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Soil Abiotic and Biotic Interactions and Impact on the Ecosystem and Human Welfare

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P.M. Huang
University of Saskatchewan, Saskatoon, Canada

A. Violante
University of Naples, Portici, Italy

J.-M. Bollag
Pennsylvania State University, University Park, PA, USA

P. Vityakon
Khon Kaen University, Khon Kaen, Thailand

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Phosphate-Induced Cadmium Release from Soils

J.O. Onyatta *and* P.M. Huang*

Abstract

Phosphate fertilizers are applied to correct phosphorus deficiency in acidic tropical soils of variable charge, which account for a large proportion of the world's arable land. They are commonly applied in bands or mixed with seeds. Within the vicinity of the phosphate fertilizer zone, the concentration of phosphate is high and can cause dissolution of soil minerals. Hence a study was conducted to investigate the degree to which phosphate may effect release of cadmium (Cd) from soil, rate of release, and formation of phosphate reaction products. Since phosphate fertilizers contain a wide range of Cd concentrations, perturbation of phosphate reaction product formation by Cd was also investigated. The surface soils used in this study were selected from tropical soils in Kenya varying widely in physicochemical properties. The study shows that 1M $NH_4H_2PO_4$ solution induced the release of Cd from natural soils and the soils treated with Idaho monoammonium phosphate (MAP)-fertilizer. The enhanced release of Cd by the phosphate was attributed to the combined effect of Cd introduced to the soils and the Cd released from the soils through the attack of protons and the complexation of phosphate. Phosphate-induced Cd release from natural soils and treated soils increased during the short reaction period of 0.25 to 1 h, then decreased with time, and tended to approach a plateau. Decrease in Cd concentration was apparently due to readsorption of the Cd released on the surface of the soil particles and/or formation of sparingly soluble reaction products in the solution. The amounts of Cd released by $NH_4H_2PO_4$ increased with increments in concentration of $NH_4H_2PO_4$. XRD analysis showed that NH_4-taranakite formed in the soils treated with 1M $NH_4H_2PO_4$ solution. However, taranakite did not form when monoammonium

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Corresponding author: Dr. P.M. Huang, Dept. Soil Science, University of Saskatchewan, 51 Campus Drive, Saskatoon SK S7N 5A8, Canada.

phosphate was spiked with Cd even at 6.4×10^{-3} M $Cd(ClO_4)_2$, indicating that Cd perturbed taranakite formation. The study indicates that at the fertilizer granule-soil interface wherein concentration of orthophosphate is high, more Cd was mobilized compared to bulk soil. The study further shows that NH_4-taranakite can form in acidic tropical soils but the formation may be perturbed if the MAP-fertilizer applied contains significantly high Cd as an impurity.

1 INTRODUCTION

The chemical characteristics of the soil and the source of phosphate fertilizer determine soil fertilizer reactions, which influence P availability to plants (Brady, 1990; Tisdale et al., 1993). When phosphate fertilizers are applied to soils and dissolved by soil water, reactions occur among the phosphate, soil constituents, and nonphosphatic fertilizer compounds. As a result, the P in the fertilizers becomes fixed due to adsorption and precipitation. The nature of the reactions and reaction intensity of phosphate fertilizers with soil constituents should vary with distance from the fertilizer granule relative to the extent of phosphate concentration and pH. The concentration of P in saturated monoammonium phosphate (MAP) solution is 2.9 M with a pH of 3.5 (Lindsay et al., 1962). In the immediate vicinity of the fertilizer granule, the pH is quite low. When the concentrated P is released into the surrounding soil, composition of the soil solution is altered, which results in the dissolution of some minerals. Dissolution of phosphate fertilizer granules is fairly rapid in soil, even under conditions of low soil moisture (Sample et al., 1980). It has been reported that large quantities of reactive cations such as Fe^{2+}, Al^{3+}, Mn^{2+}, K^+, Ca^{2+} and Mg^{2+} can be released during the dissolution processes (Lindsay et al., 1962). Cations from exchange sites may also be displaced by the cations present in these concentrated solutions. Low and Black (1947) found that treating kaolinite with ammonium phosphate solutions (up to 1.5 M) released significant amounts of Si and Al. Similar evidence for the release of cations by solutions of monoammonium phosphate (MAP) and diammonium phosphate (DAP) has been reported by Lindsay et al. (1962).

The high concentration of phosphate and low pH may cause dissolution of soil constituents such as Al and Fe oxides, kaolinite, montmorillonite, and illite (Haseman et al., 1950; Kittrick and Jackson, 1954, 1955, 1956). According to studies by Zhou and Huang (1995), monoammonium phosphate induces release of K from soils. The combined effect of phosphate and proton on the alteration of K-bearing minerals was reported to be the major mechanism of K release from the soils tested in the $NH_4H_2PO_4$ solution. NH_4^+ has nearly the same ionic radius as the K ion and can be subjected to fixation; however, release of K by NH_4^+ is possibly due to exchange reaction. Release of K^+ by NH_4^+ is relatively minor significance since NH_4Cl releases only a fraction of the K released by MAP (Zhou and Huang, 1995).

Phosphate fertilizers added to agricultural soils are also known to form various reaction products in soils (Lindsay et al., 1962; Zhou and Huang, 1995). The phosphate concentration in a soil is a key factor in determining the nature

of the reactions. Numerous phosphates are involved in these soil-fertilizer reactions and have been studied by various researchers (Bouldin et al., 1960; Lehr et al., 1959, 1967; Lindsay et al., 1962). Formation of reaction products in soils is of primary importance because plants obtain their phosphorus requirement from these reaction products (Lindsay et al., 1962).

The presence of both ammonium taranakite $[(NH_4)_3Al_3H_6(PO_4)_8 \cdot 18H_2O]$ and potassium taranakite $[K_3Al_5H_6(PO_4)_8 \cdot 18H_2O]$ in agricultural soils as P-fertilizer reaction products with soils has been reported (Lindsay et al., 1962; Taylor et al., 1963; Tamimi et al., 1964; Sakar et al., 1977; Prabhudesai and Kudrekar, 1984; Zhou and Huang, 1995). Taranakites contain N, P, and K. Formation of taranakites in soils can result in the transformation of these nutrients into forms that are slowly available. Taylor et al. (1960) investigated taranakites as a source of phosphate for plants. Formation of taranakites in soils plays an important role in nutrient dynamics, especially in the vicinity of phosphate fertilizers when applied to acidic soils.

However, little is known about the release of Cd and the formation of phosphate reaction products in phosphorus-deficient acidic soils of variable charge found in the tropics, where large amounts of phosphate fertilizers are applied to correct phosphorus deficiency. Phosphate fertilizers are applied in bands or mixed with seeds; hence the release of Cd in the region surrounding the band may differ from that of the bulk soil and consequently affect Cd phytoavailability. Therefore, the objectives of this study were to determine in selected tropical soils from Kenya: i) the degree to which phosphate may affect the release of cadmium from soils and ii) the rates of Cd release and formation of phosphate reaction products.

2 MATERIALS AND METHODS

Three surface soils (0–40 cm depth) located in Egerton (Andisol), Naivasha (Inceptisol), and Soy (Oxisol) in Kenya were used for this study. The sites from which the soils were sampled constitute major agricultural areas in Kenya that vary widely in physicochemical properties. The Egerton soils are derived from volcanic ash and pyroclastic rocks, well drained, very deep, and dark reddish-brown with humic topsoil. Naivasha soils are derived from lacustrine deposits, mainly of volcanic ash origin, imperfectly drained, moderately deep to deep, and found in the lake region (Lake Naivasha) of the Central Rift valley. Soy soils are derived from intermediate igneous rocks (syenites, trachytes, and phonolites), well drained, moderately deep to deep, dark red, friable clay over petroplinthite. All the soil samples were air dried and crushed to pass through a 2-mm sieve prior to use. Selected properties of these soils are presented in Table 19.1.

The pH of the soils in water (1:2 soil:water) was measured using a pH meter model 1820P (Fisher Scientific, Pittsburgh, PA). The cation exchange capacity (CEC) of the soils was determined after saturation with ammonium acetate solution according to the method of Jackson (1958). Mechanical analysis of the

Table 19.1: Selected properties of the soils studied (Onyatta and Huang, 1999)

Soil[†]	Parent material	pH	Mechanical analysis			Org. C	Inorg. C	CDB Fe[††]	Na-pyroph.[‡]			Ammon. Oxal[§]		Total Cd	AAAc-EDTA[¶] extractable Cd
			> 50	2–50	< 2	C	C	Fe[††]	Al	Fe	Mn	Al	Fe		
				μm											
			%					g kg^{-1}						mg kg^{-1}	
Egerton (Andisol)	Volcanic ash	6.0	20.6	26.4	53.0	26.0	1.0	35.0	1.4	0.9	0.02	1.7	6.5	0.157	0.137
Naivasha (Inceptisol)	Lacustrine	6.8	39.1	11.9	49.0	14.0	2.0	12.0	0.8	0.5	0.10	1.6	0.6	0.119	0.096
Soy (Oxisol)	Igneous rocks	5.4	34.7	11.3	54.0	20.0	2.0	17.0	1.3	0.6	0.01	1.9	0.4	0.019	0.017
LSD$_{0.05}$		0.2	0.3	0.1	0.4	0.3	0.1	0.4	0.1	0.1	0.01	0.2	0.1	0.001	0.001
LSD$_{0.01}$		0.4	0.6	0.2	0.7	0.5	0.2	0.7	0.2	0.2	0.02	0.3	0.2	0.002	0.002

[†]Surface soil sample (0–40 cm)

[††] Citrate-dithionite-hydrogen carbonate extractable Fe

[‡]Sodium pyrophosphate-extractable Al, Fe, and Mn

[§]Ammonium oxalate-extractable Al and Fe

[¶]Ammonium acetate-acetic acid-ethylene diamine tetraacetic acid extractable Cd

soils was carried out based on the method outlined by him in 1979. The total and organic carbon contents of the soils were determined by heating them without prior treatment at 1,100°C and 850°C, respectively (Wang and Anderson, 1998), using the Leco CR-12 carbon analyzer (Leco Corp., St. Joseph, MI). Inorganic carbon was determined from the difference between the two values. The Fe, Mn, and Al contents of the pyrophosphate extract (McKeague, 1967), the contents of Fe extracted by the citrate-dithionite-bicarbonate (CDB) extraction method (Mehra and Jackson, 1960), and those of the Al and Fe extracted by the ammonium oxalate-oxalic acid extraction method (McKeague and Day, 1966) were determined using a Perkin-Elmer 300 atomic absorption spectrometer (Norwalk, CT). The flame types and conditions were the same as those recommended by the manufacturer. The graphite furnace parameters used for determination of Cd are presented in Table 19.2.

