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# Organic phosphorus leaching risk from agricultural soils across China

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## Abstract

**Background:** Leaching from agricultural land is one of the major pathways of phosphorus (P) loss from soils to waterbody and may induce adverse effect on territorial environment. Past studies usually focused on the loss of inorganic P ( $P_i$ ) while ignored the role of organic P ( $P_o$ ) in leaching process. A total of 63 agricultural soil samples were collected from across China with various soil types including 21 paddy soils, 13 chernozems, 11 red soils and other type soils ( $n = 18$ ) to identify the potential risk of  $P_o$  and  $P_i$  leaching from agricultural lands and to explore their relationships with soil basic properties, Fe/Al oxides, and P status.

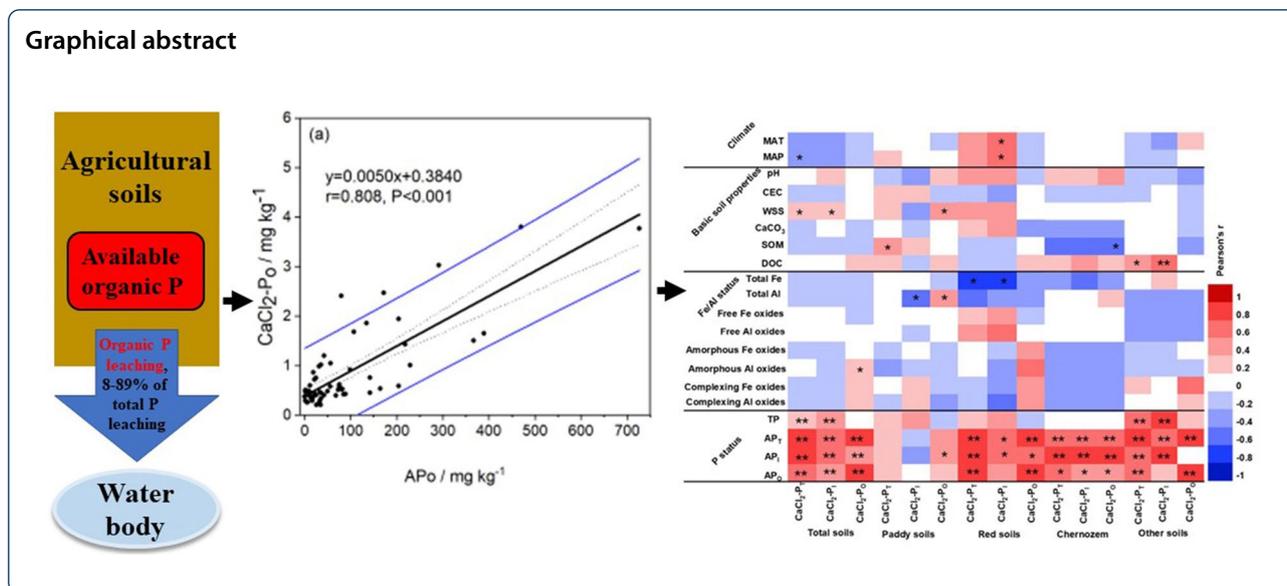
**Results:**  $\text{CaCl}_2$ -extractable organic P ( $\text{CaCl}_2\text{-}P_o$ ) accounted for 8–89% (35% on average) of  $\text{CaCl}_2$ -extractable total P ( $\text{CaCl}_2\text{-}P_T$ ) and available organic P ( $AP_o$ ) accounted to over half of available total P ( $AP_T$ ) ( $57 \pm 25\%$ ).  $\text{CaCl}_2\text{-}P_T$  was positively correlated with  $AP_T$  under all soil types except paddy soils.  $\text{CaCl}_2$ -extractable inorganic P ( $\text{CaCl}_2\text{-}P_i$ ) and available inorganic P ( $AP_i$ ) were strongly correlated for chernozem ( $r = 0.968$ ), while  $\text{CaCl}_2\text{-}P_o$  the was strongly correlated with  $AP_o$  for red soils ( $r = 0.901$ ).

**Conclusions:**  $P_o$  greatly contributed to the potential P leaching risk and should be included in the risk assessment of total P leaching. The control of soil  $AP_T$  excess accumulation in both  $P_o$  and  $P_i$  fractions in agricultural land is the key point to cut down P leaching. Mitigation measures to limit  $P_o$  leaching should be established based on the soil types.

**Keywords:** Phosphorus (P) leaching, Available organic P ( $AP_o$ ),  $\text{CaCl}_2$ -extractable organic P ( $\text{CaCl}_2\text{-}P_o$ ), Fe/Al oxides

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## Background

Phosphorus (P) is one of the limited elements for life survival and growth on earth [1]. Excessive application of P fertilizer in arable lands to guarantee crop production may induce P loss from soil to waterbody, causing adverse effect such as eutrophication [2, 3]. Leaching is one of the major pathways of P transport from soils to groundwater. It has received much attention since a large amount of P was detected in leachate [4–6]. Evaluating the P leaching risk is the prerequisite for making pollution control management. However, traditional monitoring methods like soil column or lysimeter experiments are difficult to implement because of the time- and cost-consuming [6]. Soil P tests such as  $\text{CaCl}_2$ -extractable P, water extractable P, ammonium oxalate extractable P have developed as reliable means to identify the risk of P leaching in the past studies [5].

Soil  $\text{CaCl}_2$ -extractable P ( $\text{CaCl}_2\text{-P}$ ) is highly correlated with both dissolved reactive P concentrations in surface runoff and the leached P concentration in column trials so that it can work as an indicator for assessing the potential P leaching risk [5, 7, 9]. Soil available P (AP) is usually used as an agricultural proxy index which is the soil P that potentially can be used by plants. It is less strongly bound than soil residual P so that can be easily transported in soils resulting in leaching [10–12]. Based on the relationship between AP with  $\text{CaCl}_2\text{-P}$ , the change point at which  $\text{CaCl}_2\text{-P}$  concentrations dramatically increased has been defined as the maximum acceptable AP concentrations in soils to avoid P leaching [13, 14]. It means that the P leaching risk can be evaluated by comparing the soil AP with the change point value. However, AP is not a constant value, it changes over time. For example,

after fertilizer application it increases suddenly and then declines over time. AP can be adsorbed, but adsorbed P can become plant-available over timescales ranging from months to years [15, 16]. On the other hand, organic P ( $\text{P}_O$ ) is not included in AP of change point and the relationship between available organic P ( $\text{AP}_O$ ) and  $\text{CaCl}_2$  extractable organic P ( $\text{CaCl}_2\text{-P}_O$ ) has not been explored in the past studies.

