P, F-6-P, RNA, phosphoglyceric acid and inositol mono-hexaphosphate, Wild and Oke (1966) found a better response to some of these substances than to inorganic P. Aseptic culture experiments were also used to show that the nutritional effect of RNA-P or even inositol P on rice seedling growth was superior to that of inorganic P (Sun et al. 1986; Sun and Zhang 1992). These results clearly indicate the importance of soil organic P for P nutrition of plants. Thus in order to evaluate the effects of organic manure on soil P comprehensively, both inorganic and organic P must be investigated.

The aim of the present study was to examine the fate of organic P fractions supplied in organic manure after incorporation into the soil and during incubation under anaerobic conditions. Further, the effect of the organic substances supplied with organic manure on the formation of organic P from inorganic P was investigated.

#### Materials and methods

A paddy soil on red earth (ultisol: pH 5.7; 30.9 mg organic matter  $g^{-1}$  soil; 16.4 mg Olsen-P kg<sup>-1</sup> soil) and a degleyed dark paddy soil (entisol: pH 5.9; 45.6 mg organic matter  $g^{-1}$  soil; 28.3 mg Olsen-P kg<sup>-1</sup> soil), which are widely distributed in Zhejiang Province of China, were used in the experiment.

To compare the effect of different kinds of organic manure on organic P fractions in soils, pig faeces (high P content), cow faeces (low P content), and cellulose (provides only organic substance) were used. The faeces were dried at 70  $^{\circ}$ C and ground. Some characteristics of the faeces are shown in Table 1.

The treatments comprised (1) control, (2) soil+pig faeces, (3) soil+cow faeces, (4) soil+cellulose, (5) soil+P ( $KH_2PO_4$ ), and (6) soil+cellulose+P. In treatments 2, 3, 4, and 6 the same quantitiy of organic matter (2%) was supplied. The quantity of inorganic P added as  $KH_2PO_4$  was equal to the total P in pig faeces. Treatments 5 and 6 were used to confirm the effect of the inorganic P level on the organic P fractions in the soil during incubation. In order to imitate paddy field conditions, all treatments were incubated anaerobically (flooded) for 0, 2, 4, and 6 weeks at 30 °C.

The organic P in the soils was separated into four fractions according to Bowman and Cole (1978b), comprising (1) labile organic P, extracted with 0.5 M NaHCO<sub>3</sub> (pH 8.5), with organic P determined by the increase in inorganic P after perchloric acid digestion; (2) moderately labile organic P, extracted with  $1.0 M H_2 SO_4$ , with organic P determined as for labile organic P; (3) moderately resistant and (4) highly resistant organic P, determined by transferring the  $1.0 M H_2 SO_4$ -extracted soil samples onto filter paper, then washing the samples with 3 ml ethanol, followed by drying and extraction with 0.5 M NaOH; both these organic P fractions were determined together after perchloric acid digestion (fraction I); then an aliquot of the extract was acidified with concentrated hydrochloric acid to pH 1-1.5, and moderately resistant organic P was determined after perchloric acid digestion (fraction II), with highly resistant organic P determined by subtracting fraction I from fraction II. P was determined according to the method of Murphy and Riley (1962). However, to prevent the transformation of organic P during air-drying, fresh (moist) soil samples were used for fractionation of organic P instead of air-dry soil.

To determine the change in the organic P fractions in the faeces after incorporation into the soil, a recovery experiment was conducted with three treatments, faeces mixed with fine quartz sand, faeces mixed with fine quartz sand and FeCl<sub>3</sub> (25 mg Fe g<sup>-1</sup> sample), and faeces mixed with soil. In the calculation for the treatment

of faces mixed with soils each organic P fraction was deducted from the corresponding fraction in untreated soil.

To verify the reasons proposed to explain why the moderately labile organic P fraction in soil treated with faeces increased sharply after anaerobic incubation, a supplementary fractionation experiment was performed with unincubated soil and organic manure treated with 0.1 mol SnCl<sub>2</sub> to reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>. All experiments were done with three replicates.