Table 19.2: Graphite atomic absorption parameters used for determination of Cd (Krishnamurti et al., 1994)

Steps	Temp. (°C)	Ramp time (s)	Hold time (s)	Argon flow (ml min^{-1})
Drying	200	10	20	300
Charring	300	5	20	300
Cooling	50	5	15	300
Atomization	1,600	0	10	0
Cleaning	2,700	5	5	300

For total Cd analysis the soils were ground with an agate mortar and pestle to pass through a 0.16-mm sieve and homogenized before use. The total Cd was determined after microwave digestion of the soil samples (Krishnamurti et al., 1994). The Cd availability index (CAI) of the soils (< 2 mm) was determined following the ammonium acetate-acetic acid-ethylene diamine tetraacetic acid (AAAc-EDTA) extraction procedure (Lakanen and Ervio, 1971). Cadmium in the supernatants was determined using graphite furnace atomic absorption spectrometer (GFAAS) at wavelength 228.8 nm.

2.1 Determination of Cadmium by Graphite Furnace Atomic Absorption Spectrometer

In GFAAS determination, dissolution of the sample, dissociation from the matrix, and generation of the analyte ground state occur sequentially during the following steps: drying, thermal treatment (charring), cooling, atomization and cleaning. Thus, analysis performed with GFAAS requires careful selection of step temperatures and periods to ensure that a process is carried out effectively. The furnace parameters are therefore chosen to achieve maximum accuracy and sensitivity in determination of Cd in aqueous extracts (Krishnamurti et al., 1994).

2.2 Soil Mineralogy

Soil samples were treated sequentially with 1 M NaOAc (pH 5.0) and 30% H_2O_2 prior to x-ray diffraction (XRD) analysis. Soils were not treated with dithionite-citrate-bicarbonate to remove metal oxides. The soils tested were not calcareous and the crystalline oxides present in tropical soils are known to selectively sorb heavy metals. Soil samples were fractionated to 0.2, 0.2–2, 2–5, 5–20, 20–50, and > 50 μm sizes by the sedimentation method (Jackson, 1979). Slides of 0.2, 0.2–2 and 2–5 μm size fractions were prepared for examination by Rigaku X-ray diffraction instrument (Tokyo, Japan) using monochromatic Cu-K_α radiation generated at 50 kV-150 mA. Coarse fractions (5–20, 20–50, and > 50, μm) were ground and used for powder x-ray diffraction analysis by Philips x-ray diffractometer (Model PW 1031) (Eindhoven, the Netherlands) using a Fe-K_α radiation at 35 kV-16 mA. Mineralogy of all the fractions among the soils studied showed predominance of micas and kaolinite in the 0.2 and 0.2–2 μm fractions. In the 2–5 μm fractions, micas, kaolinite, quartz and feldspars were identified and in the 5–20 μm fractions, micas, quartz, and feldspars were present. In both the 20–50 μm and > 50 μm fractions, only quartz and feldspars were identified. Oxides of Al (gibbsite), Fe (hematite) and Mn (birnessite) were detected in all the particle size fractions of the soils investigated.

The point of zero charge (PZC) of the soils was determined according to the method of Duquette and Hendershot (1993) and the specific surface area of the soil samples was determined by ethylene glycol monoethyl ether (EGME) method (Eltantawy and Arnold, 1973; Tiller and Smith, 1990) and the BET-N_2 method using the Autosorb (Quantachrome Corp., Syosset, N.Y.). These properties are presented in Table 19.3.

Table 19.3: Point of zero charge (PZC) and specific surface of the soils

Site	PZC	Specific surface (m² g⁻¹)	
		EGME[†]	BET-N_2
Egerton	6.3	66.3	32.4
Naivasha	7.2	79.0	36.0
Soy	5.0	71.1	36.0
ASE[‡]	± 0.2	± 0.3	± 0.2

[†] Ethylene glycol monoethyl ether
[‡] Average Standard Deviation

2.3 Incubation Studies

To each 100 g of the three surface soil samples, the Idaho MAP-fertilizer was added to give a Cd content of 62.4 mg kg⁻¹ soil as calculated in Appendix I (a, b). The Cd content of Idaho MAP-fertilizer was 144 mg Cd kg⁻¹. The amount of Cd added to the soils was calculated based on the fertilizer recommendation

for these soils (130 kg MAP fertilizer/ha or 67.6 kg P_2O_5/ha; fertilizer type, 11:52:0) (Annual Farmers' Recommendations, 1993), the Cd content of the fertilizer, and the amount of soil that would be in contact with fertilizer granules (Appendix 1b). The amount of MAP fertilizer added to 100 g soil used in the incubation study was calculated as described in Appendix I(c). Natural soil samples and soils treated with the Idaho MAP fertilizer were placed in plastic containers in two replicates and water added to field capacity, and the samples allowed to incubate at room temperature (25°C) for 100 days. During incubation moisture was maintained at field capacity.

2.4 Kinetics of Cadmium Release from the Soils

The concentration of orthophosphate in a saturated solution of $NH_4H_2PO_4$ fertilizer can be as high as 2.90 M (Lindsay et al., 1962). Phosphate fertilizers are often mixed with seeds or side banded; hence the concentration of orthophosphate will be high at the fertilizer granule-soil interface and especially at the soil rhizosphere. In order to simulate the effect of orthophosphate on Cd release from the soils in the vicinity of the fertilizer granules, 1.00 M $NH_4H_2PO_4$ solution was chosen for the kinetic study.

At the end of the 100-day incubation period, the treated soils were washed with 10 mL of deionized distilled water three times to remove any free salts prior to their use. In total, 30 mL of deionized distilled water was used in the leaching process. The amount of Cd removed by leaching process was not determined since incubation had been a pretreatment. One gram of each soil (natural or Idaho MAP-fertilizer treated soil), in duplicate, was placed in a polypropylene centrifuge tube and 10.0 mL of 1.00 M $NH_4H_2PO_4$ solution added. The centrifuge tube containing a soil suspension was placed in a water bath shaker at 25°C, with an agitation speed of 60 cycles min^{-1}. At the end of each reaction period (0.25, 0.5, 0.75, 1.0, 2.0, 7.0, 15.0, and 24.0 h), the suspensions were filtered through a 0.45-μm pore-size membrane under vacuum. Separate duplicate samples were used during each equilibration time. The pH of the suspensions was monitored at the end of each reaction period.

Cadmium in the filtrates was determined using a Perkin Elmer 2280 graphite furnace atomic absorption spectrometer (Norwalk, CT) at 228.8 nm using a pyrolytically coated tube. The Cd determined in the filtrates (Cd_r) was the Cd released from the soil during reaction time, t. The Cd remaining in the sample (Cd_t) at different reaction times was the difference between the total Cd present in the soil samples and the Cd released in the solution.

Under field conditions the concentration of phosphate should decrease gradually with increasing distance from the phosphate fertilizer zone. In order to investigate the influence of phosphate concentration on Cd release, 0.10 M $NH_4H_2PO_4$ and 0.01 M $NH_4H_2PO_4$ solutions were also used in the study of Cd release from the soils according to the procedure described above.

2.5 Examination of Phosphate Reaction Products in Soils and Perturbation by Cadmium

One gram of each of the natural soil samples (Egerton, Naivasha and Soy) was placed in a 50-mL polypropylene centrifuge tube and treated with 10 mL of $NH_4H_2PO_4$ solution. Soil suspensions were allowed to incubate for a period of 100 days at room temperature (25°C). Separate samples of the soils were also treated with only water using the same procedure to serve as control. The effect of Cd on formation of phosphate reaction products was also investigated by reacting the natural soils with 1 M $NH_4H_2PO_4$ solution in the presence of 6.4 × 10^{-3} M $Cd(ClO_4)_2·6H_2O$ and allowed to incubate for 100 days as described above. The concentration of 6.4 × 10^{-3} M Cd was chosen after trials using a lower Cd concentration in the range of 10^{-4} M. The trials had indicated that at 10^{-4} M Cd concentration, formation of phosphate reaction product was not perturbed; hence a concentration of 10^{-3} M was used. The choice of $Cd(ClO_4)_2$ concentration at this magnitude was based on the calculation for the incubation studies which depended on the rate of MAP fertilizer application for the three soils studied and the Cd content of the Idaho MAP fertilizer (Appendix Ia and Id). Cadmium concentration in the fertilizer granule-soil interface calculated for Soy soil at a field moisture capacity of 20% was 2.8 × 10^{-3} M (Appendix Id). This was adjusted to Cd concentration of 6.4 × 10^{-3} M, namely, the concentration at which notable perturbation on phosphate reaction formation by Cd was observed during the trials. Hence using a Cd concentration level of 6.4 × 10^{-3} M is justified, especially since the concentration of Cd at the immediate fertilizer granule-soil interface should be high. At the end of each reaction period, the soil suspensions were filtered through a 0.45-μm pore-size membrane under vacuum.