P is easily fixed in the soil through, e.g., adsorption, precipitation or biological immobilization, hence only 20% of P fertilizer is taken up by crops in arable lands [17]. The mobility and loss of inorganic P ( $\text{P}_i$ ) in soils have been explored by many studies [18–20]. Sorption is considered as the key process to controlling  $\text{P}_i$  mobility in arable lands, which is affected by certain soil properties including pH, cation exchange capacity (CEC), clay content, soil organic matter (SOM) and Al, Fe, Mn oxides [18, 21, 22]. However, the role of  $\text{P}_O$  in soil P leaching has received poor attention and is less understood [23]. In fact,  $\text{P}_O$  has been found to account for a large part of P leachates because some  $\text{P}_O$  fractions reveal smaller affinity to the soil solid phase than  $\text{P}_i$  [19, 24]. Soil  $\text{P}_O$  account for a large part of soil P pool and usually occurs as a complex mixture of monoesters (Mono-P) and diesters (Di-P), with smaller amounts of phosphonates (Phos-P) and organic polyphosphates [25, 26]. Research made by McDowell et al. [23] found that all dissolved  $\text{P}_O$  fractions, with the exception of mono-inositol hexakisphosphate leached through aquifer gravels to depth at a higher speed than orthophosphate. Thus,  $\text{P}_O$  fractions are easily transported to deep layers, and this has been proved both in montane ecosystem and agricultural lands [6, 27]. Besides, many species of  $\text{P}_O$  in soils can become available

as orthophosphate for plant via microbially mediated mineralization [28]. It means that the presence and quantity of soil  $P_O$  fractions affects the overall total P leaching. Therefore, it is necessary to consider  $P_O$  in P leaching risk assessment.

In this study, 63 samples were taken from agricultural lands with different soil types (i.e., paddy soil, red soil, chernozem, black soil and other soils) across China. The aims of the study were (1) to assess the Po leaching risk in agricultural soils across China and (2) to explore the relationship of soil Po leaching risk with soil basic properties, particularly focusing on the effect of soil available Po on P leaching.

## Materials and methods

### Soil collection

A total of 63 surface soils (0–20 cm) were point sampled by spade and pickaxes from agricultural lands across China (Additional file 1: Table S1). Soils were chosen to cover a range of soil types. All samples were air-dried at room temperature and then sieved (2, 1 and 0.15 mm) after removing the organic debris and impurities.

### Soil characterization

Soil pH was measured in water at a soil/water ratio of 1:2.5 by a FE20-FiveEasy Plus pH meter (Mettler Toledo, Switzerland). Water-soluble salt (WSS) was determined by a conductivity meter (SX-650; Tester, China) at a soil/water ratio of 1:5. The cation exchange capacity (CEC) and  $CaCO_3$  content in soils were measured by the NaOAc compulsive exchange method [29] and gasometric method [30]. Dissolved organic carbon (DOC) was extracted by 2 M KCl with the soil/water of 1:10 and the DOC in soil extracts was analyzed by a TOC/TN analyzer (Multi N/C 2100, Analytik Jena, Germany). Soil organic matter (SOM) was analyzed by wet oxidation with  $H_2SO_4$ – $K_2CrO_7$  [31]. For total Fe and Al, soils were digested by with  $HF$ – $H_2O_2$ – $HNO_3$  at 180 °C using a MARS 5 Xpress microwave system (CEM, USA), water-soluble Fe and Al were extracted by deionized water, free Fe and Al oxides were extracted by the sodium dithionite–sodium citrate–bicarbonate (DCB), amorphous Fe and Al oxides were extracted by acid ammonium oxalate, and complexing Fe and Al oxides were extracted using sodium pyrophosphate. The Fe and Al content were measured by ICP-OES (Optima 8000, Perkin Elmer, USA).

### P status

Soil samples were digested by  $HClO_4$  and  $H_2SO_4$  at 420 °C to determine the TP [32]. Extractable water-soluble P was extracted by 0.01 M  $CaCl_2$  for 30 min at a soil/water ratio of 1:5. After filtering, a part of clear

solution was taken to detect the  $CaCl_2$ -extractable inorganic P ( $CaCl_2$ - $P_I$ ) by the ammonium molybdate–ascorbic acid method immediately [33]. The other supernatant was digested with 10%  $K_2S_2O_8$  at 120 °C and 1.5 MPa for 30 min and then the total P content in water extractable P ( $CaCl_2$ - $P_T$ ) by the ammonium molybdate–ascorbic acid method was determined [34]. The organic P content ( $CaCl_2$ - $P_O$ ) was determined by the difference between  $CaCl_2$ - $P_T$  and  $CaCl_2$ - $P_I$ .

Available P (AP) was extracted by 0.5 M  $NaHCO_3$  (pH 8.5) at a soil/water ratio of 1:20 [35]. After shaking and filtering, part of clear solution was taken to measure the available inorganic P ( $AP_I$ ) using the ammonium molybdate–ascorbic acid method [33]. The other solution was digested with 10%  $K_2S_2O_8$  at 120 °C and 1.5 MPa for 30 min, and then the solution was measured by the ammonium molybdate–ascorbic acid method to determine the total content of available P ( $AP_T$ ). The difference between  $AP_T$  and  $AP_I$  was considered as available organic P ( $AP_O$ ).

### Data analysis

A one-way analysis of variance (ANOVA) was used on SPSS v22.0 software (IBM, USA) to detect differences in soil properties and P status between different soil types. Pearson correlations were used to assess the relationships between  $CaCl_2$ -extractable P with climate, basic soil properties, Fe/Al status and P status. Then, a heatmap was constructed by the Origin Pro v9.1 software (Origin-Lab, USA).

## Results

### Basic soil physicochemical properties

The soils collected across China had a wide range of physicochemical properties due to differences in soil type, climate characteristics, and agronomical variations (Table 1). The soil pH values ranged from 4.5 to 9.2 with an average of 7.2. Generally, paddy soils and red soils were neutral and chernozem soils were alkaline (Table 1). The soil CEC ranged from 6.2 to 49.3  $cmol\ g^{-1}$ , and WSS in soils were 0.01–0.95  $mS\ cm^{-1}$  (Table 1). The soils contained 0.35–14.8% soil organic matter (SOM) in weight basis and the dissolved organic carbon (DOC) varied from 0.04 to 0.36  $mg\ kg^{-1}$  (Table 1). The  $CaCO_3$  in the study soils was in a relative wide range with 0.81 to 73.7  $mg\ kg^{-1}$ . Compared with the other soil types, chernozem soils were found to be higher in CEC and in the content of SOM, DOC and  $CaCO_3$ .

