



Potassium availability and mineralogical relationships of selected Montana soil clays and silts
by Steven Jake Phillips

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Soils

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Abstract:

Soil clay mineralogical relationships of K availability were evaluated by chemical analysis, X-ray diffraction and biological extraction from 18 selected soil locations in eastern and western Montana.

Montmorillonite-vermiculite, mica, kaolin, quartz, plagioclase, and K-feldspar were identified by X-ray analysis in all soils. Allo-phane was detected in one western Montana soil. The 10 Å mica component of all eastern Montana soil clays was found to increase in peak amplitude by K-saturation at the expense of the 14 Å component.

Quantitative analysis of K fixation, percent montmorillonite and percent vermiculite of soil clays was determined by evaluating the cation exchange capacity before and after K fixation.

Potassium availability as determined by NH₄ OAc extraction was negatively correlated with cation exchange capacity, percent vermiculite in clay, percent sand, and K fixation. However, available K was positively correlated with percent clay. A decrease in the quantity of montmorillonite-vermiculite relative to mica was found to correspond to an increase in available K.

Soil K extraction by fungi was initiated in order to evaluate the release of K in soil minerals. Untreated soils, soils alternately wetted and dried, and silt and clay fractions were evaluated. Alternately wetted and dried soils were found to decrease in the amount of K extracted as opposed to the untreated soil. Approximately 2.5 times as much K was extracted by fungi in the clay fraction as compared to the silt, suggesting an increase in K release with decreasing particle size. Potassium extraction by fungi caused a transformation of mica to interstratified mica-vermiculite. The vermiculite component at 14 Å increased in peak amplitude as the mica component at 10 Å decreased in peak amplitude and sharpness.

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by

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A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

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Soils

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ABSTRACT

Soil clay mineralogical relationships of K availability were evaluated by chemical analysis, X-ray diffraction and biological extraction from 18 selected soil locations in eastern and western Montana.

Montmorillonite-vermiculite, mica, kaolin, quartz, plagioclase, and K-feldspar were identified by X-ray analysis in all soils. Allophane was detected in one western Montana soil. The 10 Å mica component of all eastern Montana soil clays was found to increase in peak amplitude by K-saturation at the expense of the 14 Å component.

Quantitative analysis of K fixation, percent montmorillonite and percent vermiculite of soil clays was determined by evaluating the cation exchange capacity before and after K fixation.

Potassium availability as determined by NH_4OAc extraction was negatively correlated with cation exchange capacity, percent vermiculite in clay, percent sand, and K fixation. However, available K was positively correlated with percent clay. A decrease in the quantity of montmorillonite-vermiculite relative to mica was found to correspond to an increase in available K.

Soil K extraction by fungi was initiated in order to evaluate the release of K in soil minerals. Untreated soils, soils alternately wetted and dried, and silt and clay fractions were evaluated. Alternately wetted and dried soils were found to decrease in the amount of K extracted as opposed to the untreated soil. Approximately 2.5 times as much K was extracted by fungi in the clay fraction as compared to the silt, suggesting an increase in K release with decreasing particle size. Potassium extraction by fungi caused a transformation of mica to interstratified mica-vermiculite. The vermiculite component at 14 Å increased in peak amplitude as the mica component at 10 Å decreased in peak amplitude and sharpness.

INTRODUCTION

Potassium (K) in agricultural soils is usually the most abundant of the plant nutrient elements. During the growing season an appreciable amount of K becomes available to plants. The amount that is not available and not exchangeable resides in the K-bearing minerals of the soil. It has long been established that one of the primary sources of K in soils, available for plant growth, is layer silicate minerals. A precise correlation between K availability, cation exchange properties, and K fixation, however, has not been totally established. This is attributed to the uncertainty of identification of micaceous and mica-like minerals which may contribute to differential behavior with respect to K exchange phenomena. To attain an understanding of K reactions in soils, it is advantageous to study the naturally occurring soil minerals including micas, vermiculites, smectites, and K-feldspars. This study was initiated with three principle objectives: 1) to correlate K-availability with soil mineralogical relationships of selected eastern and western Montana soils; 2) to determine the mineralogical effect of K saturated and K depleted soil clays; and, 3) to determine the availability of mineral K to growing fungi.

LITERATURE REVIEW

Potassium and Soil Mineralogical Factors

Potassium is normally found in great abundance in agricultural soils. The lithosphere contains approximately 2.3% K (Ernst, 1969). Potassium in most mineral soils ranges from approximately 0.05 to 3.5%. Most agricultural soils, however, average between 1 and 2% in the upper 6 inch depth (Jackson, 1964). Potassium in agricultural soils, for the most part, is derived from K-bearing feldspars and micaceous minerals. Feldspars and micas constitute greater than 63 percent of igneous rocks and 27 percent of sedimentary rocks (Ernst, 1969; Jackson, 1964).

Potassium-feldspars are tectosilicates consisting of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra linked in all directions through the O of adjacent tetrahedra. The tetrahedra are arranged in horizontal rings. These rings have been distorted, i.e., tilted and rotated from the horizontal (Deer et al., 1963). The resultant tetrahedral configuration contains large interstices which contain K ions. The tetrahedra commonly contain Si and Al ion substitutions for Si. Where a local negative charge occurs, caused by Al substitutions, it is compensated for by the positive charge of interstitial cations. The idealized formula for K-feldspars is KAlSi_3O_8 , indicating approximately 25 percent substitution of tetrahedral Al for Si (Jackson, 1964).

K-feldspar polymorphs include: sanadine, microcline, adularia, and orthoclase.

Micas are common constituents of most soils. The basic structural units as proposed by Deer et al. (1963) are hexagonally linked cation-O tetrahedra and OH-cation-O octahedra. Individual tetrahedra consist of a central cation and four coordinating O's. The octahedra consist of a central cation and 6 coordinating OH or O's. Apical O's from adjacent tetrahedra are shared by the octahedral layer providing a linkage between layers. Replacement of Si for Al via isomorphous substitution in the tetrahedral layer causes a negative charge which is then balanced by interlayer cations including K.

Two general types of micas occur. Dioctahedral micas are those having two thirds of the octahedral positions filled with trivalent cations, usually Al. Trioctahedral micas are those in which all of the possible octahedral positions are occupied primarily by divalent cations.

The idealized formulas for muscovite, biotite, and illite are $K_2Al_2Si_6Al_4O_{20}(OH)_4$, $K_2Al_2Si_6(Fe^{+2},Mg)_6O_{20}(OH)_4$, and $K_{1-1.5}(Si_{8-y},Al_y)(Al_4,Fe_4,Mg_4,Mg_6)O_{20}(OH)_4$, respectively (Grim, 1968). Muscovite and biotite are normally derived from igneous rocks, whereas illite is derived from sediments (Grim et al., 1937).

Grim (1968) suggests that all gradations can exist between illite, muscovite, and biotite, and illite and montmorillonite. It

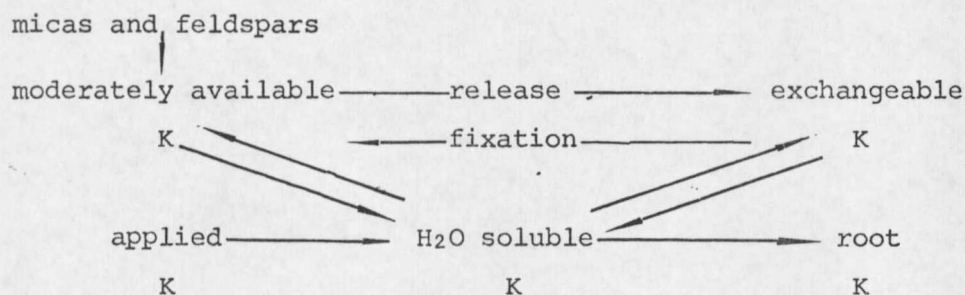
has also been suggested that illites are randomly interstratified mica montmorillonites, mica vermiculites, mica chlorites, or intergrades of any number of these mineral assemblages (Jackson et al., 1952; Mehra and Jackson, 1959). Illites differ from well-crystallized micas in that there is less substitution of Al for Si. As a consequence of less substitution, the Si to Al molecular ratio of illite is higher than that of more crystalline micas and the charge deficiency is reduced from 2 per unit cell to approximately 1.3 (Grim, 1968).

Potassium of layer silicates in the interlayer position is accommodated in pseudo-hexagonal or ditrigonal voids formed by the basal tetrahedral atomic configuration. With proxying of cations of different size and valance, distortion of the lattice occurs. When the tetrahedral layer is relatively larger than the octahedral layer, individual tetrahedra rotate and tilt from the idealized horizontal planes in order to accommodate local charge balance (Radoslovich and Norrish, 1962). The resultant basal tetrahedral voids become ditrigonal and the interlayer K coordination number is 6, consisting of 3 O's from adjacent mica layers. Coulomb's law states that for electrostatic charge, the strength varies as to the reciprocal of the distance squared between the charge and the ion. In tetrahedrally substituted clays, the distance between the K ion

and the lattice charge is approximately half that of the octahedrally substituted clays. Thus, the electrostatic force between the K ion and the tetrahedral charge is four times that of the octahedral charge. Radoslovich and Norrish (1962) concluded that K adsorption onto lattice silicates was favored by the negative charge originating in the tetrahedral layer. It was also concluded that high negative charge density favored K adsorption.

Forms of Potassium and Potassium Equilibria

Potassium equilibrium in the soil and K availability to plants is dependent, not only on the total amount of K present, but also the stage of mineral weathering and the chemical relationship of various K forms. Jackson (1964) suggests the following reactions for the chemical relationship of soil K:



Attoe and Truog (1945) concluded that 97 to 98 percent of the soil K exists in the mineral form. They also concluded that

approximately 90 percent of the available K exists in the exchangeable form. Jackson et al. (1952) indicated that K occupies interlayer positions in mica is difficultly available and release occurs when the charge of the layer is reduced and the interlayer position expands.

The immediate sources of K to plants are water soluble and exchangeable (Jackson, 1964). Nonexchangeable and strongly adsorbed K are of considerable importance to plant nutrition during the growing season. The equilibrium level of K becomes unbalanced during the growing season by K removal in the available form by plants. However, K is equilibrium quickly replenished when growth stops and nonexchangeable forms of K from K-bearing minerals become available.

Wood and DeTurk (1940) observed that fixation of K occurred when added to Illinois soils stored under moist conditions. With no K additions, these soils either fixed or released K depending on the specific soil K equilibrium level. Bolt et al. (1963), Cook and Hutcheson (1960), and Dowdy and Hutcheson (1963) have proposed an exchange equilibrium level in most agricultural soils to approximate 0.5 meq per 100 g. Potassium release from the nonexchangeable form usually maintains a somewhat constant level (Berland et al., 1950; Smith and Matthews, 1957; MacLean, 1961; Matthews and Sherrell, 1960).

According to Moss (1963), an increasing dilution of the soil water solution facilitated a greater increase in water soluble K.

Many soils have a different value for exchangeable K if the displacing solution is added to field-moist as opposed to air-dried samples. Higher values are usually found in air-dried samples. However, the opposite may occur especially in soils high in exchangeable K. Luebs et al. (1956) and Hanway et al. (1961,1962) conducted a large number of field experiments in North Central United States and obtained a higher correlation between uptake of exchangeable K by plants on undried soils as opposed to samples air-dried before analysis. These researchers concluded that analysis of exchangeable K should be on field-moist samples if used as an indication of availability to plants or of exchangeable K in the field.