## **Results and discussion**

Effect of organic manure on organic P fractions in the soil

In the Ultisol the labile and moderately labile organic P fractions increased in the control during the incubation period, while in the Entisol these two fractions decreased after 2 weeks (Table 2). This may be caused by transformation processes involving organic and inorganic P. However, the resistant organic P pools in both soils were not influenced at all by incubation. The application of pig faeces and cow faeces increased all organic P fractions in the soils to a large extent, especially moderately resistant and moderately labile organic P. Due to its higher organic P content the effect of pig faeces was more pronounced. During the incubation period in the treated soil there was a general trend for part of the moderately resistant organic P to be transferred to labile and moderately labile organic P, especially in the first 2 weeks. Then the moderately labile fraction in both soils decreased sharply. This result was a further indication of why this fraction decreased in the Entisol (control) during the incubation because both soils were rich in organic matter after applying faeces. The fluctuation in these two organic P fractions was more pronounced in the soil treated with pig faeces than with cow faeces, which may be attributed to two factors, a higher organic P content and more easily decomposable organic compounds in pig faeces. This means that under anaerobic conditions the application of organic manure increases the availability of organic P which plants can use directly (Mo et al. 1991).

Adding cellulose significantly increased all organic P fractions in soil except the highly resistant fraction. At the end of the incubation period, this increase amounted to about 80 and 34% for the labile fraction, 57 and 23% for the moderately labile fraction, and 22 and 10% for the moderately resistant pool in the Ultisol and the Entisol, respectively. These results indicate that the effect of cellulose on organic P was more pronounced in the Ultisol, which had a lower organic matter content. However, the

**Table 1** Organic matter  $(mg g^{-1})$  and P content  $(mg g^{-1})$  of faeces

Faeces	Organic matter	Labile organic P	Moderately labile organic P	Moderately resistant organic P	Highly resistant organic P	Total organic P	Inorganic P	Total P
Pig faeces	824	1.6	2.8	7.1	3.7	15.3	7.9	23.1
Cow faeces	711	1.2	0.8	1.0	0.7	3.7	2.9	6.6

Table 2Effect of organicmanure on organic P fractions $(mg kg^{-1})$  in soil and effect ofpig manure compared with $SnCl_2$ 

Treatment of soil	Incubation period (weeks)	Labile organic P		Moderately labile organic P		Moderately resistant organic P		Highly resistant organic P	
		U	Е	U	Е	U	E	U	Е
Control	0	5.6	15.5	12.7	32.7	45.5	78.3	30.3	40.5
	2	6.0	16.8	13.4	35.9	44.0	74.7	31.1	38.8
	4	7.3	12.7	14.4	31.3	44.7	75.4	31.6	39.0
	6	7.6	11.4	15.9	27.1	44.3	77.5	30.0	41.2
Pig faeces	0	23.8	33.1	124.6	127.2	225.1	267.3	63.3	69.2
C .	2	24.2	36.5	185.8	221.7	174.3	135.5	61.2	71.1
	4	29.1	47.1	114.8	185.5	159.4	139.5	66.5	68.4
	6	32.8	45.5	97.7	138.7	156.7	145.8	59.4	66.3
Cow faeces	0	17.2	26.4	27.6	46.3	91.0	119.4	51.4	62.7
	2	21.3	31.4	50.3	67.1	73.8	94.4	50.0	62.1
	4	24.5	30.5	40.2	71.2	72.3	87.9	52.1	60.7
	6	23.7	29.8	38.8	72.3	68.7	90.3	49.0	61.4
Cellulose	0	5.4	16.0	12.7	33.0	45.3	79.0	31.0	39.7
	2	9.4	19.8	17.7	36.6	41.5	77.3	30.4	40.5
	4	12.0	21.0	19.2	40.1	50.3	82.5	31.1	40.2
	6	9.9	21.4	19.9	40.7	55.4	86.8	32.3	41.7
LSD (0.05)		1.3	1.3	2.7	3.0	2.5	2.5	2.1	1.9
Pig faeces	0	24.4	32.8	126.0	128.1	225.7	264.2	62.7	70.4
$Pig faeces + SnCl_2$	0	23.3	30.7	167.4	158.6	184.6	233.7	58.4	68.8

U, Ultisol; E, Entisol; LSD, least significant difference

highly resistant organic P fraction was relatively stable and not easily modified by external conditions. These observations suggest that apart from the application of organic P with the faeces, the organic matter of the faeces may be a crucial factor in P transformation processes under anaerobic conditions.

It is well known that both organic and inorganic P are easily adsorbed, thus becoming less available to plants. However, labile organic P can be used by plants (He and Li 1987; Mo et al. 1991), and the nutritional effects of the labile organic P fractions are superior to those of inorganic P at the same concentration (Sun et al. 1986; Sun and Zhang 1992), caused by the low mobility of inorganic P in soil. Hannapel et al. (1964a, b) pointed out that the addition of bean and barley residues as well as sucrose to soil can significantly improve P movement, with more than 95% of the translocated P being organic P. Scherer and Werner (1992) showed that the distance that inorganic P can travel by diffusion from fertilizer bands in Oxisols is markedly increased by a combinated application of mineral P fertilizer and farmyard manure.

