Effects of 42-year long-term fertilizer management on soil phosphorus availability, fractionation, adsorption–desorption isotherm and plant uptake in flooded tropical rice

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Pratap Bhattacharyya[*], Amaresh Kumar Nayak, Mohammad Shahid, Rahul Tripathi, Sangita Mohanty, Anjani Kumar, Rajagounder Raja, Bipin Bihari Panda, Banwari Lal, Priyanka Gautam, Chinmaya Kumar Swain, Koushik Singha Roy, Pradeep Kumar Dash

Division of Crop Production, Central Rice Research Institute, Cuttack 753006, Odisha, India

ARTICLE INFO

ABSTRACT

Soil phosphorus (P) fractionation, adsorption, and desorption isotherm, and rice yield and P uptake were investigated in flooded tropical rice (*Oryza sativa* L.) following 42-year fertilizer and manure application. The treatments included low-input [unfertilized control without N, P, or K (C_0N_0)], farmyard manure (FYM) (C_1N_0), NP (C_0NP), NPK (C_0NPK), FYM + NP (C_1NP), and high-input treatment, FYM + NPK (C_1NPK). Grain yield was increased significantly by 74% over the control under the combined application of FYM + NPK. However, under low- and high-input treatments, yield as well as P uptake was maintained at constant levels for 35 years. During the same period, high yield levels and P uptake were maintained under the C_0NP, C_0NPK, and C_1NPK treatments. These are unique characteristics of a tropical flooded ecosystem, which is a self-sustaining system for rice production. The Fe–P fraction was highest compared to the Ca–P and Al–P fractions after 42 years of fertilizer application and was significantly higher under FYM + NPK treatment. The P adsorption capacity of soil was highest under the low-input treatment and lowest under long-term balanced fertilization (FYM + NPK). In contrast, P desorption capacity was highest under NPK and lowest in the control treatment. Long-term balanced fertilization in the form of FYM + NPK for 42 years lowered the bonding energy and adsorption capacity for P in soil but increased its desorption potential, increasing P availability to the plant and leading to higher P uptake and yield maintenance.

1. Introduction

Long-term experiments provide a means of evaluating sustainable management systems in agriculture [1]. Several long-term fertilizer experiments have been conducted to quantify changes in major and trace elements in soils [2]. Phosphorus (P) deficiency is a universal constraint to crop production and constitutes the second most important soil

fertility problem throughout the world [3]. Crop yields are often limited by low P availability in soils, owing mainly to adsorption and precipitation reactions of both indigenous soil P and applied fertilizer P with iron (Fe), aluminum (Al), or calcium (Ca) [4]. Low P uptake efficiency of plants is associated primarily with limited P availability in native soil. Consequently, large amounts of expensive inorganic P fertilizers need to be applied to many agricultural soils to attain reasonable crop yields [5]. Application of organic matter to soil increases P solubility, decreases P fixation, and thus improves P availability to plants [4].

Several additive mechanisms may be involved, including the release of inorganic P from decaying residues, blockage of P sorption sites by organic molecules released from the residues, regulation of soil pH, and complexation of soluble Al and Fe by organic molecules [6]. The adsorption behavior of P in a soil system can be determined by analysis of the adsorption data for various isotherms using equations such as the Langmuir and Freundlich equations. The P concentration in soil depends on P adsorption on the surface of soil colloids. The P availability in soil depends on the degree of P adsorption on soil colloids [7,8].

The interaction of N with P is the single most important nutrient interaction [9]. When P input from fertilizer exceeds P output in crop, P accumulates in soil over time [10]. The information obtained from P fractionation schemes has been used to estimate the fate of applied P and the relationship between forms of P and plant P nutrition [11]. Thus, for developing long-term P management strategies, it is important to ascertain the forms and characteristics of P remaining in the soil after repeated fertilizer P application in an agroecosystem.

Soil inorganic P (Pi) represents the dominant component in the soil P pool, accounting for about 75–85% of soil total P [12]. Soil Pi is represented as various fractions such as Ca–P (HCl-extractable P), Fe- and Al–P (non-occluded Fe- and Al-bound P) and O–P (P occluded within Fe oxides) [13]. Sequential Pi fractionation distinguishing labile (resin-extractable P and NaHCO$_3$-extractable P) and more stable forms (Ca–P, Al–P, Fe–P, and O–P) of Pi has been established [14]. Ca–P is generally not fractionated further into subfractions because the Ca–P fraction in non-calcareous soils is rather small [15].

However, in calcareous soils, most Pi is present in various Ca-bound forms and there are great differences in P availability among these Ca–P fractions. Huang et al [16] investigated the soil P dynamics in paddy soils in a one-season field experiment. In contrast, information about the dynamics of soil Pi fractions and P transformation under long-term fertilization in relation to adsorption and desorption isotherms is sparse. The objectives of the present study were (1) to investigate the yield and P uptake of rice in response to long-term fertilization, (2) to investigate long-term fertilization effects on soil P fractions, and (3) to evaluate P adsorption and desorption isotherms in flooded rice soil after long-term fertilizations.

