Behavior of Potassium and Sodium During the Process of Soils Formation

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TABLE OF CONTENTS

Behavior of Potassium and Sodium During the Process of Soils Formation

Hans Jenny

Introduction

The problem of soil fertility is as complicated as it is old. Great improvements in methods of soil management have been made during the last 80 years, yet it is a common belief that further progress will depend much upon a better understanding of the physical, chemical, and biological processes going on in soils. The discovery that a soil is not a static but a dynamic system in which ions, colloids, and micro-organisms play a dominant role, has greatly modified the concepts regarding soil fertility, soil formation and even soil classification. It is now realized that natural soil fertility is a product of soil formation which varies greatly in various parts of the earth, depending on differences of climate, vegetation, parent material and so forth. As a consequence, the study of weathering processes and soil development in general is receiving more attention than ever before. In this investigation an attempt has been made to organize and clarify some of the complex reactions encountered in soils on the basis of systematic experiments with soil colloids. Two definite constituents, potassium and sodium, have been selected and their behavior in various soils under a great variety of external conditions is discussed from a quantitative viewpoint. It is hoped that the results obtained will contribute toward a better understanding of soil development.

Plan of Investigation

At the outset one might ask the question whether the behavior of K and Na in soils is governed by a general underlying principle or whether the distribution of the two elements in the various soil horizons is merely a matter of chance. The viewpoint prevails—established by geologists—that K tends to accumulate in soils while Na is leached and carried to the ocean. This belief is based mainly on the comparison of analyses of igneous rocks and sedimentary rocks.[6] It can be doubted, however, whether this geological observation holds for a great many soils. Modern soil science has established fundamental differences in the chemical composition of the great soil groups on the earth. Moreover pedologists of today sharply distinguish between the various horizons of a profile, an important feature which was entirely neglected in earlier studies of soil formation. Indeed a preliminary inspection of more than

200 total soil analyses found in the literature does not reveal any consistent relationship between K and Na whatsoever. Apparently there are a great many different factors involved which affect the solubility of the K-Na-silicates, the movement of the soil solution, and the adsorption and release of the K and Na ions in soil horizons, thus making a direct application of the above principle doubtful.

It becomes necessary to approach the entire problem from a different angle. It is believed that a study of soil colloids in relation to ionic exchange might furnish a basis for a promising attack. A detailed investigation of adsorption* and release of K and Na by various soil colloids under conditions simulating those in the field should provide definite information as to the effect of the colloidal material upon the distribution of K and Na in the soil profile. These results might serve as a guide for the interpretation of total soil analyses. The first part of the paper is, therefore, devoted to experimental laboratory investigations of K and Na interchange on soil colloids, while the second part contains a characterization of soil types based on these studies.

Behavior of K and Na in Colloidal Systems

THEORETICAL CONSIDERATIONS

Most studies on soil colloids with respect to ionic exchange have been conducted along the lines of classical chemistry (Ramann[68], Bradfield[10], Magistad[51], Ganssen[26]) attempting to characterize the process by means of dissociation constants, hydrolyses constants, true chemical reactions and so forth. Relatively few (Wiegner and Jenny,[90], Cooper[19]) have approached base exchange from the viewpoint of the inherent properties of the participating ions. Not so long ago this latter method was mainly speculative, but during recent years the knowledge about molecules, atoms, and ions has become so abundant and definite that it furnishes an excellent basis for the study of the mechanism of ionic exchange in alumino-silicates. It is appropriate, therefore, to present a concise review of the fundamental concepts of K- and Na-atoms and -ions in regard to their significance in soil reactions.

On the Nature of K and Na ions

Atoms are electrically neutral systems. According to the Rutherford-Bohr model which compares atoms with planetary systems, a positively charged nucleus in the center of the atom is surrounded by one or several negatively charged electrons travelling in definite orbits around the nucleus.

*The term "adsorption" is used in the sense of Michaelis: "Adsorption is the phenomenon where some substance homogeneously dissolved in a phase accumulates at the boundary layer to a higher concentration, no statement being made whether this process is based on physical or so-called chemical forces."

The K-atom consists of a nucleus carrying 19 positive charges surrounded by 19 electrons; the corresponding number for the Na-atom is 11. If one electron is removed the atoms become positively charged *ions* (cations).

Ions are far more important in soils than atoms. In the soil solution K and Na are ionized and even after their adsorption on colloids they remain in that state. Furthermore, recent investigations on X-ray analysis of alumino-silicates indicate that the solid material including the mineral colloids is not only crystallized[36] (Kelley et al[45]) but also that the *components of the crystals are present as ions.* (Bragg[11, 12], Debye[21], and others[30]). These recent findings put the problem of ionic exchange in soils on a very broad basis. The following *properties of ions* have an important bearing upon this matter:

1. *Charge.* Cations contain one or several positive electric charges. K^+ and Na^+ are monovalent ions and contain one positive electric charge which has a magnitude of 4.775×10^{-10} electrostatic units (Millikan, 1912).

2. *Size.* Generally speaking the size of ions increases with the number of electrons, provided the comparison is made for elements of the same group in the periodic system. The K-ion is greater than the Na-ion. According to Goldschmidt[30], the radius of the K-ion is 1.33 Å, that of the Na-ion 0.98Å (1Å = 10^{-8} cm)

Different investigators report somewhat different values, and sometimes the expression "sphere of action" is preferred to "size". It should be kept in mind that these radii were obtained by X-ray investigation of crystals and refer to a coordination number of six.

