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## Responses of total, reactive and dissolved phosphorus pools and crop yields to long-term fertilization

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### ABSTRACT

Maintaining an appropriate soil phosphorus level is key to ensure sustainable phosphorus management for crop production and to minimise phosphorus losses to water bodies. However, the effects of long-term fertilization on different soil phosphorus pools, crop yields and phosphorus loss risk remain unclear. This requires insights into the responses of soil phosphorus pools, crop phosphorus uptake with related crop yields and phosphorus loss to long-term phosphorus inputs. Changes in four soil phosphorus pools ( $P_{\text{CACL}_2}$ ,  $P_{\text{OLSEN}}$ ,  $P_{\text{OX}}$  and  $P_{\text{TOTAL}}$ , respectively) and crop yield responses to various fertilization rates were examined in a 29-year long-term phosphorus fertilization experiment in China. Results showed that the increase in the four soil phosphorus pools was proportional to the accumulated phosphorus surplus, i.e., the input minus uptake.  $P_{\text{OLSEN}}$  and  $P_{\text{OX}}$  increased linearly with continuous phosphorus application and peaked at a phosphorus accumulation near  $3200 \text{ kg P ha}^{-1}$ . Beyond this threshold, continuous phosphorus application caused a gradual increase in  $P_{\text{TOTAL}}$  and a linear increase in  $P_{\text{CACL}_2}$ , which implies an increasing risk for leaching. The  $P_{\text{OX}}$  pool accounted for 87% of the accumulated phosphorus surplus until soil phosphorus saturation occurred. The crop yields of wheat and maize responded clearly to changes in  $P_{\text{TOTAL}}$ ,  $P_{\text{OX}}$ ,  $P_{\text{OLSEN}}$  and  $P_{\text{CACL}_2}$ , with  $P_{\text{OX}}$  explaining most of the yield variation. Furthermore,  $P_{\text{OX}}$  was highly correlated with  $P_{\text{CACL}_2}$ , being a risk indicator for phosphorus leaching. Given that  $P_{\text{OX}}$  explains best how much of phosphorus surplus accumulates in soil, the variation in crop yield, and the risk for P leaching, it can be used as a valuable and reliable indicator to manage phosphorus sustainably.

### 1. Introduction

Phosphorus (P) fertilizers are applied to increase crop yields since P is an essential nutrient for crop production (Langhans et al., 2022). Globally P fertilizer consumption increased by 34.5 million tons (Mt) between 1961 and 2019, producing  $26.3 \text{ Tg P}_2\text{O}_5 \text{ year}^{-1}$  surplus (MacDonald et al., 2011) and aggravated P loss to aquatic life and environment. With the projected increase in food consumption due to the global population growth from 7.8 billion in 2020 to 10.9 billion in 2100 (United Nations, 2019), sustainable P management in agriculture is crucial to maintain or even increase crop yields, while coming below a (global) planetary P boundary for the environment (Carpenter and

Bennett, 2011; Springmann et al., 2018). In addition, reducing P inputs while maintaining crop yields is key to sustainably use the limited available P reserves for food production (Gilbert, 2009; Cordell and White, 2013; Yu et al., 2021). Sustainable P management is particularly important for China, where P input for crop production has increased 13-fold in the last four decades (Liu et al., 2016). Currently, China uses 33% of the global P fertilizer consumption (Zhou et al., 2017), resulting in an annual surplus of more than  $90 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  in croplands (Zhang et al., 2019). Consequently, national average Olsen P ( $P_{\text{OLSEN}}$ ) levels in soil has reached to nearly  $25 \text{ mg kg}^{-1}$ , with increases up to  $60 \text{ mg kg}^{-1}$ , leading to serious water quality threats in those regions by enhanced P runoff (Zhang et al., 2019; Zhou et al., 2021).

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To balance increasing crop production and minimizing P loss to water bodies, soil P levels should ideally stay above a target level needed to enable high crop production and below a critical level to avoid P losses. The target level is defined as the soil P level where crop yield is set at 90–95% of the yield potential and where crops hardly respond to additional P application. The critical level is defined as the soil P level at which the dissolved P concentration increases strongly (a change point), causing enhanced P losses to surface water via leaching and runoff (Li et al., 2011). In this context soil P stands for an available P pool determined by a soil P test. The rationale for sustainable P management is to supply P: (i) in excess of crop P demand when soil P contents are below the target level (build-up), (ii) less than crop P demand when soil P contents are (far) above the target level (mining), while balanced P fertilization (P inputs equal to crop P uptake) is advised at the target level (maintain) assuming that this is sufficient to produce crops with minimal P losses (Bai et al., 2013). The implicit assumption is that the target level P for crop production is below the critical level for soil P causing leaching losses, but this assumption has not been quantified. Therefore, there is a need to identify the target and critical P levels to ensure that the target P level for crop growth is below a critical level for P leaching.

Soil P exists in several forms that can be categorized into pools reflecting its availability to plants or its safety to the environment. Labile P, extracted by calcium chloride ( $P_{\text{CaCl}_2}$ ), is strongly correlated with dissolved reactive P in soil solution (Moody, 2011) and is usually used as an indicator for P leaching. Reactive P pools, extracted with sodium bicarbonate ( $P_{\text{OLSEN}}$ ) or ammonium lactate ( $P_{\text{AL}}$ ), are often applied to monitor the soil P status and to formulate P recommendations to maintain soil fertility and boost crop production (Jordan-Meille et al., 2012; Nawara et al., 2017). The amount of P adsorbed to the soil as well as its maximum sorption capacity are often determined by an ammonium oxalate extraction, where the extractable  $P_{\text{OX}}$  (Oxalate P) represents the total reversibly bound soil P pool buffering the P in soil solution since oxalate emulates organic acids released by plants and microorganisms. Soil total P ( $P_{\text{TOTAL}}$ ), commonly extracted with strong acid, characterizes the total P stock in the soil. Although the soil P test developed by Olsen is often used to predict soil P fertility in China (Battisti et al., 2021), several studies showed that the response of crop yield to  $P_{\text{OLSEN}}$  is limited under mining conditions (McLaren et al., 2014; Johnston et al., 2016). Instead, a combination of  $P_{\text{CaCl}_2}$ ,  $P_{\text{OLSEN}}$  and  $P_{\text{OX}}$  could reflect the soil P redistribution and provides insights into soil P availability (Braun et al., 2022).

Several studies quantified soil P dynamics under controlled lab conditions (e.g., using adsorption and desorption experiments and isotopic tracing) (Frossard et al., 2014; Helfenstein et al., 2018; Braun et al., 2022). However, quantitative insights into soil P response to P addition under field conditions while accounting for soil and crop management measures are limited. Multiple studies have recognized the contribution of long-term soil P accumulation to soil P availability, reflecting the so-called legacy P effect (Jagdeep and Brar, 2022). However, limited information is available on the effect of legacy P on the distribution of P inputs over the soil P pools over time. For example, it is well known that at high soil P inputs,  $P_{\text{OX}}$  reaches a maximum (Schoumans and Chardon, 2015). Model simulations of the long-term effects of P application on P adsorption and P pool transformations also showed that the adsorbed P level peaks at a certain threshold level of accumulated P inputs, and additional inputs beyond that threshold increases the dissolved P concentration and P loss risk due to limited adsorption sites (Yu et al., 2013). Yet it is not clear whether a similar behavior also occurs for  $P_{\text{OLSEN}}$  at the same P accumulation level, although many studies have demonstrated proportional changes of  $P_{\text{OLSEN}}$  to soil P accumulation (Battisti et al., 2021; Cao et al., 2012; Jagdeep and Brar, 2022; Tang et al., 2009). A systematic comparison of the response of soil P pools to long-term fertilization and the corresponding crop response in China is thus needed to determine the adequacy of  $P_{\text{OLSEN}}$  as a soil P test as compared to  $P_{\text{OX}}$  as an indicator for optimizing P input.

