Interaction of Potassium Phosphonate Fungicide in Laterite Soil

R. ANIL KUMAR*, K. T. VELAYUDHAN*, K. VASU+, V. RAMACHANDRAN**, R. SUSHEELA BHAI[a] AND G. UNNIKRISHNAN[b]

Potassium phosphonate is a fungicide widely used to control *Phytophthora* fungi species in many crops all over the world. In this paper, an attempt has been made to study the interaction of potassium phosphonate with soil under varying pH and calcium level. Several reports available in literature indicate that the phosphonate in organic form adsorb strongly on almost all mineral surfaces and natural materials like soil and sediments. The present study conducted on laterite soil of Kerala using 2 mm sieved sample indicated that phosphonate obeys Freundlich adsorption isotherm. Though at lower concentrations, Langmuir model equally fits well, deviation was observed at higher concentrations. pH and calcium content of the soil had striking influence on the interaction of the chemical with the soil. The calcium source also appeared to influence the adsorption phenomenon. Since potassium phosphonate is extensively used to control *Phytophthora* fungi species in black pepper (*Piper nigrum*) plantations in India and liming is a standard practice followed as soil amendment in acid soils to increase the soil pH, this study may help to maintain good soil quality.

Key words : *Potassium phosphonate, adsorption, laterite soil, pH, equilibrium isotherms, black pepper*

Introduction

Great majority of phosphorus-based pesticides are organic esters of tri- and pentavalent phosphorus and thiophosphorus acids. Potassium phosphonate is a simple salt of pentavalent phosphonic ($H_3P(O)O_2$) acid, which is in isomerism with trivalent phosphorous (H_3PO_3) acid. Degradation of the compound is not expected for the reason that the compound is a simple salt. However, the compound may interact with the soil similar to other inorganic salts either by adsorption followed by ionization or by the interaction of the phosphonate or phosphite moiety, depending upon the specific condition prevailing in the soil microenvironment.

Phosphorus fixation in soil has been a subject of interest for several workers. Three types of reactions are referred to in literature to describe the phenomenon of phosphorus-soil interaction viz., adsorption, isomorphous replacement and double decomposition, involving solubility product relations. In these reactions, phosphorus is involved as one or more of ionic forms. The iron and aluminium rich laterite soil interacts strongly with orthophosphate ion by strong adsorption over the surface of oxides and hydroxides of Al and Fe[1] and on the edges of clay minerals[2].

Phosphonate ion, which results from orthophosphate by the replacement of one OH by H atom, which is directly bonded to phosphoryl-P, may exhibit more or less similar typical soil interaction shown by orthophosphate. The

* Isotope Hydrology Division, Centre for Water Resources Development and Management, Kozhikode, Kerala - 673 571, India.
** Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Mumbai - 400 085, India.
[a] Division of Crop Protection, Indian Institute of Spices Research, Kozhikode, Kerala - 673 012, India.
[b] Polymer Science and Technology Laboratory, Department of Science and Humanities, National Institute of Technology, Calicut, Kozhikode – 673 601, India.
+ Corresponding author : *Tel.*: +91-495-2355864, 2356242, *Fax* : +91-495-2357827; *E-mail id :* nhdcwrdm@eth.net (Dr. K. Vasu)

b. Equilibration study of phosphonate in soil

25 ml of 80 mg HPO_3^{2-}-P l^{-1}, prepared from phosphonate stock solution, was shaken with 2.5 g of 2 mm sieved air dry soil in stoppered 100 ml conical flasks, in triplicate, for 30, 60, 90, 120, 180 and 240 minutes over a mechanical shaker @ 180 rpm at $28 \pm 1°$ C and were centrifuged @ 4000 rpm for 20 minutes in polypropylene tubes. The centrifugates were transferred into 30 ml glass vial containing two drops of $0.1N$ H_2SO_4 (to coagulate soil colloidal particles, if any present). The contents in the glass vials were centrifuged @ 1000 rpm for 5 minutes to get clear solutions.

