

Differences in potassium forms between cutans and adjacent soil matrix in a Grey Clay Soil

Fan Liu¹, R. J. Gilkes, R. D. Hart and A. Bruand²

Department of Soil Science and Plant Nutrition, Faculty of Agriculture, The University of Western Australia, Nedlands, Perth, WA 6907, Australia

¹ Current address. Huazhong Agricultural University, Wuhan 430070, P.R. China.

² Current address. Institut des Sciences de la Terre d'Orléans, Université d'Orléans, Géosciences, BP 6759 45067 Orléans Cedex, France.

Abstract

Cutans are common fabric features in soil and represent foci of chemical and biological reactions. The influence of cutans on potassium forms and their transformations were investigated for a Western Australian grey clay soil. Cutans and matrix soil had similar clay mineral associations with kaolinite, smectite and illite being present, but had different chemical properties. The organic carbon content of cutans was higher than for matrix soil, while pH values and oxalate extractable/dithionite extractable iron (Fe_o/Fe_d) ratios were lower. Numerous SEM-EDS single point analyses of cutans and the plasma phase of the matrix soil indicated that the mean value of K concentration in cutans is greater than in matrix soil, and that the K concentration decreased with distance from cutan to matrix. Chemical extractions showed mean values of total K and latent exchangeable K were higher for cutans than for matrix soil, but both fixed K and exchangeable K values were the same for cutans and matrix soil. In a K adsorption/desorption experiment, 35% of K adsorbed by matrix soil could not be desorbed by 1 M NH₄Ac. These results indicate that cutans are relatively enriched in K and may play an important role in determining available K and latent exchangeable K due to the special physical and chemical environments they provide in the soil.

Author Keywords: Potassium; Cutans; Grey clay; Extractable Fe; SEM-EDS microanalysis

1. Introduction

Potassium forms in soil have been a key focus in studies of soil fertility. Much work has addressed bulk solution chemistry and mineralogy (Martin; Bouabid; Sharpley; Buhmann and). The influence of microscopic features of soil fabric on potassium forms and availability has not been thoroughly investigated. This is a marked deficiency as the availability of all plant nutrients is affected by the extent of soil–root contact as determined by soil structure and the associated distribution of roots and nutrients. Void cutans are argillans formed by illuviation of clay into soil voids or cracks during soil development. They are one of the common fabric features in soils and can comprise a substantial proportion of the soil volume (Brewer, 1976). Research on cutans is usually pedologically and micromorphologically focused and commonly concentrates on their mineralogical composition, formation mechanisms and relationships with water movement (Rebertus; Chartres; Jakobsen; Sullivan;

McBurnett and Venugopal). Because cutans occupy special positions in soil and are affected strongly by the external environment they are commonly different from the matrix soil much of which is within protected peds. Cutans closely interact with air, roots, microbes, soil water and dissolved ions so that cutans might be enriched in or depleted of plant nutrients relative to matrix soil. Consequently, cutans may have an important influence on the transformation and availability of plant nutrients including potassium. There may be an important link between rhizosphere and pedological processes in cutan lined voids which is generally ignored in research on plant nutrition (Martin and Sparks, 1985). We investigated the contents, forms and distribution of potassium in cutan and matrix soil of a Grey Clay Soil from Katanning Western Australia to determine if cutan and matrix soil differ in their capacities to supply K to plants and fix applied K.

2. Materials and methods

2.1. Soil sampling and descriptions

Fifteen soil samples were collected from 10 profiles to a depth of 1 m from grey clay soils on a level alluvial plain in the Katanning region of Western Australia. A description of a representative soil profile is given in Table 1. Parent material is clayey alluvium that was possibly deposited under lacustrine conditions upon a truncated lateritic saprolite. In the Katanning region, the mean daily temperature is 13–30 °C in January and is 6–14 °C in July, annual evaporation capacity is 1488 mm and the annual rainfall is 483 mm occurring mostly in June–August. The soils belong to the Grey Clay group of soils (Ug5.24, McArthur, 1991) and are commonly dry and cracked for much of the dry season (summer). Subsoil horizons usually exhibit a coarse polyhedral to columnar structure. The polyhedral peds are coated by cutans and their macro-porosity consists mainly of planar channels of 0.5–1.5 mm width. The soils also contain large vertical cracks from the surface down to a depth of 60–90 cm, which represents the limits of the coarse prismatic structure (Bruand et al., 2001). These cracks are almost totally filled by sandy-clay materials with a relatively high organic carbon content. Cutan material on ped surfaces was concentrated by scraping it off with a sterile blade and a paired sample of bulk matrix soil was taken from an adjacent ped interior.