In this study, the impact of long-term P inputs on changes in stable, reactive and labile P pools, originating from varying rates of chemical P fertilizers and P manure additions is assessed. The crop yield response to accumulated soil P surplus, which is equal to P input minus P uptake (legacy P) has been evaluated for more than 29 years in a wheat-maize crop rotation system in Qiyang county in China. More specifically, in this study, the impact of long-term P inputs on changes in  $P_{\text{TOTAL}}$ ,  $P_{\text{OX}}$ ,  $P_{\text{OLSEN}}$  and  $P_{\text{CaCl}_2}$  pools and the associated crop yield responses are investigated. The main aims of the study are the assessment of: (i) change in soil P pools and their saturation in response to P surplus, (ii) the linkage between changes in soil P pools and crop yields versus P losses to water, and (iii) the adequacy of  $P_{\text{OX}}$  and  $P_{\text{OLSEN}}$  to evaluate the agronomic yield response as well the potential losses to water.

## 2. Materials and methods

### 2.1. Site description, experimental design and fertilizer treatments

A long-term field experiment was set up in 1990 at the Qiyang Experimental Station (26°45'12", 111°52'32") of the Chinese Academy of Agricultural Sciences, Qiyang, Hunan Province, China (Fig. A1). The experimental field has a non-calcareous, slightly acidic (pH 5.7) heavy clay soil (41% clay content) with an initial low soil P status ( $P_{\text{OLSEN}}$  is 13.9 mg kg<sup>-1</sup>), classified as an upland red soil or Ferralic Cambisol in the FAO classification system (Cai et al., 2014). The cropping system is a continuous rotation of winter wheat and summer maize. Original soil properties before setting the experiment are shown in Table A1. Climate conditions during the experimental period are shown in Fig. A2, which include annual air temperatures and precipitation, and measured CO<sub>2</sub> concentrations retrieved from Mauna Loa Observatory site (Keeling et al., 1976). However, considering the focus on the impact of long-term fertilization on crop and soil P pools, the effect of climate change on inter-annual variations in crop yield was not further investigated as all treatments have the same climatic conditions.

The field experiment was designed as a randomized complete block design with two replicates. The size of each experimental plot was 200 m<sup>2</sup> (20 m × 10 m). Wheat was seeded annually in early November and harvested in early May, while maize was sown in April between wheat strips and harvested in July. No irrigation was applied for both crops, but herbicides and pesticides were used during the growing season as needed.

For this study, six fertilization treatments were selected with various combinations of fertilizer nitrogen (N), P and potassium (K) inputs, applied in organic and/or inorganic forms or combinations of both (Table 1). These include an unfertilized control (CK), a combination of N and P fertilizers (NP), N-P-K fertilizers (NPK), combinations of N-P-K fertilizers with recommended (NPKM) or high doses of pig manure (HNPKM) and only manure (M). The total P input for wheat and maize ranged from 52 to 320 kg P ha<sup>-1</sup> yr<sup>-1</sup>, with fertilizer inputs ranging from 52 to 79 kg P ha<sup>-1</sup> yr<sup>-1</sup>. Mineral fertilizers were applied at a dose of 90–300 kg N ha<sup>-1</sup> and 100 kg K ha<sup>-1</sup> per year. Of the total annual amount of fertilizer input 30% was applied to wheat and 70% to maize. All fertilizers were applied as basal fertilizers prior to seeding. Fertilizers used include urea (N, 46%), superphosphate (P<sub>2</sub>O<sub>5</sub>, 12%) and potassium chloride (K<sub>2</sub>O, 50%), and pig manure. The ratio of mineral fertilizer to manure N was about 7:3. Manure was applied at a dose of 210–315 kg N ha<sup>-1</sup> and 138–198 kg K ha<sup>-1</sup> per year for wheat and maize, respectively (Huang et al., 2021). Crop residues were left on the field and incorporated into the soil during tillage activities. All fields were ploughed twice a year before sowing.

### 2.2. Sampling and measurements

Soil samples were annually collected from the plough layer (0–20 cm) with a 5 cm internal diameter auger, approximately 15 days after the harvest but before the next seeding of wheat. Each soil sample was a

**Table 1**  
Annual application rates of P, N and K by mineral fertilizer and manure at the long-term fertilization site.

Treatments	Annual fertilization rates (1990–2019)								
	P input (kg ha <sup>-1</sup> yr <sup>-1</sup> )			N input (kg ha <sup>-1</sup> yr <sup>-1</sup> )			K input (kg ha <sup>-1</sup> yr <sup>-1</sup> )		
	Fertilizer	Manure	Total	Fertilizer	Manure	Total	Fertilizer	Manure	Total
CK	0	0	0	0	0	0	0	0	0
NP	52	0	52	300	0	300	0	0	0
NPK	52	0	52	300	0	300	100	0	100
NPKM	52	163	215	90	210	300	100	138	238
HNPKM	79	241	320	135	315	450	100	138	238
M	0	227	227	0	300	300	0	198	198

composite of 10 soil cores from the same plots. Fresh soil samples were air-dried, sieved (2.0 mm) and stored for further analysis. Due to the limited availability of historical soil samples, we selected a total of 18 archived soil samples with two replicates (except for reference soil which had only one sample) originating from different treatments over the past 29 years (Table A2). The 18 soil samples were selected to encompass the full variation in P surpluses over the duration of the experiment. Both  $P_{OLSEN}$  and  $P_{TOTAL}$  have been determined yearly.  $P_{OLSEN}$  was determined through soil extraction with 0.5 M  $\text{NaHCO}_3$  adjusting pH to 8.5 (2.5 g soil, 50 mL solution, 25 °C, shaken for 30 mins) followed by colorimetric measurement (Thermo Fisher 3020, Finland) of P using the molybdate-ascorbic acid method.  $P_{TOTAL}$  was determined after oxidative digestion with concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  (Tian et al., 2022).

The soil P contents as well as the amount of amorphous iron ( $\text{Fe}_{OX}$ ) and aluminium oxides ( $\text{Al}_{OX}$ ) of 18 selected samples were measured in 2020. The  $P_{CACL2}$  content was determined by 0.01 M  $\text{CaCl}_2$  extraction (soil: solution is 1:5, 25 °C), shaken for 15 mins followed by the molybdenum blue colorimetric method. Oxalate extractable P, Fe and Al contents were determined via extraction with 0.125 M oxalate-ammonium buffer extraction (Schwertmann, 1964) followed by P analysis via Inductive Coupled Plasma Emission Spectrometer (ICP-OES) (radial ICAP 6300 series, Thermo Scientific).

Annual grain and straw yield of maize and wheat were recorded and presented along with also historical database from the same experiment. Grain and residues were manually harvested, air-dried, weighed, ground and sieved through a 0.15-mm sieve. After digestion by concentrated nitric acid, P concentration was measured by the molybdate-ascorbic acid method. The detailed analytical methods of crop products and residues are described by Jagdeep and Brar (2022).

## 2.3. Data analysis

### 2.3.1. Soil phosphorus change calculations

Over the 29-year duration of the experiment, P uptake, P use efficiency (PUE), P surplus, and the changes in soil P pools were estimated. PUE was calculated as the percentage of total P inputs that the crop has taken up:

$$PUE(\%) = \frac{P_{uptake}}{P_{input}} * 100 \quad (1)$$

where both  $P_{input}$  and  $P_{uptake}$  are the total P input and crop P removal over a 29-year cultivation period (all in kg P ha<sup>-1</sup>).