The reacted soil samples were leached with 10 mL deionized distilled water four times to remove any free salts in the soil samples. The amount of Cd removed by leaching prior to the preparation of soil samples for XRD and IR analysis after the equilibration period was not determined. This would indeed affect calculation of the amount of Cd remaining; however, XRD and IR analyses were carried out only to identify the phosphate reaction products formed in the soils. It may be assumed that the Cd remaining after leaching and subsequently released by MAP were from the sorbed phase. The amount of Cd remaining after leaching would be essential in calculating the fraction or % Cd released but in this study, it is the actual amounts of Cd released that are relevant to food chain contamination. Each washed soil sample was air dried and ground to <5 μm with an agate mortar and pestle and used for XRD and IR analysis. The ground soil samples were directly mounted on a glass slide by adding a few drops of acetone prior to x-ray diffraction analysis by Rigaku D/MaX-RBX x-ray diffraction instrument (Tokyo, Japan) using monochromatic Fe-K$_\alpha$ radiation generated at 40 kV-130 mA. For IR analysis, 1 mg soil sample (< 5 μm) was mixed with 250 mg KBr and then pressed into a pellet. The KBr pellet with the sample was examined under a Perkin-Elmer 983 infrared absorption spectrometer (Buckinghamshire, England).

3 RESULTS AND DISCUSSION

3.1 Amounts of Cadmium Released

The amounts of Cd released from the natural Egerton, Naivasha and Soy soils during the 15-min reaction period as influenced by 1 M $NH_4H_2PO_4$ solution were very low and varied with the soils (Table 19.4). The addition of Idaho MAP fertilizer to the soils influenced the amount of Cd released from them (Table 19.5). No Cadmium was detected in the deionized distilled water in which control soils were soaked.

Soil pH is often regarded as the major factor in controlling plant uptake of Cd from soils (Chaney and Hornick, 1978). The pH effect on Cd availability in soils is largely ascribed to the marked effect pH has on retention of Cd^{2+} by soil surfaces. The initial pH of 1 M $NH_4H_2PO_4$ solution was 4.04. The pH of the soil-$NH_4H_2PO_4$ suspension at the end of a 15-min reaction period was in the order:

Table 19.4: Amount of Cd released from control soils at the end of a 15-min reaction period by 1 M $NH_4H_2PO_4$ solution

Soil[†]	pH[‡]	Cd released (mg kg^{-1} soil)	% Cd released
Egerton	4.97	0.04	25.4
Naivasha	5.09	0.03	25.2
Soy	4.66	0.01	52.6
$LSD_{0.05}$	0.08	0.01	
$LSD_{0.01}$	0.15	0.02	

[†]After 100-day incubation period with deionized distilled water at the field capacity.
[‡]pH of soil-$NH_4H_2PO_4$ suspension.

Table 19.5: Amount of Cd released from treated soils at the end of a 15-min reaction period by deionized distilled water and 1 M $NH_4H_2PO_4$ solution

Soil	Treatment[†]	DDW[‡]		1 M $NH_4H_2PO_4$	
		pH	Cd_r[††]	pH	Cd_r
			mg kg^{-1} soil		mg kg^{-1} soil
Egerton	Idaho MAP fertilizer	5.43	0.14	4.68	1.30
Naivasha	Idaho MAP fertilizer	5.04	0.13	4.46	1.10
Soy	Idaho MAP fertilizer	5.45	0.13	4.60	1.30
$LSD_{0.05}$		0.04	0.02	0.06	0.05
$LSD_{0.01}$		0.07	0.03	0.10	0.09

[†]After 100-day incubation period with Idaho MAP-fertilizer at field capacity.
[‡]Deionized distilled water.
[††]Amount of Cd released to solution.

Naivasha (5.09) > Egerton (4.97) > Soy (4.66) for the control soils. The amounts of Cd released from the soils were not in the same order as the pH of soil-$NH_4H_2PO_4$ suspensions. The Soy soil which had the lowest soil-$NH_4H_2PO_4$ suspension pH released the lowest amount of Cd (Table 19.4). Hence, pH was not the only factor influencing the amount of Cd released from soils in the system studied. In our view, the effect of pH on Cd release is important since it is one of the factors that control plant uptake of Cd. However, in terms of percent of the total soil Cd released, the Soy soil (pH of soil-$NH_4H_2PO_4$ suspension = 4.66) released the highest percent of Cd (Table 19.4). But use of the fraction of Cd released from the soils as affected by pH merely indicates how readily Cd can be released from soils, and use of absolute amounts of Cd released from the soils (mg Cd kg^{-1} soil) is more meaningful in terms of food chain contamination. The amounts of Cd released from soils treated with the Idaho MAP fertilizer by deionized distilled water and by 1 M $NH_4H_2PO_4$ solution were 0.13–0.14 and 1.10–1.30 mg kg^{-1} soil respectively (Table 19.5). Further, it was observed that the amounts of Cd released from the treated soils by deionized distilled water were one order of magnitude lower than the amounts of Cd released by 1 M $NH_4H_2PO_4$ solution (Table 19.5), indicating that phosphate substantially induced Cd release from the soils studied. However, the effect of pH cannot be discounted due to the observed difference in hydrogen ion concentration between the distilled water and the MAP treatments. Since the amount of Cd added was 62.4 mg kg^{-1}, the difference between the amount added and the amount recovered could be attributed to the fact that, within the 15-min reaction period, only a small fraction of the Cd from the sorbed phase was removed. In the process of Cd release, other factors that may account for the release of Cd include release of adsorbed Cd (II) by NH_4^+ and the chemical form of Cd (II) in the presence of 1 M phosphate. Cd forms complexes with phosphate, e.g. $[CdH_2PO_4]^+$, $[CdH_2PO_4)_2]^0$, and others, which are likely to form particularly whenever concentrations of phosphate are orders of magnitude greater than Cd, as in the case of the present study.

The amounts of Cd released during the 0.25 to 1 h reaction period from the soils increased with concentration of $NH_4H_2PO_4$ solution and also varied with soil type (Figs. 19.1 and 19.2). Irrespective of the initial Cd content in the control soils, 0.1 M $NH_4H_2PO_4$ solution appeared to release almost the same amount of Cd from control soils (Fig. 19.1). This is attributable to the low Cd contents of the soils studied and the low P concentration used. Presented in graphic form, the difference may not be significant (Fig. 19.2) even for soils treated with Idaho MAP fertilizer. However, Table 19.5 for the 15-min reaction period for the treated soils indicated a significant difference. At a concentration of 0.01 M $NH_4H_2PO_4$ no detectable amounts of Cd release were observed for the control soils. During the 0.25 to 1 h-reaction period, the lowest Cd release by 1 M $NH_4H_2PO_4$ was observed in the natural Soy soil, which is derived from igneous rocks low in Cd (Fig. 19.1). It was further observed that the amounts of Cd released by 0.10 M $NH_4H_2PO_4$ and 1 M $NH_4H_2PO_4$ solutions in natural Soy soil were almost the

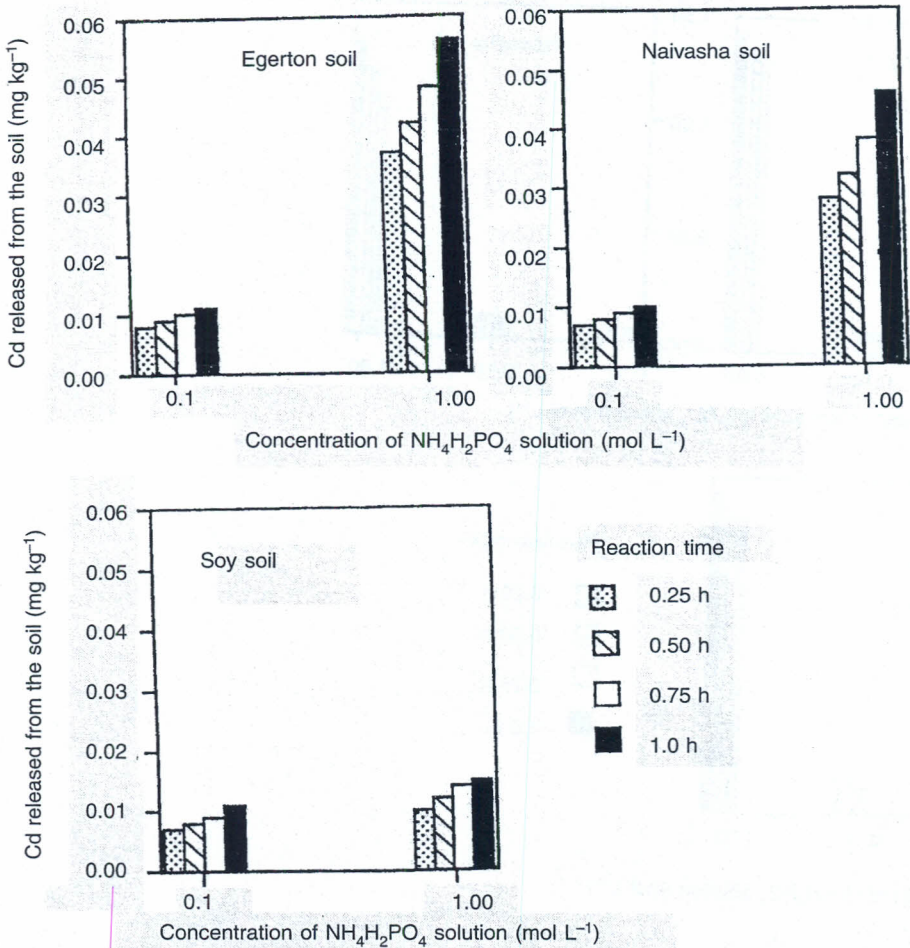**Fig. 19.1:** Amount of Cd released from control soils by $NH_4H_2PO_4$ solution at various concentrations as a function of reaction period. Cd released by 0.01 M $NH_4H_2PO_4$ solution was not detectable.