2.2. Analyses of soil and cutan properties

Samples were dried in an oven at 105 °C prior to analysis. The clay minerals of cutans and soils were investigated with a Philips PW 3020 X-ray powder diffractometer using monochromated $\text{CuK}\alpha$ radiation generated at 50 kV and 20 mA. The XRD patterns were obtained from both random powders and oriented clays after removing free Fe by the DCB method and after Mg-glycerol saturation and K saturation, respectively. The pH (H_2O) of soil and cutan samples was measured using a 1:5 sample/solution and after the samples had been equilibrated for 1 h on an end-over-end shaker. Organic carbon was determined by combustion in a LECO induction furnace after the samples had been washed once in 0.2 M HCl to remove carbonate. The particle-size distribution was determined by the pipette method after hydrogen peroxide treatment (Gee and Bauder, 1986). Extractable Fe was dissolved in ammonium oxalate (0.2 M, pH 3.0, 4 h in dark) (McKeague and Day, 1966), and dithionite–carbonate–citrate, DCB (Mehra and Jackson, 1960). Oxalate extractable iron is referred to as Fe_o and DCB extractable iron is referred to as Fe_d . Total K was extracted by digestion (125 °C) of the samples in aqua regia on an AIM500 programmable block digester. Acid-extractable K and exchangeable K were dissolved by boiling in 1.0 M HNO_3 and 1.0 M NH_4Ac for 10 min, respectively. Fixed K is considered to be total K minus HNO_3 -extractable

K. Latent exchangeable K is defined as HNO_3 -exchangeable K minus exchangeable K. K sorption and desorption measurement on matrix soil were performed as follows. Matrix soil samples were washed once with 0.2 M HCl, then were washed once with 1 M NaCl and then with water. Some of the treated sample was added to 2.5 $\mu\text{mol/ml}$ K solution in 0.01 M NaCl (soil/solution=1:25) and shaken on a reciprocal shaker at 150 cycles/min for 24 h at 25 °C. The subsamples with K adsorbed were washed twice with ethanol. Another of the HCl–ethanol treated samples, which was not added to K solution, was taken as a blank sample. Next the exchangeable K in the samples with adsorbed K and blank samples was extracted with 1 M NH_4Ac . Fe and K in the various solutions were measured with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer. Polished thin sections of soils containing ped and cutans were made by the resin impregnation method of Fitzpatrick (1984). They were polished in kerosene, carbon-coated and examined using a JEOL6400 scanning electron microscope operated at 15 kV and 5 nA, equipped with an Oxford Link systems energy dispersive X-ray analyzer. Spectra of cutan and matrix were collected at 5000–7000 counts per second for 30 live seconds, elemental compositions were determined using the ZAF correction method. Analyses are expressed on an ignited sample basis and are not directly comparable to analyses obtained on an oven dried basis (105 °C). Large numbers of single point analyses on the thin sections as well as element mapping of small areas gave detailed information about K contents and the distribution of K in cutan and matrix materials.

3. Results and analyses

3.1. General properties

Significant statistical differences existed between matrix soil and cutan (*t*-test) for pH, carbon content, Fe_o content and Fe_o/Fed ratio, but not for clay concentration and Fed content (Table 2 and Table 3). The mean clay concentration in cutans (452 g kg⁻¹) was almost identical to that (446 g kg⁻¹) of the matrix soil. As cutan materials were collected by scraping ped surfaces with a blade some matrix soil material was inevitably included in the cutan separate. However, it appears that cutans are not significantly enriched in clay.