2.5 ml each of the above clear extract was pipetted into clean 100 ml conical flasks. 5 ml of 0.1% H_2O_2 was added to all flasks and kept over sand bath for reaction to take place. The solutions were evaporated to dryness. The residue in the flasks was dissolved using distilled water. The solutions and washings were quantitatively transferred into 50 ml standard flasks. 5 ml of ammonium vanado-molybdate reagent was added and made up to 50 ml. The yellow colour intensity of the solutions was measured after 5 minutes on a spectrophotometer (Elico-SL171) at 400 nm and the amounts of P in the extracts were calculated from the standard PO_4^{3-}-P curve, which was the concentration of P as HPO_3^{2-} in the soil solution after attaining the equilibrium (C_e). The results were expressed as mean of triplicate ± SE. From C_0 and C_e, x/m was calculated.

c. Variation of soil pH with increase in phosphonate concentration

10, 20, 30 and 40 ml of 1000 mg HPO_3-P l^{-1} solutions having pH 6.2 were pipetted into 500ml standard flasks and diluted to the mark with distilled water to get 20, 40, 60 and 80 mg HPO_3^{2-}-P l^{-1} respectively. 25 ml solution, each representing 20, 40, 60 and 80 mg HPO_3^{2-}-P l^{-1} was shaken with 2.5 g of 2 mm sieved air dry soil, in triplicate, for 90 minutes in stoppered 100ml conical flasks over a mechanical shaker @ 180 rpm at $28 \pm 1°$ C. The solutions were centrifuged @ 4000 rpm for 20 minutes in polypropylene tubes. The pH values of centrifugates were measured using a digital pH meter (Systronics-335).

d. Adsorption of phosphonate and phosphate over the soil surface

2.5 g of 2 mm sieved, air dry soil, in triplicate, was shaken with 25 ml of 5, 10, 15, 20, 30, 40, 50, 60, 80 and 100 mg HPO_3^{2-}-P l^{-1} solutions for 90 minutes in clean stoppered 100 ml conical flasks over a mechanical shaker @ 180 rpm at $28 \pm 1°$ C and were centrifuged @ 4000 rpm for 20 minutes in polypropylene tubes. The centrifugates were transferred into 30 ml glass vial containing two drops of $0.1N$ H_2SO_4. The contents in the glass vials were centrifuged @ 1000 rpm for 5 minutes to get clear solutions. For comparison, 25 ml of phosphate solutions containing 20, 40, 60, 80 and 100 mg PO_4^{3-}-P l^{-1} taken in clean and stoppered 100 ml conical flasks with 2.5 g of 2 mm sieved, air dry soil were shaken for 90 minutes over a mechanical shaker @ 180 rpm at $28 \pm 1°$ C and following the same procedure as in the case of phosphonate to get a clear solution.

Equilibrium concentration (C_e) of phosphate-P and phosphonate-P present in the soil extract was determined by following exactly the same procedure as given under 'b' above by drawing suitable aliquot of the extracts, except that oxidation by H_2O_2 was not done in the case of phosphate. The analyses were performed in triplicate and the results expressed as mean ± SE. From C_0 and C_e, x was determined followed by x/m, log C_e, log (x/m) and C_e/(x/m).

e. Variation of adsorption of phosphonate over the soil surface with pH

5 g of 2 mm sieved, air dry soil, in triplicate, was taken in 100 ml wide mouthed polypropylene jars fitted with lids. 25 ml distilled water was added followed by 10 ml of 100 mg phosphorous acid P [H_3PO_3 -P] l^{-1} (to get a concentration of 20 mg H_3PO_3-P l^{-1} after dilution to 50 ml). The pH of the soil solutions were adjusted from 4 to 8 by adding $0.1N$ KOH solution drop by drop from a burette. The initial pH of the soil solutions were measured using a pH meter. The glass electrode of the meter was washed with 5 ml of distilled water and the washings were also collected in the jars. The final volumes of the soil solutions were adjusted to 50 ml with distilled water. The experiment was repeated by increasing the concentration of P to 100 mg l^{-1}.