### P status

In the present study, total content of P (TP) of soil showed higher variation from 378 to 3387  $mg\ kg^{-1}$ . There were only three soils which contained less than 400  $mg\ kg^{-1}$

**Table 1** Basic properties of soil collected across China

Soils	pH	CEC (cmol g <sup>-1</sup> )	WSS (mS cm <sup>-1</sup> )	CaCO <sub>3</sub> (mg kg <sup>-1</sup> )	SOM (%)	DOC (mg kg <sup>-1</sup> )
Total soils (n = 63)						
Min	4.47	6.23	0.01	0.81	0.35	0.04
Max	9.18	49.6	0.95	73.7	14.8	0.36
Mean	7.23	26.6	0.11	14.1	4.48	0.14
SD	1.29	9.37	0.13	14.9	2.68	0.07
Paddy soils (n = 21)						
Min	4.99	14.9	0.02	1.21	0.35	0.04
Max	8.47	41.7	0.30	41.7	5.80	0.34
Mean	6.83b	25.6b	0.09b	11.6ab	3.91b	0.12b
SD	1.25	6.27	0.08	12.38	1.52	0.07
Red soils (n = 11)						
Min	4.47	13.1	0.01	1.21	0.84	0.06
Max	8.04	49.3	0.95	16.2	7.00	0.36
Mean	6.10b	28.0ab	0.21a	6.30b	4.14b	0.16ab
SD	1.41	9.48	0.27	5.85	1.78	0.09
Chernozem (n = 13)						
Min	6.67	15.9	0.04	0.81	3.54	0.09
Max	8.79	46.0	0.26	73.7	14.8	0.23
Mean	7.87a	32.6a	0.11ab	20.6a	7.34a	0.18a
SD	0.78	9.64	0.06	22.1	3.34	0.04
Other soils (n = 18)						
Min	6.20	6.23	0.01	1.62	0.87	0.06
Max	9.18	41.4	0.17	43.7	10.6	0.17
Mean	7.92a	22.7b	0.08b	17.2ab	3.27b	0.11b
SD	0.87	10.5	0.05	13.4	2.32	0.02

Different letters indicate significant difference ( $p < 0.05$ ) between paddy soils, red soils, chernozem, and other soils

n number of soil samples, SD standard deviation, CEC cation exchangeable capacity, WSS water-soluble salt, SOM soil organic matter, DOC dissolved organic carbon

TP (Table 2). TP was higher in paddy soils than in other soil types (Table 2). However, the potentially leachable P (CaCl<sub>2</sub>-P) and AP of paddy soils were relatively lower than that of other soil types. The AP values were higher on average in red soils than the other soils (Table 2). And the highest values of CaCl<sub>2</sub>-P appeared in the group of “other soils” with 3.03 mg kg<sup>-1</sup>. Among total soil types, the average percent of AP<sub>O</sub> was 57 ± 25% of AP (Table 2).

#### Fe/Al status

As shown in Table 3, the average of total Fe (TFe) in soils was 24.8 mg kg<sup>-1</sup>, which was higher than that of total Al (TAl, 3.73 mg kg<sup>-1</sup>). However, water-soluble Fe (WFe) with an average of 1.10 mg kg<sup>-1</sup> was lower than water-soluble Al (WAl, 1.36 mg kg<sup>-1</sup>). Three types of soil Fe/Al oxides were distinguished: free Fe/Al oxides, amorphous Fe/Al oxides, and complexing Fe/Al oxides. Highest mean values of free Fe oxides (Fe<sub>fr</sub>, 72%) and free Al oxides (Al<sub>fr</sub>, 73%) was found in total Fe oxides (Fe<sub>ox</sub>) and total Al oxides (Al<sub>ox</sub>), respectively (Table 3). Compared with other soil types, the chernozem contained more TFe,

TAl, WFe, WAl, Fe<sub>ox</sub> and Al<sub>ox</sub>. The paddy soils contained highest TFe, WFe, WAl compared with other soil types while their Fe<sub>ox</sub> (14.2 mg kg<sup>-1</sup>) and Al<sub>ox</sub> (3.30 mg kg<sup>-1</sup>) were less than those of red soils (18.8 mg kg<sup>-1</sup> and 5.41 mg kg<sup>-1</sup>, respectively).

#### Relationships of CaCl<sub>2</sub>-extractable P with climate, soil properties and Fe/Al status

There was a positive correlation in the red soils between the measured climate parameters, i.e., mean average temperature (MAT,  $r = 0.730$ ) and mean average precipitation (MAP,  $r = 0.685$ ), with potentially leachable inorganic P (CaCl<sub>2</sub>-P<sub>I</sub>) (Fig. 1). Soil properties showed limited effects on the CaCl<sub>2</sub>-P. WSS was positively correlated with CaCl<sub>2</sub>-P<sub>T</sub>, CaCl<sub>2</sub>-P<sub>I</sub> under “total soils” ( $r = 0.258$ ,  $r = 0.263$ ). SOM was positively correlated with the CaCl<sub>2</sub>-P<sub>T</sub> under paddy soils ( $r = 0.460$ ), but was negatively correlated with CaCl<sub>2</sub>-P<sub>O</sub> under chernozem ( $r = -0.596$ ) (Fig. 1). DOC showed a significantly positive relationship both with CaCl<sub>2</sub>-P<sub>T</sub> ( $r = 0.589$ ) and CaCl<sub>2</sub>-P<sub>I</sub> ( $r = 0.647$ ) for the “other soils”. TFe was