3.2. K contents and forms

In plain light, the cutans appeared as a continuous parallel dark band in thin sections. The width of the bands was 200–300 μm (Fig. 2a) with clay showing strong continuous parallel orientation in cutans under crossed polarizers (Fig. 2b). Line profile chemical analyses and area chemical analyses were made using the EDS facility of the SEM including more than 160 SEM-EDS single point elemental analyses of cubic micrometer volumes of cutans and matrix soil (Fig. 3). The K concentration decreased systematically with increasing distance from the cutan (K_2O , 13 g/kg) to matrix soil (K_2O , 9 g/kg) (Fig. 3 and Fig. 4). Note that large sand grains were avoided in the EDS analysis. There was a significant statistical difference in K_2O content between cutan and matrix soil (*t*-test) for all thin sections except for sample A1. The mean values of K concentration for cutan were systematically higher than for matrix soil for all five thin sections (Table 4).

4. General discussion

The generally higher values of total K and latent exchangeable K in cutans relative to matrix soil are not related to differences in clay concentration. No systematic relationships between the latent exchangeable K concentration and the clay concentration in the cutans or the matrix soil were identified (Fig. 5). This difference in K content is also not related to differences in clay mineralogy between cutan and matrix soil as cutans and the matrix soil have the same clay mineral suite with only nonsystematic minor variations in relative abundance. The soils also do not contain significant amounts of K-bearing primary minerals such as K-feldspar, so differences in K concentration can not be associated with non-clay minerals. Cutans contain more organic matter than matrix soil and differences in K concentration may derive from more K being present in the organic matter complex. However, soil organic matter usually contains little K. Other possible reasons for a higher K concentration in cutans may include the following.

Acknowledgements

Fan Liu thanks the Gledden Visiting Senior Fellowship Scheme of The University of Western Australia for financial support and Huazhong Agricultural University, Wuhan, China, for granting sabbatical leave. Ary Bruand thanks The University of Western Australia and INRA, France for financial support. We would like to acknowledge the assistance of Ms. Melissa Narbey, Dr. Brenda Rohl and Mr. Adam Pratt of the Department of Soil Science and Nutrition, and Mr. John Hillyer of the Centre for Microscopy and Microanalysis, The University of Western Australia in sampling and analysis.

References

- Aide, 1995. M. Aide, Potassium selectivity on reference soil smectites. *Transactions of the Missouri Academy of Science* **29** (1995), pp. 23–30.
- Bouabid et al., 1991. R. Bouabid, M. Badraoui and P.R. Bloom, Potassium fixation and charge characteristics of soil clays. *Soil Science Society of America Journal* **55** (1991), pp. 1493–1498.
- Brewer, 1976. R. Brewer In: *Fabric and Mineral Analysis of Soils*, Robert E. Krieger Publishing, Huntington, NY (1976), p. 205.
- Bruand et al., 2001. A. Bruand, H. Cochrane, P. Fisher and R.J. Gilkes, Increase in the bulk density of a Grey Clay subsoil by infilling of cracks by topsoil. *European Journal of Soil Science* **52** (2001), pp. 37–47.
- Buhmann, 1993. C. Buhmann, K-fixing phyllosilicates in soils: the role of inherited components. *Journal of Soil Science* **44** (1993), pp. 347–360.
- Chartres, 1987. C.J. Chartres, The composition and formation of grainy void cutans in some soils with textural contrast in Southeastern Australia. *Geoderma* **39** (1987), pp. 209–233.
- Dhillon and Dhillon, 1991. S.K. Dhillon and K.S. Dhillon, Exchange equilibria of potassium in some red, black and alluvial soils of India: I. Effect of displacing cations. *Australia Journal of Soil Research* **29** (1991), pp. 87–94.
- Fitzpatrick, 1984. E. Fitzpatrick *Micromorphology of Soils*, Chapman & Hall, London (1984).