The accumulated P surplus (kg ha<sup>-1</sup>) was calculated as the total annual input by P fertilizer and manure minus P removal by harvested crop products (both P runoff and leaching were ignored) via:

$$P_{surplus} = \sum_{n=1}^{29} (P_{input} - P_{uptake}) \quad (2)$$

where  $yr$  is the year up to which the accumulated P surplus was calculated;  $P_{input}$  is the amount of P from fertilizer and manure per year;  $P_{uptake}$  is the total crop P removal of the maize and wheat crop (including

both grain and straw, since crop residue removal is practiced) per year (all in kg P ha<sup>-1</sup>).

The changes of soil P pools (kg ha<sup>-1</sup>) extracted with  $\text{CaCl}_2$ ,  $\text{NaHCO}_3$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  were calculated as the difference between the final and initial year of experiment (1990):

$$\Delta P_{pool} = P_{pool,fin} - P_{pool,ini} \quad (3)$$

where  $P_{pool,ini}$  is the initial pool size in the year 1990 and  $P_{pool,fin}$  the final P pool (all in kg P ha<sup>-1</sup>), where the measured P concentration ( $P_{conc}$ , mg kg<sup>-1</sup>) is multiplied by soil depth (0.2 m) and a specific soil bulk density (kg m<sup>-3</sup>) to derive the P pool:

$$P_{pool} = P_{conc} * bulk \ density * soil \ depth * 10^{-2} \quad (4)$$

where  $10^{-2}$  is a unit correction coefficient to express the pool size in kg ha<sup>-1</sup>. The soil bulk density (kg m<sup>-3</sup>) was calculated via a pedotransfer function using measured data for soil organic matter and clay content (De Vries and McLaughlin, 2013).

$$bulk \ density = \frac{1000}{(0.625 + 0.025 * SOM + 0.0015 * clay)} \quad (5)$$

where  $SOM$  is soil organic matter (%) and  $clay$  is clay content (%); soil organic matter was calculated from the measured soil organic carbon content by multiplying with a factor of 2 (Pribyl, 2010).

The relative changes in soil P pools were also calculated as a fraction of the soil P pool in the final year over the initial year:

$$Relative \ change \ of \ P \ pool = \frac{P_{pool,fin}}{P_{pool,ini}} \quad (6)$$

where  $P_{pool,fin}$  represents the P pool value at maximum accumulated P surplus.

The distributions of P over the pools  $P_{CACL2}$ ,  $P_{OLSEN}$ ,  $P_{OX}$  and stable P ( $P_{STABLE}$ , i.e., the difference in total P and  $P_{OX}$ ) were estimated as a ratio of total P, where  $P_{STABLE}$  was calculated as the difference between  $P_{TOTAL}$  and  $P_{OX}$ .

### 2.3.2. Statistical analysis

Significant differences among means were determined by Tukey test ( $P < 0.05$ ). Exponential, linear, and linear-plateau relationships were applied to examine the relationships between P surpluses and changes of the four P pools over 29-year of fertilization for multiple treatments. The relationship between the ratios of soil P pools over total P and P surplus were fitted by polynomial or exponential curves. An asymptotic regression model was fitted for the correlation between yield and soil P levels via:

$$Yield = a + b * \exp(-c * P_{pool}) \quad (7)$$

where  $a$  represents the calculated maximum yield (kg ha<sup>-1</sup>),  $b$  and  $c$  are constants, where  $c$  represents a rate constant and  $b$  represents the difference between  $a$  and the yield level with  $P_{pool}$  being zero;  $P_{pool}$  represents the soil P test with unit mg kg<sup>-1</sup>. The calibrated model constants and the explained variance for each test were evaluated to unravel the

crop response to changes in soil P. We included only observations where elements other than P are not limiting crop growth, and subsequently observations in NP and NPK treatments with pH values below 5 were skipped when doing regression between crop yield and soil P pools due to the effect of low soil pH on crop yield reductions (Zhu et al., 2020). All statistical analyses were performed in R (version 3.6.1).

### 3. Results

#### 3.1. Effects of long-term fertilization on crop P uptake, P surplus and total soil P stocks

Maize and wheat yields responded positively to P inputs. The annual average crop yield ranged from 227 to 5854 kg ha<sup>-1</sup> for maize and from 327 to 1576 kg ha<sup>-1</sup> for wheat, with the lowest crop yields observed in the unfertilized plots the highest yields found in the NPKM and HNPKM treatments receiving the highest N, P and K doses (Table A3). Compared with the non-fertilized (CK) treatment, the crop yield has increased on average 6- to 26-fold for maize and 2- to 5-fold for wheat under increasing fertilization. The NP treatment had the lowest increase while the HNPKM treatment recorded the biggest increase (Table A3). Compared with the NPK treatment, combined applications of manure and mineral fertilizers (NPKM and HNPKM) roughly doubled crop yields. The total P uptake over the 29 years varied among treatments and ranged from 96 kg P ha<sup>-1</sup> in the unfertilized plots up to 1282 kg P ha<sup>-1</sup> in the HNPKM treatment (Table 2). With an average P uptake of 450 kg P ha<sup>-1</sup> in the NPK treatments, adding manure further enhanced P uptake with an extra removal of 550 kg P ha<sup>-1</sup> in the NPKM treatment and with another extra 182 kg P ha<sup>-1</sup> in the HNPKM treatment (Table 2). The highest crop P uptake was achieved in HNPKM treatment, corresponding to the highest P supply. However, the PUE in the HNPKM treatment (14%) was less than half of that in the NPK treatment (30%). An unexplainable abrupt decrease in annual crop P uptake was observed after 6-year P fertilization in 1997 (Fig. A3) except for the unfertilized control (CK) plot. Except for the control plot, an increase in accumulated soil P surplus was observed in other treatments over the 29 years of experiment as P inputs were higher than the accumulated crop uptake. As determined by the change in P<sub>TOTAL</sub>, among the treatments, the total P accumulation in the soil was greatest in HNPKM, with 5274 kg P ha<sup>-1</sup> accumulation. Furthermore, the build-up of P was positively correlated with the annual P dose given (Fig. A4). There was an accumulated decline in total P of 24 kg P ha<sup>-1</sup> in the CK treatment. Part of the added P was lost from the topsoil (Table 2), particularly when the accumulated P surplus exceeded the 3200 kg P ha<sup>-1</sup> (Fig. 1a).

#### 3.2. Effects of long-term fertilization on soil P pools

Long-term P accumulation significantly increased the size of soil P

**Table 2**

Soil accumulated P surplus (29 years) and use efficiency in the topsoil of 0–20 cm among different treatments in Qiyang long-term experiment.

