

# Potassium release and fixation in Ferralsols (Oxisols) from Southern Togo

Roland

Paul

R. POISS, J. C. FARDEAU\*, H. SARAGONI† & P. QUANTIN‡  
ORSTOM UR 2B c/o DPVE, \*CEA, DPVE, CEN Cadarache, 13 108 Saint Paul lès Durance, France, †CIRAD/IRAT, BP 1163, Lomé, Togo and ‡ORSTOM UR 1D, 70 route d'Aulnay, 93 143 Bondy cedex, France

## SUMMARY

Potassium release and fixation were studied on Ferralsols (typic Eutruxox) of Southern Togo both by isotopic exchange with  $^{42}\text{K}^+$  ions and by exchange with 1 M ammonium acetate. Experiments were conducted on soil samples taken from surface (0-30 cm) and subsoil (80-100 cm) layers of four plots. These plots, with the same soil type, were subjected to various kinds of use: forest and crops, with or without fertilizers. A single wetting and drying of the soil samples increased the amounts of exchangeable K. This exchangeable K release could stem from clay protonation during drying. However, the K release is insufficient to allow permanent intensive agriculture without K fertilizer addition. Soil samples were therefore treated with KCl in order to study K fixation. About 20% of the applied K was fixed and the percentage increased with wetting and drying. The fixation can be explained by the presence of about 2% of interstratified clay minerals in these kaolinitic soils. Comparison of the kinetic characteristics of the isotopically exchangeable K with the amounts of ammonium exchangeable K revealed the existence of several kinds of exchange site for K ions.

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## INTRODUCTION

Because of Africa's population growth (it has doubled in the last 25 years), it is absolutely necessary that Africa's agricultural production increases. In densely populated areas, such as Southern Togo, production can only be increased by a significant improvement in efficiency. It is therefore necessary to shift from an extensive agricultural system to a sustainable intensive system.

Amounts of exchangeable K are much smaller in tropical soils than in soils under temperate climates (Von Uexkuell, 1968), but K is not often given as the first limiting factor for crop production in tropical soils (Anon., 1968). This fact can be explained both by poor crop yields and, sometimes, by the release of exchangeable K from soil particles. However, K becomes a limiting factor whenever large dry matter yields are expected. In soils with small amounts of exchangeable K, the application of K fertilizers appears to be essential in order to increase crop production.

When  $\text{K}^+$  ions are added to a soil, some of them move from the solution to the solid phase of the soil. Most of the ions retained by the solid phase of the soil remain exchangeable with  $\text{NH}_4^+$  ions, and are considered to be readily available to crops. Some others, however, enter sites where they are not exchangeable with  $\text{NH}_4^+$  ions; they are said to be 'fixed' and are considered to be unavailable to crops (Volk, 1938), although it has been observed, from greenhouse and field experiments, that some of these 'fixed'  $\text{K}^+$  ions can move into the crops and so contribute to plant nutrition (Hainnaux *et al.*, 1974; Quemener, 1986).

It was assumed, for a long time, that Ferralsols do not fix K, because their main clay mineral is kaolinite (Pedro, 1974). However, K fixation was observed in some Ferralsols. Due to the lack of K deposits in Africa and the necessity to import K fertilizers from distant areas (FAO, 1985), K

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fertilizers are very expensive in Africa, and must therefore be put to the best possible use. Thus a better understanding of exchangeable K release and fixation mechanisms in these Ferralsols is required. These mechanisms were studied on the 'Terres de Barre' of Southern Togo, where K deficiency is the main limiting factor for the crops.

## MATERIALS AND METHODS

### *Soil samples*

All soil samples were collected on the 'Terres de Barre' of Southern Togo (FAO: Ferralsols; Soil Taxonomy: typic Eustrustox) at the end of the main dry season. The sampling site was located at Davié, 35 km north of Lomé, on one of the experimental stations of IRAT (Institut de Recherches Agronomiques Tropicales). Four plots were studied: one plot under natural forest (F), one plot cropped since 1969 where K fertilizers were applied until two years ago (C), and two plots of an NPK factorial long-term experimental design (K0 and K2). The K0 plot had received no K since 1976, while the K2 plot had received 100 kg K ha<sup>-1</sup> each year since 1976. Two soil layers, 0–30 cm (S) and 80–100 cm (D), were sampled in each plot. The soil was air-dried and sieved to <2 mm. The main physico-chemical characteristics of the 8 soil samples are given in Table 1. These samples are called 'check samples' in this paper.