- Gee and Bauder, 1986. G.W. Gee and J.W. Bauder , Particle-size analysis. In: K. Klute, Editor, *Methods of Soil Analysis, Part I Agronomy Monograph* **vol. 9**, American Society of Agronomy, Madison, WI (1986), pp. 383–411.
- Jakobsen, 1991. B.H. Jakobsen , Multiple processes in the formation of Subarctic Podzols in Greenland. *Soil Science* **152** (1991), pp. 414–426.
- Klug and Alexander, 1974. H.P. Klug and L.E. Alexander *X-ray Diffraction Procedures* (2nd edn. ed.), Wiley, New York (1974) Chap. 9 .
- Martin and Sparks, 1985. H.W. Martin and D.L. Sparks , On the behavior of nonexchangeable potassium in soils. *Communications in Soil Science and Plant Analysis* **16** (1985), pp. 133–162.
- McArthur, 1991. W.M. McArthur In: *Reference Soils of South-Western Australia*, Department of Agriculture and ASSSI, Western Australia, Perth, Australia (1991), p. 163.
- McBurnett and Franzmeier, 1997. S.L. McBurnett and D.P. Franzmeier , Pedogenesis and cementation in calcareous till in Indiana. *Soil Science Society of America Journal* **61** (1997), pp. 1098–1104.
- McKeague and Day, 1966. J.A. McKeague and J.H. Day , Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* **46** (1966), pp. 13–22.
- Mehra and Jackson, 1960. O.P. Mehra and M.L. Jackson , Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals* **7** (1960), pp. 317–327.
- Rebertus and Buol, 1985. R.A. Rebertus and S.W. Buol , Intermittency of illuviation in Dystrochrepts and Hapludults from the Piedmont and Blue Ridge province of North Carolina. *Geoderma* **36** (1985), pp. 277–291.
- Ryan and Matar, 1992. J. Ryan and A. Matar , Chemistry and mineralogy of potassium in Moroccan soils: implications for fixation and release. In: *Fertilizer use efficiency under rainfed agriculture in West Asia and North Africa: Proceedings of the Fourth Regional Workshop, 5–10 May 1991, Agadir, Morocco*, ICARDA, Aleppo, Syria (1992), pp. 16–27.
- Schwertmann and Taylor, 1989. U. Schwertmann and R.M. Taylor , Iron oxides. In: J.B. Dixon and S.B. Weed, Editors, *Minerals in Soil Environments* (2nd edn. ed.), Soil Science Society of America, Madison, WI, USA (1989), pp. 379–438.
- Sharpley, 1989. A.N. Sharpley , Relationship between soil potassium forms and mineralogy. *Soil Science Society of America Journal* **53** (1989), pp. 1023–1028.
- Sullivan and Koppi, 1992. L.A. Sullivan and A.J. Koppi , Manganese oxide accumulations associated with some soil structural pores: I. Morphology, composition and genesis. *Australian Journal of Soil Research* **30** (1992), pp. 409–427.

Venugopal, 1998. K.R. Venugopal , Types of cutans in some ferruginous soils of Bangalore Plateau and their relation with soil development. *Journal of the Indian Society of Soil Science* **46** (1998), pp. 641–646.

Figures and Tables

Table 1. Description of a representative soil profile

Sample no.	Horizon	Depth (cm)	Description
1	A	0–10	Dark greyish brown (10 YR 4/2); light clay; strong polyhedral structure; very firm; regular, clear boundary to
2	B1	10–20	Grey (10 YR 5/1); heavy clay; strong polyhedral structural; some cutans; very firm; regular boundary to
3	B2	20–40	Grey (10 YR 5/1); heavy clay; coarse polyhedral; very firm; dense peds; many cutans and slikenesides; gradual to
4	B3	40–80	Grey (10 YR 5/1); heavy clay; strong coarse polyhedral very firm; dense peds; many cutans and slikenesides

Table 2. Typical properties of the matrix soil and cutans for a representative soil profile

