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Ionic Balances and Reactions of Calcium, Potassium, and Phosphorus in Soils Treated with Wasted and Organic Amendments

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ABSTRACT

Relationships between K fixation under moist conditions, which is equivalent to a reduction in CEC, and the ratio of exchangeable K to exchangeable Ca + Mg (E_p) and the K adsorption ratio (PAR) of the soil solution, provide useful characterizations of K fixation in soil profiles. The accumulation of exchangeable K in soils can be predicted from the regression between E_p and PAR. However, several such regression equations were required to characterize the accumulation of exchangeable K to a 1.05-m depth. A model for cation exchange based on two half complexation reactions provided good agreement between experimental data and calculated relationships for K-Ca and Ca-Mg exchange.

The immediate phosphate formed under alkaline conditions with continued inputs of Ca and P is DCPD ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The P in DCPD is expected to revert to the more stable compounds such as hydroxyapatite (HA) and calcium carbonate phosphate (CCP). In the presence of soluble, organically bound Ca and P, which are present in soils treated with manures, the apparent solubilities of HA and CCP were shown to be 10 to 100 fold greater than in inorganic systems.

Total salts leached from manure treated soils were significantly less than the total salt inputs. The losses of cations (difference between exchangeable cations before and after leaching of soil columns) were greater for Ca and K than for Mg and Na. A transport model, modified to include chemical reactions, provided a useful tool for predicting distribution of cations in the exchangeable and soluble forms in soil columns.

OBJECTIVES

The quantities of salts added to soils in irrigation waters, fertilizers and soil amendments to most irrigated lands is large enough that management for salinity control is essential to avoid crop yield reductions and to minimize the discharge of salts to receiving waters. Management of salinity is even more critical where saline organic amendments are used on cropland or where the land is used for disposal of animal, municipal or industrial wastes. One mechanism that reduces the impact of added salts on the salinity in the root zone and on the composition of the drainage water is precipitation of sparingly soluble compounds. The formation of these slightly soluble solids depends on the ionic composition of the soil solution, the concentrating effect of evapotranspiration and on exchange reactions. For any irrigation operation, reducing the leaching fraction (LF) increases the ionic concentrations in the soil solution and increases the formation of solids.

Prediction of the extent of precipitation of a given compound in the soil is a complex task which requires the aid of a computer. The activities of the cations and anions that form the solid must be known, but the activities of each of the other ions in solution must be known and a large set of data is needed on solubility product constants, dissociation constants, activity coefficients and exchange reactions. A chemical equilibrium model calculating the precipitation of solids of the common ions in irrigation waters has been

developed and tested. However, when large amounts of potassium (K) and phosphorus (P) are added, the physical constants and reactions involved in calculating precipitation of solids were not included. The major problem addressed by this proposal was to determine the physical constants and functions needed to simulate the solution chemistry of K and P so that computer models could be modified to more accurately represent the salinity of the soil solutions.

The main solids that are expected to precipitate in soils high in K and P are calcium carbonate (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and a number of calcium phosphates. Other compounds such as taranakite (a complex potassium-aluminum phosphate) are possible, but not likely particularly in the neutral and alkaline soils of most irrigated lands. The important physical constants needed to calculate precipitation reactions resulting from applications of K and P are i) those which describe the reactions of K that will increase CaCO_3 precipitation, and ii) those which describe the solubility and kinetics of the formation of Ca phosphates.

Specific Objectives

The major objectives were to determine the effects of K and P applications in wastes or organic amendments on the precipitation of slightly soluble compounds in soils and to assess the subsequent effects of this precipitation on salinity in the root zone and in the drainage water. Within these major objectives a number of

subobjectives were identified: i) to determine the physical constants necessary to describe K reactions in soils, ii) to determine the physical constants needed to describe P reactions in soils; and iii) to modify ionic transport and chemical computer programs to include constants for K and P reactions in the calculations of salt balance and drainage water composition when large amounts of these elements are applied.