The annual weather pattern in this part of Togo (altitude: 50 m) is tropical: two wet seasons and two dry seasons (mean annual rainfall, 1040 mm; mean annual air temperature, 27°C).

### *Treatments*

*Release of exchangeable K.* As wetting and drying are known sometimes to increase the release of exchangeable K, the soil samples were wetted at field capacity and then dried once at room temperature (22°C). The amount of exchangeable K released was determined by comparing the quantities of exchangeable K before and after wetting and drying.

*Fixation of exchangeable K.* The soil samples were thoroughly mixed with finely powdered KCl at rates of 0, 50 and 100 mg K kg<sup>-1</sup>. Quantities of exchangeable K before and after K addition were compared in order to determine K fixation. As wetting and drying are known to play a role in the transformation of K from the exchangeable form to non-exchangeable forms (Van der Marel, 1954; Scott & Hanway, 1960; Olupelu Jaiyebo, 1968; Jackson & Luo, 1986; Onchere *et al.*, 1989), one set of samples with added K was wetted and dried once as previously.

### *Determination of K content*

The K content was studied using three methods:

*Heteroionic exchange.* Two procedures were used. First, 20 g of soil were extracted by three successive additions (total of 250 cm<sup>3</sup>) of 1 M ammonium acetate buffered at pH 7. The total contact time between the soil and the acetate solution was 2 h. The quantity,  $K_{\text{exch}}$ , of K extracted was measured in the solution, after filtration, by flame photometry.

Secondly, sodium tetraphenylborate (NaTPB) is known to extract non-exchangeable K from some soils. Some samples of check soils, treatments K0 and K2, with and without wetting and drying, were treated with NaTPB (Quemener, 1979; 1988). One gram of soil was shaken with 20 cm<sup>3</sup> of 0.1 M NaTPB for 7 d at 26°C. Then 10 cm<sup>3</sup> of M NH<sub>4</sub>Cl were added and mixed with the soil. The precipitate of KTPB was dissolved with 50 cm<sup>3</sup> acetone, and K was determined by flame photometry.

*Homoionic exchange.* The method involving homoionic, isotopic exchange has frequently been used to analyse available soil phosphorus and the phosphorus-fixing capacity of soils (Morel *et al.*, 1989). This method has seldom been used to study available K because of the very short half-lives of the K isotopes (12.3 h for <sup>42</sup>K and 23 h for <sup>43</sup>K). A 1:10 soil:solution suspension was shaken for 17 h to reach a steady state (Shipley & Clark, 1972). The steady state is defined as that state of the system where the concentrations of all components of the solution remain constant, and where there is no net transfer of matter between soil and solution. A quantity of radioactivity, *R*, as <sup>42</sup>K<sup>+</sup> ions, was then added to the soil-solution mixture on a magnetic stirrer at 200 rpm. About 5 cm<sup>3</sup> of the mixture

Table 1. Physico-chemical characteristics of the surface soil (S, 0–30 cm) and subsoil (D, 80–100 cm) samples

	F <sup>a</sup>		C <sup>a</sup>		K0 <sup>a</sup>		K2 <sup>a</sup>	
	S <sup>a</sup>	D <sup>a</sup>	S	D	S	D	S	D
Clay (0–2 µm)	12	41	9	44	12	43	12	45
Silt (2–50 µm)	8	6	9	6	7	5	8	5
Sand (50–2000 µm)	80	53	81	50	81	52	80	49
pH (water)	7.2	5.3	6.2	5.1	5.6	5.3	5.8	5.7
Carbon (%)	0.55	0.17	0.45	0.17	0.41	0.17	0.51	0.20
C/N	10	5	9	5	8	4	10	4
K <sup>+</sup> (mg kg <sup>-1</sup> )	92	25	30	16	14	10	36	13
Ca <sup>2+</sup> (mg kg <sup>-1</sup> )	563	301	287	337	175	325	274	262
Mg <sup>2+</sup> (mg kg <sup>-1</sup> )	113	145	64	28	43	181	61	158
Na <sup>+</sup> (mg kg <sup>-1</sup> )	10	21	5	6	7	11	10	12
CEC (mmol <sub>c</sub> kg <sup>-1</sup> )	36	42	28	43	27	43	32	42
Base saturation (%)	100	67	79	71	48	74	67	65
K total (mg kg <sup>-1</sup> )	740	510	620	740	390	640	440	540

<sup>a</sup>F, natural forest; C, cropped since 1969; K0, no K since 1976; K2, 100 kg K ha<sup>-1</sup> a<sup>-1</sup> since 1976; S, surface soil; D, subsoil.

