

Influence of Interaction Between the Rates of Phosphorus Application and Temperature on Phosphorus Sorption-Desorption

Y.E. El Mahi, I.S. Ibrahim, A.A. Mohamed and E.A. Elamin

Department of Soil Science, Faculty of Agriculture, Shambat, Sudan

Abstract: The effect of temperature was studied during sorption-desorption of graded quantities of phosphorus in two low-P semi-arid zone montmorillonitic clay soils from the Sudan: a Vertisol (Hosh series) and an Alfisol (Hagu series). During the equilibration times used, the results indicated that at low phosphorus application, sorption increased and desorption decreased with increase in temperature from 20 to 40°C. However, at high P application, sorption decreased and desorption increased with the same increase in temperature. At high P application, there seems to be present two discrete pools of sorbed P, a fast desorbable pool and a slow desorbable one, with desorption of the first being more sensitive to increase in temperature. A kinetic equation ($P_d = a t^b$) was found to describe the release of substantial amounts of P from both pools, where P_d is the amount of P desorbed at time t , and a and b are constants.

Key words: Vertisol, Alfisol, phosphorus sorption-desorption.

It is now well established that the rate of sorption and the strength of P bonding in soils increase with increasing temperature (Barrow and Shaw, 1975; Chien *et al.*, 1982; Sah and Mikkelsen, 1986; Doula *et al.*, 1996). However, Barrow (1979) found that at a certain P enrichment point, when neither adsorption nor desorption occurred, the P concentration in solution increased with temperature and he considered this as due to the effect of temperature on the position of equilibrium between solution and adsorbed phosphate. Thus, it is not surprising that many researchers, including Singh and Jones (1977), found lower sorption and higher solubility of applied P at higher temperatures. The latter workers suggested that the net effect of temperature on P solubility depends upon the relative orders of magnitude at which the rates of fixation and release will change with temperature.

The literature on the effect of temperature on P desorption is rather conflicting. Barrow and Shaw (1975) and Sharpley and Ahuja (1982) reported an inverse relationship between the rate of P desorption and temperature. Chien *et al.* (1982) also observed a decrease of P desorption with increase in temperature when sorption and desorption were performed at the same temperature. On the other hand, the latter workers observed an increase in P desorption with increasing temperature when sorption was made at a temperature lying within the range of desorption temperature. This was also found earlier by Singh and Jones (1977) and Barrow (1979). Barrow (1983) introduced a mechanistic model, which predicts the decrease of P adsorption, and increase of desorption with increase in temperature. The validity of such a model in semi-arid zone soils of high P fixing capacity has not yet been demonstrated.

The practical implications of the effect of temperature on the sorption and solubility of fertilizer P are of paramount economic importance, especially to arid and semi-arid zone soils. Chien *et al.* (1982), after analyzing their own and Singh and Jones (1977) data, concluded that to obtain the same relative yield at a given growth temperature, a higher amount of P fertilizer is required if P is applied at higher than at lower temperature. The clay soils of central Sudan are the most extensive agricultural soils of the Sudan and are known to sorb large quantities of P (El Mahi and Mustafa, 1980). The high temperature thereof may, thus, make raising the P status of these soils to satisfactory levels hard to realize. Therefore, it is important to study the effects of temperature in these arid-zone soils with the objective of rationalizing their P fertilizer management practices.

In the present experiment, two semi-arid zone soils of low available P status were used to study the effects of temperature on P sorption and desorption from sub-samples having graded P contents with the objective of finding an overall view that may reconcile between previous conflicting results in this respect.

Materials and Methods

Two topsoil samples (0-20 cm) from southern Gezira State, Sudan were used in this study. The first sample was collected from Hagu series (fine, montmorillonitic, isohyperthermic Typic Haplustalf,) and the second from Hosh series (fine, montmorillonitic, isohyperthermic Typic Pellustert). These soils will be referred to as H and G, respectively. Some of the

physical and chemical properties of the two soils are given in Table 1.