Treatment	P input	P uptake	PUE <sup>a</sup>	P surplus	P stock change <sup>b</sup>	P losses (leaching, runoff, erosion) <sup>c</sup>
	kg P ha <sup>-1</sup>		%		kg P ha <sup>-1</sup>	
CK	0	96	-	-96	-24	-72
NP	1519	274	18	1246	843	403
NPK	1519	450	30	1070	1072	-2
NPKM	6101	1100	18	5001	2655	2346
HNPKM	9152	1282	14	7870	5274	2596
M	4266	875	21	3391	2256	1135

<sup>a</sup> P use efficiency

<sup>b</sup> the difference with the initial soil P stock

<sup>c</sup> the difference between changes of P<sub>TOTAL</sub> and accumulated soil P surplus

pools, which peaked in all reactive P pools during the experiment (Fig. 1). Both P<sub>OX</sub> and P<sub>OLSEN</sub> first increased linearly with the accumulated P surplus up to a given threshold after which the pools were stabilized. The P<sub>OLSEN</sub> pool was increased 13-fold, from 38 to 493 kg P ha<sup>-1</sup>, with the maximum value reached at a P surplus around 3200 kg P ha<sup>-1</sup>. With the same trend with P<sub>OLSEN</sub>, P<sub>OX</sub> was increased 10-fold to a maximum of about 2850 kg P ha<sup>-1</sup> and remained constant at an accumulated P surplus around 3200 kg P ha<sup>-1</sup>. Compared with the unfertilized plot, the relative increase in P<sub>OX</sub> per unit soil P surplus was lower than that of P<sub>OLSEN</sub>, while the plant available P<sub>CACL2</sub> pool had the largest relative change, increasing from < 1 to 14.8 kg P ha<sup>-1</sup> after 29 years of P fertilization (Fig. A5). Total P retention also diminished from around 3200 kg P ha<sup>-1</sup> due to the saturation of P<sub>OX</sub> and P<sub>OLSEN</sub>. Beyond this P surplus level, P<sub>TOTAL</sub> continued to increase at a lower rate (Fig. 1a) suggesting higher P losses to water. However, this was only partly reflected in P<sub>CACL2</sub> as this pool linearly increased with the P surplus (Fig. 1d).

The redistribution of the added P over the soil P pools is given in Fig. 2. Adding P resulted in a steep increase in the relative contribution of P<sub>OX</sub> and P<sub>OLSEN</sub> to P<sub>TOTAL</sub> up to an accumulated P surplus around 3200 kg P ha<sup>-1</sup>. Initially, 78% of the P<sub>TOTAL</sub> pool was in stable forms, 22% in slowly reactive forms (P<sub>OX</sub>), of which 3% was in fast reactive form (P<sub>OLSEN</sub>) and < 0.1% in labile form (P<sub>CACL2</sub>). After a long-term P accumulation following over-fertilization, most of the soil P was in reactive forms where P<sub>OX</sub> increased up to 61%, P<sub>OLSEN</sub> up to 10% and P<sub>CACL2</sub> up to 0.4%. Once the reactive P pools became saturated, adding P above the saturation point increased P<sub>STABLE</sub> fraction, thus decreasing the P fraction that is available for crop uptake (though the pool size itself is not limiting crop growth) while P<sub>CACL2</sub> continuously increased.

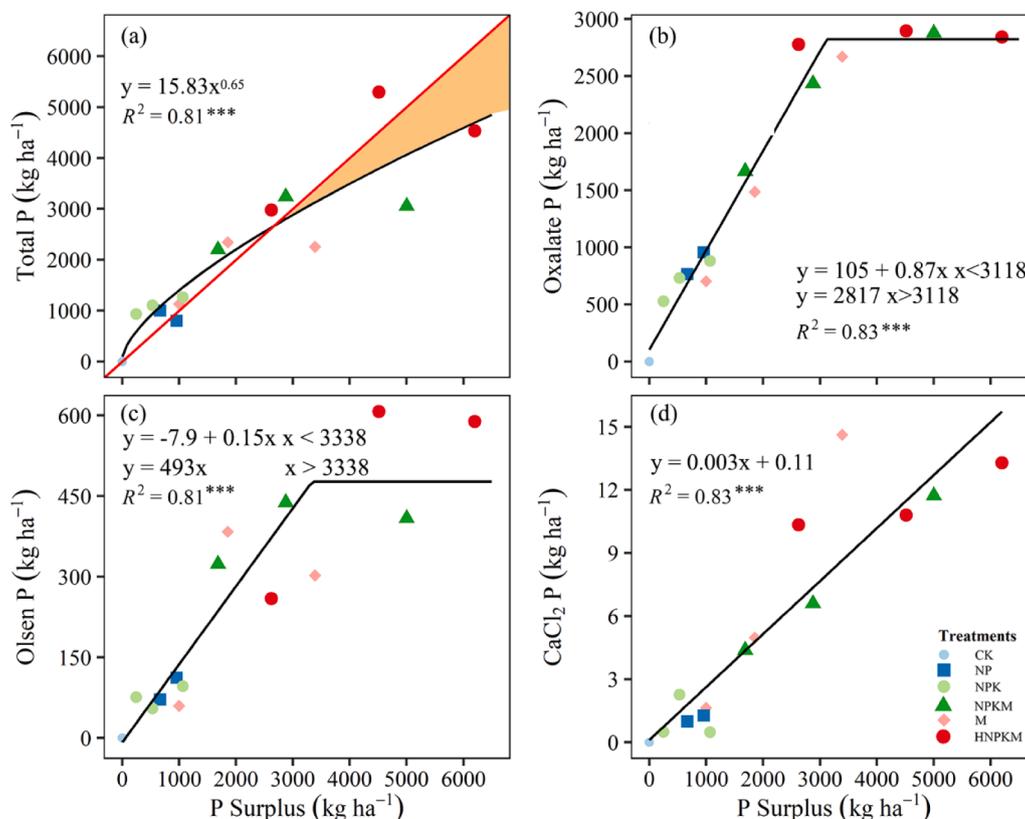
#### 3.3. Relationships between crop yields and dissolved P concentration with different soil P pools

Crop yields consistently increased with an increase in P<sub>CACL2</sub>, P<sub>OLSEN</sub>, P<sub>OX</sub> and P<sub>TOTAL</sub>, with the relationship being stronger for maize than wheat. The variation in P content explained on average 10% more of the crop yield variation for maize than wheat (Fig. 3). Changes in P<sub>TOTAL</sub> explained 59–78% of the yield variation. In contrast, changes in reactive P content (including P<sub>OX</sub> and P<sub>OLSEN</sub>) explained 59–86% and P<sub>CACL2</sub> 60–66% of the yield variation (Fig. 3). Crop yields were most sensitive to changes in P<sub>CACL2</sub>, followed by P<sub>OLSEN</sub>, whereas the sensitivity to P<sub>TOTAL</sub> and P<sub>OX</sub> was comparable (Fig. 3 and Table 3). Target soil P contents to achieve 90% of the maximum maize and wheat yield ranged from 1.5 to 1508 mg P kg<sup>-1</sup> and 1.4–1073 mg P kg<sup>-1</sup> respectively. The target P levels for 90% of the maximum yield of maize and wheat decreased in the order P<sub>TOTAL</sub> > P<sub>OX</sub> > P<sub>OLSEN</sub> > P<sub>CACL2</sub>, in line with their increased plant accessibility. The maximum yield for maize was observed when P<sub>CACL2</sub>, P<sub>OLSEN</sub> and P<sub>OX</sub> reached 0.1%, 4% and 79% of P<sub>TOTAL</sub>, respectively. Similarly, 90% of the maximum wheat yield was observed when P<sub>CACL2</sub>, P<sub>OLSEN</sub> and P<sub>OX</sub> reached 0.1%, 5% and 69% of P<sub>TOTAL</sub> (Table 3).

The relationship between P<sub>CACL2</sub> and P<sub>OX</sub> was positively piecewise-linear, whereas no significant relationship was observed between P<sub>CACL2</sub> and P<sub>OLSEN</sub> (Fig. 4). Regarding a critical level for potential leaching risk, a change point of 0.6 mg kg<sup>-1</sup> P<sub>CACL2</sub> was identified at a P<sub>OX</sub> content near 500 mg P kg<sup>-1</sup>. Notably, the critical P<sub>OX</sub> level (500 mg P kg<sup>-1</sup>) was lower than the target P<sub>OX</sub> levels required for both maize (1188 mg P kg<sup>-1</sup>) and wheat (736 mg P kg<sup>-1</sup>) crop yield (Table 3) showing that the environmental risks were elevated at soil P levels appropriate for a desired agronomic yield response.