were sampled with a syringe at various times,  $t$ , and the solution immediately filtered through a millipore filter (0.01- $\mu\text{m}$  pore diameter). The samples were generally taken at 1, 10 and 100 min. The time required for filtration was about 5 s. The quantity of radioactivity,  $r_t$ , in solution at each time  $t$  was determined by solid scintillation counting, and the  $\text{K}^+$  ion concentration,  $c$ , of the solution was measured by atomic absorption spectrophotometry.  $c$  remains constant throughout the experiment because the system is in steady state, but the quantity,  $r_t$ , of radioactivity in solution decreases as time  $t$  increases (Fardeau *et al.*, 1977; Diatta & Fardeau, 1978). The decrease in  $r_t$  is due to the homoionic exchange of  $^{42}\text{K}^+$  ions with exchangeable  $\text{K}^+$  ions located on the solid phase of the soil. The quantity,  $E_t$ , of  $\text{K}^+$  ions isotopically exchanged in the soil-solution system at each time  $t$  is calculated assuming that the isotopic composition of the  $\text{K}^+$  ions in the solution is equal to that of the total isotopically exchanged  $\text{K}^+$  in the soil-solution mixture (Morel *et al.*, 1989):

$$(r_t/10c) = (R/E_t) \quad (1)$$

or

$$E_t = (R/r_t)10c \quad (2)$$

the factor 10 taking into account the fact that 1 g of soil is mixed with 10  $\text{cm}^3$  of solution. The quantities  $r_t$  and  $R$  are expressed in units of radioactivity, the quantities  $E_t$  in  $\text{mg K (kg soil)}^{-1}$  and the concentration  $c$  in  $\text{mg K dm}^{-3}$ .

As  $r_t$  decreases with time, the quantity  $E_t$  increases. The relation  $r_t = f(t)$ , for times ranging from 1 min to 4 months, i.e. for a period of isotopic exchange of the time-scale required for plant growth, is:

$$r_t = r_1 t^{-n} \quad (3)$$

where  $r_1$  is the quantity of radioactivity remaining in solution after 1 min of isotopic exchange, and  $n$  is an empirical parameter between 0 and 0.5, which is dependent on the soil and its K fertilization. As Equation (3) can be written  $\log r_t = -n \log t + \log r_1$ , the value of  $n$  is determined by calculating the parameters of the linear regression between the values of  $\log r_t$  and the corresponding values of  $\log t$ . By combining Equations (2) and (3):

$$E_t = (R/r_1)10c t^n \quad (4)$$

Thus the quantity  $E_t$  of isotopically exchanged K at each time  $t$  is known if  $r_1/R$ ,  $n$  and  $c$  are determined.

The quantity  $E_t$  is the quantity of  $\text{K}^+$  ions that move, in a given time  $t$ , between the soil and the solution. As these ions move between the soil and the solution, they must be regarded as plant-available.

The method permits us to examine  $E_1 = (R/r_1)10c$ , i.e. those  $\text{K}^+$  ions that are isotopically dilutable during the first minute of exchange. It has been demonstrated, using simultaneous pot experiments and an indirect isotopic dilution procedure that, as for phosphate ions (Sen Tran *et al.*, 1988), the  $\text{K}^+$  ions which are taken up by crops are not significantly different from  $E_1$  (Fardeau *et al.*, 1979). In addition, and as in the case of phosphorus (Morel *et al.*, 1989), the  $r_1/R$  parameter determined during isotopic exchange is generally a good indicator of the K fixing capacity of soils (Fardeau *et al.*, 1977; Diatta & Fardeau, 1978). When  $r_1/R$  is less than 0.2 the K fixing capacity is large, and when  $r_1/R$  is greater than 0.4 the K fixing capacity is small.

#### Clay analyses

Clay analyses were performed on the  $< 2 \mu\text{m}$  fraction of each soil sample using three complementary techniques: X-ray diffraction, transmission electron microscopy and chemical analysis.

*X-ray diffraction.* Clay samples were bathed overnight in a 1 M KCl solution, and then washed three times with distilled water to eliminate chloride. The clay suspension was then spread on a glass slide and air-dried for oriented sample analyses. Diffraction diagrams for oriented samples were observed with and without treatment with glycerol and after heating up to 490°C (Robert & Tessier, 1974). The same procedure was also performed with 1 M  $\text{MgCl}_2$ .