Hydration of ions

Although the radii of K and Na ions of crystallized substances are well known, the behavior of K and Na ions in solutions is different from what one would expect on the basis of the crystal radii. X-ray analyses of ionic solutions[65] and measurements of migration velocities[46, 84] show that the ions in water act as larger units than in crystals; they have greater dimensions. Data indicate that every ion is surrounded by a shell of water molecules; in other words the ions are hydrated. Since the hydration of ions plays an important role in explaining the mechanism of base exchange it might be adequate to discuss briefly the hydration phenomenon.[13, 14, 24, 84, 86].

The hydration of ions is best understood from a consideration of electric charge and size of the ions. A combination of the two magnitudes, called electric field strength, reaches such great values in the vicinity

of an ion (for K^+ it is 180,000 volts per cm) that it exerts considerable influence upon the neighboring water molecules.

According to Debye[21], water is a permanent dipole, that is, in the neutral water molecule the positive and negative electric charges are not symmetrically arranged. Under the influence of an electric field such as exists in the vicinity of a K- or Na-ion, the water molecules become oriented and attracted, thus forming a shell of water molecules around the ion (polarization of water molecules). From the difference in radii of K and Na it is evident that the polarizing effect of the Na-ion is greater than that of the K-ion as seen from the following table:

TABLE 1.—POLARIZING EFFECT OF K^+ AND Na^+ EXPRESSED AS ELECTRIC FIELD STRENGTH

Ion	K^+	Na^+
Electric field strength $= \dfrac{1}{r^2}$	0.56	1.05

The electric field intensity of the Na-ion is more than twice as large as that of the K-ion. Na^+ will attract more water and will be more hydrated than K^+. In a water system the Na-ion including its water shell will have a greater diameter and a larger volume than the hydrated K-ion. The number of water molecules associated with K and Na is not constant and is difficult to determine experimentally. On the basis of transference experiments Remy[69] calculates that the Na-ion carries 18.4 water molecules while the K-ion carries only 11.6. This agrees well with the data of Washburn[84] who finds 18.0 molecules of H_2O for Na^+ and 11.5 for K^+. In base exchange studies of natural soil systems a difference in behavior of K^+ and Na^+ is therefore to be expected.

The Structure of the Colloidal Complex

The interaction of K- and Na-ions with soil colloids cannot be fully understood without a knowledge of the structure of alumino-silicates as revealed by the important investigations of W. L. Bragg, [11,12] Linus Pauling[63], and others.[30,59]

In the modern trend of explaining crystal structures, stress is laid on the relative sizes of the elements which make up the crystal. Fig. 1 shows the sizes of the more common constituents of silicates according to Bragg-West[11], which are based on the ionic radii given by Wasastjerna.

Ions	O^{--}, OH^-	Si^{++++}	Al^{+++}	Na^+	K^+
Diameters	2.7Å	0.6Å	1.1 Å	2.0Å	2.6 Å
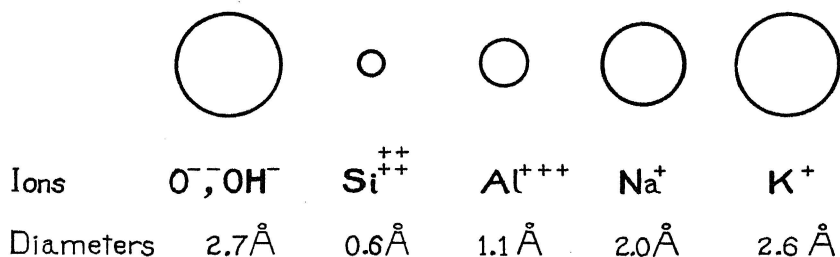
Fig. 1.—Size of ions as found in crystallized alumino-silicates.

It is clearly seen that the oxygen ion is the largest of all ions and by reason of its size and large number in alumino-silicates it forms the frame work of the crystals. Silicon ions and aluminum ions are so small in size that they will pack between the oxygen ions, cementing the structure together, but having only a secondary effect on its arrangement (Bragg). Si- and Al-tetrahedra (and octahedra) build up the alumino-silicates and are held together by the cations Na^+, K^+, Ca^{++}, Mg^{++} and others. Depending upon the arrangement, the packing of the oxygen ions is close or open.

Attention is called to Figure 2, which shows a rather closely packed structure of a chrysoberyl Be Al_2O_4 a type of mineral with little base exchange properties, while Figure 3 illustrates an open structure approaching the type of zeolites which have a very pronounced ionic exchange. In permutits and ultramarines[38] (Fig. 4) the interior cavities are so great as to permit migration of such large units as water molecules and SO_4 groups.

Aluminium   Oxygen   Beryllium
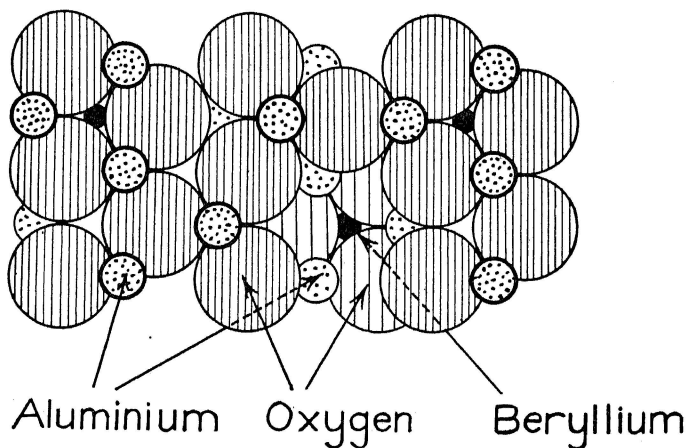
Fig. 2.—Close package of oxygen ions (Bragg-West)

O⁻⁻ and OH⁻ ions   Si or Al ions

Outer surface   Inner surface

Fig. 3.—Open package of oxygen ions (St. v. Naray-Szabo).

