A suggested fractionation scheme of inorganic phosphorus in calcareous soils

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Abstract

On the basis of a critical review on conventional fractionation schemes of inorganic phosphate and further study of chemical behaviors of Ca-P and Fe-P in calcareous soils, a systematic scheme for the separation of soil inorganic phosphates in calcareous soils is suggested. In the scheme calcium phosphate is classified into dicalcium phosphate, octacalcium phosphate and apatite types, and Ca_2-P is extracted by $NaHCO_3$ solution, Ca_8-P by NH_4Ac, Al-P by NH_4F, Fe-P by $NaOH-Na_2CO_3$, occluded-P by $Na_3Cit-Na_2S_2O_4-NaOH$, and Ca_{10}-P by H_2SO_4.

Synthetic phosphates prepared of which the chemical and physical assay show good consonance with the theoretical value were used in experiment, the recovery rates of the phosphates added into the calcareous soils by specific extractants is at the range of 85–99%.

Introduction

Since 1957 the fractionation of inorganic soil phosphate suggested by Chang and Jackson [2] has been used widely for studying the role of phosphate in soil chemistry and agrochemistry of China. [4, 7, 8, 12]. Later, Chang's fractionation system was further developed by Fife [6] and Petersen [16]. In their fractionation scheme, calcium phosphate is treated as one component and it is used rather successfully in acid soils. However, when a phosphatic fertilizer is added to a calcareous soil, the monocalcium phosphate in fertilizer is converted into dicalcium phosphate, then octocalcium phosphate [15]. The characteristics of Ca-P in calcareous soils can be summarized as follows: $CaHPO_4.2H_2O \rightleftharpoons Ca_8H_2(PO_4)_6.5H_2O \rightleftharpoons Ca_{10}(PO_4)_6F_2$ (mostly in soil parent materials). Therefore, the fractionation of inorganic phosphorus in the calcareous soils exists of a series of calcium phosphates with complex physico-chemical reactions [10, 11, 13, 17, 18, 19] and different availability to plant growth. In the present paper, on the basis of further study on the chemical behaviors of calcium phosphates and iron phosphate in calcareous soils, a new fractionation

scheme for inorganic phosphorus in calcareous soils is suggested. In the suggested fractionation scheme, the calcium phosphate is further divided into three types and corresponding extractants and procedures used in separation for the three fractions of calcium phosphate are briefly described and the method for extraction of iron phosphate is modified; finally, as compared with the conventional ones, the fractionation scheme and extraction methods of inorganic phosphate in calcareous soils suggested by the authors are discussed.

Materials and methods

Soil samples used in the present investigation include the calcareous soils (soil No 863, 864, 865 in Table 3) collected from the loessial plain of North China with $CaCO_3$ contents of 4.2–7.1% and pH of 8.5–8.8, a yellow brown earth (soil No 491) collected from Nanjing with a pH of 6.7 and a red earth (soil No 492) derived from Quaternary red clay collected from the rolling hill of Central China with a pH of 6.1.

Following are the methods for preparing syn-

thetic phosphates:

1. $CaHPO_4 \cdot 2H_2O$ [14]: slowly add 0.1 N NH_4OH into a 5% $Ca(H_2PO_4)_2 \cdot H_2O$ solution at 25–30°C with constant stirring until the pH of the solution rising up to 5–6. Keep the solution at this temperature for 1 h, filter, wash the precipitate first with distilled water and then with acetone. Dry at 40–50°C.

2. $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ [1]: add 40 g $CaHPO_4 \cdot 2H_2O$ into 800 ml of 0.5 M NH_4Ac. The initial pH of the solution is 6.9–7.0, keep the solution at 33°C with constant stirring. When the pH declines below at 6.3, then renew the NH_4Ac solution until pH of the solution is kept at > 6.7. Filter the $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ precipitated, wash first with distilled water and then with acetone. Dry at 40–50°C.

3. $Ca_{10}(PO_4)_6F_2$: weigh 8.2 g $CaHPO_4 \cdot 2H_2O$, 2.8 g $CaCO_3$, 0.7 g CaF_2 and mix thoroughly in a agate mortar. Add acetone into the mixture and grind them to form a paste. Evaporate and dry at room temperature. Transfer the dried material into a platinum evaporating dish, calcine them at 1150°C for 1.5 h, wash them with 0.5 M trisodium citrate with a pH of 8.1 to remove the excess CaO.

