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Sorption of fluoride in some soils of varying phosphate status of West Bengal and Meghalaya

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Abstract

An investigation was carried out to generate information whether long term application of phosphate, often phosphate rocks, helps accommodation of fluoride in soils. Also a comparison was made between sorption-desorption of fluoride and phosphate. There was no evidence of build-up of soluble fluoride in soil. When phosphate status of the soil was low, fluoride showed sorption-desorption hysteresis. That is the desorption curve differed from the sorption curve. When the phosphate status of the soil was higher, this was not the case. It was speculated that the fluoride ion, being smaller, might have been able to penetrate pores blocked by previous reaction with phosphate, but this did not happen probably because of increased negative charge of the surface caused by the previous application of phosphate and this appeared to be more important cause of the decreased penetration than physical blocking of pores.

Keywords: Phosphate, sorption, desorption, hysteresis, fluoride

Introduction

Fluorine (F) is a pale, yellow-green, corrosive gas which almost cannot be found in natural environment in elemental form due to its high electronegativity and reactivity. Fluoride (F⁻) is a fluorine anion characterized by small radius, great tendency to behave as ligand and easiness to form a great number of different organic and inorganic compounds in soil, rocks, air, plants and animals. Some of those compounds are quite soluble in water, so fluoride is present in surface and groundwater as an almost completely dissociated fluoride ion. Fluoride concentration in water is of great concern because of its possible accumulation and damage to the human tissues.

The presence of phosphorus (P) in agriculture is good in one way as it act as source of energy for plant growth. But the major concern here is the reduction of plant uptake of P resulting into the need for more application of P-containing fertilizers thereby increasing the cost of produce. As we apply phosphatic fertilizer more and more, we add F, as an impurity to the soil since the later constitute an integral part of mineral flouroapatite from which fertiliser- phosphorous is derived. Long-term application of phosphate fertilizers has decreased the soil's buffering capacity for phosphate (Barrow & Debnath, 2014) ^[2, 3] and for sulphate (Barrow & Debnath, 2015) ^[4] and has also stopped the slow diffusion reaction that follows an initial adsorption. If this effect is extended to fluoride it would be expected to increase fluoride retention and plant uptake. These changes in soil chemistry might be particularly relevant because phosphatic fertilizers always contain some fluoride as a contaminant and hence the fluoride content of the soil might have increased (Barrow *et al.* 2015) ^[4, 5].

Soil from tea estates in West Bengal have been fertilized for more than 100 years, often with phosphate rock. This might lead to the possibility of accumulation of Fluoride in those soils. Also because of soil acidity in the tea gardens much of soluble Al might from complex with fluoride so that large concentration of fluoride remains in solution for sorption in soil and plant uptake. Therefore we aimed to study F sorption desorption in these soils and compared with and unfertilized and uncultivated soils of Meghalaya having similar rainfall pattern.

Material & Method**Soil Used**

Surface Soil (0-20 cm) soil samples were collected from tea plantations of the state of West Bengal and soils of barren land from the state of Meghalaya in between the end of March and

the middle of April following the dry season (November–March). These soils were air-dried, thoroughly mixed and ground to pass through a 2-mm sieve. Two samples of fertilized soil were collected from tea estates in Northern West Bengal (Table 1). No detailed history of fertilizer application was available. The mean total P content was 593 mg kg⁻¹ and the mean pH (CaCl₂) was 4.08. Three samples of unfertilized soil were also taken from under forest and from barren land in the State of Meghalaya, India. These samples had a mean total P content of 225 mg P kg⁻¹ and a mean pH (CaCl₂) of 4.62.

Measurement of sorption and desorption

Samples of 5g soil (untreated and modified (see below)) were mixed in 100-ml centrifuge tubes with 50 ml 0.01 M MgCl₂ solution that contained the following concentrations of F: 0, 5, 10, 20, 30, 50, 70, 100, 150 and 200 mg F added as KF (potassium fluoride). Magnesium chloride was used rather than calcium chloride to increase the range of fluoride concentrations that could be used without risk of precipitation of calcium fluoride. The tubes were shaken gently for 48 hours in a reciprocating shaker at 25°C and the supernatant solution was separated by centrifuging and filtering with Whatman No. 42 filter paper. To measure desorption, the soil from the sorption run (after decanting the supernatant) was re-suspended with 0.01 M MgCl₂ and if shaken for 48 hours as before. In both cases, fluoride in the solution was measured using a fluoride electrode both before and after the addition of the total ionic strength adjustment buffer (TISAB) described by Larsen & Widdowson (1971).