### 4. Discussion

A schematic overview of our main results is given in Fig. 5, illustrating the impacts of: (i) long-term P fertilization on different soil P pools, including the saturation of reactive pools (P<sub>OLSEN</sub>, P<sub>OX</sub>), further discussed in Section 4.1 and (ii) the impact of changes in those pools on



**Fig. 1.** Relationship between changes in different soil P pools, i.e. changes in different pools of  $P_{TOTAL}$  (a),  $P_{OX}$  (b),  $P_{OLSEN}$  (c) and  $P_{CaCl_2}$  (d) and accumulated P surplus over a 29-year period. Treatment descriptions of CK, NP, NPK, M, NPKM and HNPKM are given in Table 1. The red line in (a) represents 1–1 line and yellow part represent the accumulated P loss from 0 to 20 cm soil. \*\*\* indicates significance at  $p < 0.001$ .

the crop yield (P uptake) and P losses, further discussed in Sections 4.2 and 4.3. Furthermore, we address the limitations of this study (Section 4.4) and discuss the implication for sustainable P management (Section 4.5).

#### 4.1. Effects of long-term fertilization on saturation of different soil P pools

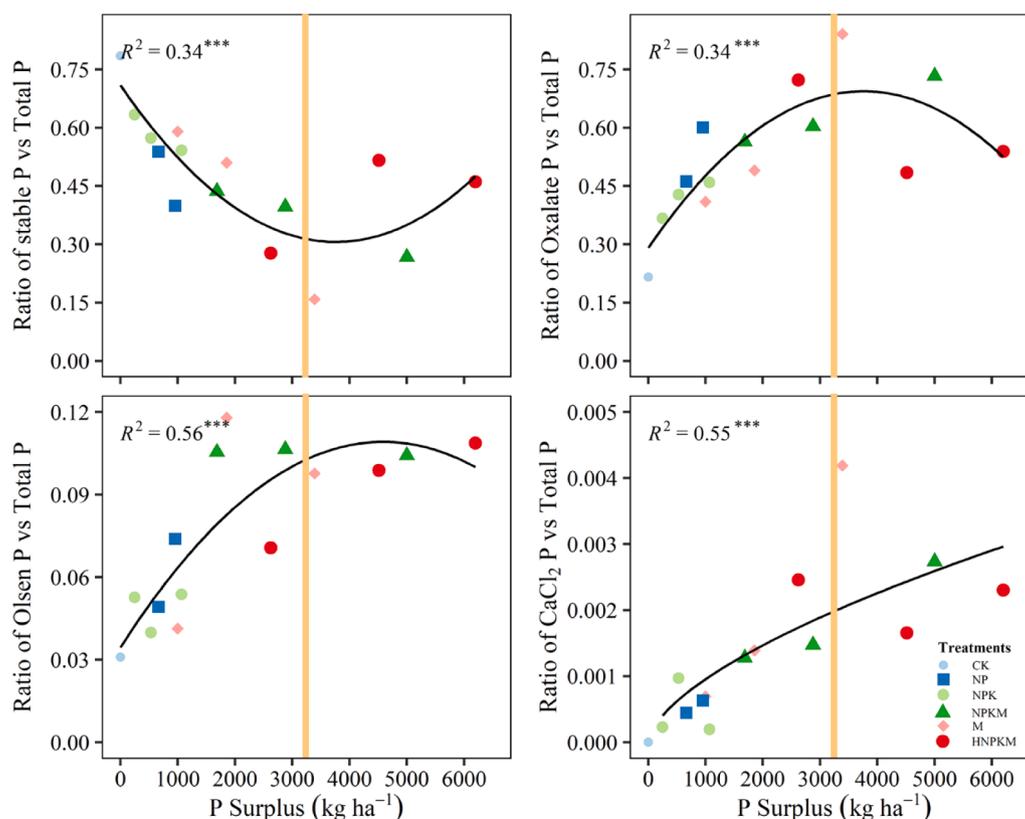
Numerous studies reported linear (or segmented linear) increases in reactive P (e.g., Olsen and Bray extracted P) in response to positive or negative P surpluses (Cao et al., 2012; Messiga et al., 2010). In this study, we also found that both Olsen and oxalate extracted P ( $P_{OLSEN}$  and  $P_{OX}$ ) increased with accumulated P surplus following a linear-plateau pattern, but the remarkable result is that both indicate a clear saturation point at an accumulation near 3200 kg P ha<sup>-1</sup>. In a previous study, soil P saturation points were determined by adding excessive P inputs under laboratory conditions (Bolster et al., 2020). Here we report that the saturation of reactive soil P pools occurred with continuous P accumulation in a long-term field, representing intensive agronomic practices adopted in China.

The increase in accumulated soil P pools varied from 0.003 kg kg<sup>-1</sup> P inputs for  $P_{CaCl_2}$  to 0.15 kg kg<sup>-1</sup> for  $P_{OLSEN}$  and up to 0.87 kg kg<sup>-1</sup> for  $P_{OX}$  (Fig. 1). This shows that most added P stays in the reactive P pool until saturation. The change in P pools per unit accumulated P was near 1 for  $P_{OX}$ , suggesting that  $P_{OX}$  is a good indicator for the legacy P pool, at least much better than  $P_{OLSEN}$ . This confirmed by a 30-day incubation study with P levels up to 10.400 kg P ha<sup>-1</sup> (Chen et al., 2022), which showed that the majority of the added P ended up in the oxalate extractable Al- and Fe-bound P pool. The measured accumulation of  $P_{TOTAL}$  in this experiment was not identical to the accumulated soil P surplus, in particular when the accumulated P surplus exceeded 3200 kg P ha<sup>-1</sup>. This is likely due to the increased sampling error for  $P_{TOTAL}$  coupled with P leaching or runoff due to P saturation (Murphy

and Sims, 2012; Oehl et al., 2002; Requejo and Eichler-Lobermann, 2014). For example, a previous study (Rubæk et al., 2013) demonstrated that soil P accumulation was visible in deeper soil layers down to 75 cm below the surface, which indirectly confirms the elevated environmental risk of excessive P fertilization (Zicker et al., 2018). Besides, more than 50% of total P loss can be attributed to erosion, which means reducing soil erosion will be a crucial management option to decrease fertilizer application and environmental impact (Alewell et al., 2020).

When P is added to soils, a series of reactions occur, ranging from the diffusion of P from fertilizer and manure into soil solution, sorption of P into soil particles, and with time, P precipitation (Hedley and McLaughlin, 2005). Earlier studies reported that at low P concentrations in non-calcareous soils, P tends to absorb through ligand exchange, whereas at higher P concentrations, P is likely to precipitate with Feox and Alox (Perassi and Borgnino, 2014). Continuous P application over 29 years increased all P pools, with the highest increases for  $P_{OX}$  and the lowest for  $P_{CaCl_2}$ , which led to an increase in total P reactivity in soil. Similar findings have been found in other field experiments (Castillo and Wright, 2008; Chen et al., 2022; Zhang et al., 2022). The distribution of soil legacy P over the P pools depends on the degree of P saturation (Allen and Mallarino, 2006; Sucunza et al., 2018), and ongoing P input triggers phosphate to precipitate into less available forms once the soil becomes saturated (Shen et al., 2011) or to leach out of the soil (Fig. 2).