4. $AlPO_4 \cdot nH_2O$ [5]: dissolve 1.6 g of powdered aluminum in 24 ml of 50% phosphoric acid. Dilute it to 60 ml. Filter, dilute the solution to 500 ml. Add 380 ml acetone into the solution with constant stirring. Filter the precipitated $AlPO_4 \cdot nH_2O$ and wash it with acetone and then with distilled water. Dry the $AlPO_4 \cdot nH_2O$ at room temperature.

5. $FePO_4 \cdot 2H_2O$ [3]: add 30 ml of 1 M NaH_2PO_4 solution to 10 ml of 1 M $FeCl_3$. Dilute to 600 ml. Digest at 90°C on a water bath for 24 h or more. Wash the precipitated $FePO_4 \cdot 2H_2O$ more than three times with acetone. Dry at room temperature.

The physical and chemical properties of the synthetic phosphates are in good consonance with their X-ray patents and chemical composition.

Results and discussions

The extractants were selected with the synthetic phosphates mentioned above based on pre-selection of a series of extractants and then the best
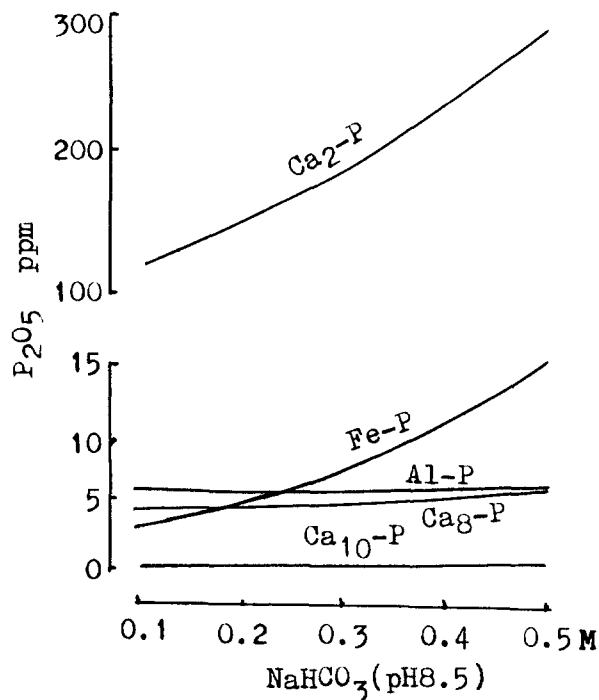

Fig. 1. Effect of concentrations of $NaHCO_3$ on the solubility of synthetic phosphates (20°C).

extractants were further selected and their optimal extracting conditions were studied. Fig. 1 shows the solubility of synthetic phosphates in $NaHCO_3$(pH 8.5) with a concentration of 0.1–0.5 M at 20°C after shaking for 1 hr (the same below unless noted). Fig. 2 shows the effects of pH on the solubility of synthetic phosphates in the solution of $NaHCO_3$(0.25 M). The solubilities of four synthetic phosphates in NH_4Ac(pH 7.0) with concentrations varying from 0.1 M to 0.5 M are shown in Fig. 3. Fig. 4 shows the effect of pH on the solubilities of synthetic phosphates in NH_4Ac solution. The extractive rates of Fe-P with NaOH(0.1 M), Na_2CO_3 (0.5 M), and NaOH(0.1 M)-Na_2CO_3 (0.5 M) under the condition of existence of $CaCO_3$ are shown in Table 1.

According to the characteristics of solubilities of various forms of synthetic phosphates in extractants mentioned above, an inorganic phosphorus fraction scheme comparatively suitable for calcareous soils can be established. In this scheme, Ca-P is divided into three types, Ca_2-P, Ca_8-P and Ca_{10}-P types, and Fe-P is extracted with NaOH-Na_2CO_3; and conventional methods are employed for determination of Al-P and occluded-P(O-P).