Fig. 4.—Elementary cell of ultramarine (Jaeger) showing a big interior cavity (in black) which is the seat of cation exchange. There is superfluous space for migrating ions and water molecules.
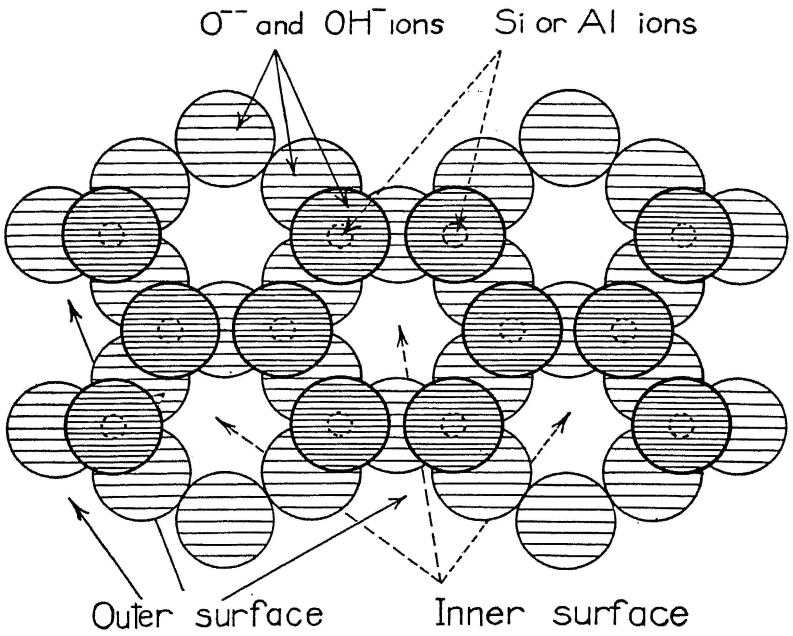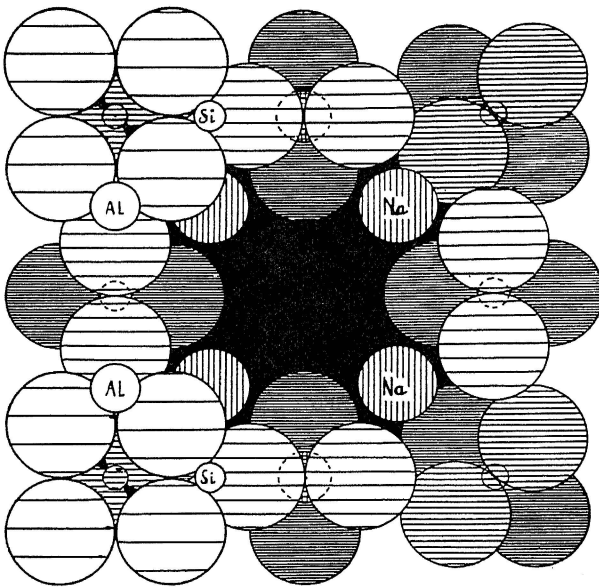
In a closely packed frame system ionic exchange is mainly restricted to the adsorptive action of the surface of the crystal, while in the case of an open structure the "interior surface" can also be the seat of ionic exchange reactions. This explains the observation that grinding may change greatly the ion exchange capacity of a closely packed mineral, but not necessarily that of a mineral of the zeolite type which has a very open structure.

The Mechanism of Adsorption and Release of K- and Na-ions*

The places of attraction in the colloidal particles are the negative O^{--} and OH^- ions† of the rigid crystal frame. Only positive ions will adhere, negative ions as a rule will be repelled and remain in the surrounding liquid. The intensity of fixation follows Coulomb's law according to which the attraction is directly proportional to the product of the charges of the ions and indirectly proportional to the square of the distance between the charges, which of course is determined by the size of the ions. Wiegner's[89] novelty in base exchange studies consists in the introduction of the *size of the hydrated ions* instead of "crystal ions" in Coulomb's equation, a feature which at once clarifies the behavior of Na- and K- ions in base exchange. The K-ion with its thin watershell can go closer to the O-ion of the crystal frame than the highly hydrated Na-ion. The attraction between the negative inner layer and the K-ion is therefore greater than for the Na-ion; in other words K is better absorbed than Na and also held more tightly. A "foreign ion," for instance Ca^{++}, will more easily replace the loosely held Na-ions than the tightly bound K-ions. On the basis of these theoretical considerations and in agreement with experimental data on ionic exchange with permutits, it can be said that:

K is better adsorbed than Na,
Na is better released than K.

The question arises as to whether the above statement might furnish a general principle for the explanation of K and Na in soil formation. In the original work of Wiegner and Jenny[90, 91] the theory was tested on artificial clays; it remains to be shown that it is also valid for soil colloids under natural conditions.

