

Reaction products of ammonium nitrate phosphate fertilizers of varying water-soluble phosphorus content in different Indian soils

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Abstract. Studies were undertaken on the isolation and identification of reaction products of ammonium nitrate phosphate (ANP) fertilizers containing 30, 50 and 70 per cent water-soluble phosphorus (WSP) of total phosphorus in representative soils of the vertisol, oxisol, alfisol, entisol, mollisol and aridisol groups of India. ANP fertilizers were applied in solid form to soil, and reaction products formed at and around the site of ANP fertilizer placement were identified after six weeks incubation in moist soils by X-ray diffraction technique. DCPD (dicalcium phosphate dihydrate- $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was the major reaction product of ANP fertilizers containing 30 and 50 per cent WSP in vertisol, entisol, aridisol, mollisol, oxisol and alfisol, and of ANP containing 70 per cent WSP in vertisol, entisol, alfisol, aridisol and mollisol. DCP (dicalcium phosphate- CaHPO_4) was detected with ANP of 30 and 50 per cent WSP in the vertisol, alfisol, entisol, mollisol and aridisol groups of soils. In addition to DCPD, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (metastrengite) and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ -monoclinic (metavariscite) were formed in alfisol and oxisol soils with ANP of 30 and 50 per cent WSP. $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ (metavariscite) were identified in alfisol and oxisol soils while $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ -orthorhombic (variscite) was formed in alfisol soils with ANP of 70 per cent WSP.

Ammonium nitrate phosphate (ANP) fertilizer in granular form is produced in India in the grades of 15:15:15 containing 30 per cent water-soluble phosphorus, and 20:20:0 containing 60 per cent water-soluble phosphorus. However, the agronomic suitability of ANP fertilizers which contained partially water-soluble and citrate-soluble phosphorus, for crops grown in different Indian soil types is controversial depending on the experimental conditions such as soil type and the growing period of the test crop [1, 4, 15, 16, 22, 23]. Water-soluble or partially water-soluble phosphorus fertilizers like ANPs undergo rapid transformation in soils to compounds which persist over several months and form the principal source of phosphorus for plants [5, 12, 14]. Identification of such reaction products helps to elucidate the fate of these fertilizers in soils and may provide information useful for recommendations on the optimum water-soluble phosphorus content of ANPs required for different soil types. Studies were undertaken to identify the specific discrete reaction products of ANP fertilizers in typical soils of the vertisol, alfisol, oxisol, mollisol, aridisol and entisol groups which form the major soil groups of India.

Materials and methods

The fertilizers used for the study were ANP fertilizers containing 30, 50 and 70 per cent water-soluble phosphorus. These fertilizers were supplied by Rashtriya Chemicals and Fertilizers Ltd., Bombay, India. MAP (mono-ammonium orthophosphate-NH₄H₂PO₄) and DCP which represent totally water-soluble and citrate-soluble phosphorus containing compounds, respectively, and form the major components of the ANP fertilizers were included for comparison. Chemical analysis of the fertilizers used are presented in Table 1.

The soils used for the study were a calcareous black (vertisol-pellustert), from Jalana, Maharashtra, a calcareous deep black (vertisol-pellustert) from Jalgaon, Maharashtra, red sandy loam (alfisol-rhodustalf) from Hyderabad, Andhra Pradesh, acidic red loam (alfisol-rhodustalf) from Raigarh, Madhya Pradesh, grey-brown alluvial (aridisol-calciorthid) from Baroda, Gujarat, an alluvial (mollisol-haplaquoll) from Pantnagar, Uttar Pradesh, solonized arid brown loamy sand of alluvial origin (alfisol-ustalf) from Ludhiana, Punjab, an alluvial (entisol-haplaquent) from Delhi and a laterite (oxisol) from Ratnagiri, Maharashtra.