To test the effects on sorption of adding phosphate to soil, five amounts of phosphate were added to Umkynseir soil, and the soil was incubated moist at 60° C for 12 days. The amounts used were: 0, 50, 200, 500 and 1000 mg P kg⁻¹ added as KH₂PO₄ (mono potassium phosphate). The Colwell method (extraction with 0.5 M NaHCO₃) as modified by Kuo (1986) was used to give an index of the phosphorus status of the soils. Aluminium concentration was measured by the method of McLean (1965) [9].

Curve Fitting

The Freundlich equation, modified by adding an intercept term (q) (Barrow, 2008) [1], was fitted to the data:

$$S = ac^b - q \quad (1)$$

Where: S=sorption of fluoride, F, in mg kg⁻¹, c= the observed solution concentration in mg F l⁻¹, and a, b and q are parameters. The intercept (q) is formally the value for desorption at zero solution concentration of fluoride. For the sorption step, sorption was calculated from the observed change in concentration.

$$S = (c_i - c) S_r \quad (2)$$

Where: S_{sr} = the solution: soil ratio, c_i =the initial solution concentration before mixing with the soil. For the desorption step, sorption was calculated from

$$S_d = S - c S_{sr} \quad (3)$$

Where: S_d = indicates the amount of fluoride retained by the soil after the desorption step. The data for both sorption and desorption were fitted simultaneously and there were, therefore, five parameters. These may be represented as: a_s, b, q_s, a_d and q_d where subscripts s and d refer to the sorption and

desorption steps. Because sorption and desorption are calculated from the observed solution concentration, the two variables of Equation (1) (S and c) are not independent. In order to fit Equation (1), it was regarded as simultaneous with Equations (2) or (3). The simultaneous solution of the two equations for a given set of parameters gives the predicted values for solution concentration for given initial solution concentrations and solution: soil ratios (Barrow, 2008) [1].

A Simplex procedure (Nelder & Mead, 1965) was used to find the set of parameters that minimized the sums of squares for the difference between the logarithms of observed and predicted concentrations. We used a logarithmic transformation because errors in measuring concentration were expected to be proportional to the mean. In general, the range of values for the desorption step was smaller than that for the sorption step. As a result the value of term b in Equation (1) was determined less precisely.

Therefore, we fitted Equation (1) to both sorption and desorption with a common value for b. Consequently, the ratio of the slopes for desorption and sorption (the hysteresis ratio of (Barrow & Debnath, 2014) [2, 3]) is given by the ratio of the a terms. To compare fluoride and phosphate, we used instantaneous slope of the sorption curves at a concentration of 0.5 mM of the element as calculated from the fitted equations and data of Barrow and Debnath (2014) [2, 3] for phosphate.

Results and Discussion

Physico-Chemical Properties of the soils

A Few properties of the soils are presented in the Table 1. This shows that the organic carbon content of the unfertilised soils were in general medium while that for the fertilised soils were high to very high.

The cation exchange capacity of the soils was below 15 cmol (p+) kg⁻¹ soil irrespective of locations. The P status of the soils, as extracted by Colwell reagent was between 9.4 and 23.6 mg kg⁻¹ soil in the unfertilised soils of the barren land of Meghalaya and between 45.6 and 80mg kg⁻¹ in the fertilised tea garden soils of West Bengal.

Figure 1 & Figure 2 shows the sorption curves of fluoride & phosphate in the soil studies. In all the soils plots of fluoride sorption against the phosphate are higher. These sorption curves were fitted to modified Freundlich equation. In general fluoride sorption is more marked in unfertilised soils than in the fertilised soils.

Figure 3 derived the relationships of hysteresis ratio for F sorption- desorption in the studied soils as well as the instantaneous slopes of the sorption curves and Colwell P of the soil. The relation shows that both the hysteresis ratio and the slope of the desorption curve decreased with increase in phosphate status of the soil.

Figure 4 and 5 summarises the sorption-desorption curves of fluoride in the unfertilised and the fertilised soils. For the unfertilised soils the desorption curves were more likely to differ from sorption curves, that is hysteresis was more likely to occur.

These desorption curves markedly differed from those arose from the fertilised soils induced via incubation. The hysteresis ratio as indicated in the method section, was calculated from the ratio of term 'a' in the equation (1) for desorption to that for sorption.

Figure 6 and Figure 7 describes the sorption-desorption of fluoride in the Umkynseir soil which was subjected to incubation with phosphate at different levels. The figures shows that with increase in levels of phosphorous addition the

desorption curves tended to become close to the sorption curves. This is similar to the behaviour of the fertilised soils as shown in figured 4 and 5. Comparison of figures 6 to 7 with the figures 4 and 5, particularly for fertilised soils, shows that even after incubation of soils with phosphate for 12 days at 60°C the reaction between them was less effective than the very long periods of reaction between soil and fertilizer for the Tea garden soils that has been fertilised for many decades. Figure 8 shows the relation of hysteresis ratio and the slope of fluoride sorption curves with the levels of phosphate incubation. The hysteresis ratio and the slope of curve as well decreased with increased value of added phosphorous. The hysteresis ratio decreases being close to unit value at the highest level of phosphorous addition. This is similar to decreased hysteresis for fluoride with increased Colwell P as described earlier.