RESULTS

The results of project activities are presented in the form of eight papers, four dealing with K chemistry, two with P chemistry and two with column studies. The major effort was on K chemistry because K exchange, whether reversible or irreversible (fixation) increases the concentration of Ca in the soil solution leading to greater precipitation of CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Ca phosphates. The research on P was designed to get an idea of the immediate P compounds that form under conditions of high P and Ca concentrations and to measure the solubilities of more stable forms of P under conditions following large applications of organic materials. The column studies were planned to measure the net effects of cation exchange and precipitation of slightly soluble compounds on the loss of cations from the water moving through the soil.

POTASSIUM FIXATION CHARACTERISTICS OF FIVE
SOUTHERN CALIFORNIA SOILS¹

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ABSTRACT

Potassium fixation in five southern California soils, sampled at 15-cm depth increments down to a depth of 105 cm, is reported. The objective was to develop quantitative relationships between K fixation and other soil and solution properties. The experiments were conducted under wet conditions only and the exchangeable cation removal done by BaCl_2 . Potassium fixation, K_f , was calculated by the difference between total initial K and total final exchangeable plus soluble K in a given system and compared to CEC, the decreases in the initial cation exchange capacity (CEC_{in}). The difference between K_f and CEC appeared small, inferring that under wet field conditions, fixation mainly occurred via the mechanism of K entrapment between clay plates. Linear increases of K_f and E_p (the ratio of adsorbed K to adsorbed Ca and Mg) and with PAR ($[\text{K}^+]/([\text{Ca}^{++}] + [\text{Mg}^{++}])^{1/2}$) were found for each depth for each soil. Potassium fixation also increased with increasing depth. Relating the fractional fixation FK_f (K_f/CEC_{in}) to E_p and PAR, a more general quantification of K fixation was obtained. Fractional fixation and E_p showed a linear relationship as $\text{FK}_f = A_2 + B_2 \cdot E_p$. Such a correlation resulted in one or two regression lines representative of fixation through a given soil profile to the 105-cm depth.

Additional Index Words: cation exchange capacity, micaceous minerals, fixation mechanism

INTRODUCTION

Potassium fixation by clays and soils is considered to occur via two main mechanisms. One mechanism is by emplacement of K between basal clay surfaces (Agarwal, 1960; Grim 1968) where it fits into the hexagonal vacancies formed by tetrahedral oxygens of 2:1 minerals. That type of fixation is accompanied by the formation of mica-like minerals (Mortland and Geiseking, 1951; Barshad, 1950, 1952, 1954; Arifin et al., 1973). The formation of the mica-like minerals is illustrated by X-ray diffraction as the d "001" spacing decreases from 1.5 nm $\rightarrow$ 1.25 nm $\rightarrow$ 1.0 nm (Everett and Ellis, 1962). As an irreversible reaction, K fixation causes a decrease in the initial CEC (Page et al., 1967; Mamy and Goultier, 1979; Deist and Talibudeen, 1967a,b).

The second fixation mechanism is considered to happen via formation of insoluble K compounds, especially aluminosilicates. According to Agarwal (1960) and Volk (1938) high pH values will accelerate the formation of such compounds. Under those circumstances the detected K-fixation will exceed the decrease of initial CEC. Such a behavior was observed by York et al. (1953), Pratt and Goulben (1957), and Page et al. (1967).

It appears that there are some dominant factors which affect K-fixation. The clay type is considered to be the most dominant factor to affect fixation. In general, micas, hydrous micas and vermiculites are considered to have the highest fixation capacities, while montmorillonites and kaolinites have low capacities (Stanford, 1947; Everett and Roscoe, 1962; Prasad et al., 1967; Agarwal, 1960; Mehrotra et al., 1972; Arifin et al., 1973).

Barshad (1954) suggested a more generalized view of fixation by attributing high fixation capacity to the high negative surface charge of clays. Mortland and Gieseking (1951) and Wear and White (1951) linked high fixation to tetrahedral negative charge as in illite or vermiculite.