*Transmission electron microscopy.* Various samples were examined between  $\times 10\ 000$  and  $\times 40\ 000$  magnification in order to observe the clay minerals.

*Chemical analysis.* The triacid digestion method was described by Harrison (1933) to determine the secondary minerals of soils (clays, oxides and hydroxides). The secondary minerals are thought to be soluble in a triacid mixture, while the primary minerals are not. The samples were digested twice by evaporating to dryness in a mixture of three concentrated acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$ ). The dry residue was dissolved with concentrated  $\text{HCl}$  and water, and the solution and residue were then separated by filtration.

The mineralogical composition was investigated as follows: the quantity of illite was determined, assuming that all the K was contained in illites the K content of which is 5.8% (Weaver & Pollard, 1973). The quantity of illite thus calculated is a minimum value, because clays derived from micas contain less than 5.8% K. The quantities of silica, aluminium and iron in the illites (Weaver & Pollard, 1973) were deduced, and the silica and aluminium residues were used to evaluate the kaolinite content. The iron oxide and hydroxide contents were calculated from the iron residue. Loss on ignition was used to set the proportion of these two components.

## RESULTS AND DISCUSSION

### *Exchangeable K in check soil samples*

The amounts of exchangeable K determined by either homoionic exchange ( $E_1$ ) or heteroionic exchange ( $K_{\text{exch}}$ ) were greater in the samples taken from wooded areas than in those taken from cultivated areas (Table 2). This indicates that deforestation and local agricultural management have led to a sharp decrease in exchangeable K in the surface layers of soils. Two factors can contribute simultaneously to this evolution: (1) under forest, the amount of dry matter and K returning to the soil is considerably larger than under cropping; and (2) the fraction of the rainfall that drains out of the rhizosphere is greater in cultivated land than in wooded soils, and thus K leaching must be slightly greater.

Table 2. Exchangeable potassium in the check samples ( $K_{\text{exch}}$  and  $E_1$  in  $\text{mg K kg}^{-1}$ ,  $c$  in  $\text{mg K dm}^{-3}$ )

	F <sup>a</sup>		C <sup>a</sup>		K0 <sup>a</sup>		K2 <sup>a</sup>	
	S <sup>a</sup>	D <sup>a</sup>	S	D	S	D	S	D
Heteroionic								
$K_{\text{exch}}$	82	25	30	16	14	10	36	13
Homoionic								
$r_1/R$	0.42	0.25	0.38	0.25	0.40	0.28	0.36	0.25
$n$	0.03	0.14	0.02	0.04	0.04	0.08	0.01	0.05
$c$	5.2	0.4	1.3	0.15	0.6	0.25	1.1	0.3
$E_1$	98	31	30	19	16	5	33	6

<sup>a</sup>See Table 1.

### *Release of exchangeable K by wetting and drying*

The quantity of exchangeable K increased after wetting and drying in the soil samples that did not receive K during long-term field experiments (Table 3). In these samples the increase in exchangeable K was of the same order of magnitude with both methods used for ionic exchange.

Various mechanisms have been invoked to explain the increase in exchangeable K with wetting and drying.

**Table 3.** Increase in exchangeable K quantities after wetting and drying (in mg K kg<sup>-1</sup>)

	F <sup>a</sup>		C <sup>a</sup>		K0 <sup>a</sup>		K2 <sup>a</sup>		Mean value
	S <sup>a</sup>	D <sup>a</sup>	S	D	S	D	S	D	
Heteroionic	25	61	40	24	29	18	0	49	31
Homoionic	24	51	40	24	36	19	2	55	31

<sup>a</sup>See Table 1.

(1) When a soil is air-dried, a pressure of the order of 1000 kg cm<sup>-2</sup> is exerted on the clay layers, which could force K<sup>+</sup> ions from illite layers (Robert *et al.*, 1988). NaTPB extracts K, particularly from illites. In the small number of samples treated with NaTPB (Table 4), the quantities of K extracted with this reagent were of the same order of magnitude as those determined by isotopic exchange or heteroionic exchange; no reserve K was extracted. From this result it can be concluded that illites were not present in large quantities in these soils. This conclusion is in agreement with data previously published on the same kinds of soil (Cabanettes *et al.*, 1973). Consequently, a mechanism involving high pressure on clay layers cannot explain the increase in exchangeable K with drying and wetting in this type of soil. In addition, NaTPB cannot be used to assess K release.