The soil solutions were shaken for 90 minutes over a mechanical shaker @ 180 rpm at $30 \pm 1°$ C and were centrifuged in polypropylene tubes @ 4000 rpm for 20 minutes. The centrifugates were transferred into 30 ml glass vials containing two drops of 0.1N H_2SO_4 after retaining a small portion in the tubes for the final pH measurement. The final pH was determined on a Systronics-335 pH meter fitted with a glass electrode. The contents in the glass vials were centrifuged @ 1000 rpm for 5 minutes to get clear solutions.

The equilibrium concentration (C_e) of phosphonate-P was determined by following exactly the same procedure as given under 'b' above by drawing suitable aliquot of the extracts. The analyses were performed in triplicate and the concentration expressed as mean $\pm$ SE. From C_0 and C_e, x/m of the adsorbate was calculated.

f. Variation in the adsorption pattern of phosphonate over the soil surface in the presence of varying amount of lime and gypsum

100 g, 2 mm sieved, air dry soil was mixed thoroughly with 1 g lime (AR $CaCO_3$), which is equivalent to 20 MT $CaCO_3$ ha^{-1}. To run the experiment, 0, 1.25, 2.5, 6.25, 12.5 and 18.75 g of the above mixture were mixed with soil to get a final weight of 25g, which represented 0, 1, 2, 5, 10 and 15 MT $CaCO_3$ ha^{-1} respectively. Similar mixtures containing gypsum (AR $CaSO_4.2H_2O$) were also prepared.

2.5 g of each of the samples were shaken with 25 ml of 100 mg HPO_3^{2-}-P l^{-1} solution for 90 minutes in clean 100 ml conical flasks over a mechanical shaker @ 180 rpm at $30 \pm 1°$ C and were centrifuged in polypropylene tubes @ 4000 rpm for 20 minutes. The centrifugates were transferred into 30 ml glass vials containing two drops of 0.1N H_2SO_4 after retaining a small portion in the tubes for determining the pH. The contents in the glass vials were centrifuged @ 1000 rpm for 5 minutes to get clear solutions.

The concentration of phosphonate-P was determined from an aliquot of 2.5 ml by following exactly the same procedure as given under 'b' above. The analyses were performed in triplicate and the results expressed as mean $\pm$ SE. From C_0 and C_e, x/m of the adsorbate was calculated.

Results and discussion

Table 1 indicates the physico-chemical characteristics of the soil under investigation. It is fairly rich in organic carbon, available nitrogen and phosphorus. The soil is acidic in reaction and low in salts.

Table 1: Physico-chemical properties of the soil under investigation

Sl. No.	Soil characteristics	
1	pH	5.2
2	Electrical Conductivity (μmhos cm^{-1})	23
3	CEC [cmol (p^+) kg^{-1}]	12
4	Organic Carbon [%]	1.2
5	Available N [mg l^{-1}]	70
6	Available P [mg l^{-1}]	7.2
7	Exchangeable K [mg l^{-1}]	33
8	Exchangeable Ca [mg l^{-1}]	230
9	Exchangeable Mg [mg l^{-1}]	28
10	Sand [%]	41
11	Silt [%]	16
12	Clay [%]	43

The concentration of potassium phosphonate in the soil is found to influence soil reaction, as observed by the increase of soil pH with increase in the concentration of potassium phosphonate. Being a salt, it undergoes ionization in the soil solution and potassium in ionic form may undergo hydrolysis into potassium hydroxide resulting in the increase of soil pH. The hydrogen ion may get adsorbed over the soil colloids **(Table 2)**.

Table 2: Variation of soil pH with increase in potassium phosphonate concentration

Sample No.	HPO_3^{2-}-P (mg l^{-1})	pH	
		Solution	Soil solution
1	20	6.2	5.4
2	40	6.2	5.5
3	60	6.2	5.6
4	80	6.2	5.7

The adsorption reactions of the phosphonate in the local soil are presented in **Fig 2** and **Fig. 3**. The equilibrium concentrations, C_e and amount adsorbed, x/m of HPO_3^{2-}-P at an interval of 0, 30, 60, 90, 120, 180, 240 minutes

respectively are given in **Table 3**. From the data, equilibrium between the soil and the solution was found to be established at 90 minutes (**Fig. 1**). **Fig. 2** and **Fig. 3** compare the adsorption of both phosphate and phosphonate over soil colloids. In both the cases, Freundlich adsorption isotherm is found to be the best option, though Langmuir adsorption model holds good at lower concentration (shown by dotted line).