Physico-chemical characteristics of these soils were determined as follows and are reported in Table 2. pH of the soil was determined in 1:2.5 soil:water suspension using a glass electrode pH meter with calomel reference electrode as described by Jackson [11]. Moisture equivalent was determined by the suction method of Bouyoucos [6]. Organic carbon was determined after oxidation by chromic acid with sulfuric acid as per the procedure of Walkley and Black [24]. Extractable phosphorus in neutral to alkaline soils was determined using the 0.5 *N* sodium bicarbonate (pH 8.5) extractant as described by Olsen et al. [17], and in acidic soils by using 0.03 *N* NH₄F + 0.025 *N* HCl extractant as per the method of Bray and Kurtz [7]. These methods were used as these are the recommended procedure for determining available phosphorus levels in soils of varying pH levels. Cation exchange capacity of soils was determined using sodium acetate extractant as described by Jackson [11]. Exchangeable calcium and magnesium were determined using sodium nitrate extractant as per the procedure of Cheng and Bray [8]. Free calcium carbonate content in the soils was estimated using HCl extractant according to the method described by Piper [18].

Table 1. Analytical data on phosphatic fertilizers

Fertilizer	Total P (%)	Water-soluble P (% of total)	Total N (%)
Ammonium nitrate phosphate	9.0	30.0	19.5
Ammonium nitrate phosphate	8.3	50.0	18.6
Ammonium nitrate phosphate	7.1	70.0	15.2
Monoammonium orthophosphate	26.9	100.0	12.2
Dicalcium phosphate	20.1	—	—

Table 2. Physicochemical characteristics of soils

Soil	pH (1:2.5)	Moisture equivalent (%)	Organic Carbon (%)	Available P (kg ha ⁻¹)	Cation exchange capacity (meq/100 g soil)	Exchange- able Ca (meq/100 g soil)	Exchange- able Mg (meq/100 g soil)	Free CaCO ₃ (%)
Vertisol (Calcareous black) Jalana	8.4	37.73	0.80	6.0	58.09	37.96	10.37	11.00
Vertisol (Calcareous deep black) Jalgaon	8.2	39.03	0.82	8.0	57.66	44.10	3.26	5.47
Aridisol (Alluvial) Baroda	8.4	28.09	0.41	34.0	19.08	5.05	3.50	3.30
Mollisol (Alluvial- Tarat) Pantnagar	7.8	32.56	1.68	42.0	24.38	8.58	2.54	2.00
Alfisol (Solonized arid brown of alluvial origin) Ludhiana	8.3	26.63	0.60	15.0	9.33	3.90	3.58	1.45
Entisol (Alluvial) Delfhi	7.6	23.00	0.74	26.0	27.56	10.70	3.24	2.05
Oxisol (Laterite) Ratnagiri	6.1	33.81	1.70	13.0	19.71	3.86	1.44	T
Alfisol (Acid red) Hyderabad	6.5	22.61	0.56	9.0	16.29	4.10	1.62	T
Alfisol (Acid red) Raigarh	5.5	22.93	0.66	0.7	5.04	1.02	0.61	n.d.

T = Traces

n.d. = not detected

For the formation of reaction products of ANP fertilizers in these soils, 2.25 g of fertilizer in granular form was placed in a small depression (2.25 cm dia.) at the centre of the soil contained in a plastic cylinder (6.5 cm dia, 5 cm height and having capacity of about 200 g soil) with a fine mesh of nylon base. The soil surface was covered with plastic sheet having holes for exchange of air. The moisture content in the soil columns was maintained by placing the plastic cylinder with its perforated base in a glass petridish to which water was added; this procedure permitted constant wetting of the soil column. The soil was then incubated for six weeks at room temperature ($25 \pm 1^\circ\text{C}$). While this procedure is broadly similar to the method used by Hinman et al. [10], relatively higher quantities of the granulated fertilizers were used in the present investigation. The procedure used for formation of reaction products in soils is similar to those used by earlier authors [19, 27]. At the end of incubation period, the soil was air dried in situ and the reaction products formed at the site of fertilizer placement and at a distance of 0.5 cm from the placement site were recovered and finely ground for X-ray diffraction analysis from which the identification of reaction products was carried out.

The diffraction patterns were obtained from Philips PW1031 wide angle goniometer tracings with a Geiger counter X-ray diffractometer, $\text{CuK}\alpha$ radiation, $\lambda = 1.5405 \text{ \AA}$, scanning rate $0.5^\circ 2\theta/\text{min}$. The "d" spacings of the X-ray diffraction patterns of reaction products were compared with those of standard compounds as listed by Lehr et al. [13]. The presence of a particular compound in the reaction product is indicated by a minimum of six to seven "d" spacings corresponding to within $\pm 0.05 \text{ \AA}$ of the values for the standard. Similar technique for identification of reaction products of phosphatic fertilizers in soils have been used by several authors [14, 21, 25, 26, 27]. The "d" spacings for the reaction product samples and for control (no P) were determined. Spacings that occurred in the treated soil, and not found in the controls were taken to be those of reaction product.