Sample no.	Depth (cm)	pH (H ₂ O)	Clay (g kg ⁻¹)	Carbon (g kg ⁻¹)	Fed ⁺ (g kg ⁻¹)	Feo ⁺ (g kg ⁻¹)	Feo/Fed	Total K (mg g ⁻¹)	BNO ₂ K ⁺ (mg g ⁻¹)	BK ⁺ (mg g ⁻¹)
Matrix 1	0–10	7.44	237	14.2	6.1	5.0	0.83	2.20	1.27	0.68
Matrix 2	10–20	9.67	400	3.4	2.5	1.8	0.71	2.76	1.38	0.63
Matrix 3	20–40	9.67	454	2.5	2.8	1.3	0.46	2.68	1.29	0.67
Cutan 3c	20–40	9.21	438	3.9	2.5	0.6	0.25	3.16	1.63	0.49
Matrix 4	40–70	10.07	467	2.4	3.3	1.7	0.53	2.52	1.21	0.61
Cutan 4c	40–70	9.43	473	3.5	2.3	0.5	0.22	2.93	1.38	0.34

Table 3. Average values of properties of the cutans and matrix soil for all profiles (all results for oven dried 105 °C samples)

Items	pH (H ₂ O)		Clay (g kg ⁻¹)		Carbon (g kg ⁻¹)		Fed (g kg ⁻¹)		Feo (g kg ⁻¹)		Feo/Fed	
	MS	Cutan	MS	Cutan	MS	Cutan	MS	Cutan	MS	Cutan	MS	Cutan
Mean	9.53	9.17	446	452	2.6	4.2	3.4	2.8	1.1	0.7	0.32	0.26
S.D.	0.42	0.27	75	74	1.0	1.6	2.0	0.9	0.4	0.2	0.14	0.08
N	15	15	15	15	15	15	15	15	15	15	15	15
T		2.81*		0.23		3.43*		1.10		3.43*		2.52
F		< 0.01		0.82		0.02		0.28		0.02		0.02

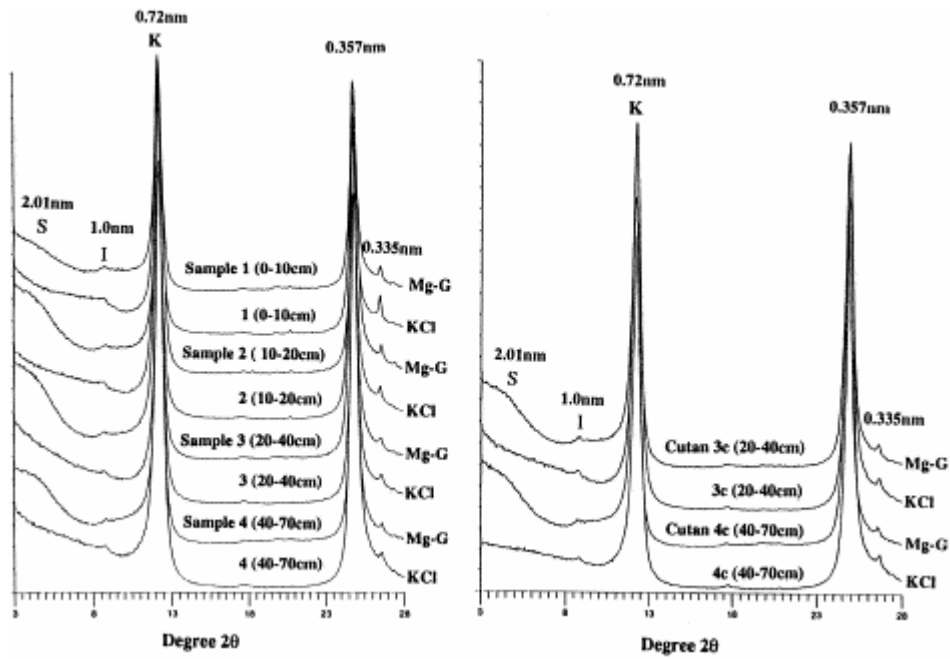


Fig. 1. X-ray diffraction patterns of the oriented clay fractions of representative samples of matrix soil from four horizons and cutans from two horizons. S, smectite; I, illite; KCl, K-saturated, Mg-G, Mg-glycerol saturated.