same (Fig. 19.1), which is also attributable to its low Cd content. However, appreciable amounts of Cd were released when 0.01 M $NH_4H_2PO_4$ solution was reacted with the soils treated with the Idaho MAP fertilizer (Fig. 19.2). Results showed that the release of Cd by $NH_4H_2PO_4$ solution of the Idaho monoammonium phosphate-treated soils was significantly higher than in control soils (Figs. 19.1 and 19.2). Although ionic strength was not determined during the study, in this case the phosphate-induced Cd release to the MAP-treated soils and the Cd impurity in the MAP apparently contributed markedly to the difference in Cd release. The results further showed that the phosphate-induced
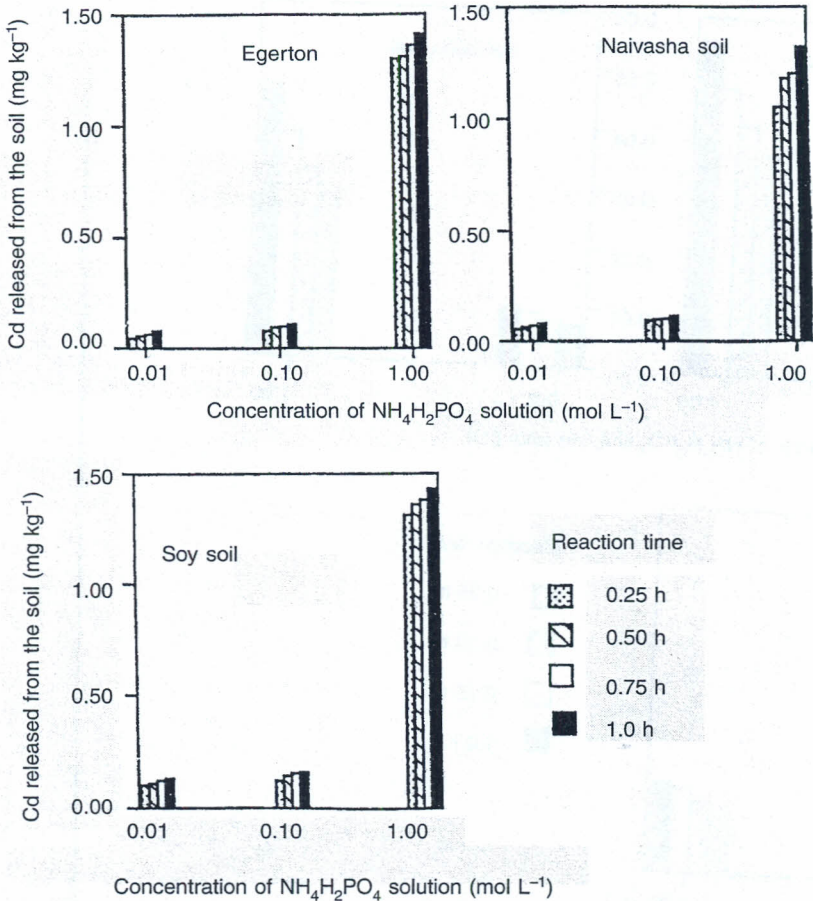
Fig. 19.2: Amount of Cd released from Idaho monoammonium phosphate (MAP)-fertilizer treated soils by $NH_4H_2PO_4$ solution at various concentrations as a function of reaction period.

Cd release increased during the short reaction period of 0.25 to 1 h and then decreased with time and tended to reach plateau in both the natural soils and soils treated with Idaho MAP fertilizer (Fig. 19.3). The decrease in Cd released could be due to readsorption of released Cd onto the surface of soil particles and/or formation of insoluble reaction products in solution.

Mortvedt and Osborn (1982) suggested that the chemical form of Cd in P-fertilizers was $Cd(H_2PO_4)_2$, $Cd(HPO_4)$, or a mixture of these salts. However, in solution Cd can precipitate as $Cd_3(PO_4)_2$ ($K_{sp} = 2.5 \times 10^{-33}$) (Dean, 1992). Formation of sparingly soluble Cd compound in solution could reduce the amount of Cd released to solution with time.
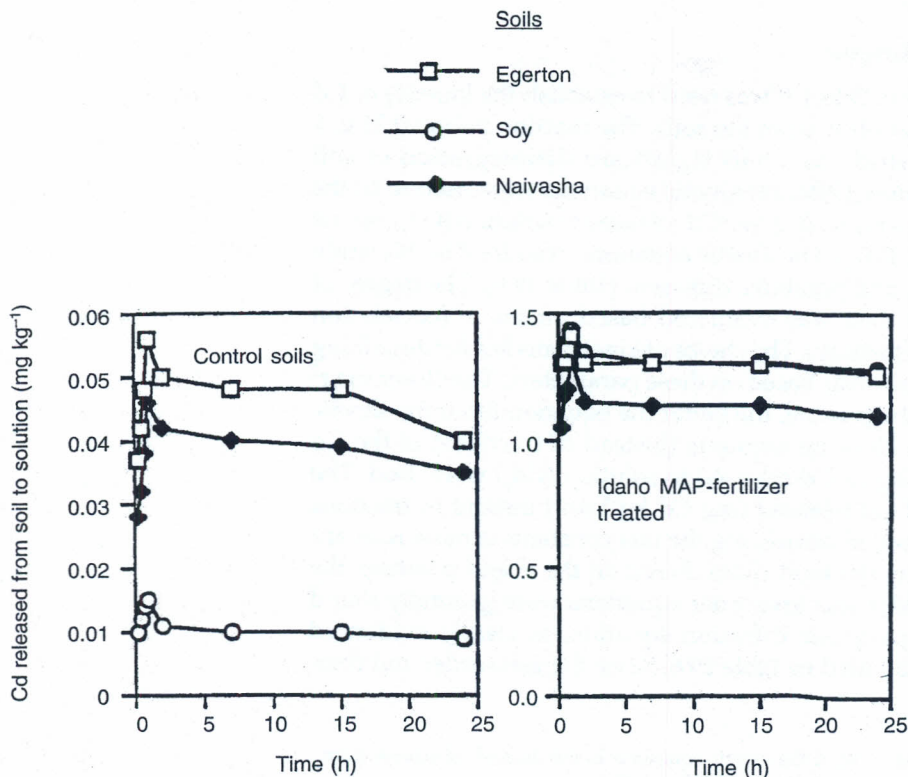
Fig. 19.3: Changes in amounts of Cd released by 1 M $NH_4H_2PO_4$ solution during the 0.25 to 24 h-reaction period from control soils and soils treated with Idaho MAP-fertilizer.

In natural soils, Cd release (Fig. 19.3) varied with Cd content (Table 19.1). For example, the Cd content of the surface horizon of the Soy soil was one order of magnitude lower than those of the Egerton and Naivasha soils. However, when the same amount of Cd was added to the soils, the Naivasha soil released the lowest amount of Cd (Fig. 19.3). The Naivasha soil compared with the other two soils retained more strongly the Cd added and thus limited its release. The manganese content of the surface horizon of the Naivasha soil was one order of magnitude higher than that of the Soy soil (Table 19.1). Heavy metals are strongly adsorbed on Mn oxides (McKenzie, 1980). Manganese oxides are very reactive components of soils; they strongly sorb cations (Huang, 1991). The added Cd was apparently adsorbed by the Mn oxides present in the Naivasha soil, which thus limited its release (Fig. 19.3). Retention of Cd by the Naivasha soil could also be attributed to the high specific area of the Naivasha soil (Table 19.3). The other soil components, e.g. organic C, oxides of Al and Fe

which could bind Cd in the surface horizon of Naivasha soil, were not higher than those of the surface horizons of the Egerton and the Soy soils (Table 19.1).

3.2 Kinetics of Cadmium Release

The short reaction period of 0.25 to 1 h was used to establish the kinetics of Cd release by 1 M $NH_4H_2PO_4$ solution from the soils. The reaction period 0.25 to 1 h was chosen for kinetic study to avoid significant disintegration of soil aggregates caused by agitation. Different kinetic equations were used to fit the data on Cd remaining in the sample (Cd_t) or Cd released to solution (Cd_r) versus the reaction time (t) (Sparks, 1989). The kinetic equations examined in this study were zero-order, first-order, and parabolic diffusion (Table 19.6). The degree of fit of each equation to the data was evaluated based on the r^2 (correlation coefficient), and p value (probability). The choice of kinetic models for describing the release of Cd from the soils was based on these parameters. The closer the r^2 value to 1.0 and the lower the p value, the better the equation fitted the kinetic data. For the kinetic study, absolute amounts (instead of fractions) of the Cd remaining in the sample (Cd_t) or Cd released to solution (Cd_r) were used. The use of absolute amounts of Cd released (mg Cd kg^{-1} soil) instead of fractions (% Cd released) of Cd released in calculating the rate constants is more relevant to the amount of Cd entering the food chain. Based on the r^2 and p values, the degree of fit for the zero-order and first-order equations were generally found to fit the data better than parabolic diffusion equation, as clearly evidenced from the r^2 and p values presented in Table 19.6. Since the zero-order and first-

Table 19.6: Comparison of degree of fit of the kinetic equations to the data of Cd release from the soils by 1 M $NH_4H_2PO_4$ solution

Soil	Treatment[†]	Kinetic equations[‡]					
		Zero-order $Cd_t = a-kt$		First-order $\ln Cd_t = a_1-k_1t$		Parabolic diffusion $Cd_r = a_2+Dt^{1/2}$	
		r^2	p	r^2	p	r^2	p
Egerton	Control	0.988	6.0×10^{-3}	0.982	9.0×10^{-3}	0.773	1.2×10^{-1}
	Idaho MAP fertilizer	0.937	3.2×10^{-2}	0.935	3.2×10^{-2}	0.878	6.3×10^{-2}
Naivasha	Control	0.978	1.1×10^{-2}	0.968	1.6×10^{-2}	0.734	1.4×10^{-1}
	Idaho MAP fertilizer	0.939	3.1×10^{-2}	0.937	3.1×10^{-2}	0.939	3.1×10^{-2}
Soy	Control	0.978	1.0×10^{-2}	0.994	3.0×10^{-3}	0.903	5.0×10^{-2}
	Idaho MAP fertilizer	0.974	1.2×10^{-2}	0.974	1.2×10^{-2}	0.968	1.6×10^{-2}

[†]After 100-day incubation period at field capacity.
[‡]Cd_t is the amount of Cd remaining in the soil sample at time t; Cd_r the amount of Cd released to solution from the soil at time t; a, a_1, and a_2 are constants in respective equations; k and k_1 are rate constants; and D is the overall diffusion coefficient.

order equations fitted the data virtually equally well, the zero-order equation was selected to establish the kinetics of Cd release during the short-reaction period of 0.25 to 1 h.