Table 1. Some physical and chemical properties of the soils

Properties	Soils	
	Hagu	Hosh
Clay, 2 μ	40.0	50.0
Silt, 2-20 μ	09.5	24.9
FS, 20-200 μ	31.0	15.2
CS, 0.2-2 mm	07.5	04.9
CaCO ₃ %	01.1	02.0
Organic carbon %	00.65	00.59
CEC meq/100 g	33.7	56.5
Extractable iron oxide %	02.4	01.7
HaHCO ₃ extractable P μ g/g soil	03.2	02.5
pH (paste)	07.9	08.3

Particle size analysis was carried out by the pipette method (Page *et al.*, 1982), free iron oxides by the method of Kilmer (1960) and phosphate by the method of Watanabe and Olsen (1965). Other properties were determined according to the methods of soil analysis (Page *et al.*, 1982).

Phosphorus sorption

Phosphorus sorption was conducted at three temperatures: 20, 30 and 40°C. Duplicate 3g soil samples were equilibrated for 6 days in 100 ml polyethylene centrifuge tubes containing 30 ml of 10, 25, 50, 100, 300 and 500 mg P L⁻¹ in 0.01M CaCl₂ solution. Two drops of toluene were added to each tube to minimize microbial activity. The tubes were then shaken longitudinally for 30-minute periods twice daily. At the end of the six-day period, the tubes were centrifuged and P in solution was

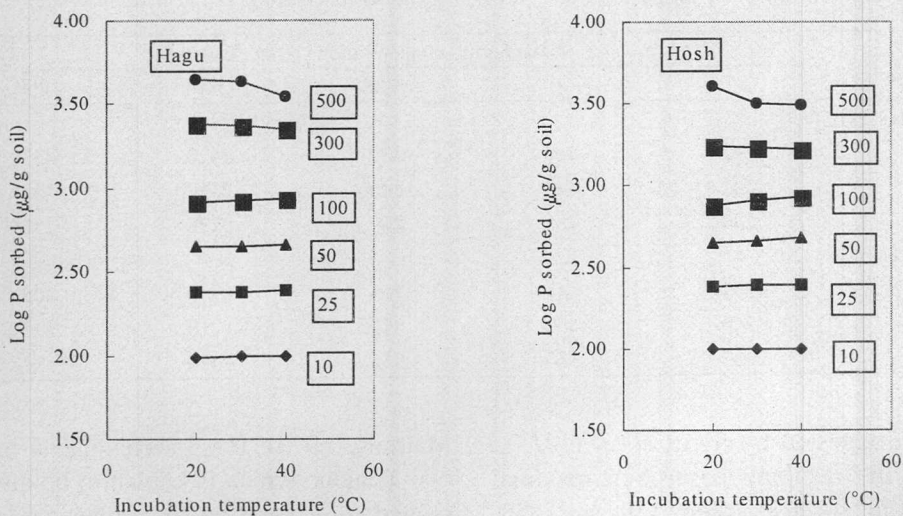


Fig. 1. Phosphorus sorption at different phosphorus solution concentrations (mg L^{-1}) and incubation temperatures.

determined. Sorbed P was estimated by the difference between the initial and the final concentrations.

Phosphorus desorption

Desorption was determined at 20, 30 and 40°C by equilibrating the previously P enriched samples with 30 ml of 0.01M CaCl_2 solution for 12 hours by continuous longitudinal shaking. The samples were centrifuged, and 28 ml of the supernatant liquid was pipetted for P determination. To each sample, a fresh 28-ml of 0.01M CaCl_2 solution was then added and the samples were resuspended for further equilibration and P determination. This equilibration cycle was repeated 10-12 times. In calculating the amount of P desorbed in each cycle, allowance was made for the two ml of the supernatant liquid carried over from the preceding cycle. The first desorption cycle was considered a

washing treatment and was thus not included in the results.