The law of mass action indicates that the amount of K released from mineral forms at equilibrium increases with increased concentration of cations other than K in solution. In addition, K release will occur with an increase in the volume of solution and with a decrease of K in the solution before the reaction (Scott and Smith, 1966).

The difference between the cation exchange capacity and the charge density for montmorillonite, muscovite, and vermiculite is 0, 230, and 50 meq per 100 g., respectively (Kardos, 1964). This is the amount of K not exchanged by normal extraction procedures.

Potassium Release

Potassium release from nonexchangeable forms is primarily a cation exchange reaction. Mortland et al. (1956) concluded that a reduction in the percentage of K from biotite after 4 successive crops of wheat increased the cation exchange capacity and was attributed to K removal by plants. Cations other than K were thought to satisfy the negative charge of the mineral layers and consequent spreading of the layers involved water entry into the interlayer position.

The vertical distribution of micaceous minerals in soils verifies the loss of interlayer K from micas. Normally, micas of sand and silt size increase with depth. The inverse is true of vermiculite. Soil vermiculite is presumably a weathering product of K micas originally present throughout the soil profile. Rich (1958) using X-ray diffraction intensities, reported that vermiculite decreased relative to mica with depth and also decreased with successively large particle size.

Conyers and McLean (1968) using X-ray analysis reported a decrease in the 10, 5, and 3.3 Å peak intensities and an increase in the intensities of the 17 and 14 Å peaks of plant degraded layer silicates. Degradation of illite to expanding layer silicates, i.e., vermiculite and smectite, was suggested due to the removal of interlayer K.

Attoe (1946) reported that air-dried samples not fertilized with K increased in exchangeable K in 9 out of 19 soils analyzed. With K fertilization, fixation occurred in 8 out of 10 samples stored in a moist condition and when air-dried, fixation occurred in all samples.

Rich (1964) and Rich and Black (1964) concluded that K removal was pH dependent. An inverse relationship was found to exist between K release and pH, i.e., K release is increased as the pH is lowered. The hydronium ion (H_3O) was reported to be more effective in replacing K than larger hydrated ions, however, after K replacement H_3O ions were rapidly replaced by other cations allowing for lattice expansion.

Potassium Fixation

Fixation of K is the conversion of the exchangeable form to the nonexchangeable form. For the most part, K fixation is a property of expanded layer-silicates. In these minerals, K is held electrostatically between layers outside the aluminosilicate structural network as a charge balancing ion subject to fixation in the ditrigonal voids in nonexchangeable form.

Potassium fixation occurs in soils containing vermiculite and vermiculite-like minerals under moist conditions, and the fixation is a consequence of prior K removal. This was demonstrated by

Mortland (1961) using mixtures of biotite and Na-saturated layer silicates. It was found that the initial K content in the layer silicates was inversely proportional to the amount of K fixed.

Luebs et al. (1956) found that K fixation was dependent on relative humidity. Soils of different H₂O vapor content were analyzed, and it was demonstrated that an increase in relative humidity caused a decrease in exchangeable K and the inverse was true of decreased relative humidity.

Potassium in Particle Size Fractions

Cook and Hutcheson (1960) reported that the total K content of the Ap, A₂ and C horizons of selected Kentucky soils decreased as the particle size decreased. Illite was found to be the predominant layer silicate mineral in the coarse fractions and less predominant in the fine fractions.

Smith et al. (1968) treated several silt and clay size fractions of Marshall soil with sodium chloride-sodium tetraphenylboron (NaTPB). It was found that as the particle size increased, the amount of K extracted increased reaching a maximum at the 20 μ equivalent spherical diameter (e.s.d.) size fraction, then decreased as the particle size was further increased. Scott (1968) analyzed micaceous minerals as to susceptibility of interlayer K to exchange

with NaTPB. It was found that as the particle size decreased from 50 to 0.08 μ (e.s.d.), the rate and the amount of K exchange increased then decreased. The maximum exchange rate was found to be considerably higher in the 0.08 to 20 μ (e.s.d.) fraction than in the 20 to 50 μ (e.s.d.) fraction.

MATERIALS AND METHODS

Potassium in Nitrogen Topdressing Study

During the years 1970 and 1971, spring N-topdressing studies were conducted at several locations throughout eastern Montana (east of the Continental Divide). Potassium-topdressing in the form of KCl applications were included in the study in order to determine the predictability of K response and to obtain qualitative and quantitative information regarding K deficiency for winter wheat and for correlation of soil properties. The study sites were seeded with Winalta, Cheyenne, Froid, Warrior, or Itana varieties of winter wheat (*Triticum aestivum* L.). Grain yield and response data for eastern Montana locations are listed in Table 1.

Soil Descriptions

Soil descriptions and classifications were obtained from the United States Soil Conservation Service, Bozeman, Montana.^{1/}

Acel soil at location 1 is a silty clay loam classified as a member of the fine, montmorillonitic family of Abruptic Aridic Argiborolls. The soil profile consists of deep alluvium over glacial

^{1/}Personal communication, Shelby Brownfield, Soil Scientist (Correlator); soil classification, a comprehensive system-7th approximation. U.S. Dept. Agr. U.S. Govt. Printing Office, Washington, D.C.; established series revised memoranda.

Table 1. Grain yield and potassium response of eastern Montana locations.

Location No.	Series	Grain yield (kg/ha)			K response (kg/ha)	
		treatment 40-40-0	treatment 40-40-40	treatment 40-40-100	maximum	average
1.	Acel	1730.40	2427.93	2222.97	697.5	595.4
2.	Scobey	1486.46	1384.99	1427.33	-101.5	- 80.6
3.	Marias	2513.28	2526.72	2674.56	161.3	87.4
4.	Bainville	2271.36	2493.12	2506.56	235.2	228.5
5.	Cherry	2358.72	2485.40	2365.44	120.9	63.8
6.	Devon	1695.45	1714.94	1745.30	47.0	32.3
7.	Dooley	873.60	1041.60	1182.72	309.1	238.6
8.	Williams	2983.68	3120.09	2984.35	154.6	68.5
9.	Giltedge	2984.35	3177.21	3105.98	166.0	177.4
10.	Amsterdam	3128.83	3307.58	3175.20	178.8	112.9
11.	Coburn	1339.96	1663.20	1548.96	323.2	266.1
12.	Absarokee	2460.86	3042.81	3049.53	588.7	585.3
13.	Cargill	1064.44	1342.65	1412.54	348.1	313.2
14.	Scobey	2921.85	3121.44	3013.92	199.6	145.8
15.	Assinniboine	2974.27	3024.81	3157.72	183.5	126.3

till. Dark green shale and siltstone of the Colorado Formation underlie the solum.

Scobey soil at location 2 and 14 is a clay loam classified as a member of the fine, montmorillonitic family of Typic Argiborolls. The lithology of the profile and substrate resemble that of the Acel series.

Marias soil at location 3 consists predominantly of clay sized minerals of the fine, montmorillonitic, calcareous, frigid family of Ustertic Torriorthents. The soil consists of alluvial clays derived from the Colorado Formation.

Bainville clay loam at location 4 is a member of the fine-silty, mixed mesic family of Ustic Torriorthents. The parent material is composed of interbedded shaly clay, mudstone and sandstone derived from the Hell Creek Formation.

Cherry soil at location 5 is a silty clay loam classified as a fine-silty, mixed family of Aridic Haploborolls. The substrate is composed of loamy and silty shales and siltstones of the Fort Union Formation.

Devon soil at location 6 is a loam classified as a member of the fine-loamy, mixed family of Aridic Argiborolls. The regolith of the Devon series is similar to that of the Cherry series.

Dooley at location 7 consists of fine sandy loam classified as a fine-loamy, mixed family of Typic Argiborolls. The profile is underlain by gravels, sand and silt of the Flaxville Gravels.

Williams heavy loam at location 8 is classified as a member of the fine-loamy, mixed family of Typic Argiborolls. The bedrock consists of clay, shale and sandstone of the Fort Union Formation.

Giltedge at location 9 is a silty clay loam classified as a fine, montmorillonitic, mesic family of Ustollic Natrargids. The lithology of the substrate consists of gravels, sand and silt deposits of fluvial terrace remnants.

Amsterdam soil at location 10 is a silt loam classified as a member of the fine-loamy, mixed family of Typic Cryoborolls. The profile consists of aeolian or lacustrine loess deposited on Tertiary undifferentiated sediments.

Coburn silty clay loam at location 11 is a fine, montmorillonitic family member of Abruptic Argiborolls. The solum is underlain by deep alluvium over weathered shale. Thermopolis dark gray-green shale and sandstone underlies the soil.

Absarokee clay loam at location 12 is classified as a fine, montmorillonitic family member of Typic Argiborolls. The soil is predominantly derived from gravel, sand and silty alluvial material deposited as valley fill sediments.

Cargill soil at location 13 is a silty clay loam member of the fine-silty, mixed family of Borollic Calciorthids. The regolith is similar to that of the Acel, Marias and Scobey soils.

Assinniboine soil at location 15 consists of fine-loamy, mixed family, classified as Aridic Argiborolls. The substrate is composed of fine textured shales much like the parent material of Bainville soil.

The sample location at township 27N, range 34W at location 16 is unclassified at this time. The parent material for this soil is composed of glaciolacustrine sediments.

The sample site at township 6N, range 20W, location 17, is unnamed at this time. It is classified as a loam member of the fine-loamy, mixed family of Typic Argiborolls. The soil profile is developed over gravely, sandy, silty valley fill sediments.

Hamilton at location 18 is a silty loam classified as a coarse-silty, mixed family member of Fluventic Haploborolls. The profile is composed of silty loess alluvium derived from valley fill sediments.

Soil Preparations

In 1972, selected soil sub-samples of the N-topdressing study experiments were obtained. In addition, 3 bulk samples from western Montana (west of the Continental Divide) were obtained and sub-samples taken. Sub-samples of these soils at 0 to 6 and 6 to 12 inch depths were oven-dried at 60°C, and passed through a 200 mesh sieve. The samples were then placed in metal containers for subsequent analysis. Sample number and appropriate locations are listed in Table 2. Sample site locations are illustrated in Figure 1.

X-ray Mineralogical Analysis

Mineral identification and mineralogical composition were determined by X-ray diffraction criteria outlined by Whittig (1965). Silt and clay separates were Mg and K-saturated and deposited on glass petrographic slides as proposed by Kittrick (1961) following glycerol solvation according to the procedure of Klages and Southard (1968).

X-ray diffractograms were obtained using a General Electric XRD5 Diffractometer with Ni-filtered Cu-radiation ($\lambda 1.5405 \text{ \AA}$). A 1° beam divergent slit, medium resolution soller slit, and a 0.1° detector slit were used. The maximum scan angle covered 60° , from 3 to $63^\circ 2\theta$. A linear recording mode of 1000 cps full scale with a 2 second time constant was used on the recording apparatus. The diffractometer and recording scan rate was 2° per minute.