The rate constants of Cd release from the soils in the 1 M $NH_4H_2PO_4$ solution and deionized distilled water were calculated from the zero-order kinetic equation. The data obtained are shown in Table 19.7. The rate of Cd release varied with the soils. The amount of Cd released based on the rate of Cd released from the soils during the 0.25 to 1 h-reaction period (Table 19.7) was lower than the amount of Cd detected in the solution at the end of 1 h-reaction period (Fig. 19.3). This indicates that the rate of Cd release in the soil system before 0.25 h was extremely fast, which accounts for the differences between the amount of Cd released after 1 h and the amount of Cd released based on the rate constant calculated from the zero-order equation. The rate of phosphate-induced Cd release from the control soils followed the order: Egerton (0.03 mg kg^{-1} h^{-1}) > Naivasha (0.02 mg kg^{-1} h^{-1}) > Soy (0.01 mg kg^{-1} h^{-1}), while for soils treated with Idaho MAP fertilizer the order was: Naivasha (0.33 mg kg^{-1} h^{-1}) > Egerton (0.15 mg kg^{-1} h^{-1}) = Soy (0.15 mg kg^{-1} h^{-1}). The rate constants are taken as a measure of the rate of Cd release from the soils. The rate of Cd release from the Idaho MAP fertilizer-treated soils, as indicated by the rate constants, was higher for the Naivasha soil than for either the Egerton or the Soy (Table 19.7). The relatively high amounts of Mn oxides and high surface area of Naivasha soil (Tables 19.1 and 19.3) apparently contributed to the strong retention of Cd, which limited its release (Fig. 19.3). However, the rate constant of Cd release in the Naivasha soil treated with Idaho MAP fertilizer as influenced by $NH_4H_2PO_4$ solution was higher than the other two soils (Table 19.7). When $NH_4H_2PO_4$ solution was

Table 19.7: Rate for phosphate-induced Cd release from soils by 1 M $NH_4H_2PO_4$ during the 0.25 to 1 h-reaction period

Soil	Treatment[+]	Rate constants (mg kg^{-1} h^{-1})	
		DDW[‡]	$NH_4H_2PO_4$
Egerton	Control	ND[‡‡]	0.03
	Idaho MAP fertilizer	0.02	0.15
Naivasha	Control	ND	0.02
	Idaho MAP fertilizer	0.02	0.33
Soy	Control	ND	0.01
	Idaho MAP fertilizer	0.01	0.15
LSD$_{0.05}$		0.01	0.02
LSD$_{0.01}$		0.12	0.03

[+]After 100-day incubation period with Idaho MAP fertilizer at the field capacity.
[‡]Deionized distilled water.
[‡‡]Not detectable.

added, dissolution of Mn oxides occurred, which resulted in release of Cd from the Naivasha soil. The ease with which dissolution of Mn oxide occurs would mean that the rate of Cd release would be higher. The strength with which Cd is bound to metal oxides depends on the metal of the adsorbent. The higher the valence : coordination ratio of the adsorbent metal, the lower the strength of adsorption of trace metals (McBride, 2000). Mn is octahedrally coordinated to six O atoms and has a valence of + 4; it thus donates a + 0.67 charge to each O atom. This creates a greater pull on the electrons between the O and Mn atoms, resulting in a large distance between Cd and the electrons in Mn oxides. This would result in a weaker bond with Cd and could, therefore contribute to the higher rate constant of Cd release in the Naivasha soil treated with Idaho MAP fertilizer, which retained Cd due to its Mn oxide content. In the natural soils, the rate constant of Cd release by 1 M $NH_4H_2PO_4$ (Table 19.7) from the Soy soil was lower than that from the Naivasha or Egerton soil. This indicates that more Cd would be released from the Naivasha and Egerton soils than from the Soy. The rate constants of Cd release from the treated soils by the deionized distilled water were much lower than those of Cd released by the monoammonium phosphate solution (Table 19.7), indicating that the application of the phosphate fertilizer substantially enhanced the rate of Cd released from the soils.

3.3 Mechanisms of Cadmium Release

Poorly crystalline Al, Fe, and Mn oxides, present in highly weathered tropical soils, are known to adsorb Cd selectively (Christensen and Huang, 1999). The mineralogy of these soils shows the presence of kaolinite and oxides of Al, Fe, and Mn. Dissolution of Al, Fe, and Mn oxides and kaolinite in these soils by phosphate would therefore enhance the release of Cd from the soils through formation of Cd-complexes such as $[CdH_2PO_4]^+$ (log $K[CdH_2PO_4]^+$ = 2.91; Martell et al., 1997). H^+ can protonate the hydroxyl groups and oxygen atoms at the broken edges or surfaces of the soil minerals to weaken the Mn–O, Fe–O, and Al–O bonds resulting in increased dissolution of Cd by phosphate. Phosphate is a strong complexing ligand. It can exchange with the OH and OH_2 groups in soil minerals to form complexes with the surface structural cations such as Al, Fe, and Mn. In the presence of H^+, phosphate ligands can thus attack these bonds more easily and replace OH_2 or OH groups to form complexes with structural cations. The mechanism of dissolution of minerals controlled by surface complexation was explained by Bloom and Nater (1991). The mechanism of enhanced Cd release from the soils by 1 M $NH_4H_2PO_4$ solution was deemed to be the combined effect of Cd introduced to soils and the Cd released from the soils through attack of the protons, the complexation effect of phosphate and the resultant solubilization effect of Al, Fe, and Mn oxides and kaolinite by the $NH_4H_2PO_4$ solution.

3.4 Reaction Products and Significance

Crystalline reaction products were found in the phosphate-treated soils by x-ray diffraction analysis at the end of the 100-day reaction period. The main d-spacings of the phosphate reaction products were: 15.88, 7.92, 7.49, 7.20, and 5.83 Å in both the Egerton and the Naivasha soils (Fig. 19.4). The d-spacings compared well with the d-spacings of the standard taranakites (NH_4-taranakite and K-taranakite) synthesized by Taylor and Gurney (1961), Frazier and Taylor, (1965), and Zhou and Huang (1995).

The standard NH_4-taranakite [$(NH_4)_3Al_5H_6(PO_4)_8 \cdot 18H_2O$] and K-taranakite [$K_3Al_5H_6(PO_4)_8 \cdot 18H_2O$] have identical main d-spacings. The peak at 6.47 d-spacing which consistently appeared in both control and treated soils indicates the presence of feldspars (Jackson, 1979). The peak at d-spacing of 3.19–3.23 Å also indicates the presence of feldspars, e.g. K-feldspars or plagioclase feldspars (Berry, 1974; Jackson, 1979). The peak at 3.74 Å, present in both control and
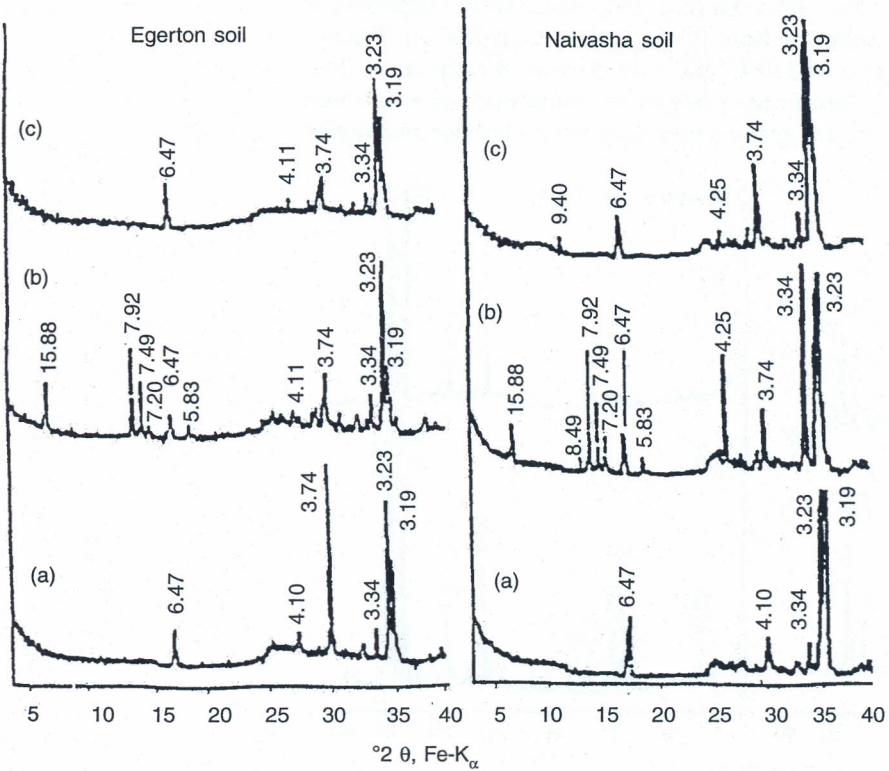