Table 3 : Equilibrium concentrations (C_e) and adsorption (x/m) of HPO_3^{2-}-P at different intervals (mean ± SE).

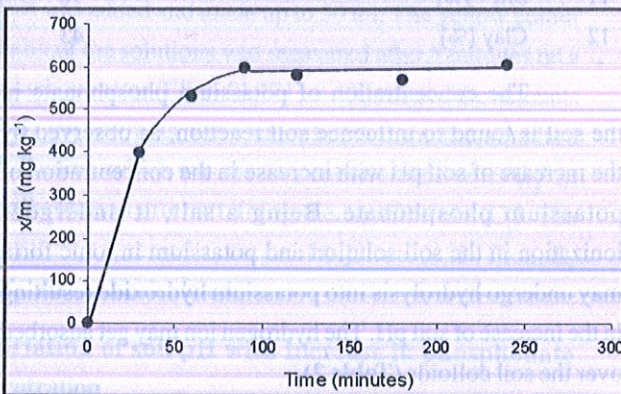| Time	HPO_3^{2-}-P	
(Minutes)	C_e (mg l^{-1})	x/m (mg kg^{-1})
0	80	0
30	40.40 ± 2.10	396
60	27.10 ± 2.95	529
90	20.45 ± 1.85	595
120	22.10 ± 0.80	579
180	23.15 ± 0.25	568
240	19.70 ± 1.60	603

Fig. 1 : Adsorption of HPO_3^{2-}-P over soil surface at different time intervals
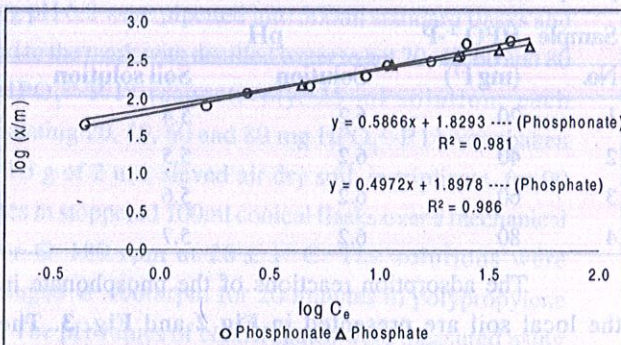

Fig. 2 : Freundlich adsorption isotherms of HPO_3^{2-}-P and PO_4^{3-}-P
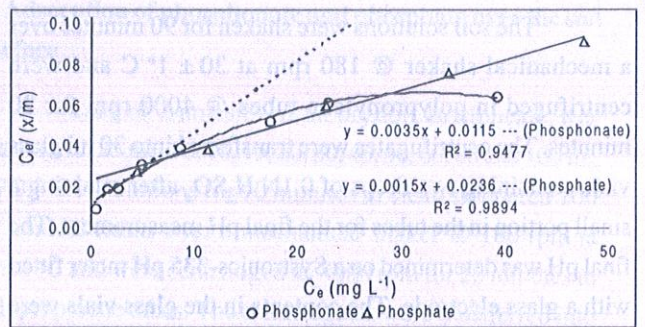

Fig. 3 : Langmuir adsorption isotherms of HPO_3^{2-}-P and PO_4^{3-}-P

The adsorption parameters, k and n of Freundlich, and k_1 and k_2 of Langmuir adsorption isotherm were determined from the experiments conducted on the adsorption of phosphonate and phosphate respectively over the soil surface from aqueous potassium phosphonate and potassium dihydrogen orthophosphate solution of different concentrations (**Tables 4-5**). The n values of 1.7 and 2 of phosphonate and phosphate respectively indicate strong and favourable adsorption of these ions over the soil surface. The Langmuir adsorption constant, k_1, which indicates the energy of adsorption is found to be higher for phosphonate (0.3040) compared to phosphate (0.0636) as indicated in **Table 6**. These results indicate that phosphate is preferably adsorbed over the mineral surfaces compared to phosphonate due to low energy of adsorption.