**Table 4.** Comparison of isotopically exchangeable potassium ( $E_i$ ) and potassium extracted by NaTPB and by ammonium acetate (in mg K kg<sup>-1</sup>, check samples)

	K0-S <sup>a</sup>		K2-S <sup>a</sup>	
	Before W-D <sup>b</sup>	After W-D	Before W-D	After W-D
$E_i$	16	52	33	35
NaTPB-extractable K	17	41	37	39
NH <sub>4</sub> <sup>+</sup> -extractable K	14	43	36	36

<sup>a</sup>See Table 1; <sup>b</sup>W-D, wetting-drying cycle.

(2) Both pH and exchangeable K increased with the wetting and drying treatment. There is a linear regression with  $r^2=0.53$  ( $P<0.01$ ), between the increases in pH ( $\Delta$ pH) and the increases in exchangeable K ( $\Delta$ K) expressed in mg K kg<sup>-1</sup>.

$$\Delta\text{pH} = 1.05 \times 10^{-3} \times \Delta\text{K} - 0.023 \quad (5)$$

Thus our results are consistent with the hypothesis that protonation of clays occurs during drying in these tropical soils (Jackson & Luo, 1986).

Exchangeable K did not increase with wetting and drying in sample K2-S, where K fertilizers had been applied for 13 years. The greatest increase in exchangeable K was observed in the F-S sample, the exchangeable K content of which was larger than in the other samples. An increase in  $K_{\text{exch}}$  with wetting and drying is not determined by the absolute amount of exchangeable K. In each soil there is an equilibrium state, as can be observed by studying the activity ratio (AR) (Beckett & Nafady, 1969). Thus the release of exchangeable K from non-exchangeable K would depend on the difference between the present AR value and its AR<sub>0</sub> value (AR<sub>0</sub> is the AR value when K distribution is in equilibrium, Beckett & Nafady, 1969; Pieri & Oliver, 1986). Therefore a release of exchangeable

K with wetting and drying would occur in all soils in a state of relative depletion. That is why the release can take place in soils that contain large amounts of exchangeable K (Bosc, 1988).

### K fixation

The fixed K is expressed as a percentage of K applied:

$$K \text{ fixed} = 100 \times [K \text{ applied} - (K_{\text{exch}} \text{ with K applied} - K_{\text{exch}} \text{ check})]/K \text{ applied} \quad (6)$$

The same calculation can be made using  $E_1$  instead of  $K_{\text{exch}}$ .

*Samples without wetting and drying.* The percentages of K fixed are given in Table 5. The results varied considerably, partly because of the small quantities involved, and partly because the quantities fixed are calculated as the difference between two quantities of exchangeable K. In Ferralsols, a fraction of the added K is transformed into a non-exchangeable form simply by wetting either with distilled water (for measurement by isotopic exchange) or with ammonium acetate solution (for measurement by heteroionic exchange). Therefore fixation, in its generally accepted sense (Volk, 1938), did occur. However, the quantities of K fixed did not exceed one-third of the applied quantities. These results are in close agreement with those obtained by homoionic exchange: the  $r_1/R$  values are greater than 0.2 for all samples (Table 2), suggesting that the fixing capacity is limited.

*Samples with wetting and drying.* Despite their variability, the fixation percentages determined after wetting and drying (Table 6) were, on average, greater than those observed without wetting and drying (Table 5).

Table 5. Potassium fixation in check soils (K fixed as a percentage of K applied)

	Dressing (mg K kg <sup>-1</sup> )	F <sup>a</sup>		C <sup>a</sup>		K0 <sup>a</sup>		K2 <sup>a</sup>		Mean value
		S <sup>a</sup>	D <sup>a</sup>	S	D	S	D	S	D	
Heteroionic	50	4	33	31	8	0	12	30	13	16
	100	18	0	15	30	10	15	14	20	14
Homoionic	50	10	0	34	32	0	0	30	12	14
	100	0	0	7	—	0	0	15	15	5

<sup>a</sup>See Table 1.

Table 6. Potassium fixation in samples wetted and dried (K fixed as a percentage of K applied)

	Dressing (mg K kg <sup>-1</sup> )	F <sup>a</sup>		C <sup>a</sup>		K0 <sup>a</sup>		K2 <sup>a</sup>		Mean value
		S <sup>a</sup>	D <sup>a</sup>	S	D	S	D	S	D	
Heteroionic	50	46	34	56	—	60	0	25	26	35
	100	24	10	34	26	0	13	13	10	16
Homoionic	50	8	0	54	—	48	0	0	18	18
	100	0	5	52	34	0	0	7	0	12

<sup>a</sup>See Table 1.