Fig. 19.4: X-ray diffractograms of soils treated with 1 M $NH_4H_2PO_4$ solution both in the presence and absence of 6.4×10^{-3} M $Cd(ClO_4)_2$ at 25°C for 100 d. (a) Control, (b) 1 M $NH_4H_2PO_4$ solution, and (c) 1 M $NH_4H_2PO_4 + 6.4 \times 10^{-3}$ M $Cd(ClO_4)_2$. Characteristic d-spacings of NH_4-taranakite: 15.88, 7.92, 7.49, 7.20, and 5.83 Å.

treated soils, could also indicate the presence of feldspars (Berry, 1974) **(Fig. 19.4)**. It has been reported that the quantities of feldspars in soils would vary with the nature of the parent material and the stage of weathering (Somasiri et al., 1971). In moderately weathered soils, there are usually considerable quantities of K-feldspars, while in strongly weathered soils, such as those in humid tropics, K-feldspars are often present in small amounts (Prabhudesai and Kudrekar, 1984).

In the Egerton soil, the peak at 4.11 Å, which appeared even in the control soils, could be goethite. Peaks at 3.34 Å indicate the presence of quartz. In the treated Naivasha soil, the peak at 4.25 Å, which did not appear in the control soil, could be due to a phosphate reaction product. Prabhudesai and Kudrekar (1984) reported that variscite ($AlPO_4 \cdot 2H_2O$) can form in soils as a monoammonium phosphate reaction product in soils and peak at 4.22 Å.

The peak observed in the x-ray diffractogram of the Naivasha soil at 9.40 Å could arise from a phosphate reaction product. Frazier and Taylor (1965) reported the occurrence of $NH_4AlPO_4OH \cdot 2H_2O$ with a d-spacing of 9.74 Å. The peak at 8.49 Å observed in the Naivasha soil (Fig. 19.5) could be a compound of ammonium aluminum phosphate hydrate [$(NH_4)_2AlH(PO_4)_2 \cdot 4HO_2)$] (Frazier and Taylor, 1965). After heating at 110°C, the 8.49 Å peak disappeared (Fig. 19.5). Formation of ammonium aluminum phosphate compounds in soils when ammonium phosphate fertilizers are applied was reported by Frazier and Taylor
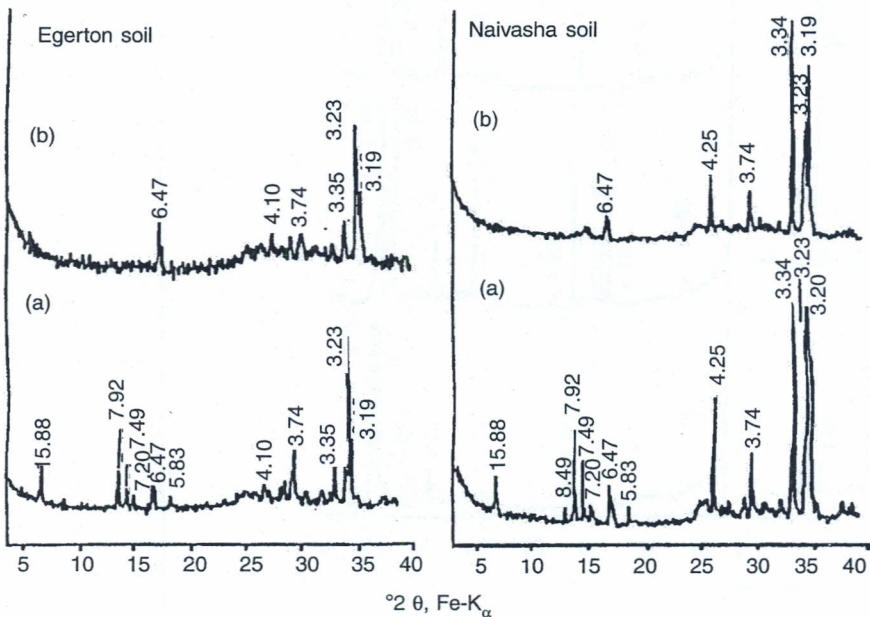

Fig. 19.5: X-ray diffractograms of NH_4-taranakite formed in soils treated with 1 M $NH_4H_2PO_4$ solution at 25°C for 100 d. (a) Before heating and (b) after heating in air at 110°C for 2 h. Characteristic d-spacings of NH_4-taranakite are: 15.88, 7.92, 7.49, 7.20, and 5.83 Å.

(1965). The 8.49 Å peak was not observed in the Egerton soil, which indicates that formation of phosphate reaction products also varies with soil type (Fig. 19.5).

When the taranakite formed was heated in air at 110°C for 2 h and then examined by XRD, the characteristic d-spacings of taranakites (15.88, 7.92, 7.49, 7.20, and 5.83 Å) disappeared, indicating that the K-taranakite transforms to new crystalline product whereas NH_4-taranakite transforms to a noncrystalline state (Fig. 19.5). The product formed in the present study was therefore identified as NH_4-taranakite. The reacting solution contained 1 M NH_4^+ and 1 M phosphate; hence if the soils released enough Al^{3+}, NH_4-taranakite would readily form. In control soils (treated only with deionized distilled water) no taranakite was detected at the end of the 100-day reaction period. Evidence of release of Cd to solution over time (§ 3.1) indicates that application of MAP fertilizers to soil should increase the Cd concentration in the soil solution whereas formation of ammonium taranakite (Figs. 19.4 and 19.5) may lead to conversion of some of the nitrogen and phosphate in the fertilizer to slowly available forms significant in plant growth. An evaluation of taranakites as sources of phosphate for plants was carried out by Taylor et al. (1960). Therefore, formation of taranakites plays an important role in nutrient dynamics of soils, especially in the vicinity of the phosphate fertilizer zone.

3.5 Perturbation of Taranakite Formation by Cadmium

Ammonium taranakite [$(NH_4)_3Al_5H_6(PO_4)_8 \cdot 18H_2O$] and potassium taranakite [$K_3Al_5H_6(PO_4)_8 \cdot 18H_2O$] have the same structure (Frazier and Taylor, 1965), although their composition differs. Lindsay et al. (1962) reported that both NH_4- and K-taranakites may be present in agricultural soils as reaction products of phosphate fertilizers. The present study shows the formation of ammonium taranakite in selected tropical soils in Kenya. When taranakites are formed, the aluminum in soil minerals becomes the source of Al in the taranakites. Phosphate fertilizers contain a wide range of Cd (0.2–345 mg kg^{-1}) as a contaminant (Alloway and Steinnes, 1999). Since large amounts of phosphate fertilizers are applied to tropical soils to correct phosphorus deficiency, the possible perturbation of Cd on taranakite formation was also investigated in this study. It was found that in the presence of 6.4×10^{-3} M $Cd(ClO_4)_2$, no taranakite formed (Fig. 19.4c), indicating that even at a concentration of 6.4×10^{-3} M $Cd(ClO_4)_2$, the formation of taranakite was perturbed.

3.6 IR Analysis

To investigate further the nature of the reaction products, infrared analysis (IR) was conducted using a Perkin-Elmer 983 infrared absorption spectrophotometer (Buckinghamshire, England), as described in § 2.5. The infrared spectra of the reaction product are shown in Figures 19.6 and 19.7 for the Egerton and Naivasha soils respectively. Ammonium ion (NH_4^+) has absorption bands that occur in
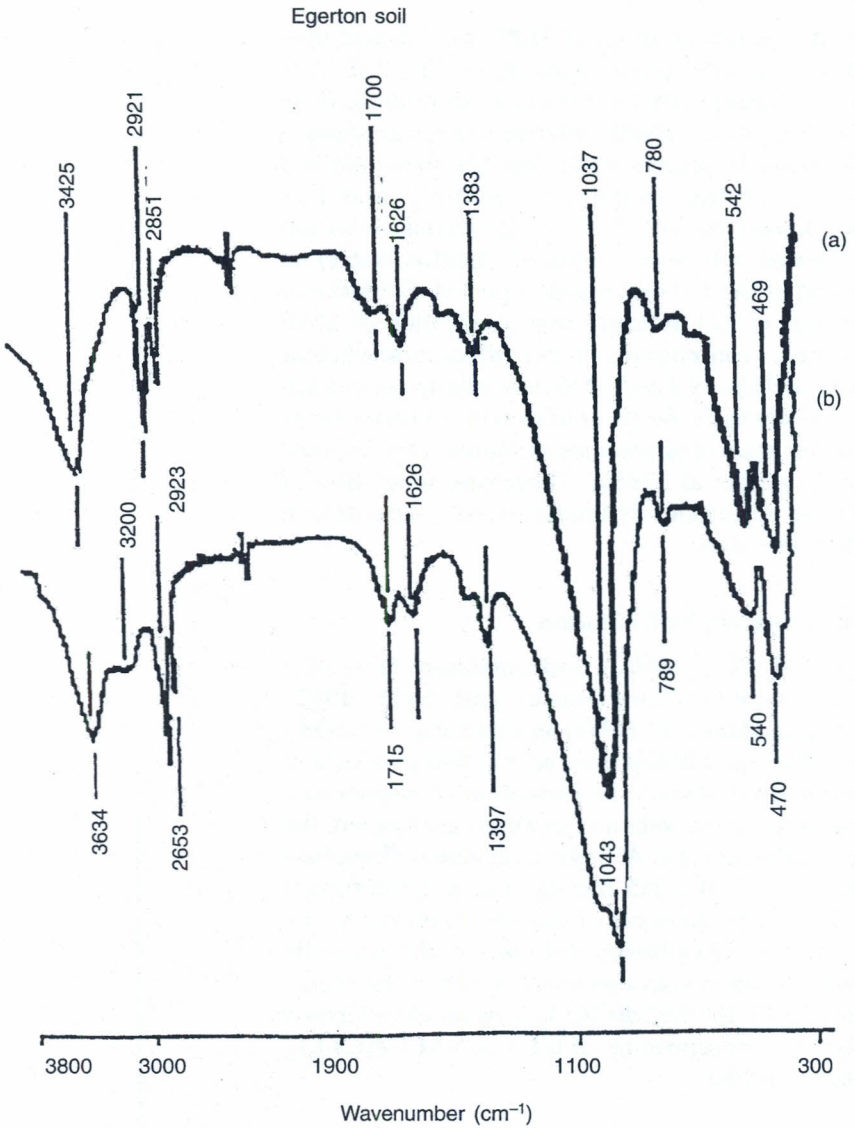
Egerton soil