**Table 2** Soil P status

Soils	TP (mg kg <sup>-1</sup> )	AP <sub>T</sub> (mg kg <sup>-1</sup> )	AP <sub>I</sub> (mg kg <sup>-1</sup> )	AP <sub>O</sub> (mg kg <sup>-1</sup> )	AP <sub>O</sub> /AP <sub>T</sub> (%)	CaCl <sub>2</sub> -P <sub>T</sub> (mg kg <sup>-1</sup> )	CaCl <sub>2</sub> -P <sub>I</sub> (mg kg <sup>-1</sup> )	CaCl <sub>2</sub> -P <sub>O</sub> (mg kg <sup>-1</sup> )	CaCl <sub>2</sub> -P <sub>O</sub> / CaCl <sub>2</sub> -P <sub>T</sub> (%)
Total soils (n = 63)									
Min	378	1.55	0.27	0.03	0.23	0.97	0.16	0.20	8.13
Max	3387	767	281	727	94.8	9.33	8.57	3.80	88.5
Mean	1118	147	58.2	89.2	56.8	2.43	1.60	0.83	34.7
SD	576	174	69.3	128	24.8	1.99	1.52	0.80	14.5
Paddy soils (n = 21)									
Min	535	12.3	2.38	4.8	19.9	1.03	0.16	0.20	17.5
Max	2690	264	107	204	92.6	1.76	1.25	1.20	88.5
Mean	1252a	72.8b	24.6b	48.2b	67.5a	1.38b	0.87b	0.52a	36.8a
SD	517.37	65.3	28.9	49.3	21.9	0.22	0.23	0.26	16.1
Red soils (n = 11)									
Min	556	1.55	0.27	1.28	15.3	1.03	0.75	0.20	15.2
Max	1797	659	271	470	84.3	7.23	5.65	3.80	77.1
Mean	1114a	253ab	110a	143a	53.9ab	2.93a	1.86ab	1.07a	32.5a
SD	373	266	104	172	21.2	2.41	1.86	1.25	20.4
Chernozem (n = 13)									
Min	378	13.1	10.6	0.03	0.23	1.26	0.75	0.37	26.2
Max	2501	506	139	367	86.2	6.40	4.72	2.41	56.8
Mean	1089a	134ab	54.5b	80.0ab	41.9b	2.89a	1.87ab	1.02a	36.9a
SD	584	148	52.5	108	27.2	2.06	1.47	0.67	8.05
Other soils (n = 18)									
Min	382	33.4	9.66	11.5	6.30	0.97	0.58	0.29	8.13
Max	3387	767	281	727	94.8	9.33	8.57	3.77	50.8
Mean	985a	179a	68.5ab	111ab	56.7ab	3.03a	2.11a	0.93a	32.0a
SD	727	182	70.7	165	24.2	2.44	1.94	0.91	12.1

Different letters indicate significant difference ( $p < 0.05$ ) between paddy soils, red soils, chernozem, and other soils

*n* number of soil samples, *SD* standard deviation, *TP* total P, *AP<sub>T</sub>* total available P, *AP<sub>I</sub>* available inorganic P, *AP<sub>O</sub>* available organic P, *AP<sub>O</sub>/AP<sub>T</sub>*%; *CaCl<sub>2</sub>-P<sub>T</sub>* total CaCl<sub>2</sub>-extractable P, *CaCl<sub>2</sub>-P<sub>I</sub>* CaCl<sub>2</sub>-extractable inorganic P, *CaCl<sub>2</sub>-P<sub>O</sub>* CaCl<sub>2</sub>-extractable organic P, *CaCl<sub>2</sub>-P<sub>O</sub>/CaCl<sub>2</sub>-P<sub>T</sub>*

negatively correlated with both CaCl<sub>2</sub>-P<sub>T</sub> and CaCl<sub>2</sub>-P<sub>I</sub> under red soils ( $r = -0.650$ ,  $r = -0.699$ ), while TAI was negatively correlated with CaCl<sub>2</sub>-P<sub>I</sub> ( $r = -0.436$ ) and positively with CaCl<sub>2</sub>-P<sub>O</sub> ( $r = 0.507$ ) in the paddy soils. However, no significant correlation was found between Fe/Al oxides with CaCl<sub>2</sub>-P under all the soil types except that Al<sub>ar</sub> had a weakly positive correlation with CaCl<sub>2</sub>-P<sub>O</sub> under “total soils” and red soils (Fig. 1).

#### Relationships between CaCl<sub>2</sub>-extractable P and soil P content

TP had significantly positive relationship with both CaCl<sub>2</sub>-P<sub>T</sub> and CaCl<sub>2</sub>-P<sub>I</sub> under “total soils” and type “other soils” while it showed no special effect on CaCl<sub>2</sub>-extractable P under paddy, red and chernozem soils (Fig. 1). The relationships between soil CaCl<sub>2</sub>-P and AP were adequately described by linear equations (Figs. 2–4). CaCl<sub>2</sub>-P<sub>T</sub> was significantly affected by AP<sub>T</sub>

under all investigated soil types (total soils:  $p < 0.001$ ; red soils:  $p < 0.001$ ; chernozem:  $p = 0.001$ ; other soils:  $p < 0.001$ ) except paddy soils (Fig. 2). Under paddy soils, CaCl<sub>2</sub>-P<sub>I</sub> also showed no relationship with AP<sub>I</sub> while there were strong positive relationships between CaCl<sub>2</sub>-P<sub>I</sub> with AP<sub>I</sub> in “total soils”, “red soils”, “chernozem” and “other soils” (Fig. 3). No relationship of CaCl<sub>2</sub>-P<sub>O</sub> and AP<sub>O</sub> was found neither in paddy soils (Fig. 4). As shown in Fig. 4, the strongest relationship between CaCl<sub>2</sub>-P<sub>O</sub> and AP<sub>O</sub> was found in red soils with the R value being 0.901 ( $p < 0.001$ ) (Fig. 4c). In chernozem, the relationship was relatively weaker (Fig. 4d).

#### Discussion

##### Role of soil physicochemical properties and Fe/Al oxides on P leaching

Many soil properties including soil pH, cation exchange capacity (CEC), organic matter, moisture, soil constituents and clay contents were considered as the factors