Results and discussion

The reaction products formed with MAP, DCP and ANP of 30, 50 and 70 per cent water-soluble phosphorus content in various Indian soil types are reported in Tables 3, 4, 5, 6 and 7, respectively. To facilitate the interpretation of the results obtained on reaction products of ANP fertilizers, it was considered necessary to present the results on reaction products of MAP and DCP formed in the experimental soils before reporting the findings on reaction products of ANP fertilizers in these soils.

DCPD was formed as reaction product with MAP in vertisols, aridisols, alfisols and entisols (Table 3). The present findings are in agreement with the results of Racz and Soper [19] and Bell and Black [2, 3] who reported that DCPD was formed when MAP was kept in contact with alkaline and slightly

Table 3. Reaction products obtained for MAP when applied in a band to soils. Incubation period: 6 weeks

Soil	pH (1 : 2.5)		Reaction products	
	Control (No P)	At placement site	At placement site	0.5 cm from placement site
Vertisol (Calcareous black)	8.4	6.8	DCPD ^a	DCPD
Vertisol (Calcareous deep black)	8.2	6.7	DCPD	—
Aridisol (Grey-brown alluvial)	8.4	6.6	DCPD	—
Mollisol (Alluvial-Tarai)	7.8	7.1	AlPO ₄ · 2H ₂ O (orthorhombic) ^b	—
Alfisol (Alluvial)	8.3	7.1	FePO ₄ · 2H ₂ O (monoclinic) ^c	—
Entisol (Alluvial)	7.6	6.5	DCPD	AlPO ₄ · 2H ₂ O (orthorhombic)
Oxisol (Laterite)	6.1	7.0	FePO ₄ · 2H ₂ O (monoclinic)	AlPO ₄ · 2H ₂ O (orthorhombic)
Alfisol (Red sandy loam)	6.5	6.6	AlPO ₄ · 2H ₂ O (orthorhombic)	AlPO ₄ · 2H ₂ O (orthorhombic)
Alfisol (Acid red sandy loam)	5.5	6.9	AlPO ₄ · 2H ₂ O (orthorhombic)	—

^a Brushite (CaHPO₄ · 2H₂O)

^b Variscite

^c Metastrengite

acidic soils. $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (metastrengite) was formed as reaction product when MAP was applied in solid form in oxisol and mollisol while $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ -orthorhombic (variscite) was identified as reaction product of MAP in alfisol, oxisol and aridisol (Table 3). Das and Datta [9] and Sarkar et al. [20] reported that $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ (variscite) was formed in acidic to neutral soils as reaction product of MAP. Yadav and Mistry [26] have identified $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (metastrengite) with MAP and DAP in red sandy loam (alfisol), laterite (oxisol) and alluvial (entisol) soils.

Data on the formation of reaction products with DCP in contrasting Indian soils presented in Table 4 indicate that transformation of DCP was not observed and this fertilizer remained chemically unchanged over a 6 week incubation period in contrasting Indian soils except in highly acidic (pH 5.5) red loam (alfisol) where partial transformation of added DCP into DCPD occurred. Bouldin and Sample [5] have reported that granules of DCP remained chemically unchanged in soil for considerable period after application. In the present study, DCP remained chemically unchanged in contrasting Indian soils which may be largely due to neutral to alkaline soil reaction or lack of H-ions in the system to favour either conversion or dissolution or hydrolysis of DCP to DCPD. Partial transformation of DCP to DCPD in highly acidic (pH 5.5) red soil (alfisol) can be largely attributed to the acidic nature of soil or higher concentration of H-ions in the soil to favour conversion of DCP to DCPD.

Data on the reaction products formed with ANP fertilizers containing 30, 50 and 70 per cent water-soluble phosphorus are presented in Tables 5, 6 and 7, respectively.