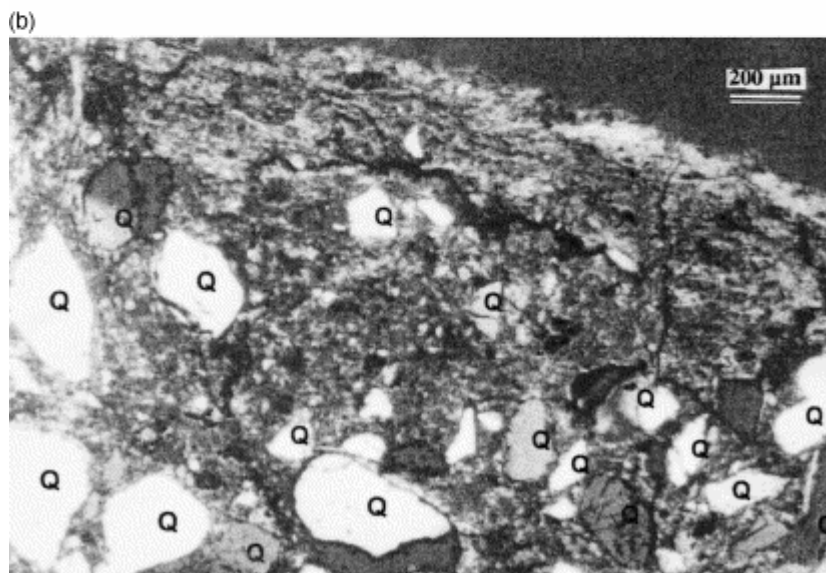
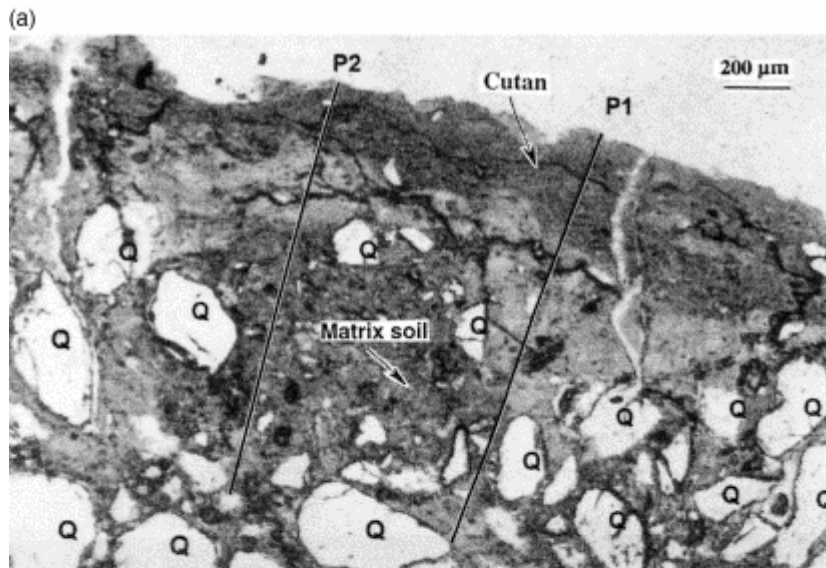


Fig. 2. (a) Optical micrograph (plain light) of a thin section of sample A4 showing the matrix soil and cutan (void argillan). The locations of the SEM/EDS scans for K presented in Fig. 3 are shown as line profiles P1 and P2. Q, quartz. (b) Optical micrograph (crossed polars) showing the highly oriented clay comprising the cutan and randomly oriented packets of clay in the matrix soil. Q, quartz.