In montmorillonites where one finds mostly octahedral negative charge, less fixation is detected. It seems that the role of pH has not been thoroughly investigated; however, it has been pointed out that under high pH values K might be precipitated with alumina and silicates (Volk, 1938). In two recent publications, Kim et al. (1983a,b) reported K fixation via formation of K-Al and K-Fe-taranakites at pH values as low as 3.0-3.5. Soils and clays saturated with Mg, Ca, and Na show higher fixation capacity, while saturation with H, NH_4 , and K ions results in a lower fixation (Wiklander, 1950; Agarwal, 1960; Grim, 1968). Drying or drying and wetting cycles were reported by many researchers to increase fixation. Chaussidon (1963) and Mama and Goultier (1979) showed that increasing the number of wetting and drying cycles increased K-fixation until a plateau value was reached.

There is evidence that under wet conditions a correlation (equilibrium?) exists between solution composition, exchangeable K and fixed K. Bolt et al. (1963) described it as a dynamic equilibrium. Everett and Roscoe (1962) refer to it as "an equilibrium process under normal field conditions." Joshi et al. (1978) showed high correlations among the different forms of K in some Indian soils. Other workers studying K fixation on Indian soils found less profound correlations among the different forms of K (Bhatnagar et al., 1973; Choudhari and Jain, 1979; Singh and Ram, 1975). Unfortunately, they used different methods to define the different K forms in soil.

The objective of the work represented here was to quantify K fixation on wet soils from southern California at pH values of 6.0 to 8.0. Fixation was related to K in solution, to the ratio of K to Ca-Mg in solution, to exchangeable K and to the decrease in the initial CEC.

EXPERIMENTAL

Fixation was studied on five profiles of southern California soils: Domino, Pachappa, Altamont, Nord and Grangeville. Each soil was sampled at 15 cm depth increments to a total depth of 105 cm. Some characteristics of the soils are shown in Shaviv et al. (1985). The experiments were done by reacting 3-g samples of soil (>1 mm size fraction) with 20 ml of KCl solution. The KCl concentration was 0, 10, 50, 100, and 200 mmole L⁻¹, ranging from 0 to 1.333 mol kg⁻¹ on the soil weight basis. Each experimental point was the mean of three replicates; the zero K treatment (blank) was replicated four times. The soil-solution suspensions were shaken for one hour and then left overnight. The solution was separated from the soil by centrifugation. The separated wet soil was weighed to correct for cations in the remaining solution and then leached four times with 25-ml portions of 0.5 M BaCl₂ solution at pH 8.2. The Ba²⁺ salt was preferred to the NH₄⁺ salt for replacement of exchangeable cations, as being considered more similar to Ca and Mg in its leaching power (Bolt et al., 1963). Cation concentrations were determined by atomic absorption spectrometry. The CEC was calculated by summing up concentration of the leached cations. Fixation was calculated in two ways. One was by subtracting the CEC of a given experimental point from the initial CEC (blank samples), setting fixation to the decrease in CEC. The second was by considering K mass balance in the

system. In that case K fixation, K_f , was defined as the difference between total initial K consisting of exchangeable, soluble and added potassium and the residual K in solution and on the solid phase (exchanged by Ba^{2+}) after equilibration. The results obtained by the two methods were compared by plotting K_f ($mmol\ kg^{-1}$) against CEC ($mmol\ (+)\ kg^{-1}$). Fixation was correlated with K concentration in the equilibrium solution with E_p and with PAR where:

$$E_p = \frac{K_s}{Ca_s + Mg_s} \quad (1)$$

in which s stands for the exchangeable cations given in $mmol\ (+)\ kg^{-1}$ and:

$$PAR = \frac{[K^+]}{([Ca^{++}] + [Mg^{++}])^{1/2}} \quad (2)$$

brackets denoting solution concentration in $mmol\ L^{-1}$.

The principal clay minerals in these soils were estimated from X-ray diffraction data obtained using a Phillips-Norelco goniometer. The soil clay samples were divided into two fractions which were saturated with Mg and K separately. The Mg-form was also X-rayed after an ethylene glycol treatment and the K form was studied after air drying and after heating at $550^{\circ}C$; according to the methods described by Jackson (1975).