Results and Discussion

Fig. 1 shows that the quantity of P sorbed increased slightly with increasing temperature at P enrichment between 10 and 100 mg P L^{-1} . This is in agreement with previous findings of Barrow and Shaw (1975), Chien *et al.* (1982) and Sah and Mikkelsen (1986). At the 300 mg P L^{-1} treatment, P sorption tended to decrease slightly in the two soils, and at the 500 mg P L^{-1} treatment there was a large decrease in adsorption and an increase in the equilibrium P concentration with increase in temperature (Fig. 2). This result supports the findings of Singh and Jones (1977) and Barrow (1979) on the effect of temperature on the position of equilibrium between solution and adsorbed P.

Ahmed (1980) showed that P adsorption of the two soils fitted a two surface Langmuir

Table 2. Phosphorus sorption (mg kg^{-1} soil) at different phosphorus concentrations and incubation temperatures

Incubation temperature $^{\circ}\text{C}$	Phosphorus concentrations (mg L^{-1})				
	25	50	100	300	500
Hosh series (G)					
20	242	448	830	2420	4373
30	241	448	840	2350	4336
40	244	466	860	2275	3509
Hagu series (H)					
20	241	444	765	1750	4059
30	246	460	810	1710	3214
40	247	480	855	1650	3135

equation suggested by Syres *et al.* (1973), and that the resulting adsorption maxima of the two surfaces were 150 and 353 g g^{-1} for Hagu and 200 and 367 g g^{-1} for Hosh series. The sums of the adsorption maxima for the two soils were, thus, far below the amounts of P sorbed by these soils from the two highest P concentration treatments. This suggests that, in this experiment, either precipitation (Lindsay and Moreno, 1960) or diffusion below the surface (Barrow, 1983) had occurred. This point will be discussed in more details later in this paper.

Table 2 presents the results of phosphorus sorption at different phosphorus concentrations and incubation temperatures. It is evident from Table 2 that P sorption from solutions of low P concentration at all temperatures was slightly higher by Hagu than by Hosh series. It is worth mentioning that this tendency was reversed at P enrichment treatments higher than 50 mg P L^{-1} . This could be explained recalling that Hagu series had a higher content of extractable iron oxides which may have a higher affinity to P at low concentration than other soil constituents (Hoford and

Mattinly, 1975). Hosh series had a higher clay content, which is known to be directly related to P sorption in similar Sudanese soils (El Mahi and Mustafa, 1980), and consequently Hosh series had a higher overall adsorption maximum as mentioned earlier. Figure 2 shows that Hagu series released relatively lower amounts of P and maintained lower equilibrium P concentration at the 25 and 50 mg P L^{-1} treatments than Hosh series. The reverse was true for the 500 mg P L^{-1} treatment. Fig. 2 also shows that, at the two lower treatments, increasing temperature produced a negative effect on the amount of P desorbed and on the equilibrium P concentration in solution in both series during the desorption cycles. The broken lines join P concentration after similar desorption cycles and show that the equilibrium P concentration in solution decreased with increase in temperature in the two series despite the higher total P content of soils equilibrated at higher temperatures (Fig. 2). The effect of temperature becomes more evident if equilibrium concentrations were compared for samples at similar total P contents (at position vertical to the X-axis). These results support the findings of Chien *et al.* (1982)