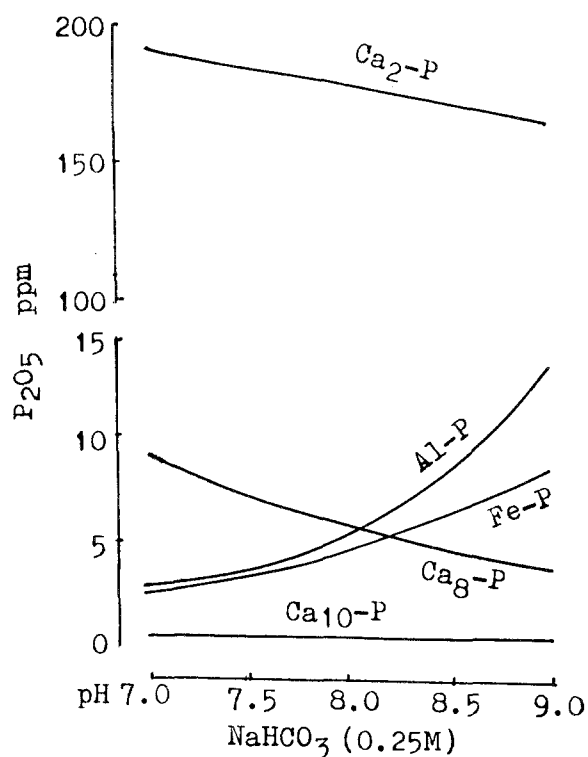Fig. 2. Effect of pH of NaHCO$_3$ on the solubility of synthetic phosphates (20°C).

Fig. 3. Effect of concentrations of NH$_4$Ac on the solubility of synthetic phosphates (20°C).

Table 2 shows the brief procedure for the extractive of various fractions of inorganic phosphates in calcareous soils.

The first fraction of inorganic phosphate extracted with NaHCO$_3$ is mainly Ca$_2$-P (Table 2), Fig. 2 shows that there are also certain amounts of other phosphates dissolved in the extractant NaHCO$_3$, but they are comparatively very small as compared with Ca$_2$-P. Therefore, this fraction can be termed as Ca$_2$-P types, or more exactly, NaHCO$_3$-soluble phosphate.

The second fraction of inorganic phosphorus extracted with NH$_4$Ac is mainly Ca$_8$-P though a small amount of Al-P and Fe-P can also be dissolved. The second fraction can be termed as Ca$_8$-P type or NH$_4$Ac-soluble phosphate. After the extraction of Ca$_2$-P and Ca$_8$-P from the original phosphates in calcareous soils, there remain the calcium phosphate insoluble in NaHCO$_3$ and NH$_4$Ac, those extracted with H$_2$SO$_4$ is mainly Ca$_{10}$-P. The recovery of synthetic Fe-P in calcareous soils with NaOH(0.1 N) is about 1-2%, indicating that severe interference exists in the reaction.
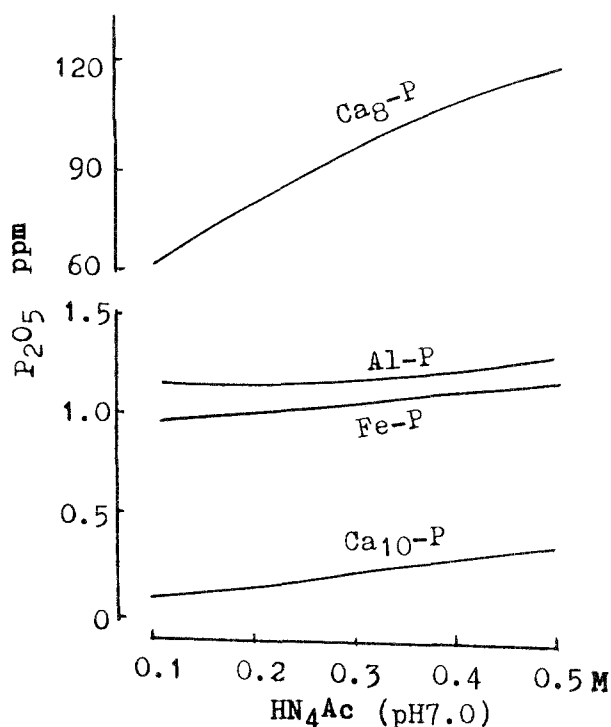
The recovery rates of various synthetic calcium and iron phosphates in calcareous soils were in the range of 85–99% (Table 3) and thus the extractants proposed in this paper could be considered reliable. When a fraction of phosphate is extracted with a specific extractant, other fractions of phosphate may also be extracted more or less, but the former fraction is absolutely predmoninant in amount. For example, the recovery rate of Ca$_2$-P with NaHCO$_3$ is about 90% and NaHCO$_3$ is reliable extractant for Ca$_2$-P.

The new scheme suggested in this paper has several advantages over that of Chang and Jackson (Table 4), for calcareous soils: (1) much Ca$_8$-P can be extracted by NH$_4$Ac in the new scheme; (2) several times more Fe-P can be extracted with the extractants in new scheme than that with the method of Chang and Jackson in calcareous soils. It can be inferred that much of non-occluded Fe-P in calcareous soils can not be extracted [9] in Chang and Jackson's scheme, possibly because of the interference of CaCO$_3$ or Ca^{2+}, or other factors.