Fig. 19.6: Infrared spectra of Egerton soil before and after treatment with 1 M $NH_4H_2PO_4$ for 100 days at 25°C. (a) Control and (b) treated soil.

the region of 3,350–3,050 cm^{-1} (Gadsden, 1975) and may be obscured or confused with absorptions arising from the presence of water. Absorption bands between 3,600 and 2,900 and 1,639–1,626 cm^{-1} (Figs. 19.6 and 19.7) indicate the presence

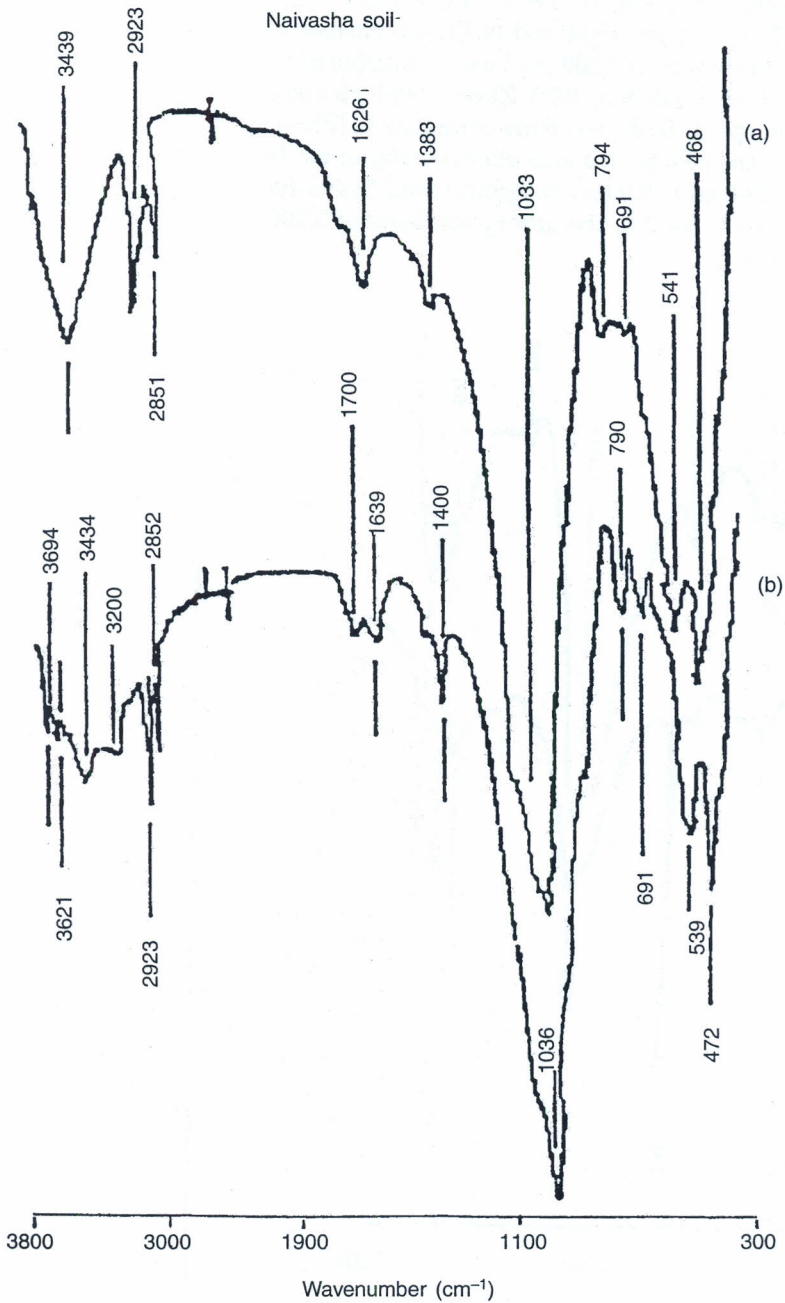**Fig. 19.7:** Infrared spectra of Naivasha soil before and after treatment with 1 M $NH_4H_2PO_4$ for 100 days at 25°C. (a) Control and (b) treated soil.

of water and hydroxyl ion (Frazier and Taylor, 1965; Zhou, 1995). The characteristic absorption band at 3,200 cm^{-1} (Figs. 19.6b and 19.7b) was attributed to NH_4-taranakite (Zhou, 1995). Bands less than 1,300 cm^{-1} can be attributed to the phosphate (Frazier and Taylor, 1965; Gadsden, 1975; Zhou, 1995). Heating did not affect the bands related to phosphate in the structure of taranakite (Zhou, 1995). Infrared analysis data of the samples before and after heating in air at 110°C for 2 h are presented in Figs. 19.8 and 19.9 for the Egerton and Naivasha soils respectively. After heating at 110°C for 2 h, the absorption band at 3,200
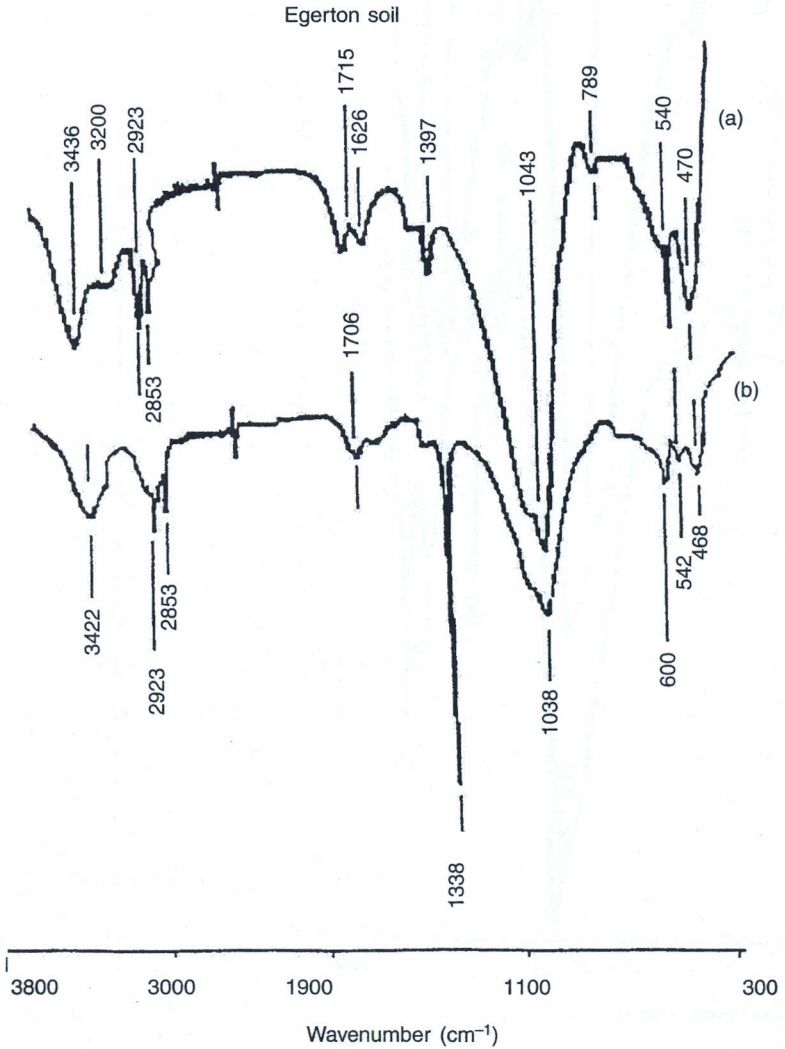