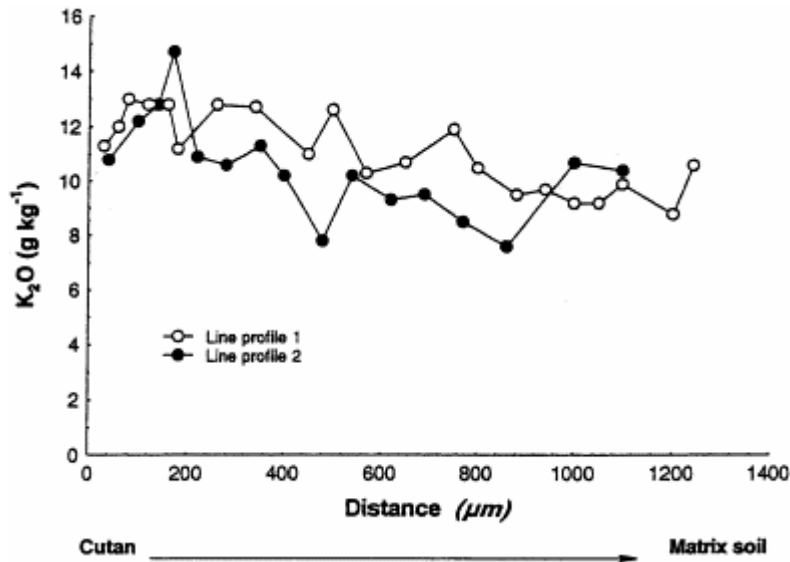


Fig. 3. The distribution of K₂O content (equivalent ignited basis) in transects across cutan into matrix soil. The data indicate that the K₂O content decreases from cutan to matrix soil.

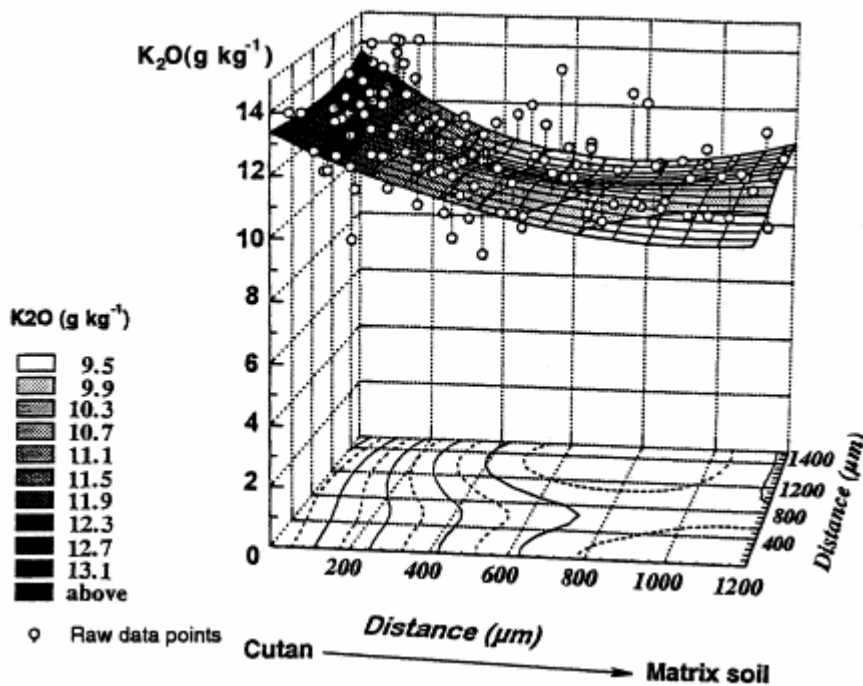


Fig. 4. The distribution of K₂O (equivalent ignited basis) over a 1.4×1.2 mm area of cutan and matrix soil. The three-dimensional surface plot indicates that the K₂O content tends to decrease with distance from cutan to matrix soil.

Table 4. Mean K concentrations (EDS data) of cutans and matrix soils in several thin sections (g kg^{-1} , ignited sample basis)

Sample no.	A1		A2		A3		A4		A5	
	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix
Depth (cm)	20-40		40-70		10-25		18-40		40-65	
Mean	11.6	10.1	8.7	7.8	8.9	5.5	10.0	8.0	11.0	8.3
S.D.	1.6	0.9	2.9	1.5	0.7	0.6	1.0	1.4	2.6	2.1
N ^a	14	13	10	11	21	9	20	14	18	11
T		1.56		3.19*		12.4*		5.05*		3.08*
F		0.13		0.01		< 0.01		< 0.01		< 0.01

Table 5. Concentration of several forms of K in cutans and matrix soil (all results for oven dried 105 °C samples)