Discussions

One of our aims in this work was to access possible contamination of soil with fluoride as consequences of long term application of phosphorous fertilizers. Table (2) shows that the 'q' value of the equation (1) applied to fluoride sorption, for the fertilised soils were similar to the value obtained from the unfertilised soils. This shows no evidence of accumulation of soluble fluoride. Perhaps this is not surprising given that annual rainfall in the Tea plantation areas of West Bengal is about 3m annually. Consequently it may be concluded that excess uptake of fluoride from the heavily fertilised acidic soils of the area is unlikely to be a problem. The higher fluoride adsorption over phosphate may be the consequences of small fluoride ions size that phosphate shows (Fluoride=0.133nm; Phosphate=0.22nm) (Bia *et. al.*, 2012). As consequences the fluoride can more easily diffuse through the pores compared to the phosphate. In addition fluoride forms inner sphere surface complexes with hydroxyl (OH⁻) ions forming single co-ordinated surface complex. In contrast phosphate may form a mono dentate and a bi-dentate surface complex. This means that when a bi-dented surface complexes is formed, phosphate anions occupy more surface size than fluoride.

For fluoride sorption the adsorption decreased as the concentration of phosphate increases in soil. This suggests that because of the above described adsorption mechanism a competition adsorption process between fluoride and phosphate occurs. Electrostatics may also play a role in the competition. Since both anions are negatively charged, an increase in phosphate concentration also increases the negative potentials of the adsorbing surface (Barrow & Debnath, 2015) [4].

Part of the explanation for this is that the mean position of the plane of adsorption for fluoride is closer to the surface, as would be expected from the relative size of the ions. Therefore, the overall affinity of fluoride for the surface might have decreased and its adsorption reduced with increase in the phosphate status. In addition to electrostatics effect, the layer size of phosphate anion might have obstructed the fluoride anion for diffusing into the pores.

It was shown by Strauss *et.al.* (1997) [11] that, when phosphate reacted with crystallised Goethite, the reaction continued for up to 3 weeks. They concluded that phosphate had penetrated into pores between the domains of the Goethite crystal. This penetration tied the domains together more firmly and increased the lag phase for dissolution. Thus there is a physical closing of pores which is consistent with the observation that prior reaction with phosphate decreased subsequent penetration of phosphate (Barrow & Debnath, 2014) [2, 3] and sulphate (Barrow & Debnath, 2015) [4]. However it seems that an increase in the negative charge is a more important cause of the decreased penetration than physical blocking of pores (Barrow *et. al.*, 2015) [4, 5].

Conclusion

We conclude that characterizing the charge on sorbed ions, its location and especially the accumulation of negative charge following long-term reaction with phosphate is important for understanding specific sorption on ions. This has led to explain the fact that despite large application of phosphate through either phosphate rock or soluble superphosphates in soils of tea plantation, there was little evidence of accumulation of fluoride. We think this is additionally favoured by intense rainfall in this area.

Table 1: Some properties of the unfertilised and fertilized soils studied.

| Parameters | Jowai | Nongpoh | Umkyenseir | Birpara | Chuapara |
|---|-------|---------|------------|---------|----------|
| pH (in 0.01M CaCl ₂) | 4.30 | 4.73 | 4.62 | 4.05 | 3.92 |
| Organic C (%) | 0.52 | 0.75 | 0.83 | 0.89 | 1.82 |
| Colwell P (mg Kg ⁻¹) | 9.4 | 21.8 | 23.6 | 45.6 | 80 |
| Water Holding Capacity (%) | 22 | 42 | 42 | 56 | 65 |
| CEC (cmol (p ⁺) kg ⁻¹) | 12.6 | 14.8 | 11.0 | 9.2 | 12.1 |

Table 2: Value of the parameters for the sorption-desorption in the soils understudy.

| Parameters | Jowai | Nongpoh | Umkyenseir | Birpara | Chuapara |
|--|----------|----------|------------|----------|----------|
| a _s | 166.72 | 95.34 | 96.85 | 54.08 | 43.64 |
| b | 0.484 | 0.724 | 0.69 | 0.55 | 0.567 |
| q | 46.34 | 0.00151 | 28.98 | 39.74 | 22.2 |
| a _d | 294.98 | 211 | 170.58 | 57.13 | 53.94 |
| q _d | 191.02 | 58.08 | 10.99 | 19.44 | 0.0037 |
| Hysteresis ratio (a _d for desorption/a _s for sorption) | 1.769314 | 2.213132 | 1.76128 | 1.056398 | 1.236022 |