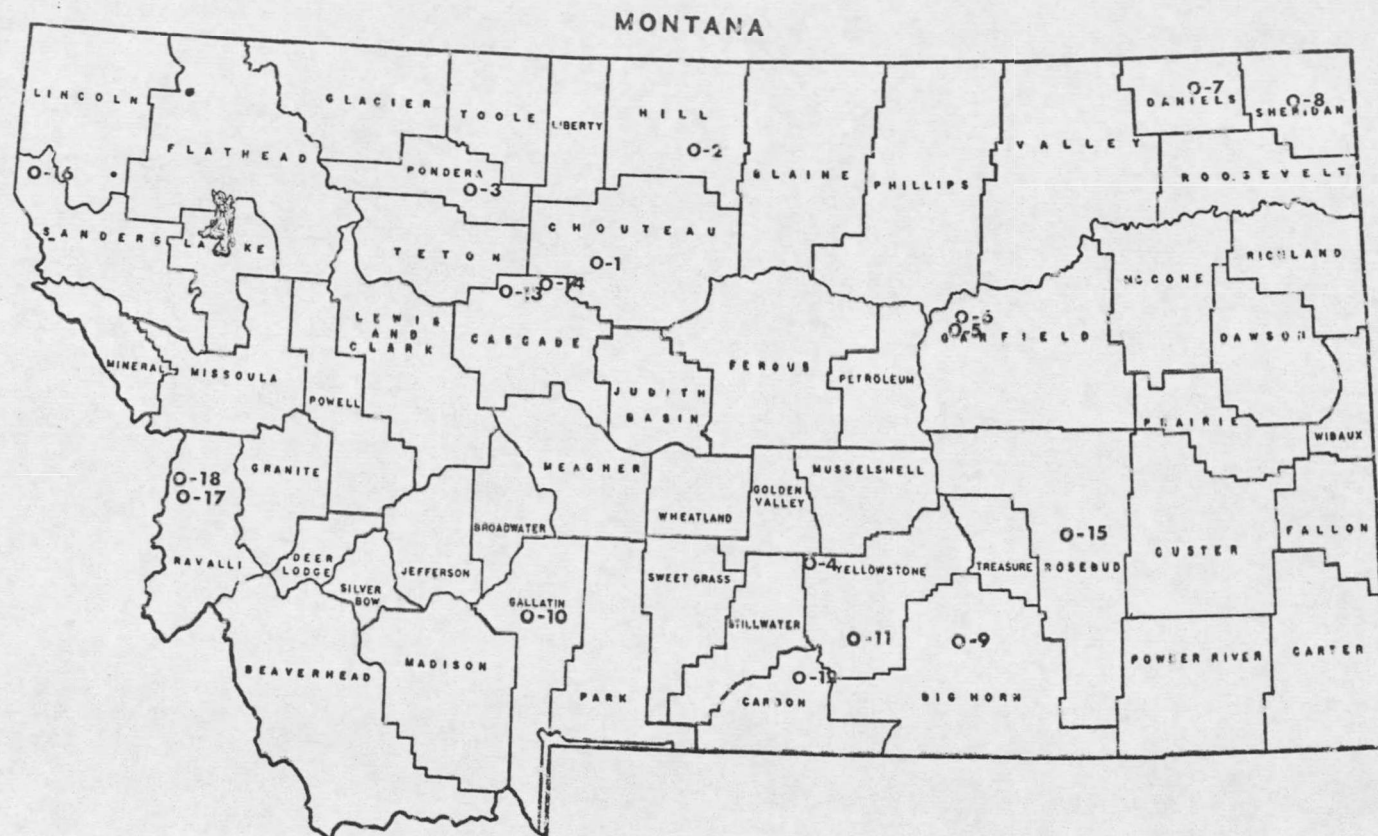
Chemical Analysis

The cation exchange capacity was determined in two ways in order to quantify the amount of montmorillonite and vermiculite in the soil following a procedure outlined by Alexiades and Jackson (1965). The cation exchange capacity was determined by saturating the clay with Ca using CaCl_2 , removal of excess salts, and replacing the Ca with MgCl_2 , designated as (C E C, Ca:Mg). For determination of the exchange capacity after K fixation, the sample was saturated by washing with

Table 2. Sample No., location, series, and cooperator names of eastern and western Montana soils.

Location		Cooperator	Legal description			
No.	Series	Name	County	sec.*	twp.†	rge.‡
1.	Acel	Gray	Chouteau	36	23N	7E
2.	Scobey	N. Station	Hill	16	31N	15E
3.	Marias	Bergstrom	Pondera	31	27N	1E
4.	Bainville	Erikson	Yellowstone	11	4N	23E
5.	Cherry	Coulter	Garfield	4	19N	34E
6.	Devon	Stanton	Garfield	31	20N	35E
7.	Dooley	Brenden	Daniels	15	35N	49E
8.	Williams	Schnitzler	Sheridan	19	31N	55E
9.	Giltedge	Torske	Big Horn	7	2S	33E
10.	Amsterdam	Bates	Gallatin	1	1S	3E
11.	Coburn	Daum	Yellowstone	7	4S	26E
12.	Absarokee	Roland	Carbon	9	4S	22E
13.	Cargill	Gettel	Cascade	17	22N	1E
14.	Scobey	Holtz	Cascade	4	22N	4E
15.	Assinniboine	Erpelding	Rosebud	15	6N	41E
16.	--	W. Station	Sanders	32	27N	34W
17.	--	W. Station	Ravalli	27	6N	20W
18.	Hamilton	W. Station	Ravalli	28	7N	20W

* sec.-section † twp.-township ‡ rge.-range



No. 1050 -- County Outline Map

Figure 1 Sample site locations

KCl, and dried at 110°C after removal of excess salts. The K was then removed by displacement with NH_4OAc , designated as (C E C, K: NH_4).

For determination of the exchange capacity after K fixation, the sample was saturated by washing with KCl, and dried at 110°C after removal of excess salts. The K was then removed by displacement with NH_4OAc , designated as (C E C, K: NH_4). Quantities of Ca and K were determined by means of atomic absorption spectrophotometry.

The percent vermiculite was determined by the following equation developed by Alexiades and Jackson (1965):

$$\% \text{ ve.} = [\text{C E C (Ca:Mg)} - \text{C E C (K/NH}_4\text{)}] / 154 \times 100$$

The percent montmorillonite was determined by the following equation modified from Alexiades and Jackson (1965):

$$\% \text{ mo.} = [\text{C E C (K/NH}_4\text{)}] / 105 \times 100$$

The values of 154 and 105 represent the cation exchange capacity attributed to vermiculite and montmorillonite, respectively.

Total K was determined after destruction of Al silicate minerals by HF following the procedure outlined by Jackson (1958). The amount of mica was calculated from the amount of total K assuming 8.3% K in mica. Atomic absorption spectrophotometry was used.

Available K was determined by equilibrium extraction with NH_4OAc by means of atomic absorption spectrophotometry.

The pH was determined in the supernatant of each sample with a soil water ratio of 1:1 by means of a glass electrode Beckman Zeromatic pH meter Model SS-3.

Particle Size Analysis

The particle size distribution of eastern Montana soils was determined by modification of the pipette method developed by Folk (1968). Oxidation of organic matter with NaOCl and washing and dispersing with Na_2CO_3 - NaHCO_3 was performed after a procedure developed by Anderson (1963). The sand size fraction was separated from the soil suspension by wet-sieving, utilizing a 44μ sieve, oven-dried at 105°C , and weighed. The silt fraction, 50 to 2μ (e.s.d.) and the clay fraction, less than 2μ (e.s.d.) were determined by sedimentation analysis. Particle settling time-centrifugal acceleration nomograms were used to determine centrifuge time (Jackson, 1956).

Soil Potassium Extraction by Fungi

Zero to 6 inch depth samples of 11 soils from eastern Montana and both 0 to 6 and 6 to 12 inch depth samples of soils from western Montana were selected for K extraction by fungi. The two soils with the highest and lowest values of, 1) available K, 2) total K, 3) cation exchange capacity (C E C, Ca:Mg), 4) K fixed, and 5) average response

were used for analysis. Untreated soils, soils alternatively wetted and dried, silt fraction and clay fractions were evaluated. In order to evaluate changes in relative humidity, soil samples were subjected to 6 repetitions of wetting at 100% relative humidity over H_2O and drying over $CaCl_2$.

Potassium extraction from soils and soil separates was performed using a procedure developed by Weed et al. (1969). Basidiomycete inoculum (*Basidiomycetes rhizoctonia* L.) was obtained from the Department of Plant Pathology at Montana State University.

Fifty mg of each soil and soil separate were placed in cellulose dialysis tubing and sealed. The dialysis tubing containing the samples was placed then into flasks containing 50 ml of nutrient solution and the fungal inoculum. The fungi served as a sink for K diffused out of the dialysis tubing by displacement from samples by Na in solution. Check samples containing the fungi, nutrient solution and dialysis tubing, excluding the sample, were included for comparison.

After a two week growth period, the fungal mat was removed from each flask and washed with approximately 10 ml of distilled-deionized H_2O dried at $105^\circ C$ for 24 hrs, and weighed. The fungal material was dry-ashed and taken up in HCl and K determined by atomic adsorption spectrophotometry. The silt and clay fractions were then removed from the dialysis tubing and prepared for X-ray analysis by Mg-saturation and

glycerol solvation. X-ray diffractograms were obtained using the same instrument settings, radiation and filter as in the previous mineralogical analysis procedure.

Correlation Analysis

The data were interpreted by means of regression analysis from a multiple regression program developed for the Sigma XDS 7 computer at Montana State University.^{2/} Correlation coefficients were used to show mutual relationships between variables. The coefficient of linear correlation (r) is a measure of the degree of relationship of variables. The confidence intervals of .01 and .05 indicate 99 and 95% probability of correct interpretation, respectively. Linear regression was used to determine the unit change of variables.

^{2/} This program was developed by Dr. R. E. Lund, Associate Professor of Statistics, Department of Mathematics, Montana State University.

RESULTS AND DISCUSSION

X-ray Mineralogical Analysis

The mineralogical composition of soil clays in this study were in part characterized by X-ray diffraction techniques. X-ray analysis revealed the presence of montmorillonite, vermiculite, mica, kaolin, quartz, and allophane. Diffraction (001) maxima from samples: Mg-saturated, air-dried; Mg-saturated, glycerol-solvated; K-saturated, air-dried; and, K-saturated, heated (500°C) were used for clay mineral identification. Magnesium-saturation of montmorillonite and vermiculite results in an (001) spacing of approximately 14 Å when air-dried. Samples were saturated with K in order to differentiate vermiculite and montmorillonite, which collapse to 10 Å when K-saturated from chlorites, which remain at 14 Å when subject to the same treatment. Glycerol-solvation was used to differentiate between montmorillonite and vermiculite. Montmorillonite, a species member of smectite minerals, expands to an (001) spacing of 17.7 Å, while the (001) spacing of vermiculite is not markedly changed by this treatment. In addition to the collapse of vermiculite to 10 Å, heating to 500°C destroys kaolin minerals that occur at approximately 7.2 Å, thereby confirming their presence. Random interstratification of montmorillonite-vermiculite produces an (001) spacing intermediate between 17.7 and 14 Å, the spacing depending on the relative abundance of each mineral in the mixture.