2. Materials and methods

2.1. Experimental site

A long-term fertilizer experiment has been continuing since 1969, involving a rice–rice cropping system in tropical Aeric Endoaquept soil on the experimental farm of the Central Rice Research Institute, Cuttack. The site is located in the alluvial tract of the Mahanadi basin at 20°25′ N and 85°55′ E at an altitude of 24 m.a.s.l. in eastern India. The climate is tropical with mean annual precipitation around 1500 mm and the predominant rainfall occurs from June to September. The soil is sandy clay loam (30.9% clay, 16.6% silt, 52.5% sand) with bulk density 1.41 Mg m^{-3}, pH (using 1:2.5, soil:water suspension) 6.6, total C 0.78%, and total N 0.08%. The cation exchange capacity is 15.2 cmol (P+) kg^{-1} and the available P content of the initial soil was 13 mg kg^{-1}.

2.2. Crop establishment and treatments

The field experiment was conducted for 42 years (there was no crop in the dry season during 1984–1993) under rice–rice cultivation and the six treatments under the study were replicated three times in a randomized block design. The field was plowed thoroughly and flooded for puddling and leveling 2–3 days before transplanting. Rice seedlings around 25 days old were transplanted at a spacing of 20 cm × 15 cm with two to three seedlings per hill in both wet (July–December) and dry (January–April) seasons. Farmyard manure was applied to the field once yearly during wet season at 5 t ha^{-1}. The total C and P content in the FYM was 245 g kg^{-1} and 3.7 g kg^{-1}, respectively. Nitrogen was applied in the form of 50% urea as basal and the rest in two equal splits as topdressing after transplanting. Topdressing with N fertilizer (urea) was performed at maximum tillering and panicle initiation stage of crop growth in both wet and dry seasons. The full doses of P and K were applied as basal just before transplanting in the form of single superphosphate and muriate of potash (KCl). All the field plots remained continuously flooded to a depth of 7 ± 3 cm during the entire period of crop growth and were drained 10 days before harvest. The crop was cultivated according to local recommended agronomic practices except for the fertilization, which was performed as described for the treatments. The treatments were as follows:

(a) Control (with no fertilizers or organic manures) (C$_0$N$_0$)
(b) FYM (5 t ha^{-1} applied only in wet season) (C$_1$N$_0$).
(c) N + P (60 kg N ha^{-1} in wet season; 80 kg N ha^{-1} in dry season and 30 kg P$_2$O$_5$ ha^{-1} in wet season; 40 kg P$_2$O$_5$ ha^{-1} in dry season) (C$_0$NP)
(d) NPK (60 kg N ha^{-1} in wet season; 80 kg N ha^{-1} in dry season; 30 kg P$_2$O$_5$ ha^{-1} in wet season; 40 kg P$_2$O$_5$ ha^{-1} in dry season and 30 kg K$_2$O ha^{-1} in wet season; 40 kg K$_2$O ha^{-1} in dry season) (C$_0$NPK)
(e) FYM + NP (5 t ha^{-1} + 60 kg N ha^{-1} in wet season; 80 kg N ha^{-1} in dry season and 30 kg P$_2$O$_5$ ha^{-1} in wet season; 40 kg P$_2$O$_5$ ha^{-1} in dry season) (C$_1$NP).
(f) FYM + NPK (5 t ha^{-1} + 60 kg N ha^{-1} in wet season; 80 kg N ha^{-1} in dry season; 30 kg P$_2$O$_5$ ha^{-1} in wet season; 40 kg P$_2$O$_5$ ha^{-1} in dry season and 30 kg K$_2$O ha^{-1} in wet season; 40 kg K$_2$O ha^{-1} in dry season) (C$_1$NPK).

2.3. Soil sampling and storage

Soil samples were collected in three replications with an auger (at a depth of 0–15 cm) in both wet and dry seasons

during 1969–2013. The soil samples collected after harvest in the wet season in the respective years were used for the study. The soils were air dried, sieved through a 2 mm sieve, and stored in sealed plastic jars for analysis.

2.4. Phosphorus adsorption

Soil samples were equilibrated with graded P levels (0, 2.5, 5.0, 10, 20, 30, 40, and 50 μg P g^{-1}) in 0.01 mol L^{-1} CaCl$_2$ solution using a soil solution ratio of 1:10. Centrifuge tubes containing the soil suspension were equilibrated for 6 days at room temperature following Singh and Jones [17]. Two drops of toluene were added to each tube to minimize microbial activity. The samples were then centrifuged at 2500 r min^{-1} for 10 min, and the P concentration was measured in the supernatant solution by the ascorbic acid method [18] on a spectrophotometer. The sorbed P was calculated as the difference between the amount of P added and that remaining in the equilibrium soil solution using the relationship

$$\frac{x}{m} \text{ or } S = \frac{VC_0}{g} \times \left(1 - \frac{C_e}{C_0}\right) \qquad (1)$$

where x/m or S denotes the amount of P adsorbed (μg P g^{-1} soil), V the volume of equilibrium solution (mL), C_0 the original concentration of P in solution (μg P mL^{-1}), C_e the equilibrium concentration of P in solution (μg P mL^{-1}) and g the mass of the soil sample (g). The residual soil was retained for desorption studies. Adsorption data were analyzed using
   (A) Langmuir equation:

$$\frac{C}{S} = \frac{1}{(k.b)} + \frac{C}{b} \qquad (2)$$

where S denotes μg P adsorbed g^{-1} soil, C the equilibrium P concentration (μg P mL^{-1}), b the Langmuir adsorption maximum (μg P g^{-1} soil) and k the Langmuir bonding energy constant (mL μg^{-1}). A plot of C/S versus C gives a straight line. The constants k and b were obtained from the intercept and slope, respectively.
   (B) Freundlich equation:

$$X = aC^{\frac{1}{n}} \qquad (3)$$

where X denotes μg P adsorbed g^{-1} soil, C the equilibrium P concentration (μg P mL^{-1}), a the extent of P adsorption (μg P g^{-1} soil) and n a constant corresponding to the degree of linearity between the solution equilibrium concentration and adsorption (g mL^{-1}). A linear plot of $\log_{10} X$ versus $\log_{10} C$ yields a and n from the intercept and slope, respectively. Differential and maximum buffering capacities were computed from the change in the quantity of P adsorbed by soil due to the change in the concentration of P in the soil solution using the relationship given by Holford and Mattingly [19].

2.5. Phosphorus desorption

The residual soils obtained from the adsorption studies were shaken with 25 mL of 0.01 mol L^{-1} CaCl$_2$ solution for 6 h on a horizontal shaker [17] and filtered through Whatman No. 1 filter paper. The equilibrium P concentration in the solution, desorbed P, was determined by the ascorbic acid method [18].

Phosphorus retained in soil (pre-sorbed P) was determined as the difference between initial sorbed P and P in the desorption equilibrium solution.

2.6. Soil P, Brays' P, uptake, and P fractionation

Soluble soil P was determined using the Olsen P method [20], based on extraction of air-dry soil with 0.5 mol L^{-1} NaHCO$_3$ at pH 8.5. Uptake of P in shoot, root, and in grain was calculated as P uptake (shoot / grain) = (P concentration in shoot / grain) × biomass. The method of Chang and Jackson [21] is widely used for estimation of soil P. Phosphorus fractionation was determined following Murphy and Riley [22]. Briefly, the Al–P fraction in a soil sample (1 g) was extracted with 50 mL of 1 mol L^{-1} NH$_4$Cl and 0.5 mol L^{-1} NH$_4$F followed by washing with saturated NaCl. Then the solution was treated with 50 mL 0.1 mol L^{-1} NaOH to yield the Fe–P fraction. The soluble P was obtained by treating the solution with 40 mL 0.3 mol L^{-1} Na$_3$C$_3$H$_6$O$_7$, 5 mL 1 mol L^{-1} NaHCO$_3$, and 1 g Na$_2$SO$_4$. The Ca–P fraction was obtained by treating the solution with 50 mL 0.25 mol L^{-1} H$_2$SO$_4$ with shaking for 1 h. The Bray's P was determined by extracting soils with 0.03 mol L^{-1} NH$_4$F in 0.025 mol L^{-1} HCl followed by spectrophotometric estimation [23].

2.7. Statistical analysis

Individual character datasets were subjected to analysis of variance and means were separated by Tukey–Kramer's HSD test at the 0.05 level of probability using the statistical software SPSS 20.0 (Statistical Package for Social Science; M/s IBM, USA).