From these results we can conclude that, in the Ferralsols studied, a fraction of any K fertilizer applied will be retained in a form that cannot be exchanged by 1 M  $\text{NH}_4$  or  $\text{K}^+$  ions. Fixation might be more marked when the soil is subjected to several wetting and drying phases, since one drying after wetting is sufficient to increase the percentage of the applied fertilizer retained in a non-exchangeable form. Similar data were obtained on soils of the same type (Koppi et al., 1987).

K fixation can be explained by the clay minerals present in these soils. On the X-ray diffraction diagram of the clays saturated with K and without glycerol treatment (Fig. 1), a wide peak appeared

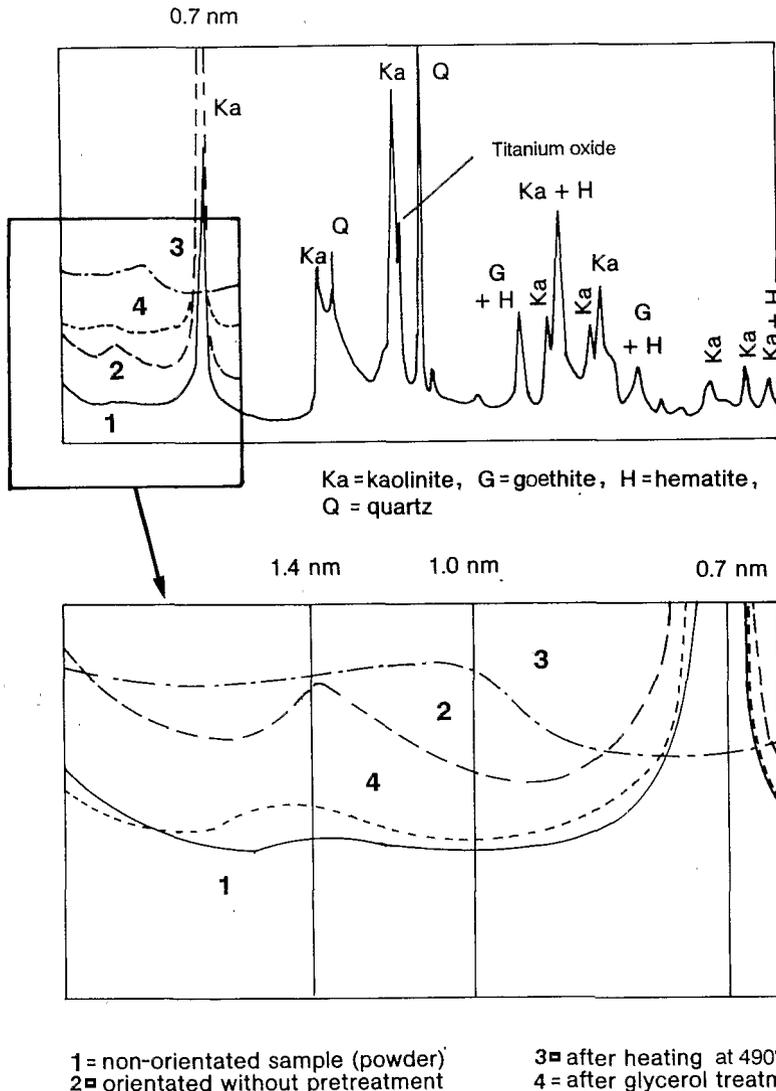


Fig. 1. X-ray diffraction diagrams of the K-saturated  $<2 \mu\text{m}$  fraction of the K0-S sample.

at 1.4 nm. This peak moved towards 1.0 nm after heating at 490°C, and almost disappeared after glycerol treatment. The same data were obtained with the clays saturated with Mg, but in this case a small peak appeared between 1.6–1.8 nm. This behaviour is more indicative of smectite than of vermiculite, since vermiculite does not swell after glycerol treatment, and K-vermiculite has a basal spacing near 1.04 nm (Grim, 1968; Brindley & Brown, 1980), while for Mg-smectite this remains near 1.4 nm. But the broad band between 1.0 and 1.4 nm could stem from an irregular

interstratification of illite-smectite components. However, there is not a complete collapse of the interlayer space to 1.0 nm after heating. This could be due either to the presence of some Al-Fe hydroxides in the interlayer space, or to the presence of chlorite. Transmission electron microscopy showed that swelling minerals were at the layer edge of small mica particles (probably muscovite). The edges of some crystals were blunted, the layers were often open and the edges rolled; ragged layers were also observed. This suggests that some expanded 2:1 clays have been formed from micas, the only primary minerals that resist ferrallitic weathering. In addition, it is known that mica-deriving vermiculite or beidellite can selectively fix K (Borchardt, 1977).