Table 3: Slope of fluoride for sorption curve at 9.5 ppm solution F concentration.

| Levels of P addition (ppm) | Slope of the curve | Hysteresis ratio |
|----------------------------|--------------------|------------------|
| 0 | 34.3372 | 1.8919 |
| 50 | 31.9157 | 1.9115 |
| 200 | 29.5098 | 1.8932 |
| 500 | 5.2824 | 1.4967 |
| 1000 | 18.9272 | 1.11620 |

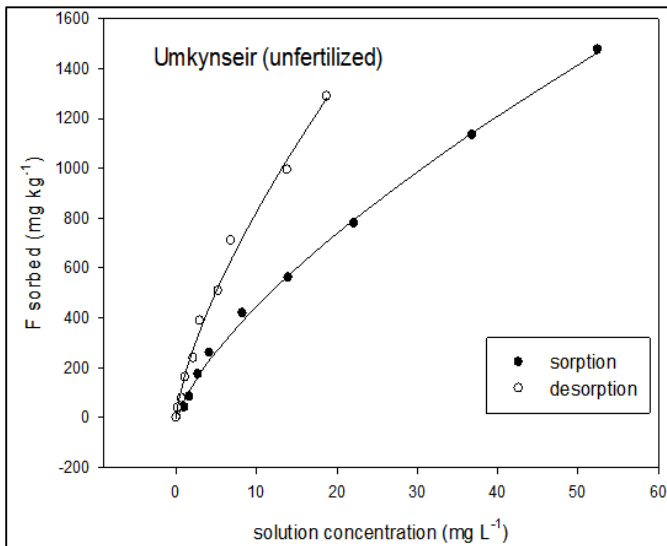
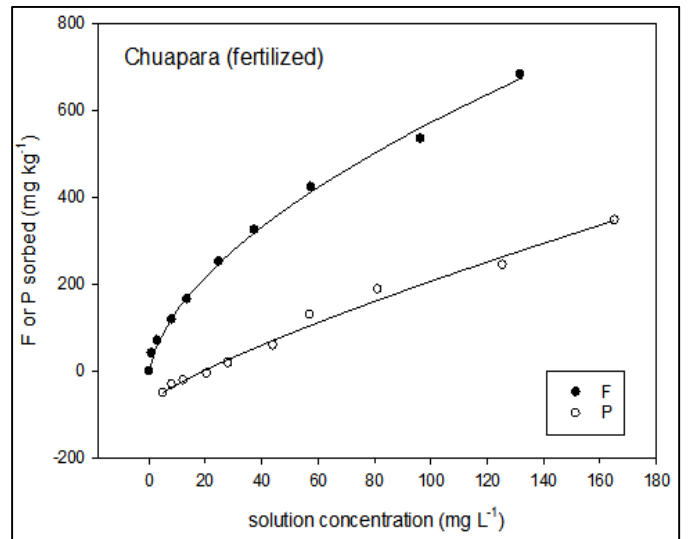
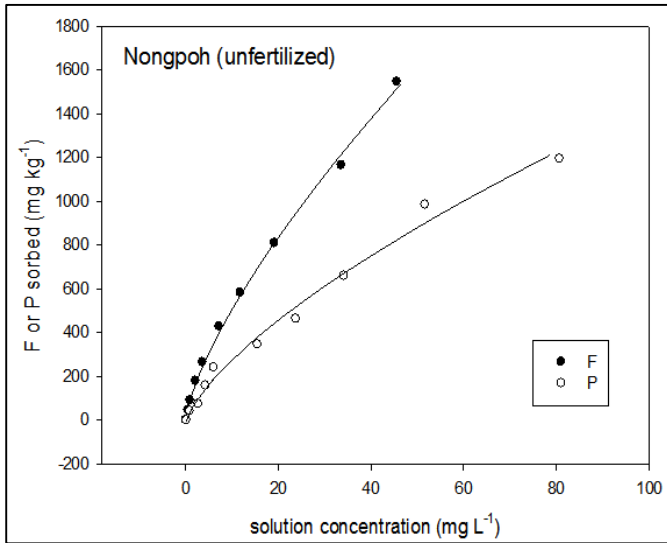
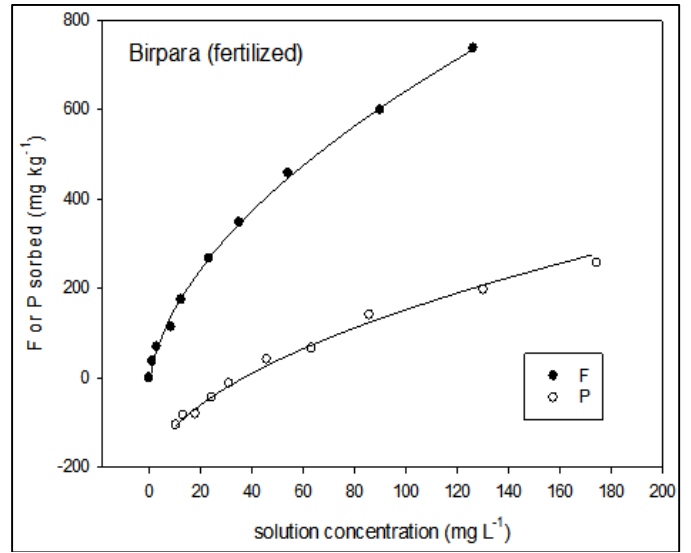
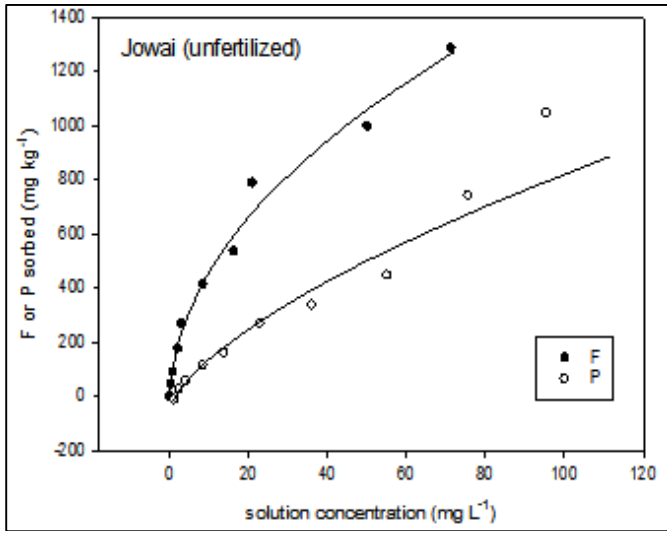