Figure 2 illustrates the change of diagnostic diffraction maxima with treatments (Sample No. 1). The silt fraction was Mg-saturated, air-dried only. Quartz was identified by the (101) peak occurring at 3.36 Å. Plagioclase and K-feldspars are identified by their (002) reflections occurring at approximately 3.18 and 3.23 Å, respectively.

Table 3 lists the X-ray peak intensity of mica, montmorillonite-vermiculite, kaolin, quartz, and feldspar in both clay and silt fractions of eastern and western Montana soils. X-ray analysis revealed the presence of mica in all soils, in both the silt and clay size fractions, with the exception of the soil at location 16 where it is absent in the clay fraction. The mineralogical composition of the soil at location 16 is in part composed of allophane, demonstrated by a low amplitude diffuse band characteristic of X-ray amorphous materials. Montmorillonite-vermiculite was detected in all soils except the soil at location 16 where it was absent in both the silt and clay fractions. Kaolin was detected in all soils from eastern Montana. The western Montana soils, for the most part, contained lesser amounts of this material. Quartz was detected in all soils and both size fractions. Feldspar was detected in the silt fraction of all soils.

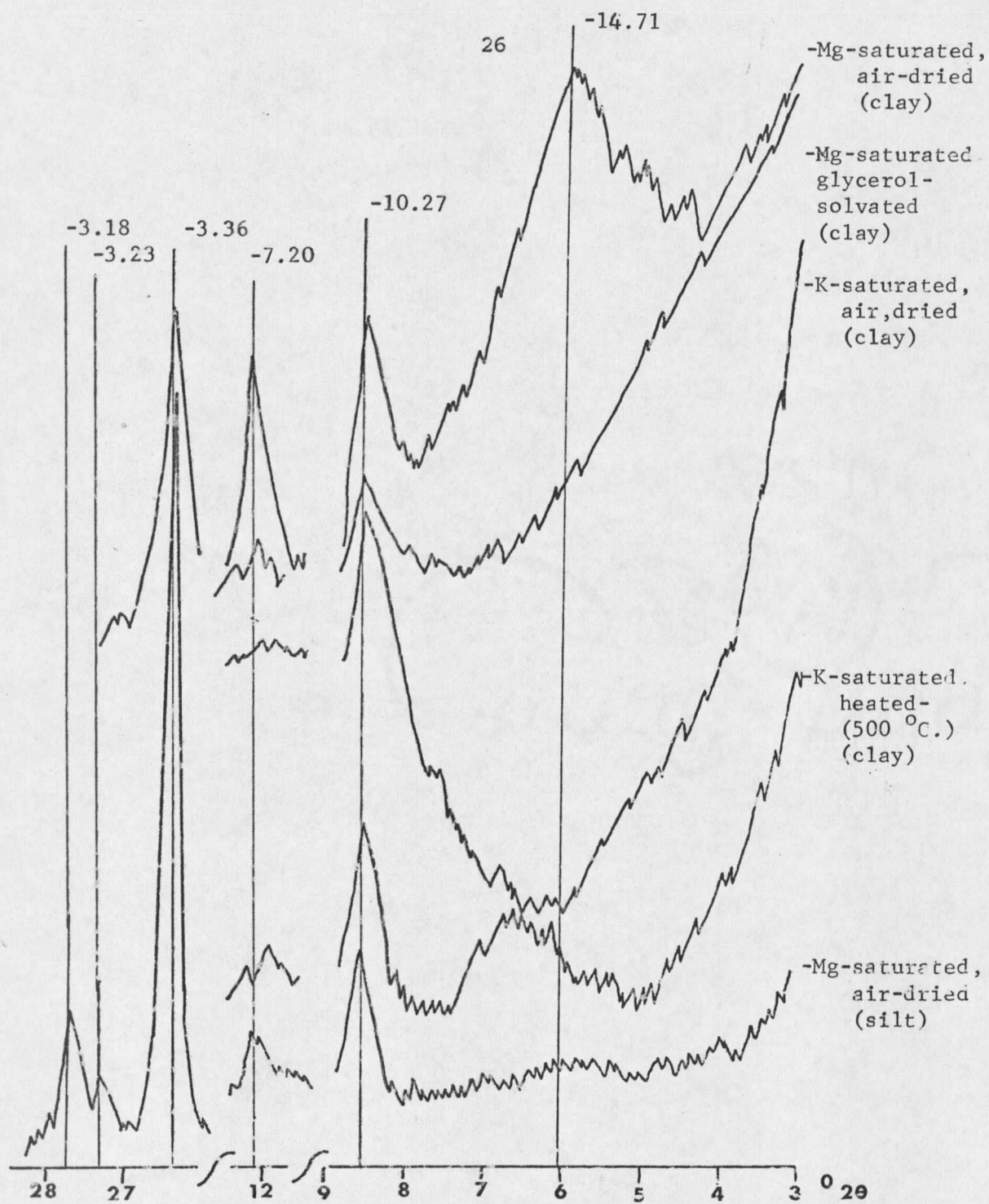


Figure 2 Mineralogical differentiation of soil clay by x-ray diffraction. Silt included.

Table 3. X-ray peak intensity of magnesium-saturated, air-dried clay and silt fractions of eastern and western Montana soils.

Sample No.	Location	Depth	Peak intensity of clay (mm)				Peak intensity of silt (mm)				
			mi.*	mo.-ve.†	ka.‡	qz.§	mi.*	mo.-ve.†	ka.‡	qz.§	fd.¶
1.	1.	C-6	90	70	45	15	35	5	10	35	25
2.		6-12	85	120	55	10	40	5	10	105	110
3.	2.	0-6	55	75	40	15	20	10	5	30	15
4.		6-12	50	135	50	10	20	10	10	20	15
5.	3.	0-6	60	90	55	10	35	10	15	70	60
6.	4.	0-6	65	180	60	10	20	10	15	45	70
7.	5.	0-6	90	140	95	10	35	10	20	50	45
8.	6.	0-6	100	125	80	10	35	5	15	15	105
9.	7.	0-6	90	110	30	5	35	5	5	110	170
10.	8.	0-6	100	100	45	5	30	15	10	25	15
11.	9.	0-6	95	75	45	15	50	10	35	60	15
12.		6-12	100	135	55	15	40	15	40	55	10
13.	10.	0-6	40	155	25	5	25	20	10	40	45
15.		6-12	55	190	25	15	20	45	10	15	10

Table 3. (continued)

Sample No.	Location	Depth	Peak intensity of clay (mm)				Peak intensity of silt (mm)				fd. π
			mi.*	mo.-ve.†	ka.‡	qz.§	mi.*	mo.-ve.†	ka.‡	qz.§	
16.		6-12	45	160	50	10	30	15	15	90	60
17.	12.	0-6	80	70	50	10	45	15	15	60	60
18.		6-12	70	55	50	10	45	20	20	35	15
19.	13.	0-6	55	50	35	15	10	5	5	45	15
20.		6-12	65	75	40	10	10	5	5	60	50
21.	14.	0-6	50	70	45	15	20	5	10	60	40
22.		6-12	55	90	60	15	15	5	10	50	35
23.	15.	0-6	75	130	60	10	15	10	10	60	50
24.		6-12	55	190	65	10	20	15	10	65	30
25.	16.	0-6	--	--	--	5	10	5	5	145	20
26.	17.	0-6	25	35	5	25	5	20	5	110	30
27.		6-12	20	30	5	20	5	15	5	100	25
28.	18.	0-6	40	90	20	30	10	30	10	130	100
29.		6-12	30	40	15	20	5	15	10	85	35

* mi.-mica † mo.-ve.-montmorillonite-vermiculite ‡ ka-kaolin § qz.-quartz
 π fd.-feldspar

Mechanism of Potassium Fixation

The characteristics of expansion and contraction of selected clay samples were evaluated by investigation of the Mg and K-saturated, air-dried X-ray diffractograms. Magnesium-saturation of soil clays gives a montmorillonite-vermiculite (001) spacing at approximately 14 Å, whereas K-saturation gives a montmorillonite-vermiculite (001) spacing between 14 and 10 Å, depending on the ratio of these minerals. Potassium-saturated samples showing a broad diffuse X-ray diffraction peak between 14 and 10 Å were interpreted to include soil clays with partial closure of the interlayer spaces resulting from mixed layering. The relationship of K-fixation and montmorillonite-vermiculite X-ray peak closure were qualitatively evaluated, examining samples with relatively high or low K-fixation ability. No quantitative data were obtained. High K-fixing soil clays exhibit a closure of the interlayer space to approximately 10 Å, thereby fixing K between layers. Low K-fixing soil clays exhibit little change in closure of the interlayer space between the 14 and 10 Å positions. Figure 3 illustrates the X-ray diffractogram of a soil clay rated high in K-fixing ability (Sample No. 15). The vertical lines at approximately 6 and $8.6^\circ 2\theta$ (14.71 and 10.27 Å) are consistent with the (001) reflections of montmorillonite-vermiculite and mica, respectively. Closure of the montmorillonite-vermiculite K-saturated peak toward the mica peak represents the