3. Results and discussion

3.1. Grain yield and P uptake

Grain yield varied under different treatments of long-term fertilizer applications in comparison to that of the control in both wet (1969–2011) and dry (1970–2010) seasons (Fig. 1). The trend of grain yield was in the order $C_1NPK > C_1NP > C_0NPK > C_0NP > C_1N_0 > C_0N_0$ in both seasons (Fig. 1). The yield was higher in the dry than in the wet season (Fig. 1). In the wet season the grain yield was in the ranges 3.18–5.78, 4.30–5.74, 3.77–5.46, 3.42–5.81, 2.57–3.48, and 1.83–3.80 t ha^{-1} under the treatments C_1NPK, C_1NP, C_0NPK, C_0NP, C_1N_0, and C_0N_0, respectively (Fig. 1-a). In the dry season the grain yield was in the ranges 2.71–5.85, 2.12–6.15, 2.08–5.01, 2.32–4.13, 1.40–4.92, and 1.03–4.04 t ha^{-1} under the same treatments (Fig. 1-b). The highest yield was found under the treatment C_1NPK and varied over the ranges 2.70–6.42 and 4.47–5.99 t ha^{-1} in the wet and dry seasons, respectively (Fig. 1). There was a reduction in the yield in the year 1999 owing to a tropical cyclone that damaged the crop and incurred a severe loss in grain yield. In the wet season, there was a jump in grain yield in 1984, 15 years after the initiation of the experiment because of the introduction of the high-yielding varieties Savitri, Pusa 2-21, IR 36, and Ratna to replace the varieties IR 8, Supriya, and Bala.
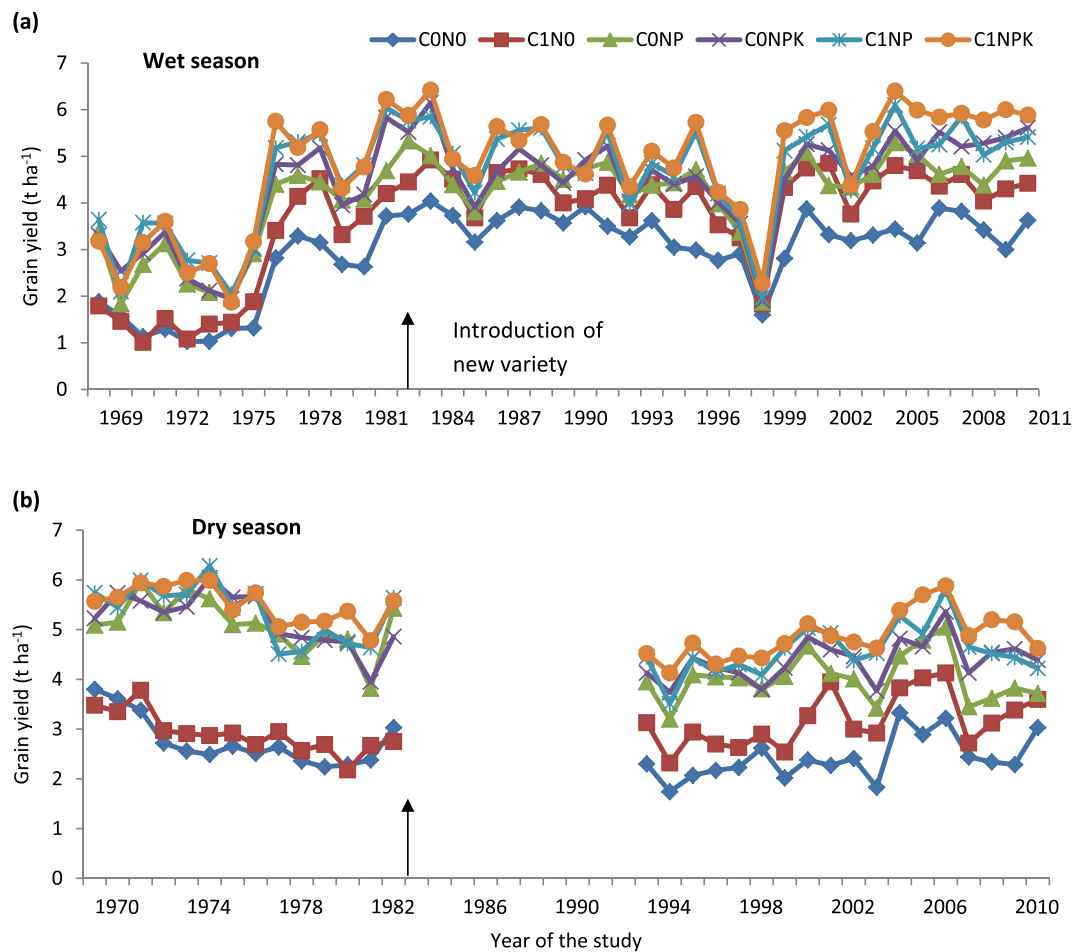
Fig. 1 – Temporal variation in grain yield (t ha^{-1}) in (a) wet season (1969–2011) and (b) dry season (1970–2010) under six long-term fertilizer treatments. The arrow indicates the introduction of new high-yielding varieties. Arrow in Fig. 1-b indicates introduction of new variety.

P uptake varied under different treatments in both wet seasons of 1969–2011 and dry seasons of 1970–2010 (Fig. 2). Grain P uptake also varied in both seasons, irrespective of treatment (Fig. 2). A positive trend in P uptake under the C_0NP, C_0NPK, and C_1NPK treatments was found but was not significant year wise. In contrast, no trend was found in the low-input treatments C_0N_0 and C_1N_0. Grain P uptake varied in the ranges 2.9–12.2, 2.9–16.3, 6.0–17.2, 5.7–20, 5.8–19.2, and 5.2–20.8 kg ha^{-1} under the treatments C_0N_0, C_1N_0, C_0NP, C_0NPK, C_1NP, and C_1NPK, respectively, during the wet seasons of 1969–2009 (Fig. 2-a). During the dry seasons of 1970–2009, grain P uptake was 4.8–7.1, 4.3–9.9, 9.1–15.2, 8.2–16.2, 9.7–15.4, and 9.5–16.9 kg ha^{-1} under the same treatments (Fig. 2-b). P uptake was highest under C_1NPK in both wet and dry seasons.

The yield response to P fertilization suggests the importance of long-term fertilizer experiments to study the potential of soil nutrient supply capacity. In the present study, grain yield was significantly higher under the C_1NPK treatment than under the other treatments. Similar trends were reported by Dawe et al. [24] and Ladha et al. [25] in a rice–wheat cropping system. In a rice–rice cropping system, a yield increase under C_1NPK was also reported by Hafele et al. [26]. Indigenous nutrient supply, particularly of P and K, showed

important effects on rice yields and fertilizer recovery rates in irrigated rice systems [27]. The carbon contents under the C_0N_0, C_1N_0, C_0NP, C_0NPK, C_1NP, and C_1NPK treatments were 6.3, 7.1, 7.5, 7.9, 7.3, and 9.3 g kg^{-1}, respectively. The N contents were 154, 218, 227, 225, 206, and 245 kg ha^{-1} under these six treatments. The higher carbon and nitrogen content under C_1NPK treatment led to increased microbial growth and higher yield in these treatments. Our long-term rice–rice system is self-sustaining, as it has the potential to store large amounts of carbon under flooded conditions as well as maintaining sustained yield over the years [28–30]. We found that the grain yield under the C_1N_0 treatment was lower than that under the other treatments except for the control. FYM applied in the wet season at the rate of 5 t ha^{-1} was applied as a supplementary dose that was lower than the full dose of NPK applied in other treatments. This low input led to a reduction in grain yield compared to that under the other treatments.