Fig 2: Sorption curves for phosphate and fluoride in fertilised soils

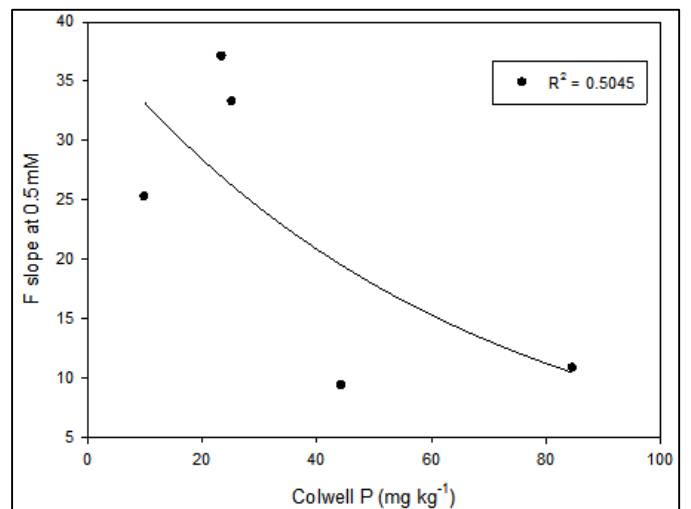


Fig 1: Sorption Curves for Phosphate and Fluoride in Unfertilised Soils.

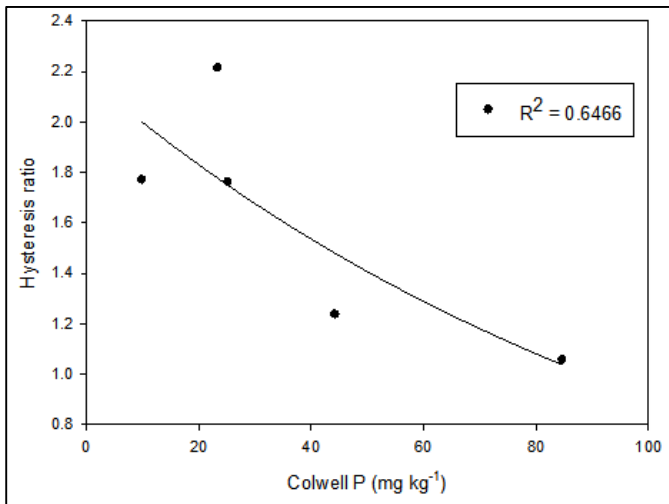


Fig 3: Relation between hysteresis ratio for sorption-desorption of fluoride and Colwell P (a) and the instantaneous slope of the sorption curves at 0.5mM and Colwell P of the soils (b).