**Table 3** Fe and Al oxides in soils collected across China

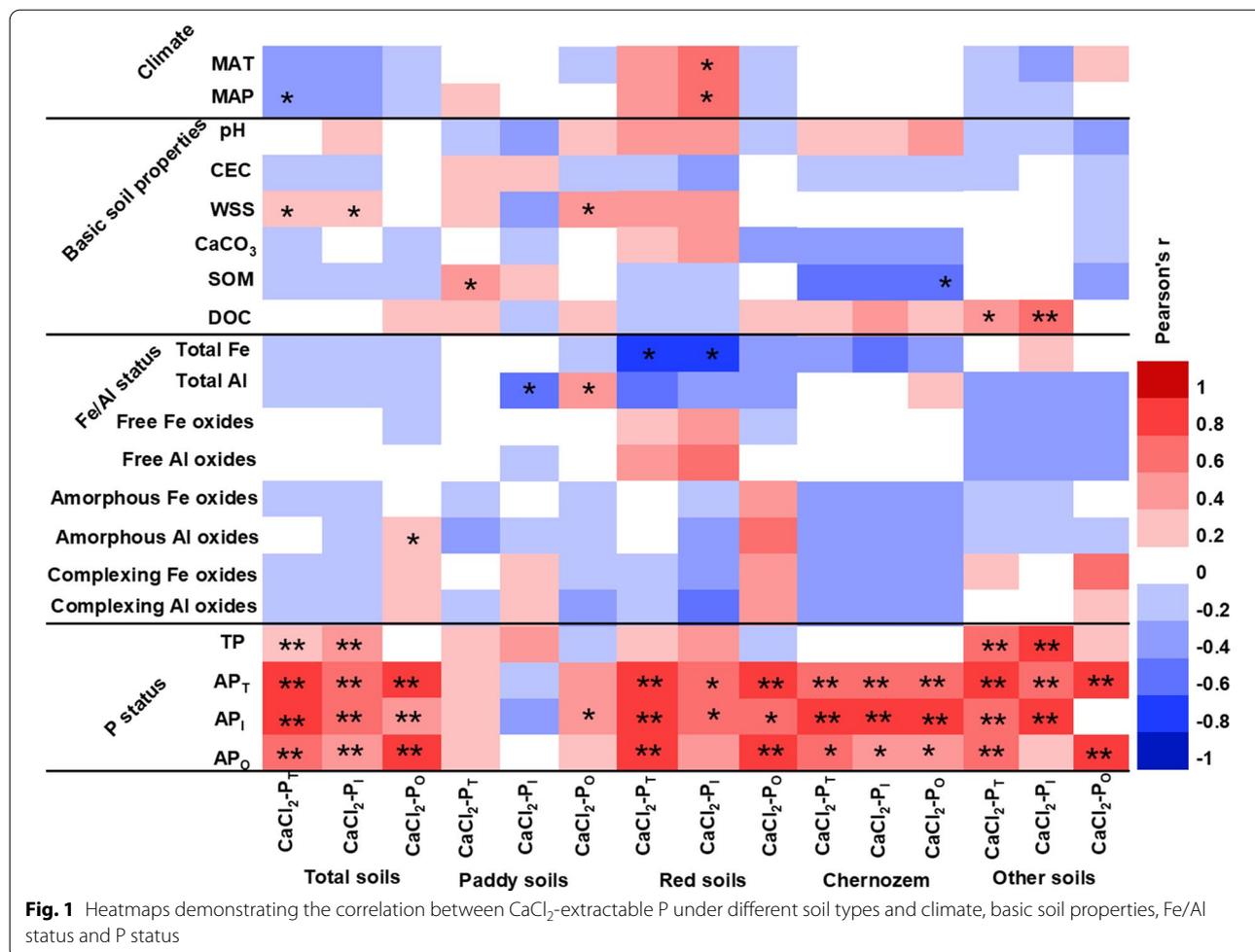
Soils	TFe (mg kg <sup>-1</sup> )	TAl (mg kg <sup>-1</sup> )	WFe (mg kg <sup>-1</sup> )	WAl (mg kg <sup>-1</sup> )	Fe <sub>fr</sub> (mg kg <sup>-1</sup> )	Al <sub>fr</sub> (mg kg <sup>-1</sup> )	Fe <sub>ar</sub> (mg kg <sup>-1</sup> )	Al <sub>ar</sub> (mg kg <sup>-1</sup> )	Fe <sub>co</sub> (mg kg <sup>-1</sup> )	Al <sub>co</sub> (mg kg <sup>-1</sup> )
Total soils (n = 63)										
Min	0.20	0.37	0.01	0.02	2.07	0.34	0.47	0.52	0.02	0.01
Max	57.7	8.72	10.7	15.5	40.3	7.73	8.70	2.72	8.48	3.42
Mean	24.8	3.73	1.10	1.36	11.8	2.07	3.36	1.51	1.11	0.69
SD	10.1	2.32	2.10	2.84	8.63	1.68	1.65	0.50	1.58	0.79
Paddy soils (n = 21)										
Min	9.55	0.58	0.02	0.02	2.07	0.34	0.86	0.52	0.09	0.06
Max	56.3	7.89	7.69	15.5	26.0	4.63	6.85	1.51	2.45	1.33
Mean	27.1a	3.55b	1.57a	2.40a	10.4a	1.66b	3.30b	1.16b	0.97b	0.56b
SD	9.26	2.47	2.56	4.34	6.92	1.31	1.43	0.27	0.67	0.36
Red soils (n = 11)										
Min	0.20	0.37	0.01	0.02	3.27	0.71	2.67	1.12	0.50	0.38
Max	25.9	6.78	10.7	8.20	40.3	6.35	8.70	2.72	8.48	3.42
Mean	15.9b	2.82b	1.13a	0.91a	11.2a	1.78ab	4.59a	1.90a	3.06a	1.73a
SD	8.29	1.93	3.19	2.42	10.6	1.59	1.83	0.52	2.79	1.22
Chernozem (n = 13)										
Min	16.6	0.53	0.15	0.12	6.03	0.93	2.14	1.19	0.02	0.01
Max	36.3	7.35	2.32	3.13	35.1	7.73	6.64	2.41	2.88	1.76
Mean	26.9a	2.86b	0.83a	1.00a	14.5a	3.10a	4.01ab	1.85a	0.90b	0.68b
SD	6.69	2.23	0.71	1.15	11.0	2.41	1.67	0.38	0.97	0.61
Other soils (n = 18)										
Min	1.68	2.33	0.01	0.03	4.70	0.70	0.47	0.54	0.03	0.02
Max	57.7	8.72	5.58	3.08	32.7	5.16	3.89	2.29	0.73	0.52
Mean	26.2a	5.12a	0.74a	0.67a	11.6a	1.95ab	2.21c	1.42b	0.22b	0.21c
SD	11.7	1.91	1.27	0.87	7.36	1.24	0.94	0.47	0.17	0.17

Different letters indicate significant difference ( $p < 0.05$ ) between paddy soils, red soils, chernozem, and other soils

*n* number of soil samples, *SD* standard deviation, *TFe* total Fe, *TAl* total Al, *WFe* water-soluble Fe, *WAl* water-soluble Al, *Fe<sub>fr</sub>* free Fe oxides, *Al<sub>fr</sub>* free Al oxides, *Fe<sub>ar</sub>* amorphous Fe oxides, *Al<sub>ar</sub>* amorphous Al oxides, *Fe<sub>co</sub>* complexing Fe oxides, *Al<sub>co</sub>* complexing Al oxides

for the P leaching by influencing P adsorption/desorption in soils [36, 37]. In our study, there was no clear correlation between soil physicochemical properties and CaCl<sub>2</sub>-P (Fig. 1). In paddy soils which were slightly acidic, SOM had a significantly positive correlation with CaCl<sub>2</sub>-P<sub>T</sub>. For paddy soil samples taken after drying conditions like our samples, some studies pointed out that organic onions increased P sorption through the formation of organic matter–Al complexes [38, 39]. In fact, many studies in other soil types showed that there was a competition of sorption sites on minerals between organic matters and phosphate [40]. A study about the colloidal phosphorus mitigation from paddy soils to waterbody also verified that the addition of organic matter increased both dissolved P and colloidal P in leachate because negatively charged organic acid bonded to particles and generated negatively hydroxyl groups, which result in both site competition and electrostatic force [41]. Other studies in acidic soils also showed that low

molecular weight organic acids increased the mobility of inorganic phosphorus (P) through the chelation of Al and high-molecular-weight organic acids showed potential to inhibit phosphate adsorption [42–44]. However, there was a negative relationship between SOM and CaCl<sub>2</sub>-P<sub>O</sub> in group of “Chernozem” with alkaline conditions in the study. Yang et al. [45] reported on the influence of SOM on P adsorption/desorption under black chernozem and concluded that OM could enhance P availability by reducing the P bonding energy and increasing the P desorption to some degree. In fact, their results also showed the adsorption capacity of soil for P increased with SOM content increased and the change of P bonding energy along with SOM content first went down and then up. It means that beyond a certain SOM value, both P bond capacity and intensity were increased so that can be a reason for negative relation between SOM and CaCl<sub>2</sub>-P<sub>O</sub> in the alkaline chernozem soils studied. Besides, some studies made in alkaline