As compared with Chang and Jackson's scheme (Table 5), the total amount of three types of cal-

Table 1. Effect of $CaCO_3$ on the amount of Fe-P extracted (%)

Extractants Treatment	NaOH (0.1N)	Na_2CO_3 (0.5 M)	$NaOH-Na_2CO_3$ (0.1 N–0.5 M)
Fe–P	93.4	48.6	97.4
Fe–P + $CaCO_3$	73.4	48.9	94.8

* Shake 1 hr. 20°C

cium phosphates extracted in the new scheme approximate the total amount of NH_4Cl-soluble and H_2SO_4-soluble phosphate in Chang and Jackson's scheme. It is indicated that the methods for fractionating Ca-P into three types of calcium phosphates with different chemical behavior are reliable and thus very helpful in the study on transformation of phosphates applied in calcareous soils.

It can also be seen from Table 5 that the total amounts of Fe-P and occluded phosphate in the two schemes are also approximately the same, but in Chang and Jackson's scheme a large part of Fe-P can not be extracted with NaOH in calcareous soils and is considered as occluded phosphate. Using $NaOH-Na_2CO_3$ in various soils with the new scheme revealed that a considerable amount of Fe-P could be extracted from calcareous soils. Therefore, the new scheme may promote greatly the study on the transformation of different forms of phosphates in weathering processes and is of significance in stuyding the effect of Ca-P and Fe-P on plant phosphorus nutrition in calcareous soils.
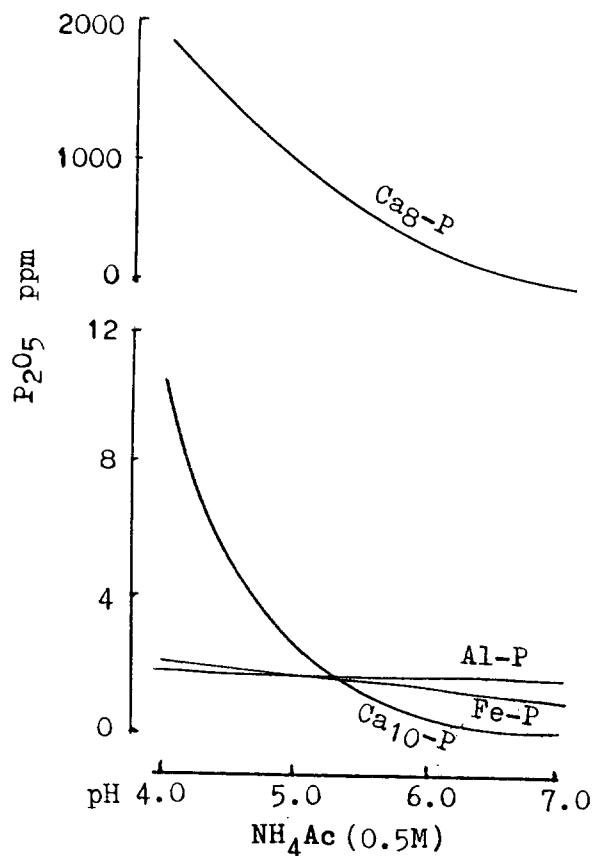
Fig. 4. Effect of pH of NH_4Ac on the solubility of synthetic phosphates (20°C).

Table 2. Scheme of inorganic-P fractionation in calcareous soil

Soil	pH 7.5, 0.25 M $NaHCO_3$					
S1	ppt 1* pH 4.2, 0.5 M NH_4Ac					
	S2	ppt 2** pH 8.2, 0.5 N NH_4F				
		S3	ppt 3 0.1 N $NaOH$–0.1 N Na_2CO_3			
			S4	ppt 4 0.3 M Na_3Cit-$Na_2S_2O_4$–Na OH		
				S5	ppt 5 0.5 N H_2SO_4	
					S6	ppt 6
(Ca$_2$–P)	(Ca$_8$–P)	(Al–P)	(Fe–P)	(O–P)	(Ca$_{10}$–P)	

* ppt 1 wash with 95% alcohol
**ppt 2–5 wash with saturated NaCl solution

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Table 3. Recovery of synthetic phosphates added in soils (%)