From our results we conclude that the effect of organic manure in improving P nutrition through promoting organic P in soil cannot be ignored. This means that a comprehensive view of the effect of organic manure in improving P nutrition to plants must include the effect of organic substances on organic P.

Recovery of organic P from organic manure after incorporation into the soil

The results of the experiment to determine the recovery of organic P indicated that immediately after the organic

manure was mixed into the soil large changes occurred in the different organic P fractions of the organic manure (Fig. 1). While less than 40% of the labile fraction and 40-67% of the moderately labile fraction were recovered from pig and cow faeces, the moderately resistant fraction increased to 164 and 149% for cow faeces and 450 and 470% for pig faeces in the Ultisol and Entisol, respectively. The highly resistant fraction increased by 12-29%.

In pig faeces about 70% and in cow faeces about 45% of the total Po is inositol P (Sun and Zhang 1992). In pig faeces 80% and in cow faeces 46% of the total inositol P is Ca-inositol P or Mg-inositol P which may attribute to the moderately labile organic P pool. However, in paddy soils 98% occurs as Fe-inositol P which is considered a resistant organic P fraction (He and Li 1987). That means that after the faeces was mixed into the soil, labile and moderately labile faecal organic P (Ca- and Mg-inositol P) were largely transformed to moderately resistant organic P (Fe-inositol P). These results were supported by a further experiment in which FeCl<sub>3</sub> was supplied together with faeces (Fig. 2), demonstrating the role of Fe in the transformation of organic P. Nevertheless, the higher recovery of organic P after the addition of FeCl<sub>3</sub>, compared with the treatment without the addition of Fe, shows that the transformation process is rather complicated. Although chemical precipitation of Fe-inositol P may contribute to the effect, other factors may be involved, such as adsorption of soluble organic P compounds by clay minerals and humic complexes (Bowman and Cole 1978a).

However, with the reduction of  $Fe^{3+}$ , as a consequence of the low redox potential during the flooding, the moderately labile organic P fraction increased steeply within 2 weeks, while the moderately resistant organic P

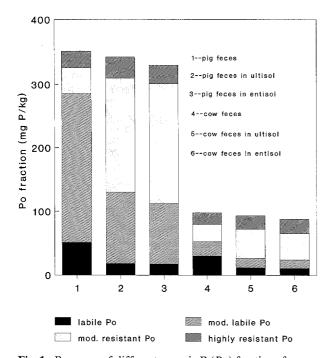


Fig. 1 Recovery of different organic P (Po) fractions from organic manure after mixing with soil; mod., moderately

fraction decreased (Table 2), which may have been related to the reduction of  $Fe^{3+}$ -inositol P to  $Fe^{2+}$ -inositol P. This conclusion was supported by the results of a supplementary experiment in which the moderately labile organic P fraction was increased and the moderately resistant organic P fraction was decreased by adding SnCl<sub>2</sub> to the soils treated with organic manure, so that  $Fe^{3+}$  was reduced to Fe<sup>2+</sup> artificially (Table 2). The effect of SnCl<sub>2</sub> on the transformation of organic P was more pronounced in the Ultisol with the higher Fe content. However, since the change after 2 weeks of flooding was larger in the treatment with pig faeces than with SnCl<sub>2</sub> it cannot be

Fig. 2 Influence of  $Fe^{3+}$  on the recovery of different organic P

10000

1--pig feces

3--cow feces

2--pig feces plus FeCl a

4--cow feces plus FeCl,

3

mod. labile Po

highly resisant Po

Effect of organic matter combined with inorganic P on organic P fractions in the soil

The added inorganic P was partly converted to organic P. especially to the labile and moderately labile organic P fractions, during the incubation period (Table 3). However, this effect was more pronounced when inorganic P was

Treatment	Incubation period (weeks)	Labile organic P	Moderately labile organic P	Moderately resistant organic P	Highly resistant organic P
Ultisol	0	5.7	12.8	45.7	30.0
+ inorganic P	2	7.4	16.2	43.4	31.3
-	4	10.3	18.4	51.7	32.4
	6	9.7	18.0	50.4	31.8
Ultisol	0	5.5	13.0	45.3	30.4
+ inorganic P + cellulose	2	14.7	20.4	41.9	33.7
	4	18.2	25.4	56.4	35.4
	6	17.6	28.3	60.8	33.4
Entisol + inorganic P	0	15.6	33.0	79.1	40.3
	2	18.1	37.4	77.4	40.7
	4	20.4	42.1	84.1	44.3
	6	19.3	38.0	86.7	42.7
Entisol	0	15.3	32.7	80.0	40.8
+ inorganic P + cellulose	2	22.3	40.4	81.9	43.3
	4	26.7	48.3	90.5	43.9
	6	25.0	46.6	94.4	44.8
LSD (0.05)		1.2	2.1	2.7	2.0