Fig. 19.8: Effect of heat treatment on infrared spectra of the Egerton soil treated with 1 M $NH_4H_2PO_4$ for 100 days at 25°C. (a) Control soil and (b) heat treatment at 110°C in air for 2 h.
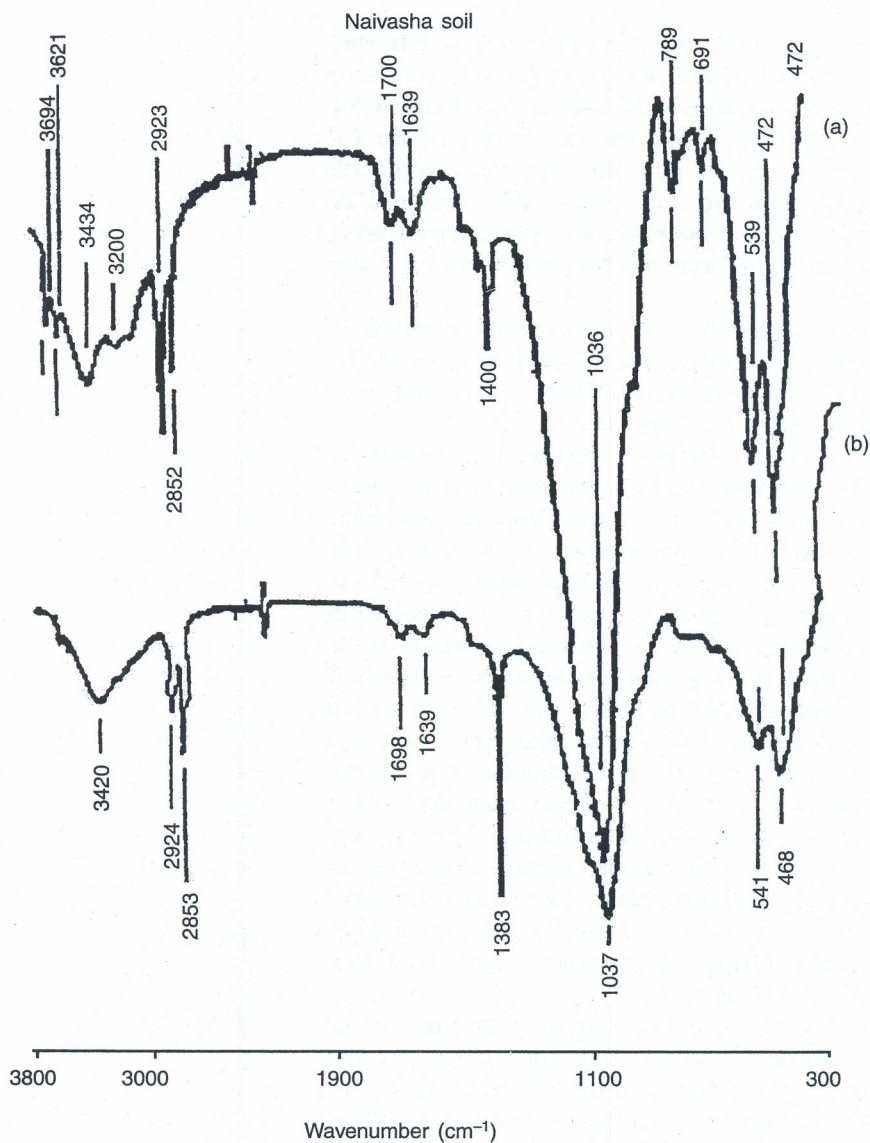
Fig. 19.9: Effect of heat treatment on infrared spectra of Naivasha soil treated with 1 M NH$_4$H$_2$PO$_4$ for 100 days at 25°C. (a) Control soil and (b) heat treatment at 110°C in air for 2 h.

cm^{-1} disappeared (Figs. 19.8 and 19.9), indicating that the ammonium taranakite structure was destroyed (Zhou, 1995). This IR evidence was in accord with the x-ray evidence that NH$_4$-taranakite was formed in the reaction products.

4 SUMMARY AND CONCLUSIONS

The amounts of Cd released from natural soils and Idaho MAP fertilizer-treated soils were significantly enhanced by $NH_4H_2PO_4$ solution. The rate constants for Cd released by 1 M $NH_4H_2PO_4$ solution from soils treated with Idaho MAP fertilizer were one order magnitude higher than the rate constants for Cd released by deionized distilled water from soils with the same treatments. This indicates that the rate of Cd release from the soils was greatly enhanced by application of the Idaho MAP fertilizer. The combined effect of attack by proton, Cd present in Idaho MAP fertilizer, and dissolution by phosphate would enhance the rate of Cd release from the soils.

Increase in the amounts of Cd released with increments in the concentration of $NH_4H_2PO_4$, would imply that at the fertilizer granule-soil interface in the soil rhizosphere where the concentration of orthophosphate is expected to be high, more Cd would be released compared to the bulk soil.

In the immediate vicinity of the fertilizer granule the phosphate concentration is saturated. High concentrations of phosphate can cause substantial alterations of soil constituents and subsequent release of metal ions. Phosphate fertilizers contain Cd as a contaminant and their application to soils is known to lead to Cd accumulation in soils. Application of phosphate fertilizers to soils may promote Cd release from soils, thus increasing the Cd content in soil solution. This may lead to increased Cd uptake by plants and adverse effects on human health. Using x-ray diffraction analysis, NH_4-taranakite was identified in the Egerton and Naivasha soils treated with 1 M $NH_4H_2PO_4$ solution for 100 days. However, taranakite did not form when monoammonium phosphate was spiked with Cd even at 6.4×10^{-3} M $Cd(ClO_4)_2$, indicating that Cd perturbs the formation of taranakites in soils. The nature of the soil-fertilizer reaction products depends largely on the acidity developed during dissolution of the applied fertilizer and may vary with distance from the fertilizer granule because of change of phosphate concentration. Since plants obtain most of their fertilizer phosphorus from the reaction products and not from the fertilizer per se, identification of reaction products is of primary importance in understanding the nature and behavior of phosphorus in soils.

The results presented in this study highlight the influence of the Idaho MAP fertilizer applied to agricultural soils on Cd release. Cd mobilized in the soil rhizosphere can be transported to the plant roots and then be taken up by the plant. The study also shows that NH_4-taranakite can form in the acidic tropical soils when monoammonium phosphates is applied to these soils. However, in the fertilizer-granule interface, Cd may perturb formation of taranakite, if the applied MAP fertilizer contains significantly high Cd as impurity.

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Appendix I

(a) Calculation for the amount of cadmium added to the soil in the incubation study:

Recommended rate of monoammonium phosphate (MAP) fertilizer application

$$= 130 \text{ kg kg}^{-1}$$

Cd content of Idaho MAP fertilizer $\quad = 144 \text{ mg kg}^{-1}$

Amount of Cd introduced to soil from the fertilizer: 130 kg ha^{-1} MAP × 144 mg kg^{-1}

$$= 18{,}720 \text{ mg Cd/ha}^{-1}$$
$$= 18.72 \text{ g Cd/ha}^{-1}$$

Amount of fertilizer in 1 m^2 plot $\quad = 130 \text{ kg } 10^4 = 0.013 \text{ kg}$

$$= 13 \text{ g of fertilizer}$$

(b) Amount of soil in contact with fertilizer granules:

For a spherical fertilizer granule with diameter of 3 mm (0.3 cm), i.e., radius of 1.5 mm (0.15 cm)

Volume of a fertilizer granule $\quad = 4/3 \, \pi \, r^3$

$$= 4/3 \, (3.14)(0.15 \text{ cm})^3$$
$$= 0.0141 \text{ cm}^3$$

Thickness of soil around fertilizer granule

$$= 1 \text{ mm} = 0.1 \text{ cm}$$

Radius of fertilizer granule and soil around it

$$= 0.15 \text{ cm} + 0.1 \text{ cm} = 0.25 \text{ cm}$$

Total volume (fertilizer + soil around it)

$$= 4/3 \times 3.14 \, (0.25 \text{ cm})^3 = 0.0654 \text{ cm}^3$$

Vol. of soil around fertilizer granule

$$= 0.0654 \text{ cm}^3 - 0.0141 \text{ cm}^3$$
$$= 0.0513 \text{ cm}^3$$

Bulk density of soil $= 1.49$ g cm^{-3}

Weight of soil around 1 fertilizer granule

$$= 0.0513 \text{ cm}^3 \times 1.49 \text{ g cm}^{-3}$$

$$= 0.0764 \text{ g soil}$$

Weight of MAP fertilizer in 1 m^2 plot $= 13$ g (equivalent to 392 MAP fertilizer granules)

Therefore, wt. of soil in 1 m^2 plot around granules

$$= 0.0764 \text{ g} \times 392 = 30 \text{ g}$$

Amount of soil around fertilizer granules in 1 ha

$$= \frac{30 \text{ g} \times 10^4}{1000}$$

$$= 300 \text{ kg soil}$$

Hence 18.72 g Cd (from Idaho MAP fertilizer) is present in 300 kg soil

Amount of Cd in 1 kg soil

$$= \frac{18.72}{300}$$

$$= 0.0624 \text{ g Cd kg}^{-1} \text{ soil}$$

Hence amount of Cd used in the incubation study

$$= 62.4 \text{ mg Cd kg}^{-1} \text{ soil}$$

$$= 6.24 \text{ mg Cd}/100 \text{ g soil}$$

(c) Calculation for amount of MAP added to 100 g soil

Wt. of soil around MAP granules in 1 m^2 plot calculated as 30 g.
Wt of MAP fertilizer added to 100 g soil calculated as:
30 g soil around 13 g MAP fertilizer granules

Hence, 100 g soil $=$

$$\frac{100 \text{ g} \times 13 \text{ g MAP fertilizer granules}}{30 \text{ g}}$$

$$= 43.3 \text{ g MAP fertilizer}$$

This is equivalent to 6.24 mg Cd/100 g soil as calculated in Appendix I (b).

(d) Sample calculation for solution Cd concentration in fertilizer granule-soil interface:

Field capacity of soils: Egerton: 30%, Naivasha 29%, and Soy 20%.

$Cd(ClO_4)_2 \cdot 6H_2O$ FW = 419.3

Therefore, weight of Cd perchlorate added to 100 g soil

$$= \frac{419.3 \text{ g} \times 0.0062 \text{ g}}{112.4 \text{ g}}$$

$$= 0.0231 \text{ g cadmium perchlorate}$$

For example, solution Cd concentration at 20% field capacity

$$= \frac{0.0231 \text{ g} \times 1,000 \text{ g}}{419 \text{ g} \times 20 \text{ mL}}$$

$$= 2.8 \times 10^{-3} \text{ M}$$