Table 4 : Adsorption of HPO_3^{2-}-P over the soil surface from aqueous potassium phosphonate solutions of different concentrations (mean ± SE).

C_0 [mg l^{-1}]	C_e [mg l^{-1}]	log C_e [mg l^{-1}]	x/m [mg kg^{-1}]	log (x/m) [mg kg^{-1}]	Ce/(x/m)
5	0.45 ± 0.03	-0.347	46	1.658	0.010
10	1.62 ± 0.06	0.210	84	1.923	0.019
15	2.52 ± 0.30	0.399	125	2.096	0.020
20	4.81 ± 0.24	0.681	152	2.182	0.032
30	8.53 ± 0.36	0.931	215	2.332	0.040
40	10.70 ± 0.36	1.029	293	2.467	0.037
50	17.19 ± 1.08	1.234	328	2.516	0.053
60	22.84 ± 1.20	1.358	372	2.570	0.062
80	24.76 ± 0.24	1.394	552	2.742	0.045
100	39.18 ± 1.20	1.593	608	2.784	0.064

Table 5 : Adsorption of PO_4^{3-}-P over the soil surface from aqueous potassium dihydrogen orthophosphate solutions of different concentrations (mean ± SE).

C_0 [mg l^{-1}]	C_e [mg l^{-1}]	log C_e [mg l^{-1}]	x/m [mg kg^{-1}]	log (x/m) [mg kg^{-1}]	Ce/(x/m)
20	4.40 ± 0.36	0.642	156	2.193	0.028
40	11.19 ± 0.24	1.049	288	2.460	0.039
60	22.62 ± 1.19	1.354	374	2.572	0.061
80	34.52 ± 0.24	1.538	455	2.658	0.076
100	47.62 ± 1.19	1.678	524	2.719	0.091

Table 6 : Freundlich and Langmuir adsorption constants of phosphonate and phosphate over the soil surface at 28 ± 1° C after 90 minutes of shaking.

Adsorption Isotherm	Adsorption Constant	Adsorbate	Value
Freundlich	k	HPO_3^{2-}-P	67.5
		PO_4^{3-}-P	79.0
	n	HPO_3^{2-}-P	1.7
		PO_4^{3-}-P	2.0
Langmuir	k_1	HPO_3^{2-}-P	0.3040
		PO_4^{3-}-P	0.0636
	k_2	HPO_3^{2-}-P	286
		PO_4^{3-}-P	667

Table 7 gives the effect of pH variation on the adsorption of HPO_3^{2-}-P. The influence of soil pH on the adsorption of phosphonate over the mineral surface is presented in **Fig. 4**. Adsorption decreases regularly with the increase in pH. At lower pH, which is generally encountered in acid soils like laterite, adsorption is quite high. Large decrease in the amount adsorbed was seen when pH of the soil-solution system attained a value ranging between 4.5 and 6.5. In other words, in soil of high pH like those of saline and alkali soils, phosphonate is expected to be more in the solution, which moves down through the percolating water.

Table 8 shows the variation in the concentration of HPO_3^{2-}-P adsorbed from the solution over the soil surface with increase in Ca ion concentration applied as lime ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$). Application of chemicals containing calcium is a usual practice in acid and alkali soils as a measure of amendment. Calcium salts as burnt lime and

Table 7: Effect of variation of pH on the adsorption of phosphonate over the soil surface (mean ± SE).