Grain yield and P uptake were higher under the C_0NP, C_0NPK, and C_1NPK treatments than under the low-fertilizer input treatments (C_0N_0 and C_1N_0). There were significant differences in yield and uptake under C_0N_0, C_1N_0 compared to the C_0NP, C_0NPK, and C_1NPK treatments. Under both low- and high-input treatments, yield and P uptake were maintained for 35 years.
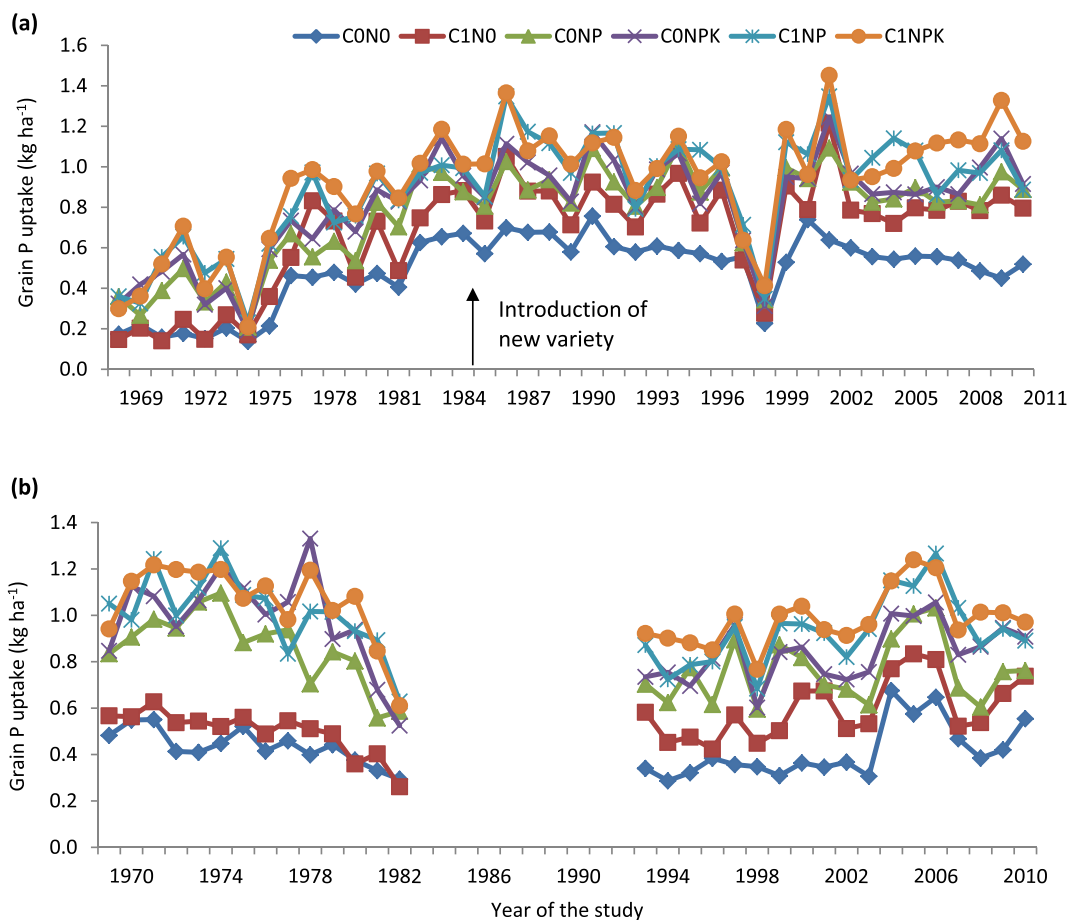
Fig. 2 – Temporal variation in grain P uptake (kg ha^{-1}) in (a) wet season (1969–2011) and (b) dry season (1970–2010) under six long-term fertilizer treatments. Arrow in Fig. 2-a indicates introduction of a new variety.

This result indicates that a low level of grain yield and P uptake in the control was sustained for three decades. High yield and P uptake levels (in the C_0NP, C_0NPK, and C_1NPK treatments) were maintained during the same time. This maintenance of yield and P levels is a unique characteristic of lowland submerged rice ecology in eastern India, and is due to the low rate of decomposition of organic matter in soil and inputs of C and other nutrients in the form of algae, weeds, and plant biomass.

Nitrogen application had a yield-increasing effect compared with the control, and the application of P significantly increased yields of rice compared with the P-omitted treatments. There was no significant effect of K application on rice yields, owing to the high inherent soil K levels in excess of crop K demand at present yield levels, a finding in agreement with those of other studies [27]. The P uptake was significantly higher both in shoot and grain under the C_1NPK treatment. In P-sufficient soils such as that of the present study, application of NPK alone or in combination with FYM led to a higher P uptake level than observed under the other treatments, as also reported by Singh et al. [7].