EXPERIMENTAL PART‡

In order to approach natural conditions in the field, the adsorption and release of K and Na was studied under a great variety of conditions. The following factors were taken into consideration:

a) Nature of colloidal complex
b) Variation in salt concentration
c) Effect of dilution
d) Influence of varying pH values
e) Effect of anions
f) Effect of cations
g) Temperature influence
h) Presence of calcium carbonate

Investigation of the above factors should furnish exact data as to the relative importance of parent material and climate in affecting the release and adsorption of the two ions.

The Behavior of K and Na as Effected by the Nature of the Colloidal Complex

The following colloidal complexes were studied:

Permutit (Riedel)
Artificial zeolite (Folin)
Colloidal clay (Putnam silt loam subsoil.)
Natural soil (Putnam silt loam.)
Colloidal bentonite
Colloidal AL(OH)$_3$
Humus (Wisconsin peat).

TABLE 2.—ADSORPTION AND RELEASE OF K AND NA BY COLLOIDAL
ALUMINO-SILICATES
(Symmetry values)*

	Permutit		Putnam clay		Bentonite clay	
	K	Na	K	Na	K	Na
	%	%	%	%	%	%
Adsorption of KCl and NaCl by NH$_4$-colloids__	48.0	32.5	54.0	35.7	53.0	50.6
Adsorption of KCl and NaCl by H-colloids____	8.0	2.7	13.0	6.2	18.4	14.6
Release of adsorbed K and Na by NH$_4$Cl_____	37.5	55.0	20.6	51.6	39.6	49.4
Release of adsorbed K and Na by HCl_____	----	----	69.6	80.3	50.4	60.4

*Symmetry values indicate the magnitude of ionic exchange as expressed in percentage when the number of ions added to the system is equal to the number of ions adsorbed on the colloid.

Permutit and zeolite were commercial products. They were converted into systems containing only one exchangeable cation through leaching with the respective chlorides as previously described[39]. An NH$_4$-Putnam silt loam soil was similarly prepared. Colloidal clay and colloidal bentonite were extracted from natural products by churning and sub-

sequent centrifuging with a Sharples supercentrifuge according to the method developed by Bradfield[10]. After electrodialyses in a three-compartment cell[9], which removed ionic impurities and adsorbed ions, the resulting H-colloids were converted into the desired K^+, Na^+, NH_4^+, Ca-systems by adding definite amounts of the corresponding hydroxides. Intake and outgo of ions were studied according to methods previously described.

Results.—The inspection of Figures 5-21 clearly reveals that the relative behavior of K and Na is consistent and not affected by the nature of the colloidal complex. Even in such extreme types of materials as permutit and bentonite or humus, K and Na maintain their individuality in ionic exchange. *In every case studied more K is adsorbed than Na (Figures 5-11) while on the other hand more Na is released than K (Figures 16-19).* This is also evident from the symmetry values listed in Table 2. It is true that in some experiments the difference between K and Na is less pronounced than in others,* but the differences are always observed and their trend is in the same direction. Whether the material is an artificial or natural product, a soil or only its colloidal portion, a weak clay acid or a strong one, or whether it has a wide or narrow $SiO_2:Al_2O_3$ ratio, it does not matter; the hydration of ion effect is always exhibited. From the viewpoint of soil formation, these findings are very striking in that they emphasize the dominance of the K and Na ion over the variations of the colloidal soil material.†

A search of the literature for comparable investigations revealed the following:

Ramann and collaborators[68] working with permutits, but using entirely different methods report similar results as those shown in Figures 6 and 10. An ammonium permutit was leached with mixtures of KCl and NaCl solutions, containing equal numbers of K and Na ions as expressed in normalities (0.5 m). The resulting K-Na-permutit had a K/Na ratio of 7.38, that is to say, about seven times more K than Na had been taken up. Ramann also studied release of K and Na against exchange with MgCl₂ and his data show that after the reaction had taken place the K-permutit contained 0.1832 equivalents K (per 100 gr. permutit), while the Na-permutit contained only 0.1710 equivalents Na, indicating that Na is easier replaced than K.

Ilse Zoch[93] treated a natural zeolite (Desmin of Berufjord) with NH₄Cl and found that in the mineral the K:Na ratio had increased from 1 to 1.064, and that 7.74 per cent of the Na present had been exchanged, while only 1.40 per cent of the K was released.

The work of *Magistad*[51] dealing with hydrolysis of artificial and natural zeolites also shows that more Na is lost than K. *H. Kappen's*[44] studies on a loam soil from Germany, (Annaberg), *Miyake's*[57] experiments with Hagerstown loam (Maryland) and *Daikuhara's*[20] researches also indicate that K is much more strongly adsorbed than Na.

*For an explanation see footnote on page 11.
†The exchange experiments with electrodialysed peat from Missouri revealed the following data: 4g H-peat + KCl, NaCl, total volume 500 cc.

Milliequivalents of salt added	Milliequivalents of H released	
	by KCl	by NaCl
10.00	0.729	0.675
20.00	0.790	0.705
60.00	0.913	0.793

Küllenberg[49] treated 100 grams of soil with various K- and Na-salts and found that for 0.01 normal solutions, 3.2-5.3 times more K than Na is adsorbed; in 0.2 normal solutions 1.7-2.9 times more K than Na is adsorbed, the range depending on the salt used.

Schuhmacher[73] found that humus adsorbed twice as much $K_2 SO_4$ as $Na_2 SO_4$.