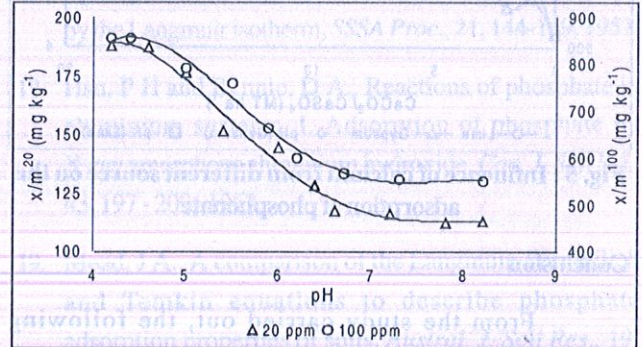| 20 mg H_3PO_3-P l^{-1}			100 mg H_3PO_3-P l^{-1}		
pH	C_e [mg l^{-1}]	x/m [mg kg^{-1}]	pH	C_e [mg l^{-1}]	x/m [mg kg^{-1}]
4.2	1.24 ± 0.06	188	4.2	14.38 ± 1.88	855
4.6	1.32 ± 0.22	187	4.4	14.06 ± 0.31	854
5.0	2.36 ± 0.36	176	5.0	19.38 ± 0.63	791
5.4	4.92 ± 0.18	151	5.5	22.19 ± 0.94	758
6.0	5.45 ± 0.24	144	5.9	31.76 ± 3.64	663
6.4	6.93 ± 0.18	128	6.2	43.13 ± 1.25	600
6.6	7.82 ± 0.12	117	6.7	44.38 ± 1.25	566
7.2	7.64 ± 0.18	116	7.3	42.50 ± 1.25	555
7.8	7.76 ± 0.18	112	8.2	39.06 ± 1.56	552
8.2	7.46 ± 0.24	113	—	—	—

Fig. 4 : Influence of soil pH on the adsorption of phosphonate

limestone are usually applied to acid soils, whereas gypsum is a good amendment in the case of alkali soils. In the experiment, calcium carbonate and gypsum were treated with the soil, which show same trend in the adsorption of phosphonate. Soil when treated with calcium carbonate increased the pH, possibly due to conversion of carbonate to bicarbonate leading to adsorption of calcium with soil colloids, increasing the percentage base saturation of colloidal complex correspondingly pushing up the pH of the soil solution. The reverse is the effect of gypsum in the soil, which ultimately results in lowering of the pH. The adsorption of phosphonate in the presence of calcium as calcium carbonate increases corresponding to the increase in soil pH, whereas under gypsum application, there is less adsorption **(Fig. 5)**. Thus, the loss of the chemical in soil of high pH like saline and alkali soil should be high.

Table 8 : Effect of pH and calcium (from different sources) on the adsorption of phosphonate over the soil surface (mean ± SE).

$CaCO_3$ (MT)	pH	C_e [mg l^{-1}]	x/m [mg kg^{-1}]	$CaSO_4$ (MT)	pH	C_e [mg l^{-1}]	x/m [mg kg^{-1}]
0	5.9	47.6 ± 3.2	524	0	5.9	47.6 ± 3.2	524
1	6.2	37.7 ± 0.3	623	1	5.8	40.9 ± 1.2	591
2	6.4	39.1 ± 0.6	609	2	5.7	42.6 ± 0.6	574
5	7.1	37.4 ± 1.8	626	5	5.5	28.3 ± 0.9	717
10	7.7	28.9 ± 0.9	711	10	5.4	26.0 ± 1.5	740
15	7.7	16.6 ± 2.0	834	15	5.3	22.5 ± 2.0	775
20	7.7	15.2 ± 1.2	848	20	5.2	28.6 ± 2.3	714
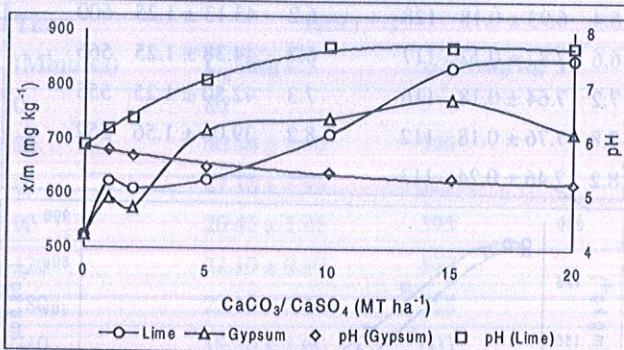
Fig. 5 : Influence of calcium from different source on the adsorption of phosphonate

Conclusion

From the study carried out, the following conclusions are arrived.