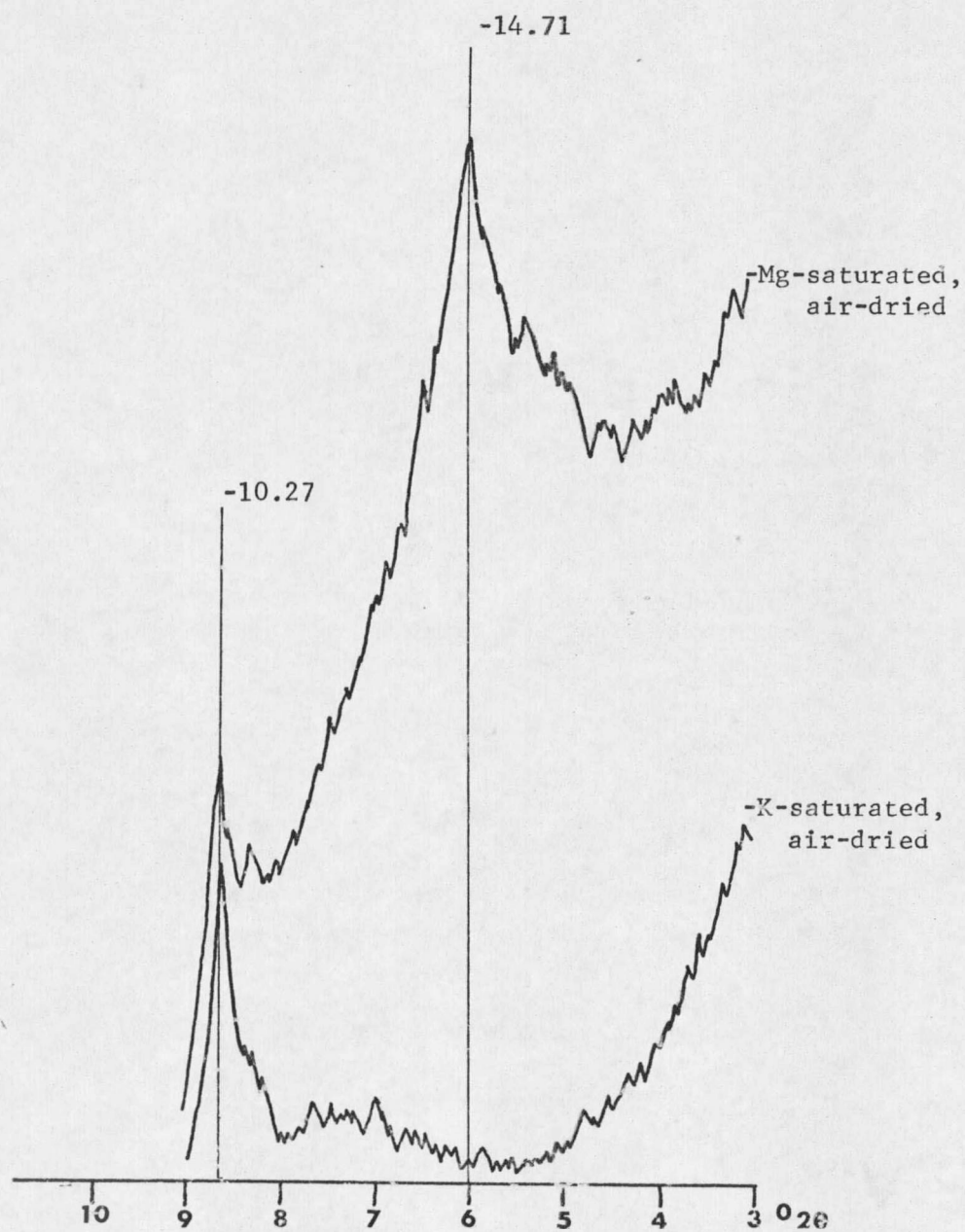


Figure 3 X-ray diffractogram of high K fixing clay

transformation of mineral species, i.e., montmorillonite-vermiculite to mica. The intensity of the mica peak is greatly increased in amplitude by K-saturation due to an increase of K ions in the interlayer positions of expanding layer silicate minerals resulting in a 10 Å d-spacing. Figure 4 illustrates an X-ray diffractogram of a low K-fixing soil clay (Sample No. 22). The vertical lines at approximately 6 and $8.6^\circ 2\theta$ (14.71 and 10.27 Å) are consistent with the reflections of montmorillonite-vermiculite and mica, respectively. There occurs only a slight increase in the K-saturated mica peak amplitude.

Chemical Mineralogical Analysis

Quantitative analysis of K-fixation, percent vermiculite and percent montmorillonite was determined by evaluating the cation exchange capacity of soil clays by chemical means (Table 4). The difference between the values of cation exchange capacity (Ca:Mg) and (K:NH₄) is attributed to the amount of K fixed in the interlayer positions of vermiculite.

The cation exchange capacity (Ca:Mg) was positively correlated with the intensity of the montmorillonite-vermiculite X-ray diffraction peak in the clay, and negatively correlated with the intensity of the mica X-ray diffraction peak in the clay, both correlations being statistically significant at the .05 level.

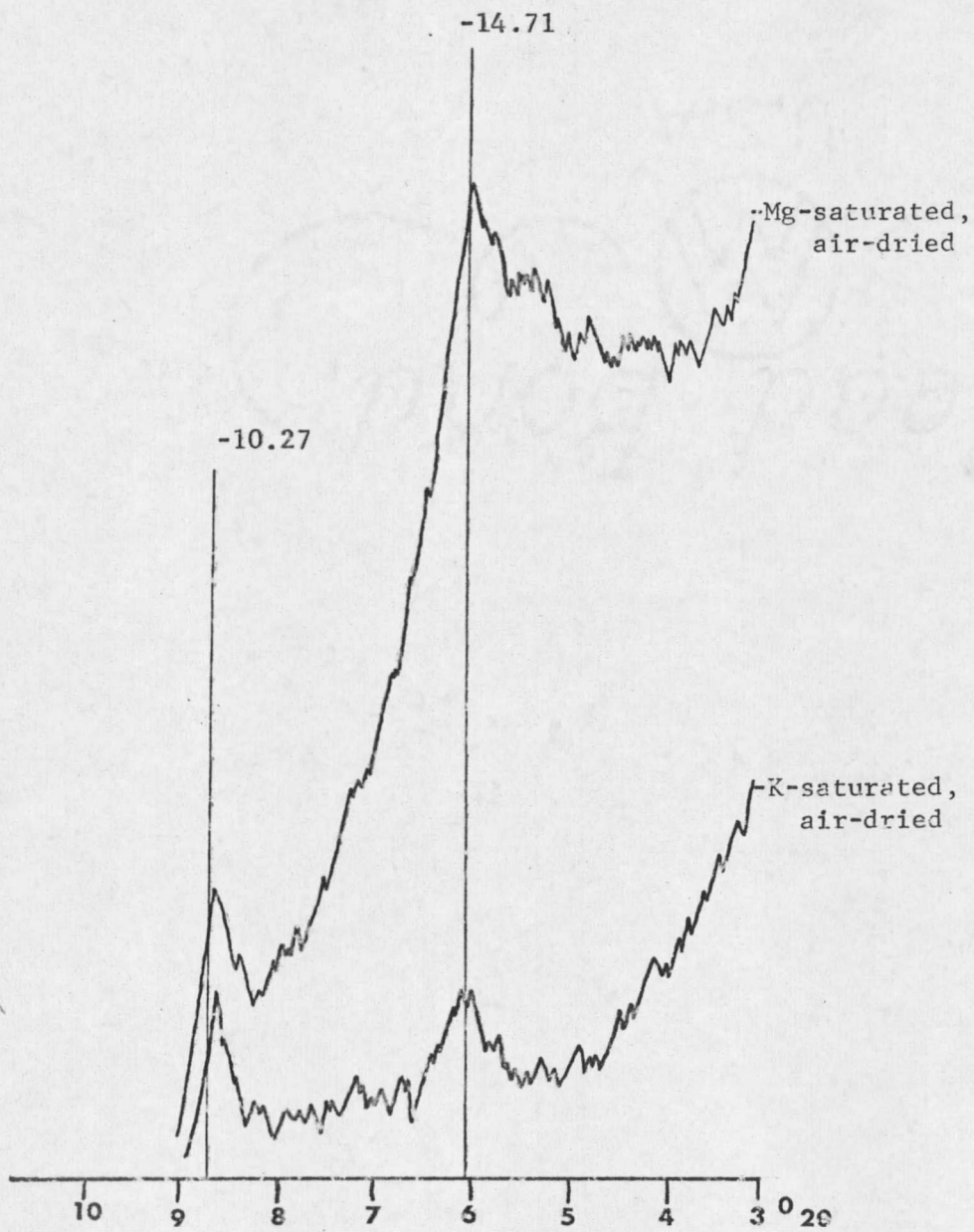


Figure 4 X-ray diffractogram of low K fixing clay

Table 4. Cation exchange capacity Ca:Mg, K:NH₄, K fixed, and percent montmorillonite and vermiculite of eastern Montana soils.

Sample No.	Location	Depth	Series	C E C Ca:Mg	C E C K:NH ₄ (meq per 100g.)	K fixed	mo.*	ve.†
							(%)	(%)
1.	1.	0-6	Acel	78.8	41.5	37.3	39.5	24.2
2.		6-12		85.5	43.1	43.4	41.1	27.5
3.	2.	0-6	Scobey	96.0	48.5	47.5	46.5	30.8
4.		6-12		107.3	40.8	66.5	38.9	43.2
5.	3.	0-6	Marias	90.0	41.5	48.5	39.5	31.5
6.	4.	0-6	Bainville	96.0	38.5	57.5	36.9	37.3
7.	5.	0-6	Cherry	96.0	26.9	69.1	28.1	44.9
8.	6.	0-6	Devon	84.0	30.0	54.0	28.5	35.1
9.	7.	0-6	Dooley	93.8	46.2	47.6	44.0	30.3
10.	8.	0-6	Williams	83.5	35.4	48.1	33.7	31.2
11.	9.	0-6	Giltedge	71.3	36.2	35.1	34.4	22.8
12.		6-12	Amsterdam	87.0	36.9	50.1	35.1	32.5
13.	10.	0-6		97.5	48.5	49.0	46.1	31.8
14.		6-12		114.6	34.6	80.0	32.9	51.9
15.	11.	0-6	Coburn	96.0	38.8	57.2	36.9	37.1
16.		6-12		81.0	34.2	46.8	32.5	30.4
17.	12.	0-6	Absarokee	75.0	27.3	47.7	26.0	31.0
18.		6-12		80.5	32.3	48.2	30.7	31.3
19.	13.	0-6	Cargill	96.0	30.0	66.0	28.6	42.0
20.		6-12		101.9	29.2	72.7	27.8	47.2
21.	14.	0-6	Scobey	72.8	35.0	37.8	33.3	24.6
22.		6-12		73.8	36.9	41.9	35.1	27.2
23.	15.	0-6	Assinniboine	85.5	37.7	47.8	35.9	31.0
24.		6-12		92.3	37.7	54.6	35.9	35.5

* mo.-montmorillonite † ve.-vermiculite

All eastern Montana soils were found to contain appreciable amounts of vermiculite and montmorillonite and subsequently K-fixation was appreciable, i.e., greater than 35 meq per 100 g.

Quantitative analysis of mica was evaluated by determining the total quantity of K in the clay fraction. Although small amounts of K-feldspars possibly occur in this size fraction, the contribution of K from these minerals was assumed to be negligible. Percent mica in clay was negatively correlated, statistically significant at the .05 level, with percent clay. Total K in the clay, however, was positively correlated with percent clay, significant at the .05 level. Figure 5 presents the results of linear regression of total K in clay and percent clay. In all soil sampled to 12 inches, mica was more abundant in the 6 to 12 inch depth. The analysis of total K and the calculated percent mica are listed in Table 5.

Potassium Availability

The Montana Agricultural Experiment Station and Cooperative Extension Service at Montana State University^{3/} lists the following recommendations for K fertilization of non irrigated small grains:

^{3/} Montana Agricultural Experiment Station, Plant and Soil Science Department, Bozeman, Montana. Mimeographed Circular No. 59D.