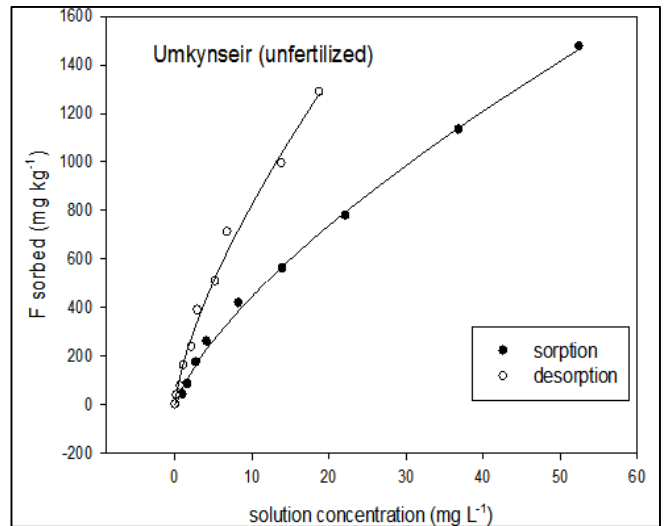


Fig 4: Sorption-Desorption of Fluoride in the Unfertilised Soils.

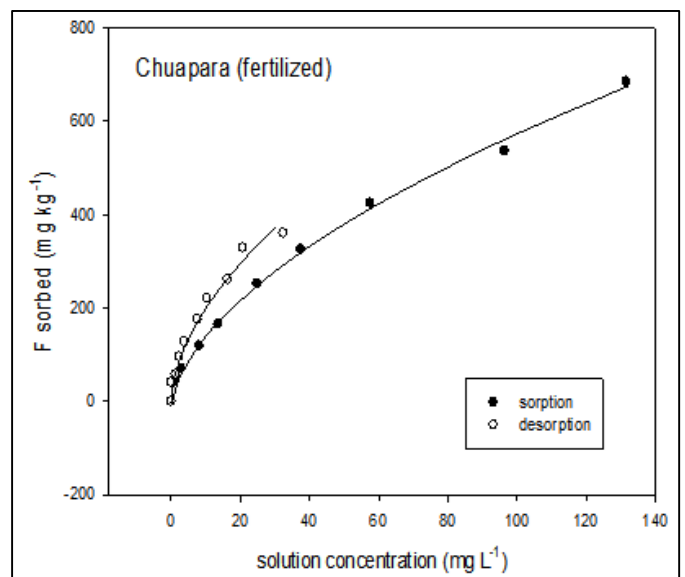
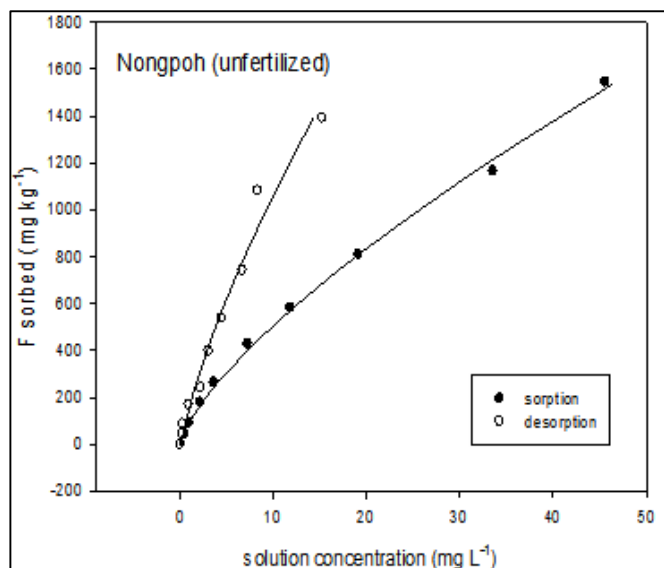
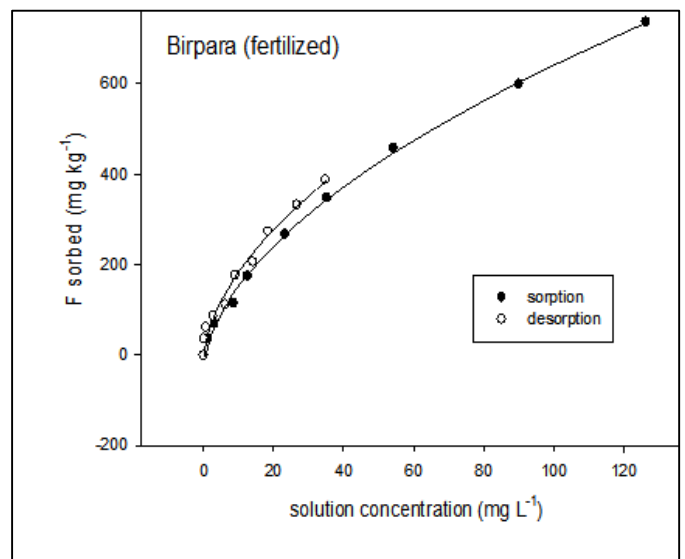
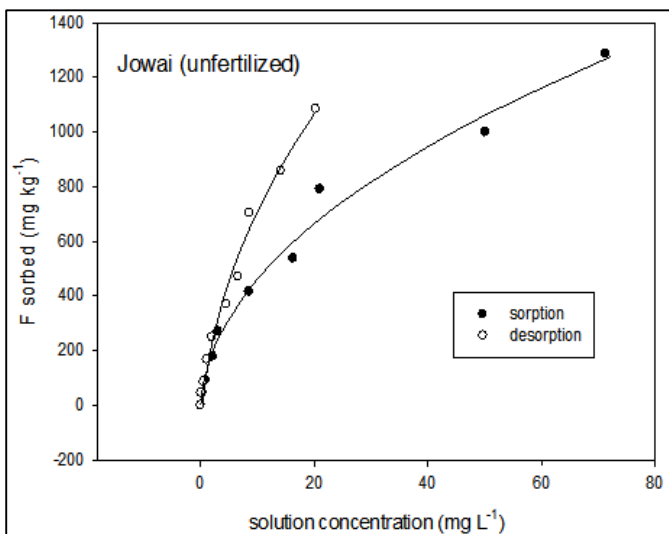