3.2. Soil available P and fractions of P

Soil available P varied significantly among the treatments during 1969–2009 (Fig. 3). The maximum P content was found

under C_1NPK and varied in the range 13.0–28.2 kg ha^{-1} (Fig. 3). Available P content varied in the ranges 10.3–13.7, 13.0–15.6, 13.0–18.8, 13.0–21.2, 13.0–27.3, and 13.0–28.2 kg ha^{-1} under C_0N_0, C_1N_0, C_0NP, C_0NPK, and C_1NP; respectively (Fig. 3). Soluble P and Brays' P were in the respective ranges 7.0–12.0 mg kg^{-1} and 9.9–33.7 mg kg^{-1} among the treatments and were highest under C_1NPK (Table 1). Three fractions of P were quantified from different treatments: Al–P, Fe–P, and Ca–P. The highest content of fractioned P was found in the form of Fe–P (Table 1). Each P fraction was highest under the C_1NPK treatment and the lowest under the C_0N_0 treatment. The contents of P in different fractions were in the ranges 53–94, 72.1–181, and 51.0–116.5 mg kg^{-1} in the form of Al–P, Fe–P and Ca–P; respectively, among the treatments. The largest amount of fractionated P was found under the C_1NPK treatment, with values of 94, 181, and 117 mg kg^{-1} for Al–P, Fe–P, and Ca–P, respectively (Table 1).

Fractionation of Pi sheds light on soil Pi availability and Pi interconversion among different fractions and Olsen-P gives an indication of soil P availability [31]. Accordingly, soil Pi has been partitioned into fractions including Ca–P (HCl extractable P), Fe–P, and Al–P. Sequential Pi fractionation for distinguishing labile (resin-extractable P and NaHCO$_3$-extractable P) and more stable forms (Ca–P, Al–P, and Fe–P) of Pi has been established [14]. In this study, among all soil P fractions, Fe–P was highest in all the
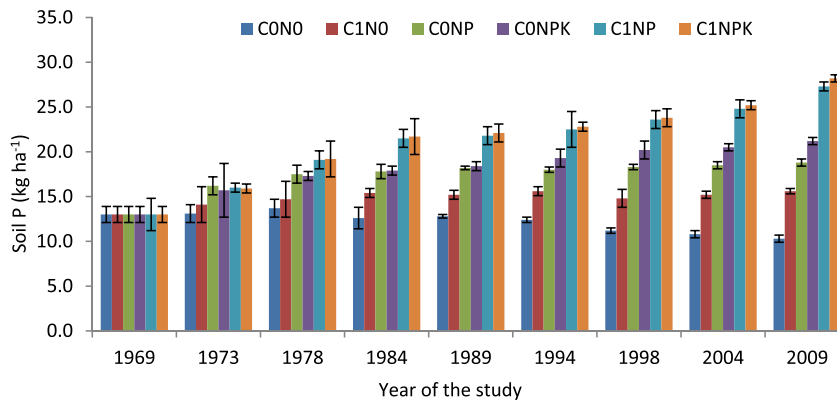
Fig. 3 – Temporal variation in soil P content (kg ha⁻¹) under different long-term fertilizer treatments in the year 1969–2009.

treatments. Among the six long-term treatments, where P fertilizers were applied for 42 years along with FYM and K, P fractions followed the trend Fe–P > Ca–P > Al–P. However, the application of P fertilizer along with NK and organic manure favors the fixation of P equally in Fe and Ca sites in soil at nearly neutral pH (6.6) under flooded conditions. In contrast, where P fertilizer was not applied or was applied only with N, P fractions followed the trend Fe–P > Al–P > Ca–P. This difference may represent the promotion of soil acidification by N fertilization even in flooded soil, perhaps favoring the Al–P over the Ca–P fraction under the N and NP treatments. In the present study, the Pi fractions in the form of Ca–P, Fe–P, and Al–P were at the highest levels in the C_1NPK treatment. Schmidt et al. [32] reported that fertilizer P and manure applied annually for many years resulted in accumulation of inorganic P and organic P fractions in soil. Comparing the treatments with and without P application at 0–15 cm depth, the increase in Fe–Pi concentrations was greater than that in Al–Pi concentrations. This difference was due to the NaOH-extractable inorganic P that served as a primary sink for fertilizer P added to tropical soil and was also observed for continuous fertilization of soils with fertilizer P for 9 or more years under some cropping systems [33]. Under the NPK treatment, plant P uptake resulted in a marked decrease in available soil P with time, possibly enhancing P release from sparingly soluble P forms because of a change in the balance between available P and sparingly soluble P [34]. Phosphorus is an important plant nutrient needed for realizing optimum yields in agroecosystems including rice–wheat [35] and rice–rice. In most lowland rice soils, P availability initially increases on flooding [36], and rice may meet its P requirement from the residual P applied in the preceding season of cultivation. Drainage following submergence induces P deficiency, owing mainly to changes in the inorganic fractions [37]. The availability of native P depends on the degree of reduction of soil, as rice grows under waterlogged conditions [35].