Gedroiz[27] in 1916, treated a soil with a mixture containing 0.5 n NaCl and 0.5 n KCl and reports that K and Na were adsorbed in the ratio of 1.46: 0.81. In another experiment (1918) he studied the replacement of Ca from various Russian cherno-zems, using 0.1 n KCl and 0.1 n NaCl solutions, respectively. K replaced 93 per cent of the adsorbed Ca and Na only 83 per cent. The same relationship was found with Mg, Ca, and Ba-chernozems. Gedroiz makes a general statement saying that K is more energetically adsorbed than Na.

Joseph and Oakley[43] isolated clay from a badob soil (Sudan) and saturated one portion of it with K and another portion of it with Na. These K and Na clays were then subjected to electrodialysis, a process in which the adsorbed cation (K, Na) is replaced by hydrogen ions of water. They found that Na is easier replaced than K.

Puri[66] working in India also observed that K is better adsorbed than Na.
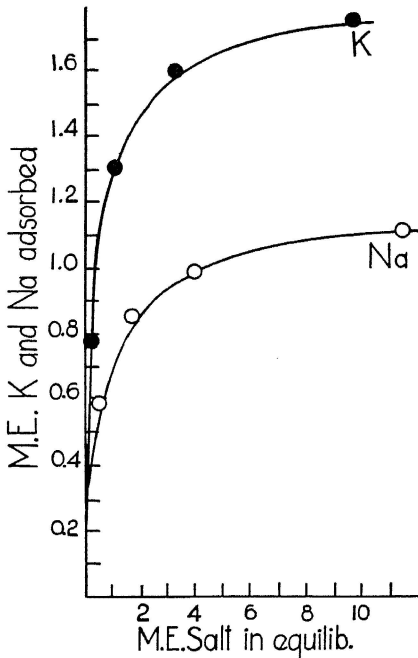
Fig. 5.—ADSORPTION OF K AND Na BY NH₄-H-SOIL (PUTNAM). Procedure: 10g. of soil containing 2.28 milliequivalents exchangeable NH₄. K and Na added as chlorides. Total volume 250cc. Time of reaction one week. Adsorption based on outgo of NH₄. pH 4.5-5.7.
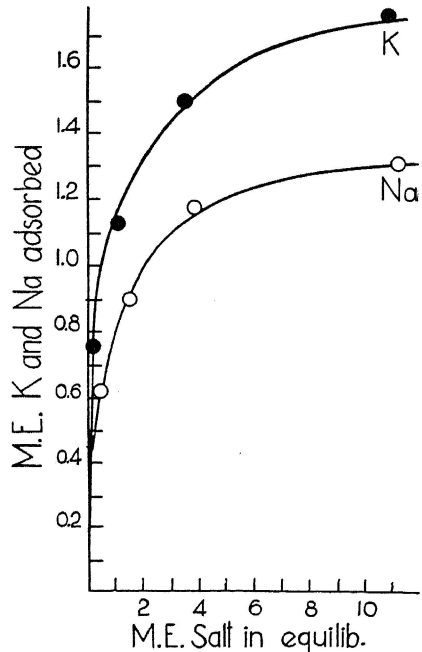
Fig. 6.—ADSORPTION OF K AND Na BY NH₄-H-PERMUTIT (FOLIN). Procedure: 0.6291 g. permutit containing 2.07 milliequivalents exchangeable NH₄; KCl, NaCl added, volume 250cc. NH₄ released was determined—as usual—by distillation. Time of reaction one week.