Soil P transformations between P pools are mainly regulated by adsorption-desorption and precipitation-dissolution, which are indicative of a dynamic equilibrium between those P pools (Shen et al., 2011). This applies to both accumulation and mining (Wang et al., 2007). For example, Beck and Sanchez (1994) concluded that soil reactive P pools (including P pool extracted by 0.1 M NaOH extraction) could contribute to crop uptake through fast desorption of P into the soil solution, whereas Chen et al., (2021) indicates that even the very stable P pools might become available given long-term tillage and root activity. This is



**Fig. 2.** Relationship between ratios of different soil P pools vs  $P_{TOTAL}$ , i.e. in  $P_{STABLE}$  (a),  $P_{OX}$  (b),  $P_{OLSEN}$  (c) and  $P_{CaCl_2}$  (d), and accumulated P surplus over a 29-year period. The descriptions on treatments of CK, NP, NPK, M, NPKM and HNPKM are given in Table 2. \*\*\* indicates significance at  $p < 0.001$ .

confirmed by the mining treatments in our long-term experiment where  $P_{OLSEN}$  and  $P_{CaCl_2}$  remained remarkably constant over time (data not shown). Given the strong linear response of  $P_{OX}$  to the legacy P surplus,  $P_{OX}$  might be a valuable indicator of legacy P.

#### 4.2. Effects of long-term fertilization on P losses

Observations over the experimental period show that P losses to the environment or soil sub-layers will most likely increase over time, as evidenced by the increased  $P_{CaCl_2}$  content (Fig. 1d), and the fact that substantial amounts of added P were lost from the topsoil (Fig. 1a) as soon as P inputs exceed the maximum retention capacity. Strong increases in  $P_{CaCl_2}$  in response to high P inputs are often observed and might be linear (our study) or non-linear (Chen et al., 2022), dependent on the P buffer capacity, which in turn is affected by the content of oxalate extractable Fe and Al (Van Rotterdam et al., 2012).

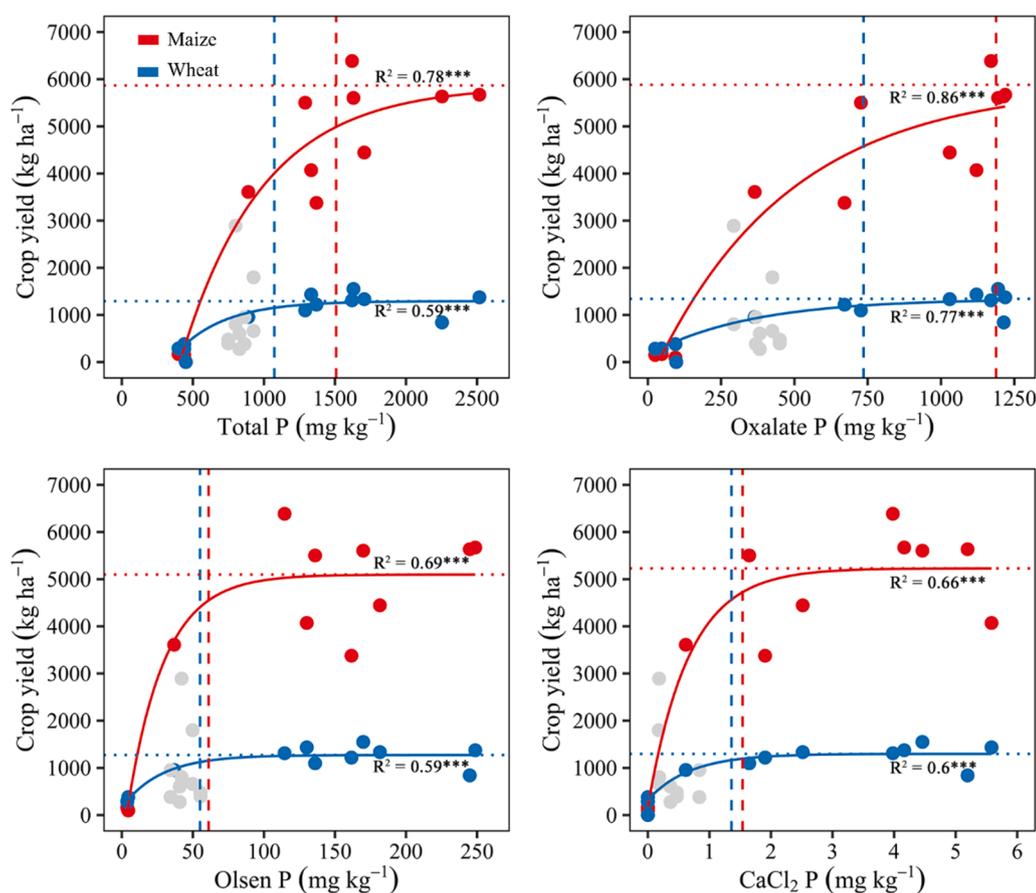
The increase in  $P_{CaCl_2}$  is indicative for greater risks of P leaching and runoff (Xie et al., 2021) because of its relationship with the P concentration of soil solution or leachate and to the total dissolved P in surface runoff (Dougherty et al., 2008; Schindler et al., 2009). Saturated soils resulting from overfertilization will lead to substantial P losses. Unlike the results of excessive long-term fertilization for pomelo orchards (Chen et al., 2022), where  $P_{CaCl_2}$  steeply increased when the P surplus exceeded approximately 4100 kg P ha<sup>-1</sup>, the current study did not find such a tipping point. Similarly, Ulén (2006) also found a close linear relationship between dissolved P in runoff and soil P status. However, we did find a change point for  $P_{CaCl_2}$  when  $P_{OX}$  reached saturation (Fig. 4). The change point was found at 0.6 mg kg<sup>-1</sup>  $P_{CaCl_2}$  in  $P_{CaCl_2}$  and  $P_{OX}$  association, with  $P_{OX}$  content approaching 500 mg P kg<sup>-1</sup> (Fig. 4), a threshold below the target P levels derived for maize (1188 mg P kg<sup>-1</sup>) and wheat (736 mg P kg<sup>-1</sup>). This is in contrast to the findings of Bai et al. (2013) who assumed that the critical threshold for P leaching is present above the target P level for crop yield. Note, however, that

$P_{CaCl_2}$  is only a proxy of the P concentration in leachate and soil solution. The actual P leaching also depends on hydrological properties, precipitation surplus and topography (Djodjic et al., 2004; Davis et al., 2005). Furthermore, erosion exacerbate the risk of eutrophication by P losses to surface waters (Messiga et al., 2015; Shen et al., 2011; Zicker et al., 2018), implying that the change point is not the same as a critical level for environmental risk.

#### 4.3. The performance of soil P pools in predicting crop yield

Our long-term field experiment allowed to identify and quantify target soil P levels for both maize and wheat under field conditions. In all cases, crop yield responded positively to increases in available and reactive soil P (Fig. 3). Target values for  $P_{OX}$ ,  $P_{OLSEN}$  and  $P_{CaCl_2}$  were consistently higher for maize than wheat given the differences in root biomass and associated P response, which is consistent with other field studies in China (Bai et al., 2013). However, other studies (Colomb et al., 2007; Sucunza et al., 2018; Tang et al., 2009) reported higher (or equal)  $P_{OLSEN}$  thresholds for wheat than for maize. This difference might be explained by the fact that P uptake varied with the climatic conditions across regions (e.g., precipitation). In addition, maize is more responsive than wheat due to its higher P demand and uptake (Fig. 3). This means that maize requires higher P availability and subsequently higher P fertilizer inputs when soil P contents are below target values. Note that where 90% of the maximum crop yield was obtained, the target soil P level was closer to a P surplus of 2500 kg P ha<sup>-1</sup> (Fig. A6), which was well below the P saturation point of 3200 kg P ha<sup>-1</sup> and far below the calculated maximum P accumulation of 6000 kg P ha<sup>-1</sup>.