- Freundlich isotherm can explain the adsorption of phosphonate over the surface of the laterite soil of Kerala and the adsorption is found to be favourable and strong.

- Adsorption of phosphonate over soil clay is influenced by soil pH, which decreases with increase in soil pH.

- Adsorption of phosphonate over the soil surface increases as Ca ion concentration increases, irrespective of the calcium source.

All the above chemical interactions shown by phosphonate ion in soil are similar to that shown by phosphate ion in soil. This clearly indicates that there exists a similarity between phosphonate and phosphate ions.

The present study indicates that the fungicide is adsorbed strongly and is retained in the soil for more time.

The effect of lime intensifies the adsorptive capacity of the soil for the chemical. These effects make the chemical the most popular among the farmers of Kerala, Tamil Nadu and Karnataka States of India for the control of *Phytophthora* fungi species, which cause foot rot disease in black pepper (*Piper nigrum*), in the plantations, as the chemical is retained in the soil and thus ensuring the destruction of the fungi species.

There is a remote chance of percolation of the chemical through the soil to ground water because of strong adsorption on the soil particles. If the pH of soil gets increased by some means or the pH of soil is high, then there might be some movement of the chemical in soil, may be to a small extent. If lime is used in soil for increasing pH, then there is a little chance of movement of the chemical in soil to ground water, because Ca ion itself chemisorbs phosphonate ion strongly. Thus, the possibility of ground water contamination by the chemical is also the least.

References

1. Breeuwsma, A, Adsorption of ions on hematite (α-Fe$_2$O$_3$), Ph.D. Thesis, Wageningen, 1973.

2. De Hann, F A M, The interaction of certain inorganic anions with clays and soils, *Agri. Res. Rep.*, Wageningen, 655, 167, 1965.

3. Bolt, G H, Physico-chemical models, *Soil Chemistry B*, Elsevier Scientific Publishing Company, Amsterdam, The Netherlands, 1982.

4. Hingston, F J, Atkinson, R J, Posner, A M and Quirk, J P., Specific adsorption of anions on goethite, *Trans. 9th Int. Congr. Soil Sci.*, 1, 669-678, 1968.

5. Chen, Y S R, Butler, J N and Stumm, W, Adsorption of phosphate on alumina and kaolinite from dilute aqueous solutions, *J.Colloid Interface Sci.*, 43, 421-436, 1973.

6. Huang, C P., Adsorption of phosphate at the hydrous ψ-Al_2O_3 – electrolyte interface, *J. Colloid Interface Sci.*, 53, 178-186, 1975.

7. Lopez-Hernandez, D and Burnham, C P,. The effect of pH on phosphate adsorption in soils, *J. Soil Sci.*, 25, 207–216, 1974.

8. Lehr, J J and Van Wesemael, J., The influence of neutral salts on the solubility of soil phosphate, *J. Soil Sci.*, 3, 125-135, 1952.

9. Pissarides, A, Stewart, J W B and Rennie, D A., Influence of cation saturation on phosphorus adsorption by selected clay minerals, *Can J Soil Sci.*, 48, 151-157, 1968.

10. Barrow, N J, Influence of solution concentration of calcium on the adsorption of phosphate, sulphate and molybdate by soils, *Soil Sci.*, 113, 175-180, 1972.

11. Volkweiss, S J, Robarge, W P and Corey, R B., Effect of associated cations on phosphate sorption by minerals and soils, *Agron. Abstr.*, 87, 1973.

12. Ryden, J C and Syers, J K., Rationalization of ionic strength and cation effects on phosphate sorption by soils, *J. Soil Sci.*, 26, 395-406, 1975.

13. Ryden, J C, McLaughlin, J R and Syers, J K., Mechanism of phosphate sorption by soils and hydrous ferric oxide gel, *J. Soil Sci.*, 28, 72-92, 1977.

14. Stoop, W A., Interactions between phosphate adsorption and cation adsorption by soils and implications for plant nutrition, Ph. D. Thesis, University of Hawaii, 1974.