Table 7. Mineralogical composition of the clay fraction in the 'Terres de Barre' of Davié

	0-30 cm	80-100 cm
Interstratified illite-smectite minerals	2.1	1.4
Kaolinite	76.0	85.2
Fine quartz and amorphous silica	3.5	0.0
Goethite	8.0	11.4
Hematite	5.0	0.0
Titanium oxide	3.9	1.6
Other oxides	1.5	0.6
Total	100.0	100.3

Values are expressed as a percentage, determined by triacid attack.

The amounts of the different clay minerals in the soil samples were determined from the results of the triacid digestion (Table 7). The most abundant mineral was kaolinite (about 80%), while interstratified clays represented around 2% of the  $<2 \mu\text{m}$  fraction. A similar content of interstratified clays was observed in other Ferralsols from Brazil, by means of microcalorimetric measurements (Arkcoll *et al.*, 1985), and in a Ferralsol from Kenya (Kwale series) by XRD observations (Onchere *et al.*, 1989). This small content of K-selective material appears to be sufficient to explain the fate of K in these soils, which are definitely not 'pure' kaolinitic soils (Goulding & Talibudeen, 1980; Sparks, 1987; Delvaux *et al.*, 1988; Van Oort, 1988).

*Relationships between compartments determined by isotopic exchange kinetics and physico-chemical exchange sites for  $K^+$  ions*

A compartment, or pool, is defined as an homogeneous unit in which all the ions, or molecules, have the same properties. Each compartment of an heterogeneous system can be defined by its volume and its rate of exchange,  $k$ , with all the other compartments (Zilversmit *et al.*, 1943). The relationship observed for isotopic exchange in a system in steady state (Equation 3), where no net fixation or release of K occurs, can be obtained if, and only if, the radioactive ions injected are exchanged at various rates with identical but non-radioactive ions located in different compartments of an heterogeneous system (Sheppard, 1962; Shipley & Clark, 1972). Equation (3) is a power function and the system of exchangeable  $K^+$  ions contains more than two compartments (Sheppard, 1962). The analysis of such a pluricompartamental system must be realized using stochastic analysis. Equation (3) then appears to be the Laplace transform of a gamma function (Barrow & Shaw, 1975; Fardeau *et al.*, 1985). This gamma function is the probability function, giving the probability of each individual rate,  $k_p$ , of exchange between the compartment of  $K^+$  ions in which the isotope was injected (the soil solution) and all the other compartments,  $k=0$  and  $k=\infty$  being excluded.

The value  $k=0$  for the rate of exchange corresponds to the pool of  $K^+$  ions determined by the double inverse isotopic dilution method (Sen Tran *et al.*, 1988), i.e. the pool  $E_1$  which exchanges over a time period shorter than that required for the first determination.

The values  $0 < k < \infty$  define another compartment. From the Laplace transform method, it is possible to calculate the mean mathematical rate of exchange,  $k_m$ , between the ions located in the  $E_1$  pool and the other isotopically exchangeable  $K^+$  ions:

$$k_m = n/(r_1/R)^{1/n} \quad (7)$$

The value  $k = \infty$  for the rate of exchange corresponds to a pool of  $K^+$  ions that are unable to move towards the soil solution.

Therefore, in these soils, there are three distinct pools of  $K^+$  ions defined by their rates of exchange,  $k = 0$ ,  $0 < k < \infty$  and  $k = \infty$ . These pools, defined by the ability of the  $K^+$  ions they contain to move towards the soil solution, would correspond to at least three types of site for K.

It would be useful to link these pools to exchange sites deduced from crystallographic or mineralogical data. This may not be possible, because a similar attempt undertaken over a much longer period to identify sorption sites for phosphate ions was unsuccessful. In this last case, a pool identified by isotopic exchange did not correspond with a well-defined single chemical form of P, and various types of linkage of phosphate ions with soil components, identified by chemical analysis, sometimes had the same isotopic composition, i.e. corresponded to the same compartment defined by the method of isotopic exchange (Gachon, 1973).