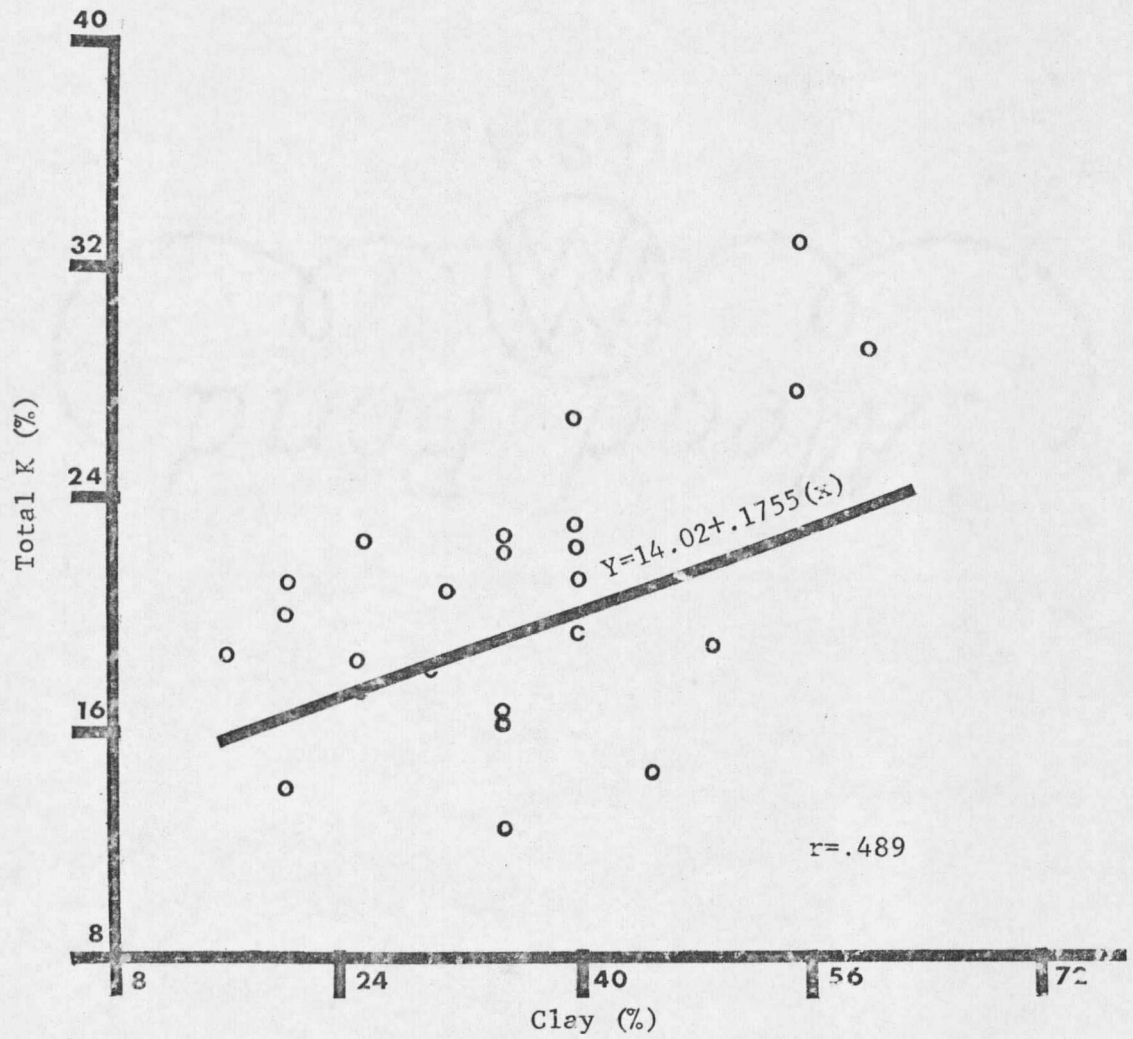


Figure 5 Correlation of total K and percent clay

Table 5. Analysis of total potassium of eastern Montana soil clays and calculated % mica.

Sample No.	Location	Depth	Series	Total K (%)	Mica (%)
1.	1.	0-6	Acel	2.20	26.5
2.		6-12		2.26	27.2
3.	2.	0-6	Scobey	2.22	26.7
4.		6-12		2.67	32.2
5.	3.	0-6	Marias	2.20	26.5
6.	4.	0-6	Bainville	1.73	20.8
7.	5.	0-6	Cherry	1.84	22.2
8.	6.	0-6	Devon	2.08	25.1
9.	7.	0-6	Dooley	1.85	22.3
10.	8.	0-6	Williams	1.89	22.8
11.	9.	0-6	Giltedge	2.11	25.4
12.		6-12		2.30	27.7
13.	10.	0-6	Amsterdam	1.39	16.7
14.		6-12		1.66	20.0
15.	11.	0-6	Coburn	1.62	19.5
16.		6-12		1.93	23.2
17.	12.	0-6	Absarokee	1.26	15.2
18.		6-12		1.45	17.5
19.	13.	0-6	Cargill	1.80	21.7
20.		6-12		2.22	26.7
21.	14.	0-6	Scobey	2.78	33.5
22.		6-12		2.91	35.1
23.	15.	0-6	Assinniboine	2.00	24.1
24.		6-12		2.10	25.3

<u>MSU soil test</u>	<u>Rating</u>	<u>Rate K₂O</u>
<u>K (ppm)</u>		<u>lbs/A</u>
0-75	very low	50-60
75-125	low	30-50
125-250	medium	0 or 30
> 250	high	0

All of the eastern Montana soils (0 to 6 inch depth) occurred in the high range (Table 6). Of the western Montana soils, the Hamilton soil (location 18) was rated high, and the soils at locations 16 and 17 rated a medium classification. The availability of K, as measured by NH₄OAc extraction, was greater in the 0 to 6 inch depth than in the 6 to 12 inch depth of all soils studied, except the Hamilton soil (location 18), where approximately equal concentrations were extracted at both depths.

Available K was negatively correlated with: 1) cation exchange capacity (Ca:Mg), 2) percent vermiculite in clay, 3) percent sand, and 4) K-fixation, the first two relationships being statistically significant at the .05 level, the third at the .01 level, and the last at the .05 level. Available K was, however, positively correlated with percent clay, significant at the .05 level. As the mineral constituents in the soil range from montmorillonite and vermiculite to mica in relative abundance, the cation exchange capacity is decreased, i.e., from 154 and 100 to 40 meq per 100 g;

Table 6. Available potassium and pH values for eastern and western Montana soils.

Sample No.	Location	Depth	Series	Available K (ppm)	pH
1.	1.	0-6	Acel	464	6.10
2.		6-12		432	7.20
3.	2.	0-6	Scobey	304	7.78
4.		6-12		106	7.89
5.	3.	0-6	Marias	914	7.99
6.	4.	0-6	Bainville	438	8.02
7.	5.	0-6	Cherry	458	7.97
8.	6.	0-6	Devon	352	7.48
9.	7.	0-6	Dooley	256	6.77
10.	8.	0-6	Williams	736	7.07
11.	9.	0-6	Giltedge	688	7.63
12.		6-12		464	7.88
13.	10.	0-6	Amsterdam	656	7.72
14.		6-12		320	8.00
15.	11.	0-6	Coburn	448	6.79
16.		6-12		432	7.50
17.	12.	0-6	Absarokee	528	7.69
18.		6-12		368	7.90
19.	13.	0-6	Cargill	560	7.99
20.		6-12		352	8.00
21.	14.	0-6	Scobey	784	7.71
22.		6-12		608	7.82
23.	15.	0-6	Assinniboine	336	7.51
24.		6-12		240	7.60
25.	16.	0-6	--	129	6.70
26.	17.	0-6	--	224	7.59
27.		6-12		208	7.65
28.	18.	0-6	Hamilton	384	7.61
29.		6-12		385	7.67

therefore, a decrease in the quantity of montmorillonite and vermiculite corresponds to an increase in available K. The relationship between available K and percent sand is inversely proportional due to a dilution effect imparted by sand sized particles. Figure 6 presents the results of linear correlation between available K and percent sand in selected eastern Montana soils. The relationship between available K and percent clay suggests that clay holds available K, and with increasing amounts of clay in the soil more K will be available. Figure 7 presents the results of linear correlation between available K and percent clay in selected eastern Montana soils. Figure 8 presents the results of linear correlation between available K and K fixed.

An attempt was made to evaluate geologic formations as to K availability without success due to similarity in clay mineral assemblages of all eastern Montana soils.

Soil pH

The pH values of eastern and western Montana soils range from 6.1 to 8.02 (Table 6). This suggests a range of approximately 65 to 100 percent base saturation and an exchangeable cation population composed primarily of Ca and Mg (Buckman and Brady, 1969). The pH values of all soils were greater in the 6 to 12 inch depth. This is attributed to the abundance of alkali and alkali earths translocated out of