DCPD (brushite) was formed as reaction product in vertisols, aridisol, mollisol, entisol, oxisol and alfisol groups of Indian soils with ANP fertilizers containing 30 and 50 per cent water-soluble phosphorus and with ANP of 70 per cent WSP, DCPD was identified predominantly in vertisols, aridisol, mollisol, alfisol and entisol soils. In addition to DCPD formation, DCP (monetite) was detected with ANP of 30 per cent WSP in vertisols, aridisol, mollisol, alfisol, entisol, and with ANP of 50 per cent WSP in vertisol, aridisol, mollisol and alfisol soils. DCP was not identified when ANP of 70 per cent WSP was applied to contrasting Indian soils.

The ANP fertilizers used in the present study are primarily composed of MAP, DCP, NH_4NO_3 and CaSO_4 and water-soluble phosphorus content in these fertilizers increases with increase in the MAP : DCP ratio. Formation of DCPD in vertisols, entisol, mollisol, aridisol and alfisol groups of India with ANP fertilizers in the present study may be largely due to the presence of MAP in ANP fertilizers, these effects are similar to those obtained with MAP fertilizer where DCPD was identified as reaction product in the same groups of soil as mentioned above (Table 3) in the present study. DCPD formation even in acidic red (alfisol) and laterite (oxisol) soils with ANP of 30 and 50 per cent WSP may be largely due to hydrolysis or conversion of DCP to

Table 4. Reaction products obtained for DCP when applied in a band to soils. Incubation period: 6 weeks

Soil	pH (1:2.5)		Reaction products	
	Control (No P)	At placement site	At placement site	0.5 cm from placement site
Vertisol (Calcareous black)	8.4	8.3	DCP ^a	—
Vertisol (Calcareous deep black)	8.2	8.0	DCP	—
Aridisol (Grey-brown alluvial)	8.4	8.2	DCP	—
Mollisol (Alluvial-Tarai)	7.8	8.1	DCP	—
Alfisol (Alluvial)	8.3	8.3	DCP	—
Entisol (Alluvial)	7.6	7.6	DCP	—
Oxisol (Laterite)	6.1	6.4	DCP	—
Alfisol (Red sandy loam)	6.5	7.1	DCP	—
Alfisol (Acid red sandy loam)	5.5	6.9	DCP	—
			DCPD	—

^a Dicalcium phosphate anhydrous (CaHPO₄·monetite)

Table 5. Reaction products obtained for ANP (30 per cent water-soluble phosphorus) when applied in a band to soils. Incubation period: 6 weeks

Soil	pH (1:2.5)		Reaction products	
	Control (No P)	At placement site	At placement site	0.5 cm from placement site
Vertisol (Calcareous black)	8.4	7.8	DCPD	—
Vertisol (Calcareous deep black)	8.2	7.6	DCPD	—
Aridisol (Grey-brown alluvial)	8.4	7.4	DCPD	—
Mollisol (Alluvial- Taraí)	7.8	8.1	DCPD	—
Alfisol (Alluvial)	8.3	7.4	DCPD	—
Entisol (Alluvial)	7.6	6.9	DCPD	—
Oxisol (Laterite)	6.1	7.6	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic) ^a	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic)
Alfisol (Red sandy loam)	6.5	7.0	DCPD FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic)	AlPO ₄ · 2H ₂ O (monoclinic)
Alfisol (Acid red sandy loam)	5.5	7.2	DCPD FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic)	—

^a Metavariscite

Table 6. Reaction products obtained for ANP (50 per cent water-soluble phosphorus) when applied in a band to soils. Incubation period: 6 weeks

Soil	pH (1 : 2.5)		Reaction products	
	Control (No P)	At placement site	At placement site	0.5 cm from placement site
Vertisol (Calcareous black)	8.4	7.6	DCPD	—
Vertisol (Calcareous deep black)	8.2	7.2	DCPD DCP	—
Aridisol (Grey-brown alluvial)	8.4	6.8	DCPD DCP	—
Mollisol (Alluvial-Tarai)	7.8	7.2	DCPD DCP	—
Alfisol (Alluvial)	8.3	7.4	DCPD DCP	—
Entisol (Alluvial)	7.6	6.5	DCPD	—
Oxisol (Laterite)	6.1	7.2	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic)	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic)
Alfisol (Red sandy loam)	6.5	7.0	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic) DCPD	—
Alfisol (Acid red sandy loam)	5.5	7.2	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (monoclinic) DCPD	—