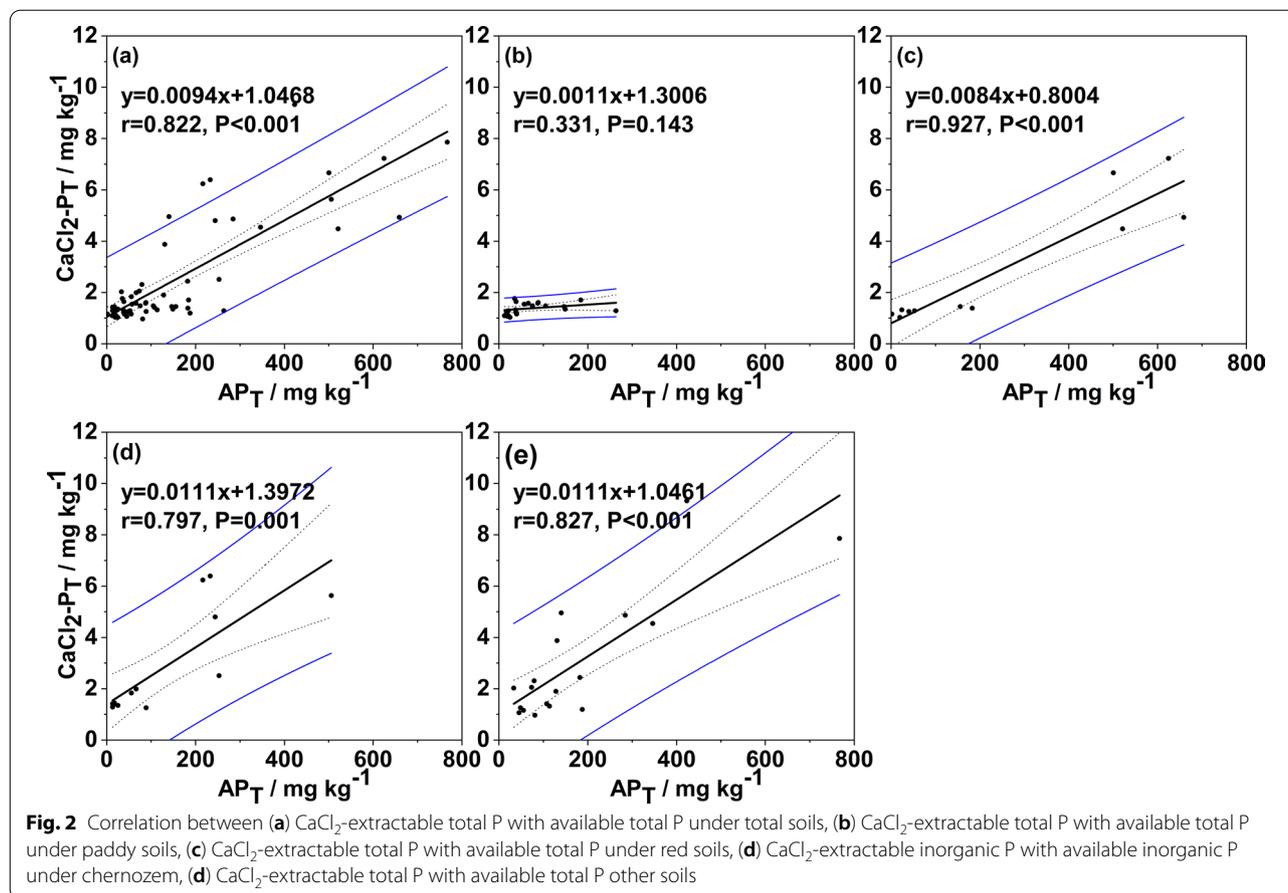


soils suggested that SOM was beneficial to P adsorption because of anionic character of SOM which can bind electrostatically cations such as  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  and these cations promote P retention [46, 47]. Overall, the influence of SOM on P adsorption depends on the type and concentration of organic material and the soil types, respectively, which is in accordance with the idea made by Debicka et al. [48].

Limited effect of Fe/Al oxides on  $\text{CaCl}_2$ -P was detected under all soil types in our study maybe due to the relatively limited number of soil samples. In fact, the process of phosphate sorption was affected by multiple soil constituents such as, carbonate content, organo-mineral complexes, metal oxides and clay minerals, because they all worked as adsorbents [18, 49, 50]. Abundance of metal oxides and their crystallinity were considered as the key factor for P adsorption [51, 52]. Higher free Al/Fe oxides usually means higher P retention and amorphous Al oxides with higher specific area is better to adsorb phosphate [51–54].