Fig 5: Sorption- Desorption of Fluoride in Fertilised Soils.

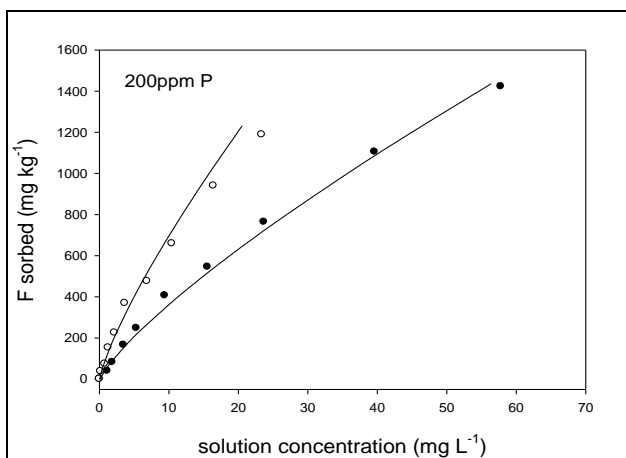
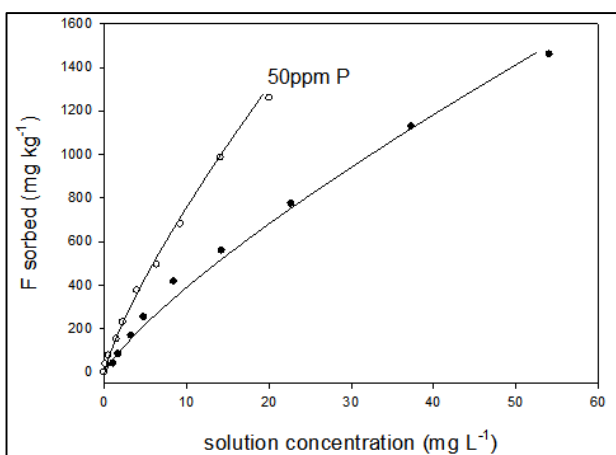
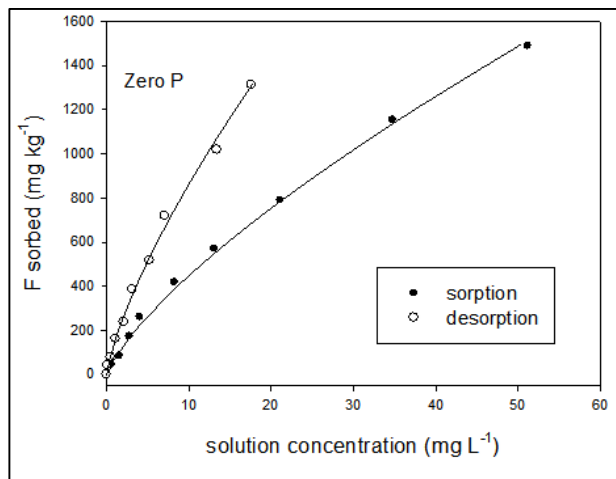


Fig 6: Sorption-Desorption curves of fluoride in the Umkynseir soil as affected by the incubation with phosphate at different levels.