All these data reported by numerous investigators in various countries working with entirely different soils agree with the experimental results found in the present study and show that the qualitative behavior of K and Na in ionic exchange reactions is not affected by the nature of the soil colloids studied.
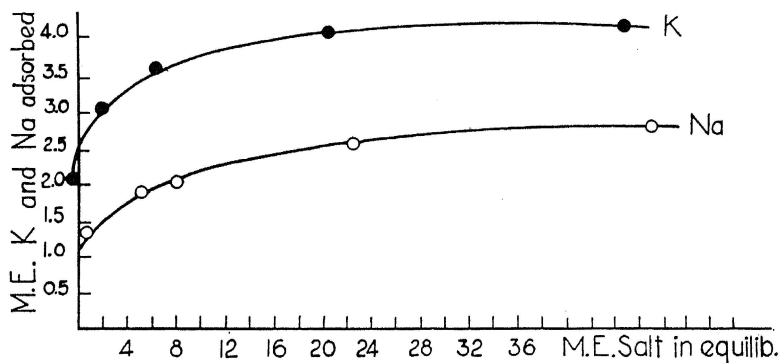
Fig. 7.—ADSORPTION OF K AND Na BY NH₄-CLAY (pH 8.5). Procedure: 4.96g. NH₄-clay containing 4.15 milliequivalents exchangeable NH₄; KCl, NaCl added, volume 500cc.; pH range 7.7-8.3; adsorption based on NH₄ exchange including hydrolyses.
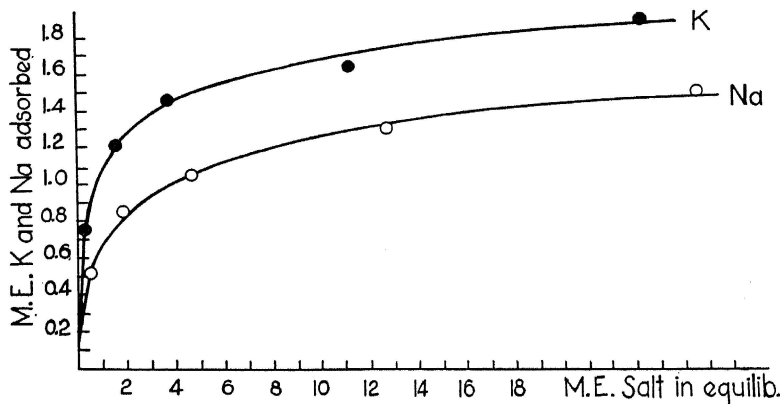
Fig. 8.—ADSORPTION OF K AND Na BY NH₄-H-CLAY. Procedure: 6.90 g. clay containing 2.07 M. E. exchangeable NH₄; KCl, NaCl added; total volume 500cc.; time of reaction one week; pH at equilibrium varies from 4.1-5.2. Adsorption of K, Na based on exchange of NH₄.
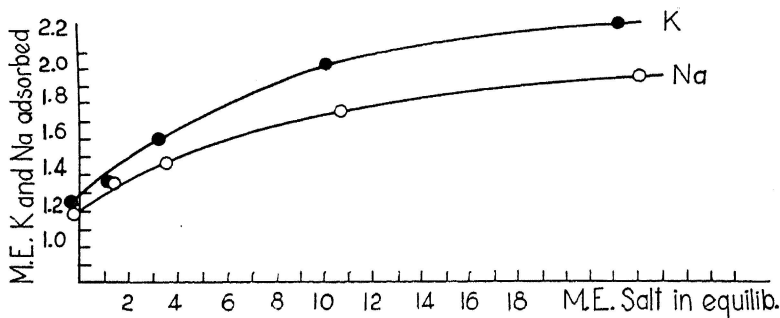
Fig. 9.—ADSORPTION OF K AND Na BY NH₄-H-BENTONITE. Procedure: 2.45g. bentonite containing 2.195 milliequivalents exchangeable NH₄; KCl, NaCl added; volume 500cc. pH range 4.9-6.0. Time of reaction one week. NH₄ determined by distillation, as usual.
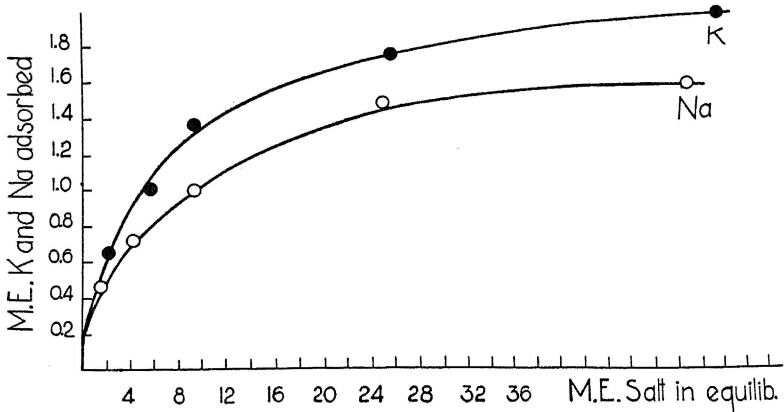
Fig. 10.—ADSORPTION OF K AND Na BY Ca-PERMUTIT. Procedure: 1g Ca-permutit containing 3.99 milliequivalents exchangeable Ca was treated with increasing amounts of KCl, NaCl. Volume 100 cc. Time of reaction one week. Adsorption of K and Na based on outgo of Ca.
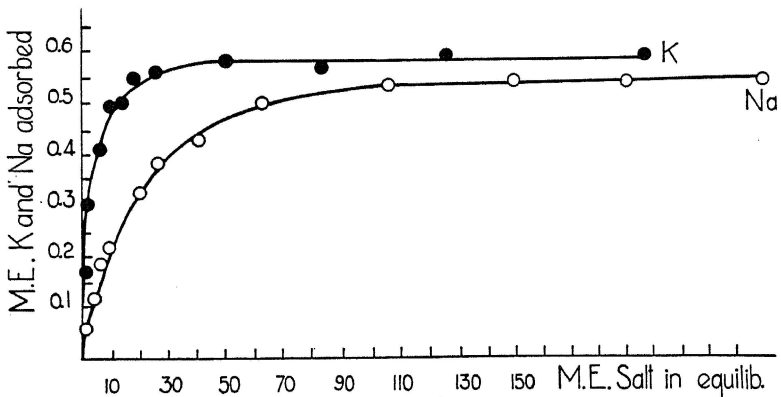
Fig. 11.—ADSORPTION OF K AND Na BY H-CLAY. Procedure: 3.69g. H-clay+KCl, NaCl in 250 cc. volume. Titration of exchanged H after one week reaction time. Indicator: phenolphtalein. pH varies between 3.30-3.85. Graph based on 1g clay.