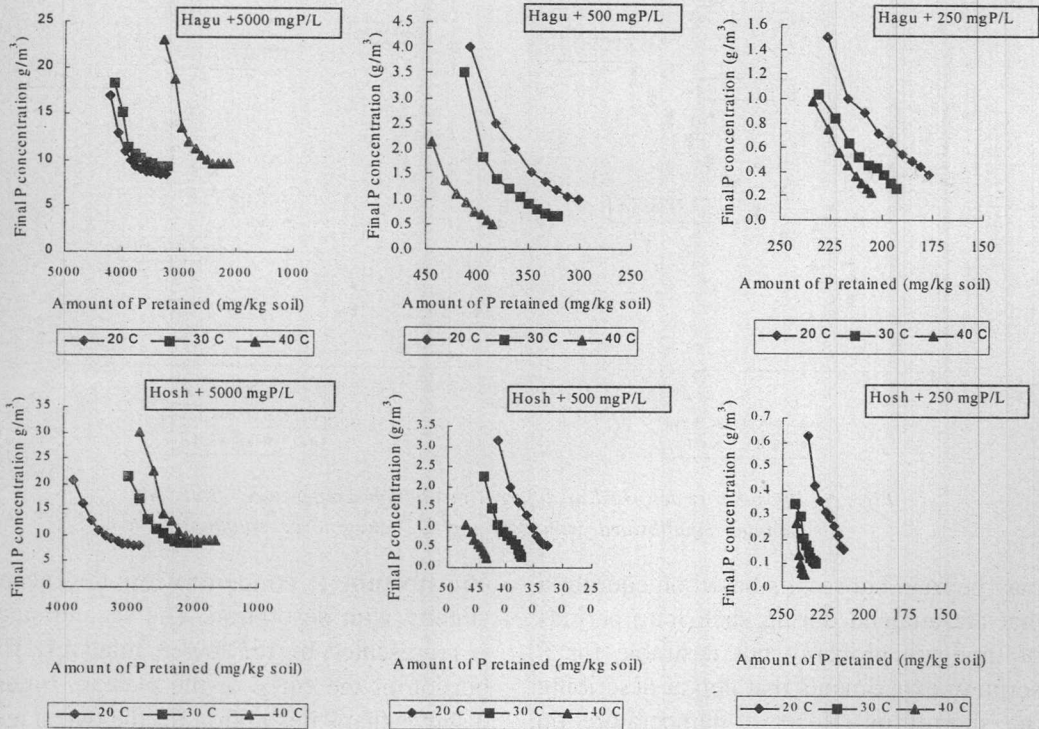


Fig. 2. Effect of temperature on phosphorus desorption.

on the effect of temperature on desorption when P adsorption and desorption were performed at the same temperature, and those of Sharpley and Ahuja (1982) who found a decrease in the amount of desorbable P and in the rate of P desorption with increase in temperature. On the other hand, increase in temperature increased the equilibrium P concentrations during desorption cycles from the 500 mg P g⁻¹ treated samples. The broken lines show that the P concentration increased with temperature despite the lower total P content of the samples equilibrated at higher temperatures (Fig. 2). The effect of temperature becomes more evident when

equilibrium concentrations during desorption were compared at similar total P contents. These results confirmed the previous findings of Singh and Jones (1977) and Barrow (1979).

Using the model described by Barrow (1983), the results obtained in this experiment for P sorption and desorption at treatments lower than 300 mg L⁻¹ might have been influenced by lack of equilibration; and that given the required time of reaction (which may extend for weeks or months), samples equilibrated at lower temperatures should show more sorption and less desorption than samples equilibrated at higher temperatures. This

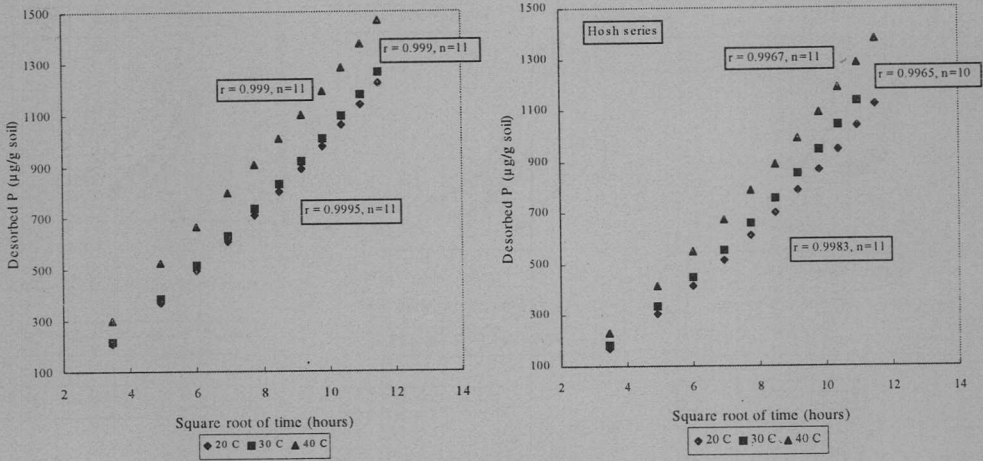


Fig. 3. Phosphorus desorbed at different incubation temperatures from soil samples equilibrated with 500 mg L^{-1} phosphorus solution.