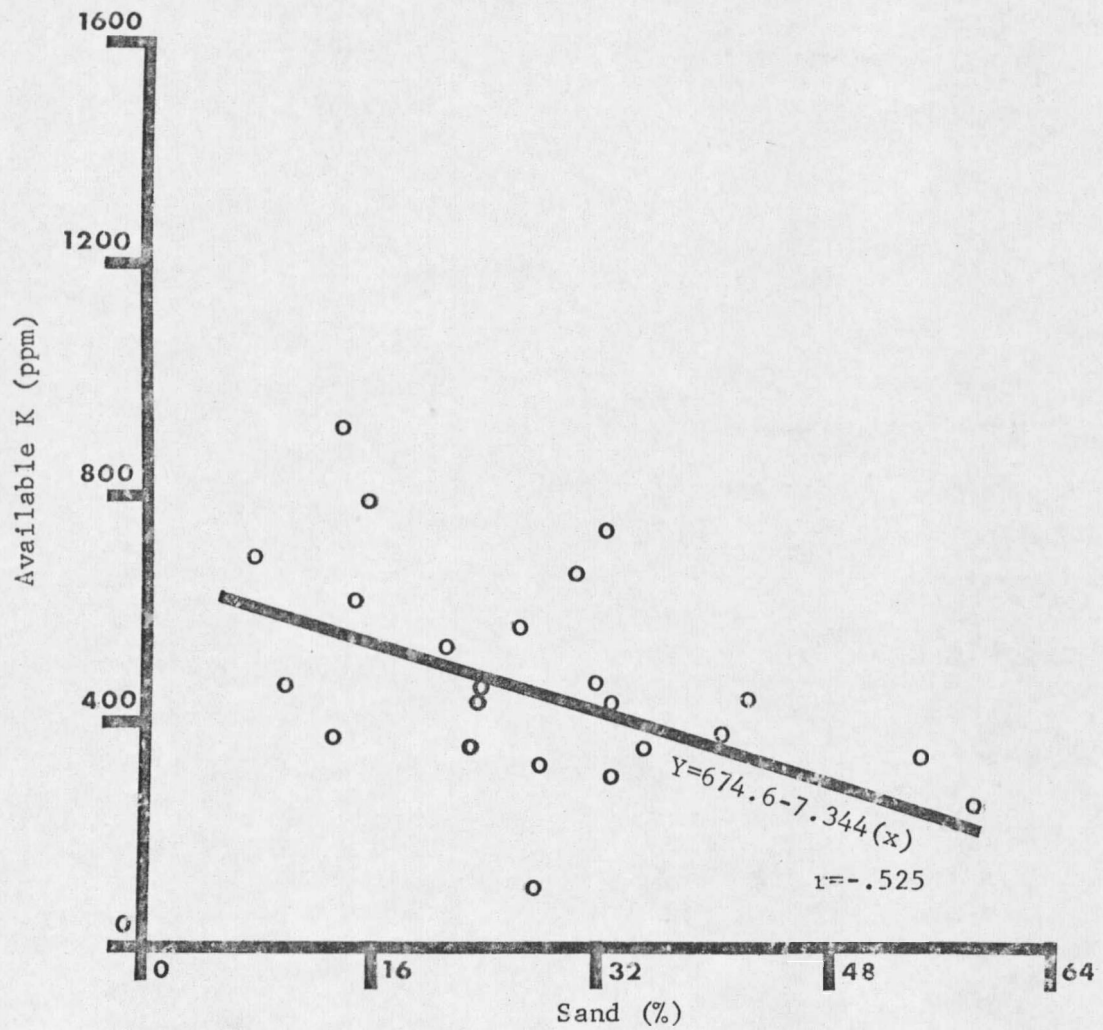


Figure 6 Correlation of available K and percent sand

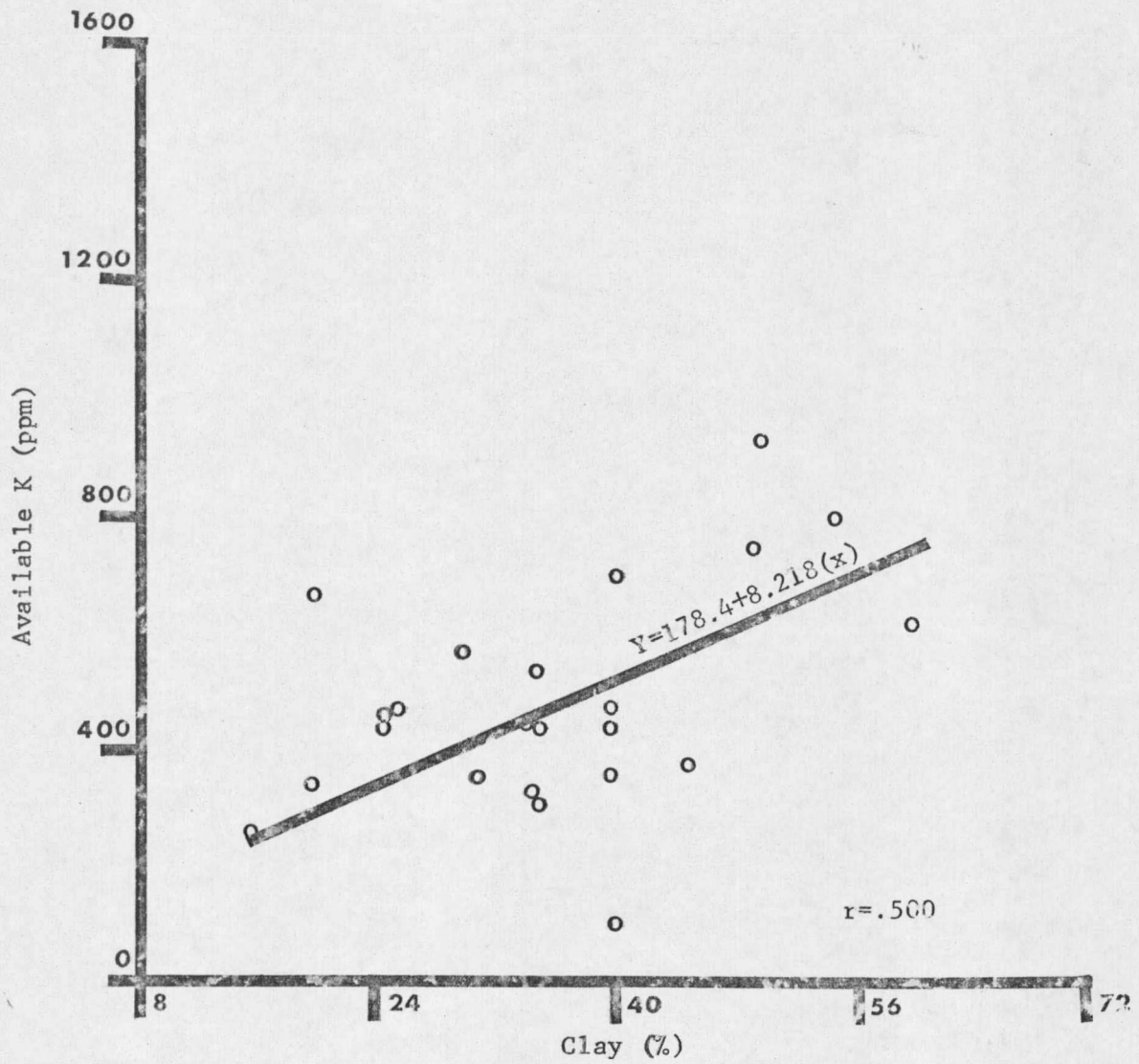


Figure 7 Correlation of available K and percent clay

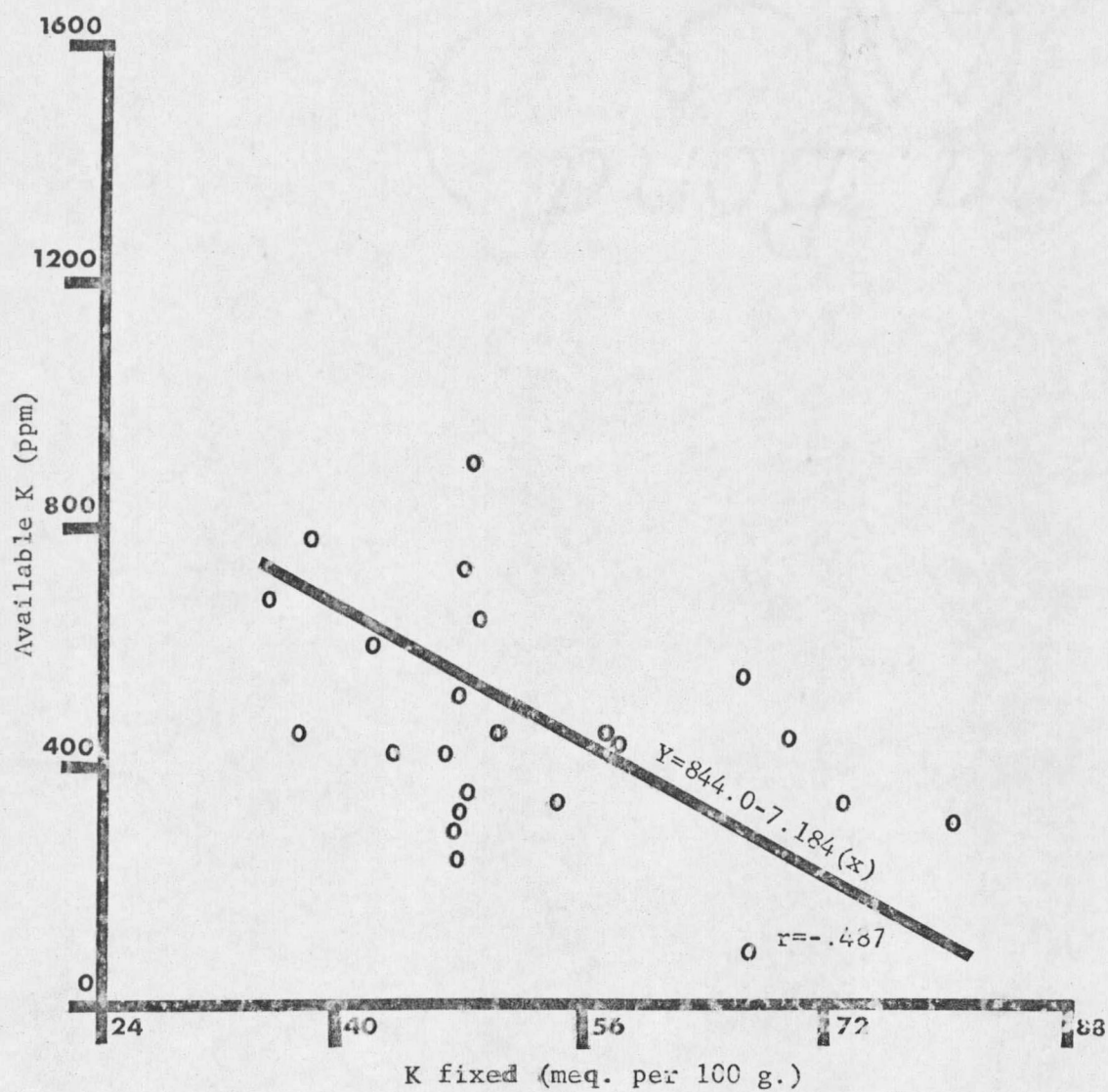


Figure 8 Correlation of available K and K fixed

the surface 6 inch layer into the lower depths of the soil profile by leaching.

Particle Size Analysis

The 0 to 6 inch depth of all soils studied contained more sand except the Acel (location 1), Giltedge (location 9), and the Assinniboine (location 15) where greater accumulations of sand were found in the 6 to 12 inch depth. Silt was more abundant in the 0 to 6 inch depth of all soils except the Scobey (location 2) soil, where it was more abundant in the 6 to 12 inch depth, and the Coburn soil (location 11), where it occurred in approximately equal concentrations at both depths. The clay content was higher in the 6 to 12 inch depth as opposed to the 0 to 6 inch depth of all soils except the Giltedge (location 9) and Assinniboine (location 15) soils where it was found in approximately equal concentrations at both depths. It is noted that these soils were subject to cultivation practices and subsequent mixing of particles to a depth of 6 inches is probable. Table 7 lists the quantity of each soil separate and the appropriate texture of eastern Montana soils with depth.

Soil Potassium Extraction by Fungi

Soil K extraction by fungi was initiated in order to evaluate the release of K from soil minerals. The mechanism of K release

Table 7. Particle size and textural designations of eastern Montana soils.

Sample No.	Location	Depth	Series	Particle size fractions(%)			Texture
				sand	silt	clay	
1.	1.	0-6	Acel	31.4	43.2	25.4	clay
2.		6-12		23.4	41.4	35.1	clay
3.	2.	0-6	Scobey	32.4	32.6	35.1	clay loam
4.		6-12		27.0	33.1	39.9	clay loam
5.	3.	0-6	Marias	13.7	36.1	50.1	silty clay loam
6.	4.	0-6	Bainville	41.8	33.3	24.9	clay loam
7.	5.	0-6	Cherry	23.5	51.5	25.0	clay
8.	6.	0-6	Devon	34.7	34.3	31.1	clay loam
9.	7.	0-6	Dooley	57.8	26.2	16.0	sandy clay loam
10.	8.	0-6	Williams	32.1	18.7	49.2	loam
11.	9.	0-6	Giltedge	7.6	52.1	40.3	silty clay
12.		6-12		9.9	50.1	40.0	silty clay
13.	10.	0-6	Amsterdam	30.0	49.9	20.1	clay
14.		6-12		27.4	37.7	34.9	clay loam
15.	11.	0-6	Coburn	27.4	37.6	35.0	clay loam
16.		6-12		23.2	37.8	40.0	clay loam
17.	12.	0-6	Absarokee	20.9	44.1	34.9	clay
18.		6-12		13.3	41.8	45.0	silty clay
19.	13.	0-6	Cargill	26.1	43.8	30.1	clay
20.		6-12		22.8	37.1	40.0	clay loam
21.	14.	0-6	Scobey	15.6	29.5	55.0	silty clay loam
22.		6-12		14.7	25.4	59.9	silt loam
23.	15.	0-6	Assinniboine	53.9	26.1	20.0	sandy clay loam
24.		6-12		54.5	25.4	20.1	sandy clay loam

involved the exchange of Na in solution for K in the soil K-bearing minerals. The fungi functioned as a sink for soil K by maintaining K in solution at appropriately low concentrations, whereby K could continue to be released to the fungi from K-bearing soil minerals through exchange with solution Na.

Table 8 lists the amount of K extracted from selected soil samples subjected to alternate wetting and drying and untreated samples. In comparing the results of Table 8, it is seen that, for the most part, wetting and drying caused a decrease in the amount of K extracted as opposed to the untreated soil. Table 9 lists the amount of K extracted from silt and clay separates. Approximately 2.5 times more K was extracted from the clay fraction as compared to the silt (mean values), suggesting an increase in K release with decreasing particle size.