RESULTS AND DISCUSSION

Fixation Mechanism

To check the existence of a significant contribution of K-fixation due to formation of insoluble K compounds, the K_f results (based on K balance) were plotted against ΔCEC . As can be seen from Fig. 1 and Table 2, the correlation between the fixation results obtained by the two different methods was very close to the 1:1 line. This correlation indicates that the main contribution to fixation came from the irreversible adsorption of K between the clay planar sheets. However, it appears that for the high fixation values ΔCEC is slightly higher than K_f . Two possible explanations can be given; the first is that part of the exchangeable Ca and Mg ions were trapped by the closure of the interplanar spacing between clay particles as K-fixation occurred (Deist and Talibudeen, 1967a,b); however, by calculating the mass balance for Ca, almost no Ca fixation was detected when the soils were reacted with the low KCl concentration and a small amount of Ca release was observed when reacting the soil with the high KCl concentration. The second explanation can be given by assuming K release from nonexchangeable forms during the equilibrium process.

From a practical point of view, under the experimental conditions, results from both methods were identical. For convenience we have chosen to represent K fixation by the parameter K_f (based on K mass balance).

Potassium Fixation vs. Potassium Concentration in Equilibrium Solution

One possible way to describe K fixation is by correlating this parameter to K concentration in the equilibrium solution to the amount of K added to a given weight of soil. In Fig. 2A-2B, the increase of K with K in solution is shown for the Domino and Altamont soils at three different depths (1, 3 and 7). The general trend of these fixation isotherms is that the percent of the added K that was fixed was high at low levels of additions, but decreased with increase in amount of K added, ending in some of the cases with a plateau. The same results were obtained with the other three soils. Similar behavior was reported by Page et al. (1967) and Arifin et al. (1973). In general, the deep layers showed higher fixation capacities than the surface layers. Table 1 shows that the surface samples were, in all cases, richer in exchangeable K which infers higher amounts of previously fixed K (Bolt et al., 1963). That assumption will be proved later in this paper.

The increase of the initial CEC with depth may also account for the increase in fixation with depth.

Fixation Correlated with PAR and Ep

If one considers fixation to be irreversible it would then be expected to see the K ions disappearing from solution as long as the fixation sites were not "saturated". As seen from Fig. 2A-2B, we found K in solution even when fixation was far from saturation. In such a case, the exchange of K with Ca-Mg may compete with the fixation process so that both types of sites are populated at the same time, even when the irreversible adsorption is incomplete. If that is true, then a

correlation between fixed K and the PAR or E_p values may be found. By plotting K_f , the fixed K, vs. PAR we get a linear relation in the form of:

$$K_f = A_1 + B_1 \cdot \text{PAR} \quad (3)$$

Figure 3A-3B demonstrates the behavior of the Domino and Altamont soils. The values A_1 and B_1 increase with soil depth, indicating again that fixation increases with depth. That linear behavior is typical for each of the five soils investigated. Employing such a relation as in Eq. (3) makes it possible to quantify the fixation of each 15-cm layer separately. However, in some cases adjacent layers show similar behaviors, i.e., depths 4-7 in Fig. 3A or depths 1-3 in Fig. 3B.

A linear relation between E_p and PAR was found for the five soils investigated, (Shaviv et al., 1985) implied that a linear correlation should also exist between K_f and E_p where:

$$FK_f = \frac{K_f}{\text{CEC}_{in}} \quad (4)$$

CEC_{in} being the initial CEC. The correlation was in the form:

$$FK_f = A_2 + B_3 \cdot E_p \quad (5)$$

Using such an approach resulted in a general basis for describing fixation.