Table 3 Effect of organic substrate combined with inorganic P on organic P  $(mg kg^{-1})$  fractions in soil

LSD, Least significant difference

(Po) fractions from organic manure; mod., moderately

2

400

300

200

100

0

1

labile Po

mod. resistant Po

Po fraction (mg P/kg)

explained completely by the redox reaction.

combined with cellulose compared with the application of inorganic P alone or cellulose (Table 2). The results of the present study thus appear to show that the mechanism by which cellulose increases soil organic P is principally the transformation of inorganic to organic P by microbes stimulated by the cellulose, which provides the necessary energy source and organic substrate (Hannapel et al. 1964a, b; Zhang et al. 1992).

Therefore we conclude that the application of organic manure can considerably increase organic P fractions in soil under flooded conditions. When inorganic P is supplied together with organic manure the formation of organic P is promoted. Further, the application of inorganic P fertilizer combined with organic manure should be regarded as an effective way of the plant availability of inorganic P in soils. To evaluate the actual effects of organic manure on soil P nutrition, both inorganic and organic P should be investigated.

Acknowledgments We thank the Volkswagen-Stiftung for financial support.

## References

- Azar KE, Laag AE, Pratt PF (1980) Bicarbonate-extractable phosphorus in fresh and composted dairy manure. Soil Sci Soc Am J 44:435-437
- Bowman RA, Cole CV (1978a) Transformation of organic phosphorus substrates in soils as evaluated by NaHCO<sub>3</sub> extraction. Soil Sci 125:49-54
- Bowman RS, Cole CV (1978 b) An exploratory method for fractionation of organic phosphorus from grassland soils. Soil Sci 125:95-101
- Hannapel RJ, Filler WH, Bosma S, Bullock JS (1964a) Phosphorus movement in a calcareous soil: I. Predominance of organic forms of phosphorus in phosphorus movement. Soil Sci 97:350-357

- Hannapel RJ, Filler WH, Fox RH (1964b) Phosphorus movement in a calcareous soil: II. Soil microbial activity and organic phosphorus movement. Soil Sci 97:421-427
- He T, Li SJ (1987) On the fractionation of organic phosphorus in soil by Bowman Cole's method. Acta Pedol Sinica 24:152–159
- Meek BD, Graham LE, Donivan TJ, Mayberry KS (1979) Phosphorus availability in a calcareous soil after high loading rate of animal manure. Soil Sci Soc Am J 43:741-743
- Mo SX, Qian JF, Qian CJ (1991) Studies on phosphorus of organic manure and its reutilization. Acta Pedol Sinica 28:309-316
- Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31-36
- Sah RN, Mikkelsen DS (1986a) Effects of anaerobic decomposition of organic matter on sorption and transformation of phosphate in drained soils. 1. Effects on phosphate sorption. Soil Sci 142:267-274
- Sah RN, Mikkelsen DS (1986b) Effects of anaerobic decomposition of organic matter on sorption and transformation of phosphate in drained soils. 2. Effects on amorphous iron content and phosphate transformation. Soil Sci 142:267-274
- Scherer E, Werner W (1992) Phosphatverfügbarkeit und Phosphatdynamik in Latosolen bei kombinierter Stallmist- und Phosphatdüngung in Abhängigkeit von Plazierungsverfahren. VDLUFA-Schriftenr 35:709-712
- Sun X, Zhang YS (1992) Study on inositol phosphate in organic manure and paddy soils and its effect on rice growth. Acta Pedol Sinica 29:365-369
- Sun X, Zhang YS, Ying QC, Tang CX (1986) Effect of organic manure on soil fertility and crop production. In: Current Progress in Soil Research in People's Republic of China. Jiangsu Sci Tech Press, pp 199–206
- Wild A, Oke OL (1966) Organic phosphate compounds in calcium chloride extracts of soils: Identification and availability to plants. J Soil Sci 17:356-371
- Zhang JH, Tan SW, Liu XY, Hong F (1988) A study on oxidation status and organic phosphorus components of organic substances in soils of different levels of fertility. Chin J Soil Sci 19:60-62
- Zhang YS, Werner W, Sun X (1993) Effect of organic manure on P adsorption and desorption in the paddy soils. Agribiol Res (in press)