3.3. Phosphorus adsorption

The results indicated that the amount of P sorbed was higher under C_0N_0 than under the other long-term fertilizer treatments (Fig. 4). The long-term fertilizer experiment soils varied with respect to P adsorption behavior. Phosphorus adsorption data for different long-term fertilized soils were fitted to the Langmuir (R^2: 0.970–0.988) and Freundlich equations (R^2: 0.933–0.983) (Table 2). The Langmuir P adsorption maxima (b) and bonding energy constant (k) showed a wide variation among treatments (Table 2). The values of the adsorption maxima, which are measures of the P adsorption capacities of soil, were highest under the C_0N_0 treatment (8.19 μg P g⁻¹), decreased with levels of P applied, and were lowest (3.02 μg P g⁻¹) under C_1NPK. Bonding energy, which is a measure of resistance to P release in soils, varied from 0.320 to 0.560 mL μg⁻¹ (Table 2). The Freundlich constants a and n also showed wide variability in the different long-term fertilizer treated soils (Table 2). The constant a, which is a measure of the extent of P adsorption at

| Table 1 – Effect of long-term use of inorganic fertilizers and farmyard manure on soluble-P, Brays' P, and different soil P fractions.					
Treatment	Soluble P (mg kg⁻¹)	Bray-P (mg kg⁻¹)	Al–P (mg kg⁻¹)	Fe–P (mg kg⁻¹)	Ca–P (mg kg⁻¹)
C_0N_0	7.0 a	9.9 a	53.0 a	72.1 a	51.0 a
C_1N_0	7.1 a	18.8 b	75.0 b	104.5 c	62.5 b
C_0NP	10.5 c	18.3 b	86.0 c	93.5 b	84.0 c
C_0NPK	9.5 b	22.7 c	76.1 b	114.1 c	87.0 c
C_1NP	10.5 c	33.7 d	86.5 cd	169.5 d	99.5 d
C_1NPK	12.0 d	33.2 d	94.0 d	181.0 e	116.5 e
LSD (P < 0.05)	0.50	0.39	5.01	6.7	6.1
In each column, means followed by common letters are not significantly (P < 0.05) different by Tukey's-HSD test.					
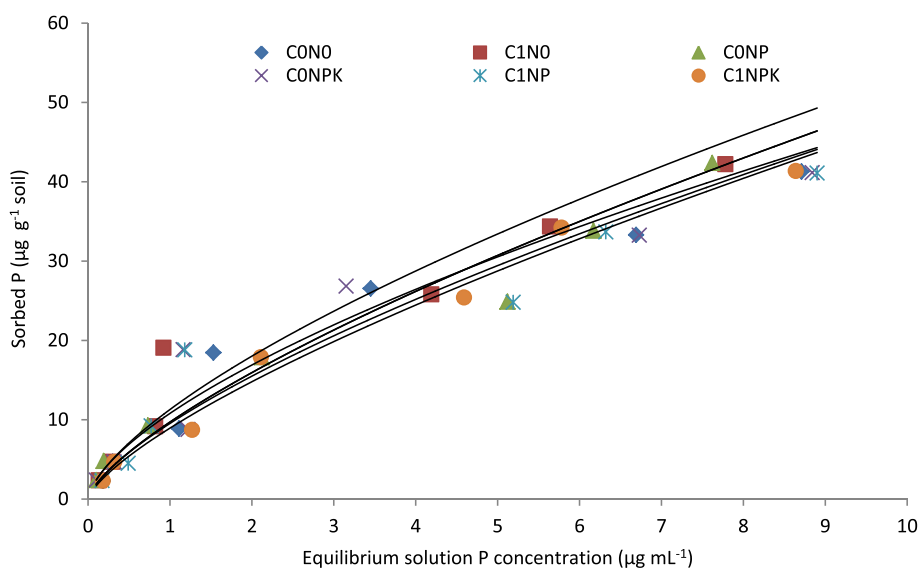
Fig. 4 – Phosphorus adsorption at different P substrate concentrations under different long-term fertilizer treatments over 40 years of study.

the unit equilibrium concentration, ranged from 8.93 to 10.16 $\mu g\ g^{-1}$ soil. The n values were highest (0.725 g mL^{-1}) under C_1NPK and lowest (0.674 g mL^{-1}) under C_1N_0 (Table 2).

The flux of P from the soil as well as the amount and type of water-soluble P sources applied to plant roots determine the bioavailability of P to growing plants. The intensity factor, the measure of P concentration in soil solution, is one of the major factors that governs this flux and is associated with P adsorption on the surface of soil colloids. Thus, P reactions and its retention in soil have important implications to plant growth and fertilizer use efficiency [38]. The extent of adsorption is one of the important factors in P supply capacity of soil [7] and in fertilizer recommendations [8]. The adsorption behavior of P in a soil system can be determined by analysis of adsorption data for various isotherms using equations such as the Langmuir, Freundlich, Brunauer–Emett–Teller (BET), and Temkin equations [8]. These analyses give an idea of the adsorption capacity as well as the energy with which the nutrient is retained in the soil system. The amount of P adsorbed was higher under C_0N_0 than under the other treatments. Higher adsorption in C_0N_0 compared to rest of the treatments were ascribed to the presence of more exchange sites because of the 42-year stress on the soil P

reserves for meeting crop requirements. The Olsen P content of C_0N_0 was also lower than that of the fertilized soils, resulted in higher adsorption of P in C_0N_0 soil [39]. The NPK treatment either alone or in combination with FYM showed lower adsorbed P than the other treatments. Thus, an increase in the rates of long-term P fertilization led to marked reduction in P adsorption. Sharma et al. [40] also reported reduced P adsorption under continuous application of P during 11 cycles of maize–wheat crop rotation. It is interesting to note that P adsorption was lowest under the C_1NPK treatment. This observation could be due to a relatively large amount of residual P in C_1NPK [39]. The application of FYM played a key role in keeping the applied P in a more available form and, consequently, in reducing P adsorption. Organic acid anions released during the decomposition of FYM accumulate in the rhizosphere and compete with orthophosphates for adsorption sites, thereby making more P available and decreasing P adsorption [41].