In Fig. 4A-4C, FK_f values for Domino, Nord and Grangeville soils were plotted against E_p values of the different layers of each of the soils. The results of that correlation are summarized in Table 3. Fixation by the Domino, Altamont and Grangeville soils was characterized by two lines, one line corresponding to the first three layers and the

second line to the following layers. The fixation results of the Pachappa soil seem to be more scattered, hence the two lines drawn appeared to differ only slightly and the correlation coefficients $r_1 = 0.77$ and $r_2 = 0.78$ were the lowest obtained among the five soils (Table 3). In case of the Nord soil (Fig. 4B), a single line represented fixation through the whole profile with $r = 0.86$ (Table 3). The regression lines obtained for the different profiles were used to calculate the fractional fixation FK_f for $E_p = 2.0$ which appeared in most of the cases to be the point for fixation to reach a plateau value. The results were summarized in Table 3, showing FK_f values which correspond to a decrease of about 50 percent of the initial CEC.

Actually one can plot FK_f vs. PAR and get a similar general quantitative correlation as obtained with E_p . In Fig. 5, FK_f was plotted vs. PAR for the Altamont soil. The high correlation between FK_f and E_p or PAR suggests a strong relationship between fixed K and the exchangeable K. Examining the behavior of the deep layers (4-7) where the prior fixed K is expected to be low, we found a very high selectivity for the fixed K at lower exchangeable K coverage (Fig. 4A-4C). This confirms our assumption that the K fixation sites have a priority compared to the exchangeable sites which is highest at low K coverage, and that higher E_p values indicate higher amounts of K fixed.

There were some points in the work that were not considered but may appear significant under natural conditions. All experiments were done under wet conditions only, even though as indicated in the introduction higher fixation is likely to occur under drying or wetting and drying cycles. Potassium release from nonexchangeable forms was not measured, but we found in general much lower amounts of soluble and exchangeable

K in the blank samples (no K added) compared with the amounts added to the soils. Sodium was ignored in all our correlations, mainly because it contributed a negligible amount to the samples studied. Calcium and Mg were treated similarly regarding the exchange with K.

CONCLUSIONS AND SUMMARY

The surface layers in the five profiles studied had significantly lower fixation capacity than the deep layers despite the high quantities of mica in the surface. This seems to be a reflection of the fact that these cultivated soils were treated with fertilizers and organic manures, which caused partial saturation of the K-fixation capacity.

Because the mineralogy was not studied quantitatively, it was impossible to account for the contribution of each mineral type of K fixation. However, all the profiles investigated consisted of either mica or vermiculite or both in a combination with montmorillonite. Considering that the minerals appear in a mixed interstratified form in soil, the micas or vermiculites might have induced high K fixation even when a profile was relatively rich in montmorillonite.

It appears that under wet conditions, the mechanism of K emplacement between clay plates has the major contribution to fixation. The contribution of the K precipitation mechanism to fixation was evaluated by comparing the K_f values to CEC values which appeared very close.

The relations FK_f vs. E_p and FK_f vs. PAR provide a useful tool for evaluating fixation through a given profile. Sampling a soil profile at 30 to 50 cm depth increments appears to be enough for practical estimation of the K fixation capacity (of a soil) by the method used in this work.

The relation FK_f vs. E_p or PAR can be used to estimate the CEC decrease caused by K fixation in an ion transport model under continuously wet conditions.

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Table 1. Some characteristics of the Domino, Pachappa, Altamont, Nord and Grangeville soils.

Table 2. The parameters, A-intercept and B-slope, for the linear correlation between K_f and CEC.

Table 3. Intercepts (A_2), slopes (B_2), linear correlation coefficients (r), and the FK_f value at $E_p = 2.0$, based on the correlation between FK_f vs. E_p (Eq. 6) for the five soils.

Table 1. Some characteristics of the Domino, Pachappa, Altamont, Nord and Grangeville soils.