### Effects of soil P status on P leaching

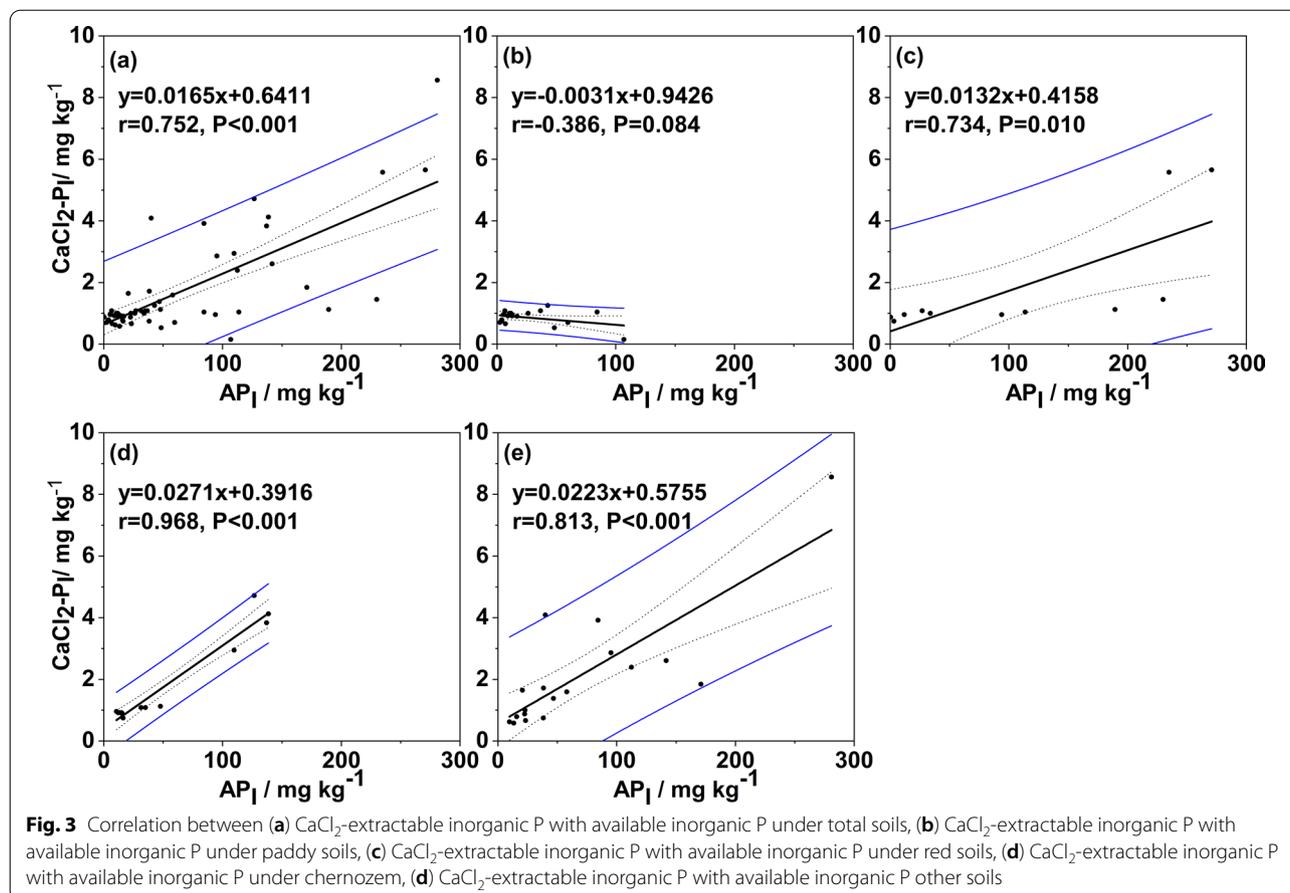
More P stored in soils resulted in the higher concentration of  $\text{CaCl}_2$ -P and thus higher risk of P loss (Fig. 1). Such a significant relationship of TP with  $\text{CaCl}_2$ -P could have been expected, when all studied soil samples ( $n = 63$ ) were taken in consideration. P is easily accumulated in soils when P inputs exceed crop requirement because of the discrepancy between high P fixation capacity and low P use efficiency by plants. The unbalance between application of fertilizer and crop P removal also decreases the availability of P sorption sites in soils [55]. Therefore, the P concentration in surface soils was demonstrated as a key factor for P leaching in some studies [56, 57]. It works as one of the major continuous sources for P pollution in waterbodies [17, 58]. In the study, we tested arable soils from all over the China and found the  $\text{CaCl}_2$ - $\text{P}_1$  were  $0.16\text{--}8.57 \text{ mg kg}^{-1}$ , which was higher than that reported in the study by Zhao et al. [59]. They investigated 23 agricultural soil samples across China and found  $0\text{--}2.5 \text{ mg kg}^{-1}$   $\text{CaCl}_2$ - $\text{P}_1$ . The mean available inorganic



P (AP<sub>I</sub>) value that we analyzed (58.2 mg kg<sup>-1</sup>) was also higher than that reported (20.7 mg kg<sup>-1</sup>) in a study in 2006 [60]. Only 9.3% of the arable land in 2006 was over 40 mg AP<sub>I</sub> kg<sup>-1</sup>, while that proportion is currently 38%. The increased application of P fertilizer resulted in the accumulation of P in arable land [11]. In comparison, 549 mg AP<sub>I</sub> kg<sup>-1</sup> was found in Danchi catchment [6] and 106 mg AP<sub>I</sub> kg<sup>-1</sup> was detected in Beijing suburbs [61], higher than that detected in an earlier study referred previously by Li et al. [60].

AP<sub>I</sub> was identified as important parameter for the P transport [12]. Our results also confirmed the significant correlation between AP<sub>I</sub> and CaCl<sub>2</sub>-P<sub>I</sub> under “total soils” ( $r=0.752$ , Fig. 3). In the past research, a split-line model was usually used to describe the relationship between AP<sub>I</sub> and CaCl<sub>2</sub>-P<sub>I</sub>. There was a specific point (change point) that can be used to determine the optimal AP<sub>I</sub> concentrations in soils without causing P<sub>I</sub> leaching [13, 14]. However, less study focused on the organic forms both in AP and CaCl<sub>2</sub>-P. In fact, organic P transport with subsurface flow plays a vital role in P transport and organic P was identified as the main form in leachate [19, 24, 62, 63]. In our study, the

CaCl<sub>2</sub>-P included both inorganic P and organic P, with the average 34% of organic P under all soils (Table 2). However, the AP in all soils consisted of more organic P (57 ± 25%). A relatively high correlation between AP and CaCl<sub>2</sub>-P under “total soils” was found when considered both the organic and inorganic forms ( $R=0.822$ , Fig. 2). Furthermore, a significant positive relationship of AP<sub>O</sub> with CaCl<sub>2</sub>-P<sub>O</sub> was found among all soil types except paddy soils (Fig. 4). The  $r$  value was up to 0.901 in red soils, which revealed that AP<sub>O</sub> was one of the key factors for P leaching in that soil type. A study conducted in red soils under arable crops found that AP<sub>I</sub> was positively correlated with deposition capacity and negatively with the maximum P adsorption capacity, which may result in more P leaching [64]. Fewer studies did research about the role of organic part in AP on P leaching and our results showed the mean AP<sub>O</sub> was more than mean AP<sub>I</sub> in red soils (Table 2). Change point is a useful tool when assessing the need for implementing P leaching control management. Different with the change point can be found from the relationship between AP<sub>I</sub> and CaCl<sub>2</sub>-P<sub>I</sub>. No critical level of AP<sub>O</sub> was identified where CaCl<sub>2</sub>-P<sub>O</sub> increased dramatically. It