15. Amarasiri, S L and Olsen, S R, Liming as related to solubility of P and plant growth in an acid tropical soil, *SSSA Proc.*, 37, 716-721, 1973.

16. Bolt, G H and Bruggenwert, M G M,. *Soil Chemistry A*, Basic Elements, Elsevier Scientific Publishing Company, Amsterdam, The Netherlands, 1978.

17. Olsen, S R and Watanable, F S,. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm, *SSSA Proc.*, 21, 144-149, 1957.

18. Hsu, P H and Rennie, D A., Reactions of phosphate in aluminium systems, I. Adsorption of phosphate by X-ray amorphous aluminium hydroxide, *Can. J. Soil Sci.*, 43, 197 - 209, 1962.

19. Mead, J A., A comparison of the Langmuir, Freundlich and Temkin equations to describe phosphate adsorption properties of soils, *Austral. J. Soil Res.*, 19: 333-42, 1981.

20. Polyzopoulos, N A, Keramidas, V Z and Kiosse, H., Phosphate sorption by some alfisols of Greece as described by commonly used isotherms, *SSSA Proc.*, 49: 81-4, 1985.

21. Bhuiyan Jr., L R and Sedberry, J E, Phosphorus sorption characteristics of selected soils of Louisiana, *Comm. Soil Sci.Plant Anal.*, 26 (7-8): 1059-72, 1995.

22. Ioannou, A, Dimirkou, A and Papadopoulos, P., Phosphate sorption by goethite and kaolinite-goethite (k-g) system as described by isotherms, *Comm. Soil Sci. Plant Anal.*, 29 (13-14): 2175-90, 1998.

23. Dodor, D E and Oya, K,. Phosphate sorption characteristics of major soils in Okinawa, Japan, *Comm. Soil Sci. Plant Anal.*, 31 (3-4): 277-88, 2000.

24. Treybal, E R., Mass Transfer Operations, 3rd edition, McGraw Hill International editions, Chemical Engineering Series, Singapore, 1981.

25. Rao, M and Bhole, A G,. Chromium removal by adsorption using fly ash and bagasse, *J. Indian Water Works Asso.* XXXIII (1), 97-100, 2001.

26. Raji, C, Shubha, K P and Anirudhan, T S., Use of chemic ally modified sawdust in the removal of Pb (II) ions from aqueous media, *Indian J. Environ. Hlth.*, 39 (3), 230-238, 1997.

27. Ramu A, Kannan, N and Srivathsan, S, Adsorption of carboxylic acids on fly ash and activated carbon, *Indian J. Environ. Hlth.*, 34 (3), 192-199, 1992.

28. Ajmal Mohammad, Ali Mohammad, Rehana Yousuf and Anees Ahmad, Adsorption behaviour of Cadmium, Zinc, Nickel and Lead from aqueous solutions by *Mangifera indica* seed shell, *Indian J. Environ. Hlth.*, 40 (1), 15-26, 1998.

29. Horstmann, B and Grohmann, A., Investigations into the biodegradability of phosphonates, *Vom Wasser*, 70, 163-178, 1988.

30. Fischer, K., Sorption of chelating agents (HEDP and NTA) onto mineral phases and sediments in aquatic model systems. Part II: Sorption onto sediments and sewage sludges, *Chemosphere*, 24, 51-62, 1992.

31. Held, S,. The environmental behavior of chelating agents on phosphonic acid basis, *Textilveredlung*, 24, 394-398, 1989.

32. Nowack, B and Stone, A T., Influence of metals on the adsorption of phosphonates onto goethite, *Environ. Sci. Technol.*, 3, 3627-3633, 1999.

33. Sprankle, P, Meggit, W and Penner, D, Rapid inactivation of glyphosate in the soil, *Weed Sci.*, Lawrence, 23, 224-228, 1975.

34. Jackson, M L., *Soil Chemical Analysis*, Prentice-Hall of India Pvt. Ltd, New Delhi, 1967.

35. Vogel, A I., A textbook of quantitative inorganic chemistry including elementary instrumental analysis, Longman Group Ltd., London, 1978.