K form	Total K ^a (mg g^{-1})		HNO ₃ K ^a (mg g^{-1})		ExK ^a (mg g^{-1})		FK ^a (mg g^{-1})		LK ^a (mg g^{-1})		EK/LK ratio		Topsoil
	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix	Cutan	Matrix	
Mean	2.70	2.45	1.35	1.14	0.41	0.46	1.35	1.31	0.94	0.68	0.43	0.72	1.22
S.D.	0.58	0.71	0.34	0.39	0.12	0.15	0.31	0.35	0.26	0.29	0.12	0.23	0.64
N	15	15	14	15	15	15	14	15	14	15	14	15	10
T		3.03*		3.08*		1.00		0.04		2.63*			
F		< 0.01		< 0.01		0.33		0.97		0.01			

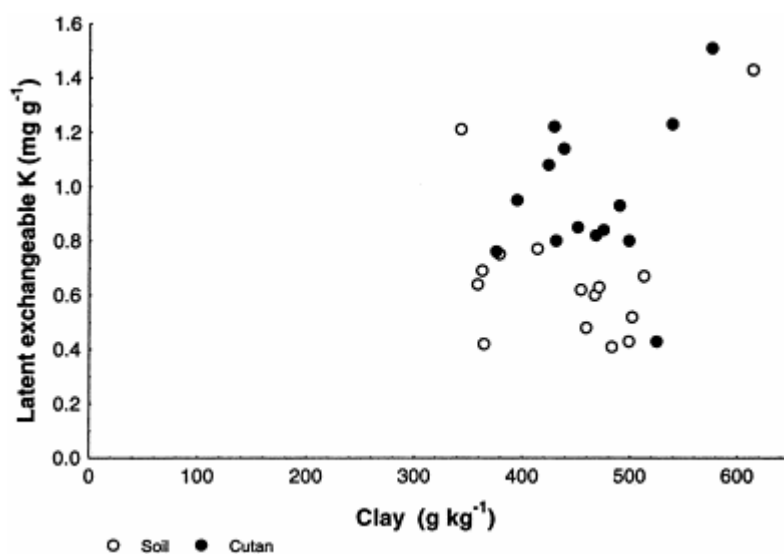


Fig. 5. The relationship between latent exchangeable K content and clay concentration for cutans and matrix soil. These data indicate that differences in latent exchangeable K content are not simply due to difference in the clay concentration and that cutans generally contain more exchangeable K than matrix soil.

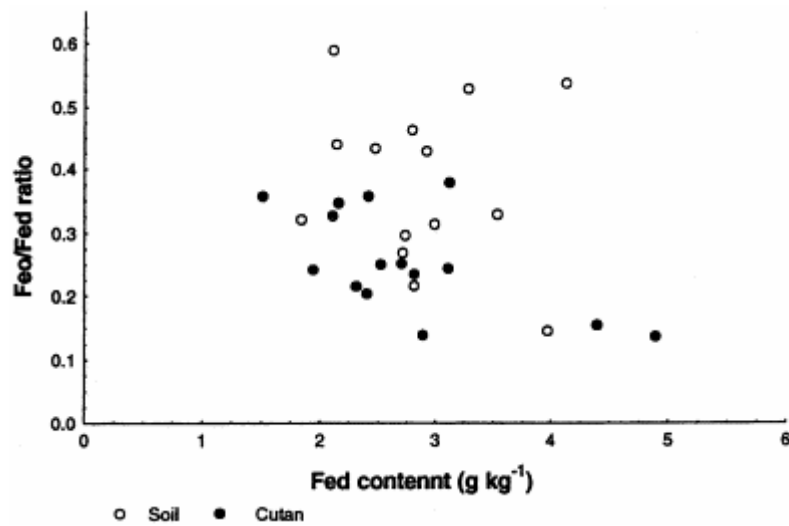


Fig. 6. The relationship of Feo/Fed ratio with Fed for cutans and matrix soil. These data indicate that the Feo/Fed ratio for the cutans is generally lower than that for the matrix soil.

Table 6. K sorption and desorption by matrix soil

	Sorbed K (mg g^{-1})	Desorbed K (mg g^{-1})	Fixed K (mg g^{-1})	K desorption ratio (%)	FK_f/SK^2 ratio (%)
Mean	1.63	1.05	0.58	65	35
S.D.	0.07	0.03	0.08	3.5	3.5
N ^b	12	12	12	12	12