3.4. Phosphorus desorption

The practical reliability of using adsorption isotherms is questionable if this is not compared with the P desorption

Table 2 – Effect of long-term use of inorganic fertilizers and farmyard manure on adsorption (Langmuir and Freundlich) constants.

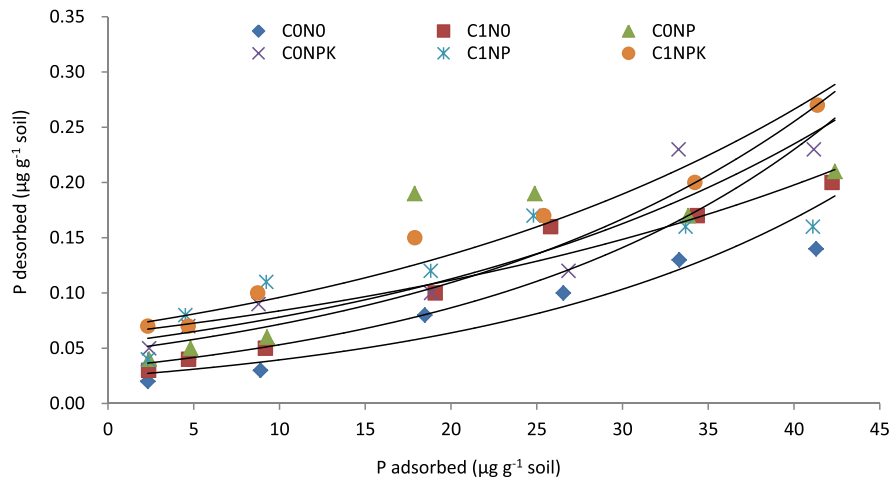| Treatment	Langmuir parameters			Freundlich parameters		
	b ($\mu g\ g^{-1}$)	k (mL μg^{-1})	R^2	a ($\mu g\ g^{-1}$)	n (g mL^{-1})	R^2
C_0N_0	8.19	0.560	0.987	10.16	0.682	0.974
C_1N_0	5.74	0.421	0.988	11.27	0.674	0.941
C_0NP	5.52	0.390	0.984	10.00	0.678	0.972
C_1NP	4.71	0.356	0.982	10.13	0.694	0.936
C_0NPK	3.10	0.320	0.970	9.46	0.703	0.933
C_1NPK	3.02	0.338	0.981	8.93	0.725	0.983

Fig. 5 – Phosphorus desorption at different P substrate concentrations under different long-term fertilizer treatments in 40 years of study.

behavior of the soils. The degree of reversibility of the adsorption–desorption reaction cannot be ignored. The relationships between P adsorption and desorption in the long-term experiment soils under investigation are presented in Fig. 5. It is evident that only a fraction of the sorbed P was desorbed. The results showed that during the past 42 years, the quantity of P desorbed was far less under the C_0N_0 than under the C_1NPK treatment. The higher P desorption under NPK alone compared to that under FYM alone at higher P concentration may have be due to higher organic molecule-P complexes with FYM. The soils that adsorbed a high proportion of applied P during the adsorption reaction tended to release a lower proportion during the desorption reaction, and vice versa.

There is, however, a disagreement [42] as to whether or not adsorption–desorption reactions are reversible. If they are irreversible or partially reversible, the indication of the replenishing ability of soils by the P adsorption isotherms may be misleading. Distinct hysteresis in adsorption–desorption behavior of the long-term experiment soils suggests that overestimation of the adsorption–desorption reaction is unavoidable when the P adsorption isotherm is used to estimate the P-supplying ability of the soils to crops. Raven and Hossner [43] observed hysteresis in P adsorption and desorption processes in soils. In addition, the possibility of precipitation of the added P as sparingly soluble P compounds must not be overlooked. These results revealed that the amount of desorbed P was far less than that of adsorbed P and was of a relatively high order in the treatment C_1NPK. Also, P desorption increased with an increase in added fertilizer P. The results explicitly indicate that the adsorption and desorption of applied P are inversely related and that soils that adsorb P the most readily release it the least readily into the soil solution. Thus, the plots receiving continuous P additions had higher potential to release P to meet the P requirements of the subsequent crops. These results indicate that the continuous addition of higher P doses and FYM decreased resistance to P release and thus increased the P supply in the soil.

4. Conclusion

Long-term balanced fertilization lowers the bonding energy and adsorption capacity for P in soil as well as increasing its desorption potential. This process in turn increases P availability to plants and leads to increased P uptake and yield sustainability. There is a future scope to quantify soil organic P pools in addition to inorganic fractions. There is also a scope for introduction of P-responsive rice varieties in this region that exploit the native soil P effectively, not only maintaining yield at higher levels but reducing the cost of external fertilizer application.

Acknowledgments

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