The time of access to the pool  $E_1$  must be considered to be instantaneous (1 min or less). The amounts of  $K_{\text{exch}}$  and  $E_1$  were closely correlated. Including all the samples:

$$K_{\text{exch}} = 0.88E_1 + 0.1 \quad (8)$$

with  $r^2 = 0.96$  ( $P < 0.01$ ). Thus the amount of isotopically exchangeable  $K^+$  ions is about 10% larger than that of  $NH_4^+$  exchangeable K ions. This conclusion is in agreement with results obtained for soils of the neighbouring Ivory Coast (Cabanettes *et al.*, 1973). The difference between the quantities  $K_{\text{exch}}$  and the quantities  $E_1$  can be explained by making two different assumptions. According to the first hypothesis, this difference can result from incomplete extraction of isotopically exchangeable ions by the ammonium acetate. According to the second hypothesis, the pool  $E_1$  would contain on the one hand  $K^+$  ions located on sites accessible to both  $NH_4^+$  and  $K^+$  ions, and on the other hand  $K^+$  ions located on sites accessible only to  $K^+$  ions, and not to  $NH_4^+$  ions. However, all these  $K^+$  ions have the same ability to enter the soil solution. According to the literature on soil thermodynamics, the first sites could correspond to the external, planar sites of clay minerals, whose selectivity for  $K^+$  is weak, and the second sites could correspond to the edge sites, whose selectivity for  $K^+$  is higher (Mengel & Kirkby, 1980). As the extraction of  $K_{\text{exch}}$  is realized by three successive extractions with acetate, the first hypothesis is unlikely.

The second pool consists of  $K^+$  ions for which  $0 < k < \infty$ . It could be assumed that the corresponding sites would be the interlayer exchange sites, particularly those in 'wedge zones' (Mengel & Kirkby, 1980; Andreoli, 1989), although the mechanisms of exchange between sites are only partially understood (Goulding, 1983).

The difference between the quantity of total K in a soil and the quantity of K present in these two pools indicates the presence of a third pool. This last compartment contains  $K^+$  ions that must be regarded as immobile. They are probably  $K^+$  ions entrapped in the hexagonal oxygen network of tetrahedral sheets, compensating tetrahedral charges (Al for Si substitution). This has already been shown for illite, vermiculite and some smectite clay minerals.

## CONCLUSIONS

Wetting and drying of typical Ferralsols from Southern Togo, so-called 'Terres de Barre', increased exchangeable K in all soil samples taken from plots where no K was applied during cultivation. This release of exchangeable K appears to be caused by the protonation of clays which occurs during the drying phase. The quantity of K released can be equivalent to an application of K fertilizers of about 100–150 kg K ha<sup>-1</sup>. This release can explain the difficulties encountered by agronomists when, in tropical agrosystems, they compare crop uptake and decrease in exchangeable K in soil samples (Pieri, 1987). The determination of exchangeable K can provide an estimate of the quantity of K

available to a crop for the next cropping season, but this determination cannot predict what will be available after one crop and several successive wetting and drying cycles.

Such K release might encourage the idea of cultivating without K fertilizers; this could be a serious mistake. The rate of transfer of K from the clay matrix to the interlayer sites is slower than that from interlayer sites to solution. There is therefore a limit to the rate of release of fixed K that would constrain plant growth, particularly those plants that require high levels of K. Also, in the long term, the repeated removal of K without return reduces the available K content of soils, as observed on all the cultivated plots, compared to the forest plot. Therefore the release of fixed K can provide only a very short-term solution to crop needs. The development of a sustainable intensive agriculture, a prerequisite for increasing agricultural production on the 'Terres de Barre', must involve the application of K fertilizer which returns to the soil at least the same amount of K as that which is exported in the crops.

About 20% of the K applied as fertilizer to the 'Terres de Barre' soils became non-exchangeable to either  $\text{NH}_4^+$  or  $^{42}\text{K}^+$  ions. Thus, according to the general definition of K fixation, these soils fix K, whereas for a long time it was considered that they do not do so. This fixation is probably due to a small quantity of interstratified illite-smectite clays, detected by a combination of physical separation methods and crystallographic and chemical analyses. The fixed quantities are small in relation to the quantities required by crops, and therefore K fertilization will not be greatly hindered by fixation.

In addition, clay mineral analysis and the comparison of data obtained on exchangeable K, either by heteroionic or homoionic (isotopic) exchange, showed the presence of at least three types of exchange site for K. These are primarily characterized both by their ability to adsorb  $\text{K}^+$  or  $\text{NH}_4^+$  ions and by the rate of exchange between the  $\text{K}^+$  ions that they contain and the  $\text{K}^+$  ions in the soil solution.

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