Table 7. Reaction products obtained for ANP (70 per cent water-soluble phosphorus) when applied in a band to soils. Incubation period: 6 weeks

Soil	pH (1:2.5)		Reaction products	
	Control (No P)	At placement site	At placement site	0.5 cm from placement site
Vertisol (Calcareous black)	8.4	7.5	DCPD	—
Vertisol (Calcareous deep black)	8.2	6.9	DCPD	—
Aridisol (Grey-brown alluvial)	8.4	7.5	DCPD	—
Mollisol (Alluvial-Tarai)	7.8	7.3	DCPD FePO ₄ · 2H ₂ O (monoclinic)	—
Alfisol (Alluvial)	8.3	6.8	DCPD	AlPO ₄ · 2H ₂ O (orthorhombic)
Entisol (Alluvial)	7.6	6.4	DCPD	—
Oxisol (Laterite)	6.1	7.4	FePO ₄ · 2H ₂ O (monoclinic)	AlPO ₄ · 2H ₂ O (monoclinic)
Alfisol (Red sandy loam)	6.5	7.1	FePO ₄ · 2H ₂ O (monoclinic) AlPO ₄ · 2H ₂ O (orthorhombic)	—
Alfisol (Acid red sandy loam)	5.5	7.3	AlPO ₄ · 2H ₂ O (monoclinic)	—

DCPD because of acidic nature of soil as well as acidic pH of the saturated solution of ANP fertilizers (pH 5.8 for ANP 30 per cent WSP; pH 4.0 for ANP 50 per cent WSP) at and in close proximity to the site of placement of the fertilizer pellet. DCPD was not formed with ANP of 70 per cent WSP in acid red (alfisol) and laterite (oxisol) soils which can be ascribed to the low content of DCP in this fertilizer. The presence of DCP in vertisols, entisol, mollisol, aridisol and alfisol soils with ANP fertilizers containing 30 and 50 per cent WSP can be accounted for by the presence in these fertilizers of relatively large amount of DCP which subsequently might not have hydrolyzed or converted to DCPD due to neutral to alkaline reaction of soils.

In addition to DCPD formation with ANP of 30 and 50 per cent WSP, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ -monoclinic (metastrengite) and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ -monoclinic (metavariscite) were formed as reaction products in acid red loam (alfisol) and laterite (oxisol) soils. With ANP of 70 per cent WSP, metastrengite, metavariscite and variscite were identified as reaction products in acid red loam (alfisol) and laterite (oxisol) soils. Formation of metastrengite, metavariscite and variscite with ANP fertilizers in alfisol and oxisol soils may be largely due to the presence of MAP in ANP fertilizers, these effects are similar to those obtained for MAP fertilizer where metastrengite and variscite were identified as reaction products of MAP (Table 3) except that in place of variscite, metavariscite was identified as reaction products with ANP of 30 and 50 per cent WSP fertilizers. It is of interest to note that although the two aluminium phosphate, namely, variscite and metavariscite have similar chemical composition, their crystallographic properties are different. Variscite is orthorhombic in nature while metavariscite is monoclinic in nature. The differences in the formation of variscite with MAP, and metavariscite with ANP of 30 and 50 per cent WSP in soils may be probably due to the rapid dissolution of predominantly water-soluble phosphorus fertilizers such as MAP while with ANP of 30 and 50 per cent WSP dissolution of phosphorus component of ANP fertilizers may be slow because of relatively low content of water-soluble phosphorus compound in ANP of 30 and 50 per cent WSP fertilizers.

Variscite was identified with ANP of 70 per cent WSP mainly in alfisols while metavariscite was formed in laterite (oxisol) and highly acid red loam (alfisol) soils.

The reaction products formed in proximity of the site of fertilizer were generally not detected at a distance of 0.5 cm from the fertilizer placement site which can be ascribed to the likely interference from soil particles present in the reaction product sample which rendered identification of the reaction products through X-ray diffraction techniques rather difficult as well as to the general lack of mobility of orthophosphate ions in soils.

Current research in our laboratory is aimed at synthesis of the major persistent reaction products of ANP fertilizers in major Indian soil types identified in the present investigation, namely, brushite, variscite,

metavariscite and metastrengite and evaluation of these reaction products as sources of phosphorus to plants grown in contrasting soil types.

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