Potassium extraction by fungi in part produced a transformation of micas to vermiculite in all soil clays evaluated. Interpretation of mica transformation was, for the most part, qualitative due to the variability of soil clay quantities and properties. Figure 9 illustrates a soil clay (Sample No. 13) with the expansion of the mica component forming vermiculite and interstratification of mica and vermiculite layers. The vertical lines at approximately 6, 8.6, and 28 °2 θ (14.71, 10.27 and 3.18 Å) represent montmorillonite-vermiculite and

Table 8. Potassium extracted by fungi from selected soils untreated and alternately wetted and dried from eastern and western Montana.

Sample No.	Location	(mg.)		(ppm)		(ug)	
		Dry matter produced		K in fungi		Total K extracted	
		ut.	wd.	ut.	wd.	ut.	wd.
1.	1.	77	6	2202	2034	170	12
5.	3.	49	110	925	1430	45	157
7.	5.	27	5	5413	1626	146	13
8.	6.	31	27	2441	1292	76	35
9.	7.	41	8	1293	2397	53	19
11.	9.	35	41	5093	1846	178	76
13.	10.	91	99	498	853	45	85
17.	12.	16	26	5737	2911	92	75
19.	13.	12	51	5145	1142	62	58
21.	14.	58	27	2009	1679	117	45
23.	15.	34	44	872	2077	30	91
25.	16.	74	76	2786	321	206	24
26.	17.	16	58	4840	974	77	57
27.		52	66	872	754	45	50
28.	18.	83	89	2229	713	85	63
29.		57	131	1053	618	60	81
		47 = $\bar{x}$	54 = $\bar{x}$	2713 = $\bar{x}$	1416 = $\bar{x}$	93 = $\bar{x}$	59 = $\bar{x}$

Table 9. Potassium extracted by fungi from silt and clay fractions of selected soils from eastern and western Montana.

Sample No.	Location	(mg.)		(ppm)		(ug)	
		Dry matter produced		K in fungi		Total K extracted	
		silt	clay	silt	clay	silt	clay
1.	1.	19	137	2386	651	45	89
5.	3.	3	161	2325	405	7	65
7.	5.	3	70	1162	498	4	35
8.	6.	91	139	755	382	69	52
9.	7.	48	182	400	369	19	67
11.	9.	25	120	2260	703	57	84
13.	10.	55	126	1028	780	56	98
17.	12.	22	2	1189	963	26	2
19.	13.	30	121	1279	1574	38	190
21.	14.	73	155	478	635	35	98
23.	15.	12	136	1308	1113	16	151
25.	16.	10	16	2615	654	26	10
26.	17.	57	82	992	574	57	47
27.		12	81	1598	656	19	53
28.	18.	92	94	550	1332	51	125
29.		7	95	498	687	4	65
		35 = $\bar{x}$	107 = $\bar{x}$	1301 = $\bar{x}$	748 = $\bar{x}$	33 = $\bar{x}$	74 = $\bar{x}$

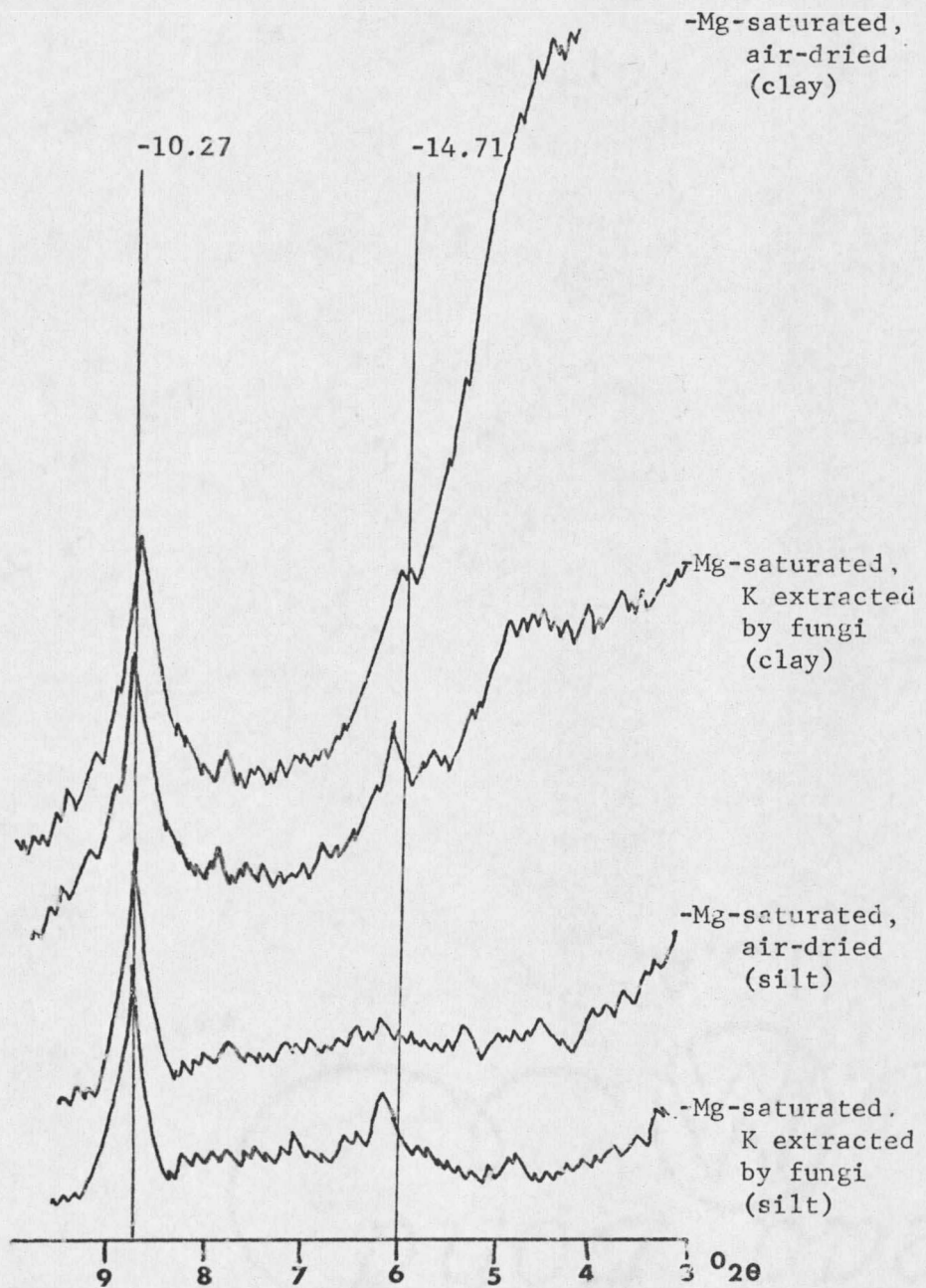


Figure 9

X-ray diffractogram of soil clay mica-vermiculite transformation. Silt included.

mica, respectively. The $14 \text{ \AA}$ X-ray diffraction peak at approximately $6^\circ 2\theta$ increased as the peak at approximately $10 \text{ \AA}$ ($8.6^\circ 2\theta$) decreased in amplitude and sharpness. The process of mica transformation to vermiculite is explained by the replacement of more accessible K by Na and interlayer H_2O molecules. With further replacement of K, the attractive forces between layers decrease and the (001) spacing increases. A mixed layer structure occurs with increasing numbers of layers converted to vermiculite type minerals.

Available K and the quantity of K extracted by fungi from alternately wetted and dried soil are positively correlated, statistically significant at the .05 level. There is a strong negative correlation between the quantity of dry matter produced from alternately wetted and dried soil and the X-ray peak intensity of mica in the clay fraction, significant at the .01 level. The relationship between the amount of dry matter produced by fungal extraction of K in the untreated soil and the quantity of montmorillonite-vermiculite in the clay fraction is positively correlated and significant at the .01 level. This suggests that K becomes more available when there is a corresponding increase in the amount of expanding lattice minerals in the soil.

SUMMARY AND CONCLUSIONS

The influence of soil mineralogy on K availability is considered of primary importance in the understanding and characterization of soils. Soil clay mineralogical relationships of K availability were evaluated by chemical analysis, X-ray diffraction and biological extraction from 18 selected soil locations in eastern and western Montana.

Montmorillonite-vermiculite, mica, kaolin, quartz, plagioclase, and k-feldspar were identified by X-ray analysis in all soils. Allophane was detected in one western Montana soil.

The characteristics of lattice expansion and contraction of selected soil clay samples were evaluated by comparison of the Mg and K-saturated X-ray diffractograms. High K fixing soil clays when K-saturated were found to exhibit closure of the interlayer space to approximately $10 \text{ \AA}$, thereby fixing K between layers. A subsequent increase in the $10 \text{ \AA}$ peak amplitude was also found. Soil clays with a lower K fixation capacity exhibited little change in the interlayer space between 10 and $14 \text{ \AA}$. Closure of the montmorillonite-vermiculite K-saturated peak toward the mica peak represents a transformation of mineral species, i.e., montmorillonite-vermiculite to mica.

The cation exchange capacity Ca:Mg was positively correlated with the intensity of the montmorillonite-vermiculite X-ray diffraction

peak in the clay and negatively correlated with the intensity of the mica X-ray diffraction peak in the clay, both correlations being statistically significant at the .05 level.

Percent mica in clay was quantitatively determined and found to be negatively correlated, statistically significant at the .05 level, with percent sand. Total K in the clay, however, was positively correlated with percent clay, significant at the .05 level.

Potassium availability as determined by NH_4OAc extraction was negatively correlated with cation exchange capacity Ca:Mg, percent vermiculite in clay, percent sand, and K fixation. A decrease in the quantity of montmorillonite-vermiculite relative to mica was found to correspond to an increase in available K.

Soil K extraction by fungi was initiated in order to evaluate the release of K in soil minerals. The two soils with the highest and lowest values of available K, total K, cation exchange capacity Ca:Mg, K fixed, and average grain yield response were used for analysis.

Untreated soils, soils alternately wetted and dried, and silt and clay fractions were evaluated. For the most part, soils wetted and dried caused a decrease in the amount of K extracted as opposed to the untreated soil. Approximately 2.5 times as much K was extracted from the clay fraction as compared to the silt, suggesting an increase in K availability with decreasing particle size.

Potassium extracted by fungi in part caused a transformation of mica to vermiculite. When subject to K extraction by fungi, the mica component at 10 Å was transformed to interstratified mica-vermiculite. The vermiculite X-ray diffraction peak at approximately 14 Å increased in amplitude as the mica peak decreased in amplitude and sharpness. With increased replacement of K, the attractive forces between layers decreased and the c-axis spacing increased.

Ammonium acetate available K and the quantity of K extracted by fungi from alternately wetted and dried soil were positively correlated, statistically significant at the .05 level. There was a negative correlation between the quantity of dry matter produced from alternately wetted and dried soil and the X-ray diffraction peak intensity of mica in the clay fraction, significant at the .01 level. The relationship between the amount of dry matter produced by fungal extraction of K in the untreated soil and the quantity of montmorillonite-vermiculite in the clay fraction was positively correlated and significant at the .01 level. This suggests that K becomes more available when there is a corresponding increase in the amount of expanding lattice minerals in the soil.

An attempt was made to evaluate geologic formations as to K availability without success due to similarity in clay mineral assemblages of all eastern Montana soils.

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