Target P levels for crop yields of maize and wheat vary from 1.4 to 1.5 mg P kg<sup>-1</sup> for  $P_{CaCl_2}$ , 55–60 mg P kg<sup>-1</sup> for  $P_{OLSEN}$  and 736–1188 mg P kg<sup>-1</sup> for  $P_{OX}$ . The levels derived for  $P_{CaCl_2}$  are in line with the results of Sánchez-Alcalá et al. (2015) and Van Rotterdam et al. (2012), who showed that  $P_{CaCl_2}$  levels above 2–4 mg kg<sup>-1</sup> are



**Fig. 3.** Relationship between crop yield of maize (red) and wheat (blue) and different soil P test, i.e.,  $P_{TOTAL}$  (a),  $P_{OX}$  (b),  $P_{OLSEN}$  (c) and  $P_{CaCl_2}$  (d) over 29-year period. Data points in grey colour were skipped from calibration regression lines because of severe crop yield reduction due to acidification. Vertical dashed lines represent target soil P contents for reaching 90% of the maximum yield. Horizontal lines represent the maximum yield level predicted by asymptotic regression model. \*\*\* indicates significance at  $p < 0.001$ .

**Table 3**

Maximum yields and target P values associated with target yields, modelled with the asymptotic regression curve on data for all treatments and years.

Soil P test	Maize				Wheat			
	Yield <sub>max</sub> <sup>a</sup> (kg ha <sup>-1</sup> )	Rate <sup>b</sup>	TargetP <sub>90</sub> <sup>c</sup> mg kg <sup>-1</sup>	TargetP <sub>95</sub> <sup>d</sup> mg kg <sup>-1</sup>	Yield <sub>max</sub> <sup>a</sup> (kg ha <sup>-1</sup> )	Rate <sup>b</sup>	TargetP <sub>90</sub> <sup>c</sup> mg kg <sup>-1</sup>	TargetP <sub>95</sub> <sup>d</sup> mg kg <sup>-1</sup>
$P_{CaCl_2}$	5230	1.49	1.54	1.96	1297	1.46	1.36	1.78
$P_{OLSEN}$	5096	0.039	60	112	1272	0.036	55	71
$P_{OX}$	5882	0.002	1188	1551	1343	0.003	736	986
$P_{TOTAL}$	5866	0.002	1508	1865	1294	0.003	1073	1334

<sup>a</sup> Predicted Maximum Yield by  $Y = Asym + (R_0 - Asym) \cdot \exp(-\exp(\text{lrc}) \cdot X)$ , X and represents soil P level and crop yields; Asym represents the maximum values;  $R_0$  represents the response when X is 0; lrc represents the ln transform of the rate constant

<sup>b</sup> Calculated by  $\exp(\text{lrc})$

<sup>c</sup> Target P level for 95% of Yield<sub>max</sub>

<sup>d</sup> Target P level for 90% of Yield<sub>max</sub>

agronomically excessive. However, the values for  $P_{OLSEN}$  are generally higher than those reported in the literature, being close to 20 mg P kg<sup>-1</sup> for both maize and wheat (e.g., Bai et al., 2013). Due to low pH and high clay content, the strong soil P adsorption in the Qiyang experiment could partly explain the need for higher target soil P levels.

It is important to note that none of the existing soil P tests is superior to another for predicting crop response to P inputs (Nawara et al., 2017; Van Rotterdam et al., 2012). Although the crop yields of maize and wheat were more sensitive to changes in the concentration of P forms with high availability, i.e.,  $P_{OLSEN}$  and  $P_{CaCl_2}$ , the overall variation in crop yield response to changes in soil P contents was less well explained by  $P_{OLSEN}$  and  $P_{CaCl_2}$  ( $R^2$  varying from 0.59 to 0.69) than by  $P_{TOTAL}$  and  $P_{OX}$  ( $R^2$  varying from 0.59 to 0.86) (Fig. 3 & Table 3). The  $P_{OX}$  content was the most reliable soil P test for explaining the crop yield response to changes in soil P concentrations for both maize and wheat (Fig. 3 & Table 3). In contrast, Nawara et al. (2017) demonstrated that  $P_{OX}$  was inferior to other soil P tests. This could be explained by the fact that

oxalate extractant is better suited for red non-calcareous soils (being rich in aluminium and iron oxides) in Qiyang than for the soils in Europe. In addition, differences in the sensitivity of crops to P deficiency need to be considered when comparing crop dose response trials.

#### 4.4. Limitations in the study

Inevitably, there are some limitations that may have affected the derived saturation points and target values for soil P levels, especially from the variable N and K inputs between treatments and soil pH. Crop yield may have been influenced by differences in soil N and K availabilities apart from P since the inputs were not the same among all treatments. In addition, differences in acidification rates, induced by high mineral N fertilizer inputs, might also have affected crop yield. To reduce these confounding effects, we removed outlier observations before the analysis of the relationship between crop yield and soil P content when differences in N and K availability were substantial (e.g.,

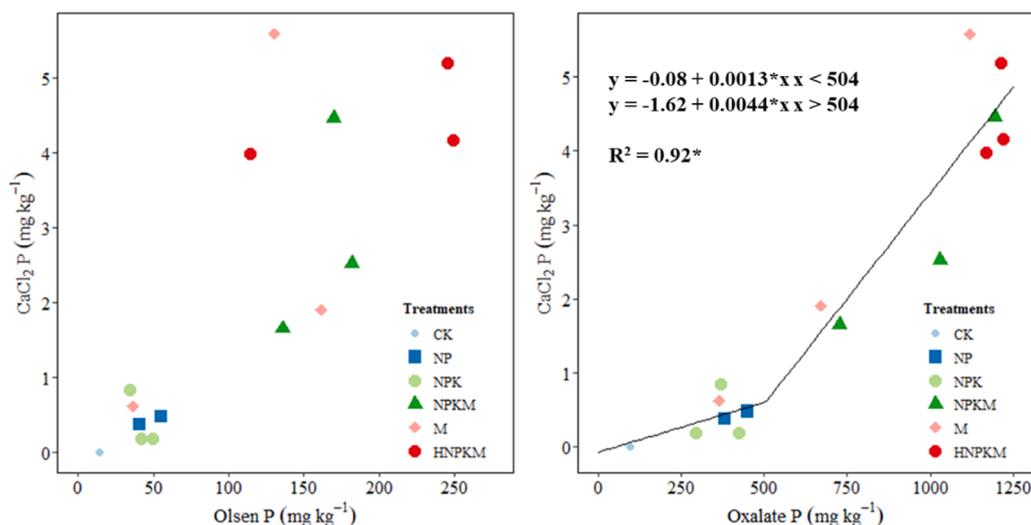


Fig. 4. Relationship between  $P_{CaCl_2}$  and  $P_{Olsen}$  (left) and  $P_{Ox}$  (right) over 29-year period. \* indicates significance at  $p < 0.05$ .