Effect of Concentration of Salts Added

The peculiar shape of the exchange isotherm shows that in dilute salt solutions the relative adsorption is greatest, while under higher salt concentrations the reaction tends to become independent of the amount of salt added. This is typically shown in Figure 11, where H-clay was treated with increasing amounts of KCl and NaCl; the highest concentrations were saturated solutions. Although the curves run parallel to the X-axes at high concentrations, the K-line remains consistently above the Na-line in agreement with the better adsorbability of the K-ion.
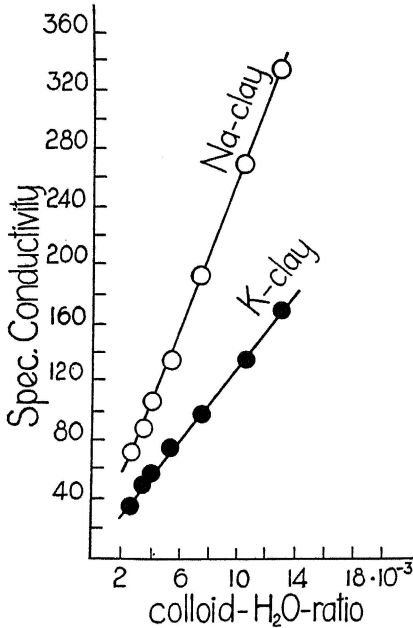
Fig. 12.—Effect of dilution on specific conductivity of K and Na-clay (60 M. E. K, Na per 100g of colloid). Data not corrected for cell constant (0.50).
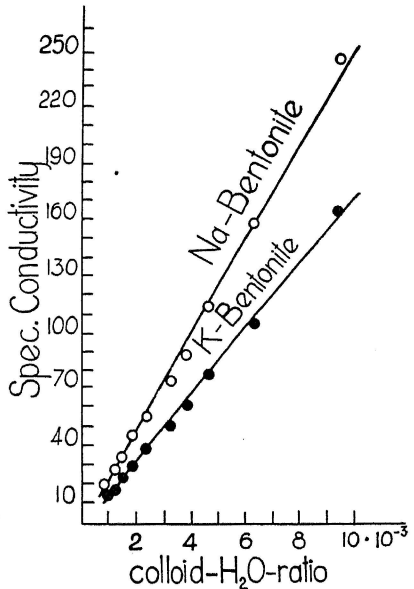
Fig. 13.—Effect of dilution on specific conductivity of K- and Na-bentonite (60 M. E. K, Na per 100 g of colloid). Data not corrected for cell constant (0.50).

In the study of the release of K and Na from colloidal clay against NH_4 a somewhat different type of curve was encountered (Fig. 17), but here also as well as in Figures 16, 18, 19, the Na-curve remained above the K-curve demonstrating the better release of the Na-ion.

The difference in behavior of K and Na is manifested at all concentrations investigated.—The fact that many of these adsorption curves can be described by Freundlich's adsorption formula does not prove that the process includes physical adsorption; on the other hand, the observation[39] that these ionic exchange reactions occur stoichiometrically is, of course, no proof that only chemical forces* are involved.

Effect of Dilution

Ganssen[26], Ramann[68], Rothmund[72], and recently Wiegner and Jenny[90] claim that base exchange reactions are independent of dilution, especially if polyvalent and heavy monovalent cations are considered. For lighter monovalent cations activity coefficients of the added salt and "hydrolysis effects", must be taken into consideration.

*Electron pair bonds.
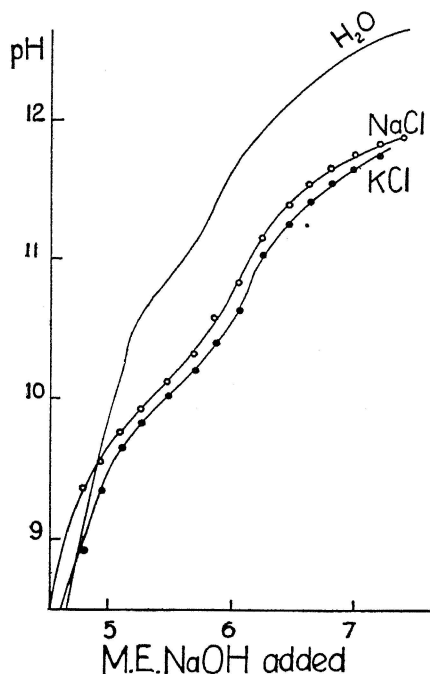
Fig. 14.—EFFECT OF KCl AND NaCl ON TITRATION OF AlCl₃. 4.85 M. E. AlCl₃ titrated with NaOH in presence of 25 M. E. KCl, NaCl. Presence of neutral salts decreases the hydrolyses of aluminates (as compared with the H₂O curve) but Na-Al(OH)₃ is more hydrolysed than K-Al(OH)₃.
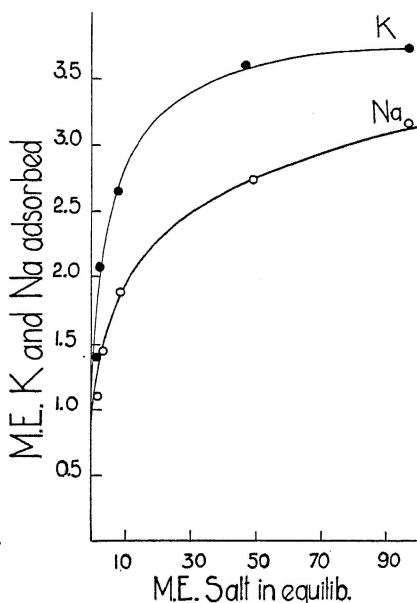
Fig. 15.—ADSORPTION OF K AND Na BY PURE NH₄-PERMUTIT. (Riedel) 1g permutit containing 4.15 M. E. exchangeable NH₄; KCl, NaCl added; volume 100 cc.; reaction time one week. Adsorption based on outgo of NH₄ as determined by distillation.