Added Phosphates	Soil No.*	NaHCO₃	NH₄Ac	NH₄F	NaOH Na₂CO₃	H₂SO₄
Ca₂–P	863	91.8				
	864	91.2				
	865	91.0				
	492	88.4				
	491	87.0				
Ca₈–P	863	10.1	85.1			
	864	10.3	85.7			
	865	9.75	87.1			
	492	6.91	80.8			
	491	3.37	81.6			
Al–P	863	6.51	2.55	75.2		
	864	6.97	2.55	82.5		
	865	5.66	2.73	74.7		
	492	7.58	3.17	91.8		
	491	3.54	2.95	88.2		
Fe–P	863	8.37	2.45	7.32	92.9	
	864	8.19	2.47	8.35	92.2	
	865	8.21	3.30	8.39	92.6	
	492	7.65	3.08	14.0	90.8	
	491	5.95	2.76	11.8	91.2	
Ca₁₀–P	863	0.0678	0.194	0.116	0.0519	99.4
	864	0.0519	0.0293	0.152	0.361	99.0
	865	0.00991	0.299	0.123	0.129	95.2
	492	0.0291	–	0.146	0.0826	94.4
	491	0.0947	0.954	0.133	0.585	97.9

* 863, 864, 865- fluvo-aquic soil (clayey, loamy, sandy); 492- Red soil: 491- Yellow brown earth

Table 4. Comparison of results determined by two fractionation schemes (ppm P₂O₅)

Soil No.*	NaHCO₃ (Ca₂–P)	NH₄Ac (Ca₈–P)	NH₄F (Al–P)	NaOH–Na₂CO₃ (Fe–P)	H₂SO₄ (Ca₁₀–P)	O–P	Total
863	14.9	115	46.2	52.1	850	172	1250
864	6.67	138	36.5	38.9	857	163	1240
865	1.52	55.4	14.1	24.2	893	113	1101
492	1.28	16.7	31.0	136	36.9	294	516
491	2.79	23.7	44.0	236	80.5	267	654

(Chang and Jackson's scheme)

Soil No.*	NH₄Cl	NH₄F (Al–P)	NaOH (Fe–P)	H₂SO₄ (Ca–P)	O–P	Total
863	19.7	33.4	4.57	976	216	1250
864	12.0	40.3	4.32	1016	207	1279
865	9.01	12.8	6.04	947	130	1105
492	1 22	25.9	121	61	306	515
491	1.82	49.9	225	108	283	667

* 863, 864, 865- Fluvo-aquic soil (clayey, loamy, sandy); 492- Red soil; 491- Yellow brown earth

Table 5. Comparison of results for Ca–P and Fe–P determined by two fractionation schemes (ppm P_2O_5)

Soil No.*	$NaHCO_3$ (Ca$_2$-P)	NH_4Ac (Ca$_8$-P)	H_2SO_4 (Ca$_{10}$-P)	Total Ca-P	suggested scheme NaOH–Na$_2$CO$_3$ (Fe-P)	O-P	Total Fe-P
863	14.9	115	850	980	52.1	172	224
864	6.67	138	857	1002	38.9	163	202
865	1.52	55.4	893	950	24.2	113	137
492	1.28	16.7	36.9	54.9	136	294	430
491	2.79	23.7	80.5	107	236	267	503

Soil No.*	NH_4Cl (Ca$_2$-P)		H_2SO_4 (Ca$_{10}$-P)	Total Ca-P	Chang and Jackson's scheme NaOH (Fe-P)	O-P	Total Fe-P
863	19.7		976	996	4.57	216	221
864	12.0		1016	1028	4.32	207	211
865	9.01		947	956	6.04	130	136
492	1.22		61.0	62.2	121	306	427
491	1.82		108	110	225	283	508

* 863, 864, 865- Fluvo-aquic soil (clayey, loamy, sandy); 492- Red soil; 491- Yellow earth

Summary

A new scheme for the fractionation of calcium phosphate in calcareous soil is suggested, in which calcium phosphate is subdivided into three types, i.e. dicalcium phosphate, octacalcium phosphate and apatite by extracting with $NaHCO_3$, NH_4Ac, and H_2SO_4 solution respectively; the Fe-P is extracted by $NaOH—Na_2CO_3$.

The recovery rates of synthetic phosphates in calcareous soils are in the ranges of 85–99%.

As compared with Chang and Jackson's scheme, no remarkable difference in amount is found between the total amount of three types of calcium phosphate in this scheme and the total amount of NH_4Cl-soluble and H_2SO_4-soluble phosphate in Chang and Jackson's scheme; the total amount of Fe-P and occluded-phosphate between two schemes are approximately the same but more Fe-P is identified in the new scheme.

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