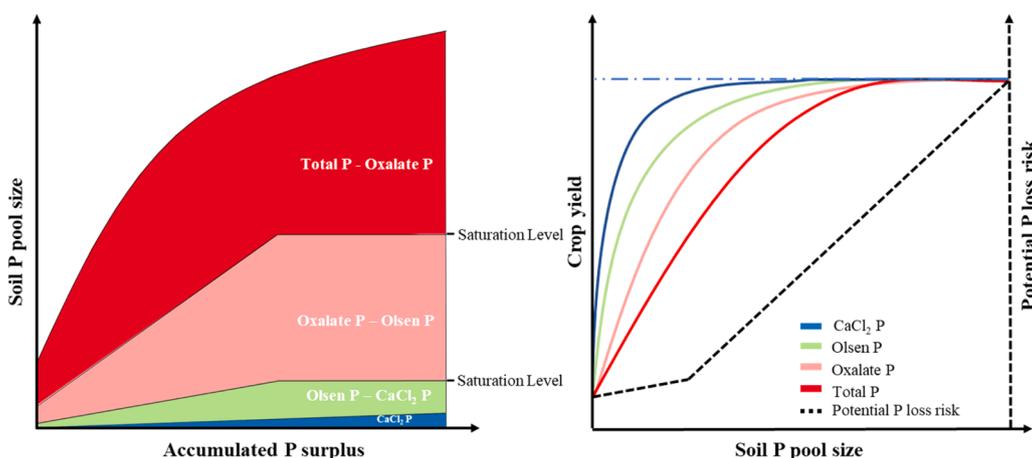


Fig. 5. Schematic overview of the responses of soil P pools to long-term accumulated P surplus (left) and the impact of changes in those pools on the crop yield (P uptake) and P losses (right).

in NP and NPK treatments) or the crop production was strongly hampered by low pH levels. In the remaining treatments (NPKM, HNPKM and M), the K application was around  $200 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (see Table 1), being much higher than the K uptake (Fig. A7). Besides, the confounding effects could also be from the different N inputs. For example, the NPKM and M treatments have equal annual N input of  $300 \text{ kg N}$ , but considering the limited N uptake (see Fig. A8), situations of N deficiency are very unlikely. Besides, strong agreement for both maize and wheat yield between NPKM and HNPKM implies that those confounding factors had a limited impact on the derived target P level assessment (Fig. A9).

The uncertainties of this work could also be arising from the soil P balance calculation. In this study, soil P surpluses were determined annually by the difference between total P input and crop P uptake, while the P contents in manure were assumed to be constant based on literature data. Given the duration of 29 years, this might have led to a bias and the propagation of associated error in the estimated total P input, although the average is likely plausible since the P concentration in manure matches the range found in China (Qin et al., 2020). In addition, P transport from soil sub-layers to the topsoil by crop uptake (and subsequent incorporation of crop residues) and earthworms were not considered. Similarly, the P input via deposition was neglected given that this is usually less than 1% of the total P input in agricultural

systems (Oenema et al., 2003). Both factors could cause a higher observed P accumulation than estimated via the P surplus (Fig. 1a). Furthermore, the increase in atmospheric  $\text{CO}_2$  concentrations during the experimental period from  $\sim 350 \text{ ppm}$  in 1990 to around  $415 \text{ ppm}$  in 2019 may have influenced crop yield and thereby P uptake. In two long-term (15 and 9 years) free air  $\text{CO}_2$  enrichment (FACE) experiments of rice in China, receiving a  $\text{CO}_2$  concentration of  $200 \text{ ppm}$  above the ambient concentration, Wang et al. (2023) observed a nearly 25% decline in soil available P, mainly due to enhanced P uptake. However, in our study the  $\text{CO}_2$  increase over the experimental period was more than 3 times lower that applied by Wang et al. (2023). The impact of climate on the soil P balance is thus likely very limited when compared to the effects of the accumulated P input. In addition, this study was only conducted in a single non-calcareous soil in China, where soil P retention is mainly regulated by the adsorption of Al/Fe oxides and hydroxides. Therefore, further research is needed to assess whether the observations of our study are representative for other soil types as well.

Overall, we do acknowledge the inherent uncertainties and limitations due to confounding errors or non-systematic errors in our study. Yet, it clearly demonstrated that continuous long-term P fertilization would increase soil P pools and saturate reactive P pools, which exacerbate environmental risks. We also found that crop yields responded differently to changes in soil P pools. These findings have considerable

practical significance in guiding sustainable P fertilization strategy.

#### 4.5. Implication for sustainable phosphorus management

In this study, we made a comprehensive assessment of the effects of long-term fertilization on crop yield in response to changes in different soil P pools under field conditions. The results indicate that long-term and excessive P input will saturate soil reactive P pools while crop yield does not respond to added P far before that saturation point. Considering that a large fraction of external P inputs is not immediately available to plants, it is crucial that P fertilization strategies should be based on available soil P pool, influenced by the legacy of the past P accumulation, using an appropriate soil P indicator. Our results provide valuable field-based insights to guide fertilizer recommendation using  $P_{OX}$  as a robust estimate of the soil legacy P effects to attain a target  $P_{OX}$  value using several assumptions. The assumptions are that the target P level for crop yield is below the critical P level for environmental risk (Bai et al., 2013), and the 0–20 cm layer is the relevant layer for evaluating P availability in a wheat-maize cropping system. Knowing the current  $P_{OX}$  content, and the target  $P_{OX}$  content to maximize crop production, one can determine the P needed to bring the soil P status up to the desired level for a given crop P requirement (target yield times crop P content) and the link between P surplus and P accumulation, which is affected by the soil P retention capacity. This retention capacity can be determined by measuring not only P but also Al and Fe in the oxalate extraction, with the ratio of  $P_{OX}$  divided by  $Al_{OX}$  and  $Fe_{OX}$ , being called P Saturation Index (PSI). As suggested by Kleinman (2017), the PSI can be used to define the remaining sorption capacity and subsequently define and assess strategic trajectories for P accumulation. Thus, a precise fertilization strategy for large scale crop production could be developed based on the current and target  $P_{OX}$  level, possibly combined with  $P_{CACL2}$  to better determine the target level for crop yield. It is also possible to predict the duration required to attain the target  $P_{OX}$  under the assumption that P input will remain constant throughout, this providing guidance for policy making for long-term P management.

## 5. Conclusions

Our 29-year field experiment showed that long-term P accumulation significantly increased the size of available, reactive and stable P pools, with the largest relative change occurring for  $P_{CACL2}$  (more than 100-fold), followed by  $P_{OLSEN}$  (13-fold),  $P_{OX}$  (11-fold) and  $P_{TOTAL}$  (5-fold). The responses of these pools to long-term P accumulation gradually decreased, and even declined to zero for reactive P pools ( $P_{OX}$  and  $P_{OLSEN}$ ). Both  $P_{OLSEN}$  and  $P_{OX}$  did not further increase at an accumulated P surplus around 3200 kg P ha<sup>-1</sup>, indicating saturation of the soil P retention capacity at that level. Added P accumulated more in available P forms before the reactive P pools were saturated, and once the soil was saturated, continuous additional P inputs promoted soil P transformation into more stable P forms and P leaching. Crop yields were most sensitive to changes in  $P_{CACL2}$ , whereas  $P_{OX}$  and  $P_{OLSEN}$  were more reliable in explaining crop variation. The change in  $P_{OX}$  was a better indicator for the legacy P pool size (being close to it, i.e., 87% of added P) and crop yield changes than  $P_{OLSEN}$ , thus become a better candidate to guide sustainable P management. Considering that  $P_{CACL2}$  was the most sensitive soil P indicator to identify situations for P deficiency and crop yield limitation, a combination of  $P_{OX}$  and  $P_{CACL2}$  could be most appropriate to accurately assess the size and availability of soil P.

## Declaration of Competing Interest

We declare that we have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

## Acknowledgements

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2023.108658.

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