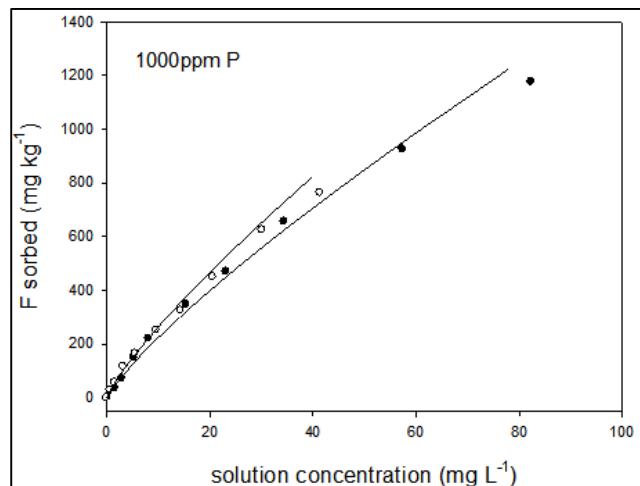
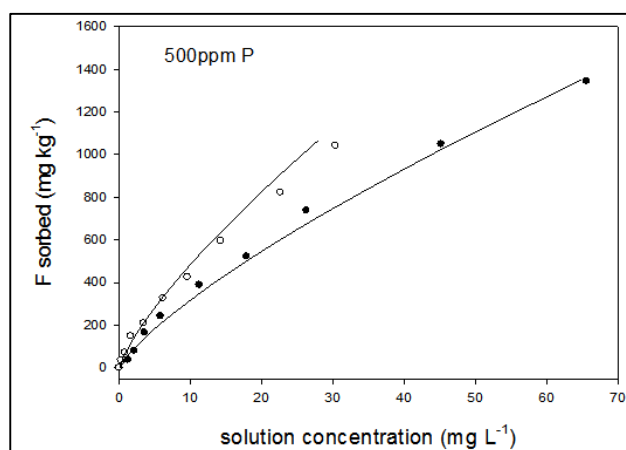


Fig 7: Sorption-Desorption curves of fluoride in the Umkynseir soil as affected by the incubation with phosphate at different levels.

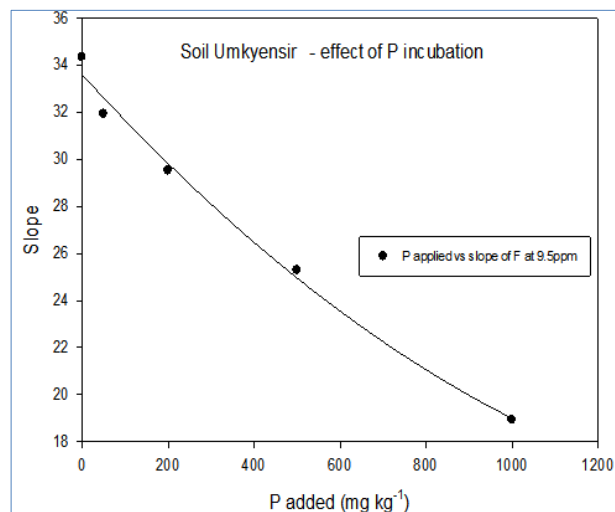
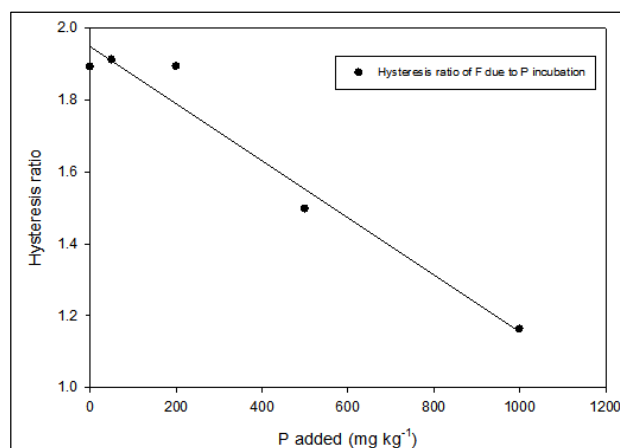


Fig 8: Relation of the hysteresis ratio and slope of sorption of fluoride with the levels of incubated phosphate.

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