Soil	Depth layer no.	Initial CEC	Initial exchange K+	pH	Principal clay minerals			Clay %	Organic matter %
					Mi	Mt	Vr		
-----mmol (+)/kg----									
Domino - fine-loamy, mixed thermic Xerollic Paleorthids	#1	150.0	8.5	7.3	0.75	0.25	-	22.5	0.94
	#3	181.0	5.6	7.0	0.75	0.25	-	23.7	0.6
	#7	424.9	1.1	7.7	0.25	0.75	-	28.7	0.35
Pachappa - fine-loamy, mixed thermic Typic Haploxeralfs	#1	75.5	6.6	7.4	1.0	--	-	12.5	0.32
	#3	79.1	3.1	7.6	0.75	0.25	-	10.0	0.15
	#7	123.9	0.9	7.6	0.50	0.50	-	11.2	0.08
Altamont - montmorillonitic thermic Typic Chromoxerets	#1	155.5	12.0	5.8	0.50	0.50	-	22.5	1.99
	#3	167.8	4.3	6.2	0.25	0.50	0.25	22.5	0.70
	#7	205.8	0.10	6.4	trace	0.25	0.75	22.5	0.26
Nord - coarse-loamy, mixed thermic Cumulic Haploxerolls	#1	111.5	10.6	8.0	0.75	0.25	-	15.0	0.84
	#3	122.4	11.5	8.0	0.75	0.25	-	15.0	0.43
	#7	121.0	1.0	9.0	0.25	0.75	-	12.5	0.14
Grangeville coarse-loamy, thermic Fluvaquentic Haploxerolls	#1	52.5	4.0	7.2	0.75	0.25	-	7.5	0.29
	#3	42.0	2.4	7.8	0.50	0.50	-	7.5	0.15
	#7	68.5	0.8	8.2	0.25	0.50	0.25	8.8	0.05

On semi-quantitative basis only; Mi = mica, Mt = montmorillonite; Vr = vermiculite.

Table 2. The parameters, A-intercept and B-slope, for the linear correlation between K_f and ΔCEC .

Soil	Intercept A	Slope B	Linear correlation coefficient r
Domino	1.162	0.821	0.880
Pachappa	0.117	0.983	0.937
Altamont	0.273	0.875	0.850
Nord	0.600	0.770	0.902
Grangeville	0.038	0.909	0.942

Table 3. Intercepts (A_2), slopes (B_2), linear correlation coefficients (r), and the FK_f value at $E_p = 2.0$, based on the correlation between FK_f vs. E_p (Eq. 6) for the five soils.

Soil	Layer no.	Intercept A_2	Slope B_2	Linear correlation coefficient r	FK_f at $E_p=2.0$
Domino	1-3	-.043	.271	0.875	0.499
	4-7	.107	.216	0.974	0.593
Pachappa	1-3	.083	.163	0.772	0.409
	4-7	.188	.095	0.780	0.378
Altamont	1-3	.065	.280	0.950	0.495
	4-7	.146	.119	0.878	0.384
Nord	1-7	-.044	.248	0.864	0.452
Grangeville	1-3	-.110	.407	0.847	0.704
	4-6	.172	.181	0.869	0.532

LIST OF FIGURES

Figure 1. Potassium fixation - K_f (calculated by K mass balance) vs. CEC - the decrease in initial cation exchange capacity. Pachappa soil; all depths represented. The solid line represents the 1:1 slope.

Figure 2. Potassium fixation - K_f vs. K^+ concentration in equilibrium solution. A. Domino soil, depths ($\square$) 1; (Δ) 3; ($\circ$) 7. B. Altamont soil, depths: ($\square$) 1; (Δ) 3; ($\circ$) 7.

Figure 3. Potassium fixation - K_f vs. PAR for the seven layers sampled. A. Domino soil, depths: ($\bullet$) 1; ($\circ$) 2; ($\blacksquare$) 3; ($\square$) 4 to 7. B. Altamont soil, depths: ($\bullet$) 1 to 3; ($\circ$) 5; ($\blacksquare$) 6; ($\square$) 7.

Figure 4. Fractional fixation - FK_f vs. E_p for three different soils. A. Domino, depths: ($\bullet$) 1 to 3; ($\circ$) 4 to 7. B. Nord, ($\bullet$) all depths. C. Grangeville, depths: ($\bullet$) 1 to 3; ($\circ$) 4 to 7.

Figure 5. Fraction fixation - FK_f vs. PAR, Altamont soil, depths: ($\bullet$) 1 to 3; (Δ) 4; ($\circ$) 5 to 7.

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