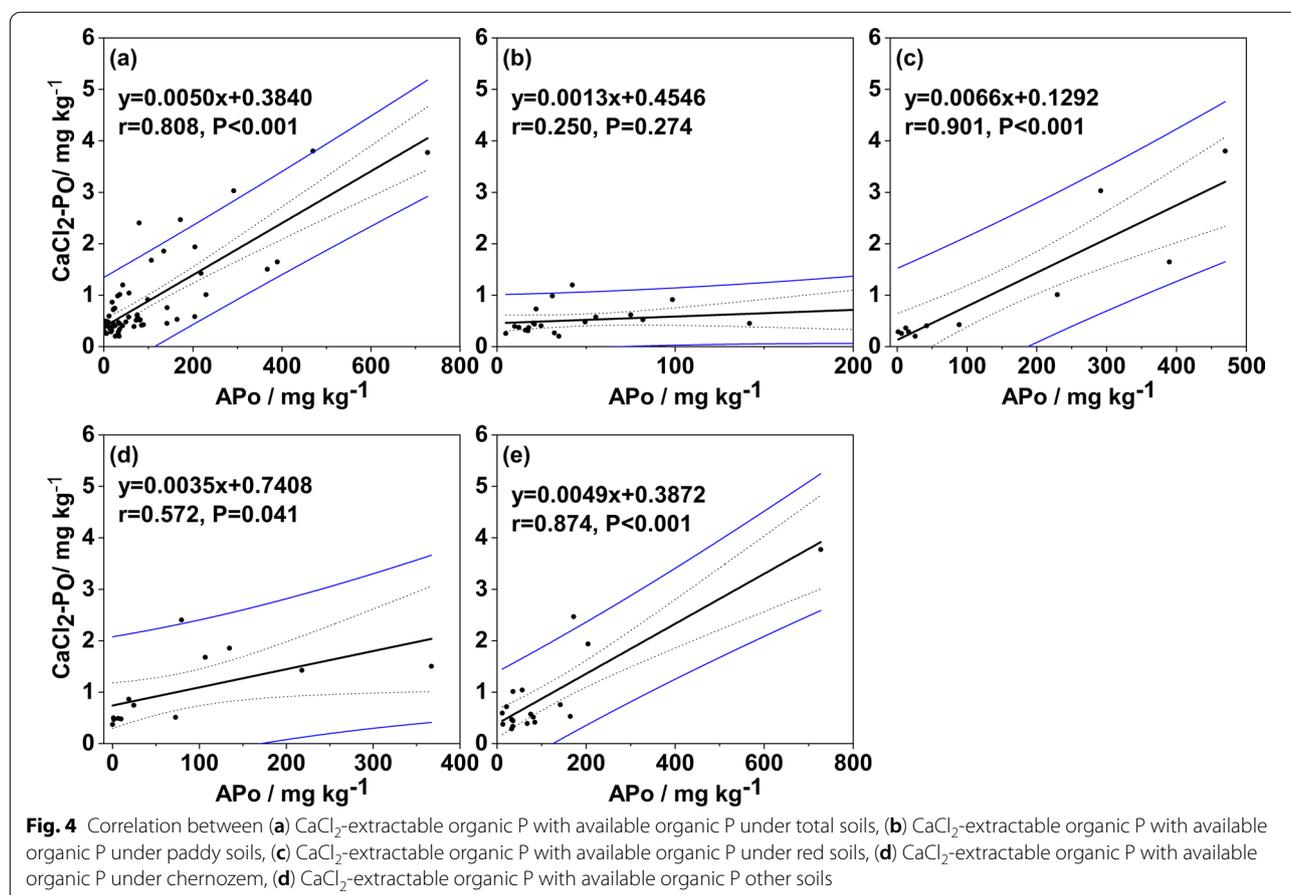
means that the leaching risk of organic P is harder to predict and thus control than that of inorganic P.

Paddy soils showed different results from other soil types (Figs. 2–4). AP had no correlation with  $\text{CaCl}_2\text{-P}$  neither with organic or inorganic form. In fact, some studies believed that soil P test measured in the topsoil should not be used alone for P leaching risk assessment [56]. But fewer studies suggested that AP should not be used in P leaching prediction. Paddy soil is a special type of agricultural land which experiences waterlogging during rice growing period for over 6 months in the double-cropping rice system, resulting in the alternating redox cycles [65]. The shift of redox condition may alter the P adsorption and desorption by changing organic fractions and anions related to P bonded [66]. The alteration may affect AP behavior without affecting P leaching.

## Conclusions

$\text{CaCl}_2$  extractable total P ( $\text{CaCl}_2\text{-P}_T$ ) in arable soils sampled from all over the China was in a large range of  $0.97\text{--}9.33\text{ mg kg}^{-1}$  with 35% of them in organic forms on average. The mean percentage of organic P was

over half of available total P ( $\text{AP}_T$ ) ( $57 \pm 25\%$ ) and the maximum even reached 88.5%. Therefore, the potential risk of organic P ( $\text{P}_O$ ) leaching from arable land is higher and  $\text{P}_O$  should be included in P leaching proxy measurements. Positive correlation was found between  $\text{CaCl}_2\text{-P}$  (organic forms, inorganic forms and total forms) with AP (organic forms, inorganic forms and total forms) under all investigated soil types except paddy soils.  $\text{CaCl}_2$  extractable inorganic P ( $\text{CaCl}_2\text{-P}_i$ ) and available inorganic P ( $\text{AP}_i$ ) was highly correlated in the type of chernozem ( $r=0.968$ ). And the relationship of  $\text{CaCl}_2$  extractable organic P ( $\text{CaCl}_2\text{-P}_O$ ) with available organic P ( $\text{AP}_O$ ) was strong in the type of red soils ( $r=0.901$ ) which both  $\text{CaCl}_2\text{-P}_O$  and  $\text{AP}_O$  of it were significantly higher than those of other soil types. It means that the control of  $\text{AP}_O$  accumulation in arable land may be the key point to limit  $\text{P}_O$  leaching and the mitigation measures should be constructed based on the soil type. However, rare effects of soil basic properties and Fe/Al oxides on  $\text{P}_O$  leaching was found in our study because of the limited number of samples, thus increasing the sample size is necessary for further study.



## Supplementary Information

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**Additional file 1: Table S1.** Soil sampling information.

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## Author contributions

XS analyzed the data and drafted the manuscript. ML designed the experiment and contributed to the chemical analysis of soil sample. RB and EK improved the manuscript. All authors read and approved the final manuscript.

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All data are presented in the manuscript.

## Declarations

### Ethics approval and consent to participate

The manuscript is an original work that has not been published in other journals. The authors declare no experiments involving humans and animals.

## Consent for publication

All authors agreed to the publication.

## Competing interests

The authors declare that they have no competing interests.

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