may be true, but results based on equilibria that are attained during such long periods of time are probably not desirable for P sorption experiments that aim at describing the short-term effects of temperature on P fertilizer conditions. Intermittent shaking of a 1:10 soil suspension for 6 days will probably be equivalent to P equilibration for several weeks in natural fertilized soils at field moisture level (Barrow and Shaw, 1979). Thus, it may be concluded that the application of small amounts of P for cool season crops in a hot arid climate, like that of the Sudan before sowing, which is more hotter than the actual growing season, may cause a substantial decrease in the availability of P applied later to crops.

Figure 2 shows also that in the 500 mg P L^{-1} treatment there was a first stage of rapid P desorption during which equilibrium P concentration in solution decreased rapidly, followed by a second stage of slower desorption where the

equilibrium P concentration decreased slightly with desorption. The second stage is represented by the lower, relatively flat portion of the curve or the plateau. Figure 3 shows that P desorption for the two stages can be described by the equation :

$$P_d = a t^b$$

where,

P_d is the total amount of P desorbed at time t , and a and b are constants. The rate of P desorption remained almost constant or tended to decrease with increase in temperature, as shown by the regression equations presented in Figure 3. It is evident that there is a marked positive effect of temperature, especially between 30 and 40°C , on the most easily desorbable P of the first stage (Fig. 3), which was solubilised during the first desorption cycle. The values of the regression equations estimate the equilibrium P concentrations in solution as desorption time approaches zero. This value was in the order of 25, 27, and 39 mg

P L⁻¹ for soil G and 36, 37, and 66 mg P L⁻¹ for soil H at the 20, 30 and 40°C, respectively. This supports the idea of Barrow (1983). Results in Fig. 2 indicate that in the 500 mg P L⁻¹ treatment there seems to be present two pools of sorbed P. The first pool is an easily desorbable pool, presumably the pool of adsorbed P, that maintains a decrease in the equilibrium P concentration in solution with increased desorption. The second pool is a less easily desorbable pool which is presumably a larger pool of fixed or precipitated P compounds since it maintained a nearly constant P concentration in solution ranging between 8 and 9 mg P L⁻¹, depending on temperature. The equilibrium P concentration increased in both pools with increase in temperature, but to a lesser extent in the second than in the first pool. Phosphorus solubility calculations, according to the procedure of Lindsay and Moreno (1960), showed that at the plateau the actual PH₂PO₄ exceeded the theoretical value for both octacalcium phosphate and hydroxyapatite. The actual equilibrium values were in the order of 4.92 and 4.94 for Hosh and Hagu series, respectively, which were very close to the calculated PH₂PO₄ equilibrium values at 20°C for octacalcium phosphate which were 4.76 and 4.70 for Hosh and Hagu series, respectively.

Thus, it seems that sorbed P on the plateau is in equilibrium with a poorly crystalline or with the dissolution of super saturation phase of octacalcium phosphate described by Lindsay and Moreno (1960). Arambari and Talibudeen (1959) found an increase in labile phosphate with increase in temperature in the fraction that has lowest exchange rate of P³² in solution, and they

ascribed this to increased hydrolysis of an insoluble mixture of precipitated orthophosphates.

In conclusion, in soils from Sudan that readily sorb P, the effect of temperature on P sorption and desorption at the time of equilibrium used depended upon the quantity of P added. When small amounts were added the sorption increased and desorption decreased with increasing temperature, but when large amounts of P were added, the situation was reversed with sorption decreasing and desorption increasing with increase in temperature. These results probably apply for many other soils that sorb P, but the amount of P required to generate an increase or decrease of solution P in a particular soil with increase in temperature will probably depend upon the initial P status of that soil before P application.

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