The effect of dilution upon the outgo of K and Na from soil colloids is of particular importance in the present study because it relates directly to the influence of various amounts of percolating water on the removal of K and Na. This process is commonly called "hydrolysis of alumino-silicates". It is a special case of ionic exchange in which only the H ions of the water participate, according to the following scheme:

$$\begin{array}{|c|c}\hline \text{soil} & Na^+ \\ \text{colloidal} & Na^+ + H^+\ OH^- \\ \text{particle} & Na^+ \quad \text{Intermicellar liquid} \\ \hline \end{array} \rightleftharpoons \begin{array}{|c|c}\hline \text{soil} & H^+ \\ \text{colloidal} & Na^+ + Na^+\ OH^- \\ \text{particle} & Na^+ \quad \text{Intermicellar liquid} \\ \hline \end{array}$$
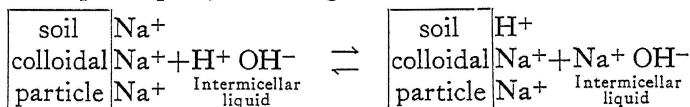
The intermicellar liquid in this example would exhibit an alkaline re-action due to the Na OH formed. According to the theory of hydration of ions, Na-clay should hydrolyze more than K-clay, since the Na-ion is less firmly bound on the surface of the colloid and therefore easier exchanged by the H ions of the water; also, the pH of the suspension should be different for the two systems.* Percolating water should re-move more Na than K.

*This pH difference cannot be simply attributed to differences in the degree of surface dissociation of K- and Na- clays, as has been claimed.
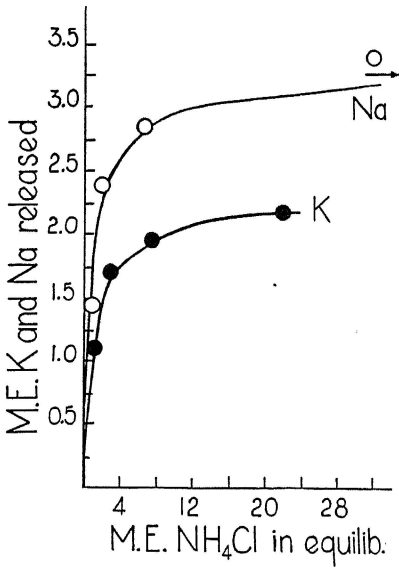
Fig. 16.—RELEASE OF K AND Na FROM K- AND Na-PERMUTIT. Procedure: 1g. Na-permutit (3.99 M. E. exchangeable Na) and 1g K-permutit (4.46 M. E. exchangeable K) treated with various amounts of NH₄Cl. Total volume 100 cc. Time of reaction one week. Release of K and Na based on adsorption of NH₄.
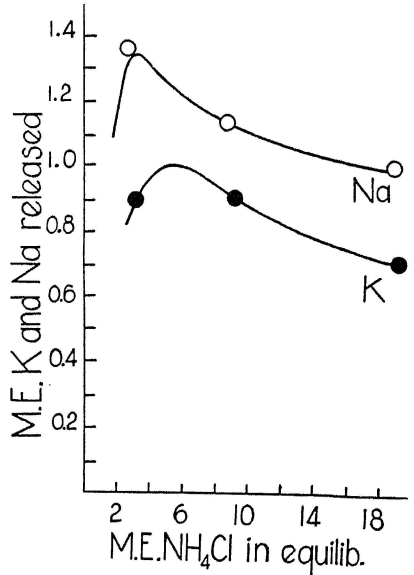
Fig. 17.—RELEASE OF K AND Na FROM K- AND Na-CLAY. Procedure: 2.20g. clay containing 1.38 M. E. exchangeable K, Na respectively. Various amounts of NH₄Cl added; total volume 500 cc. Time of reaction one week. Release of K, Na, determined by adsorption of NH₄.
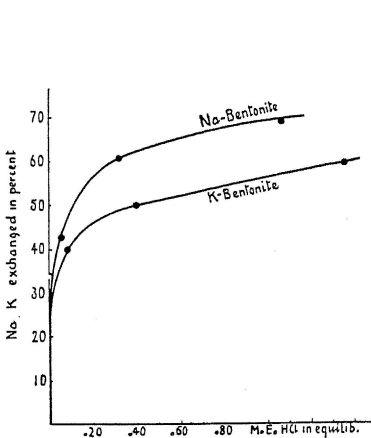
Fig. 18.—RELEASE OF K AND Na AGAINST H FROM BENTONITES. Procedure: 0.950 g K-, resp. Na- bentonite containing 0.8075 milliequivalents exchang. K, Na. Volume 250 cc. time of reaction 1 week, temperature 28°C. Release of K and Na determined by HCl adsorption.
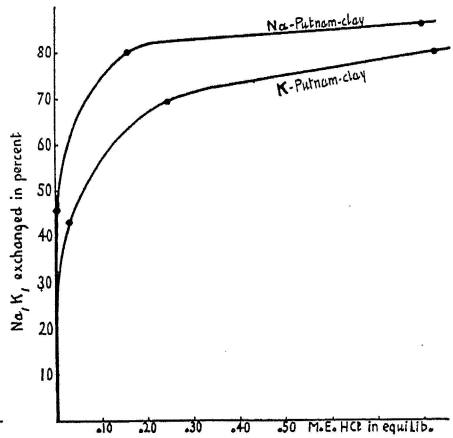
Fig. 19.—RELEASE OF K AND Na AGAINST H FROM PUTNAM CLAY. Procedure: 1.420g colloid containing 0.8075 milliequivalents exchangeable bases. Volume 250 cc. time of reaction 1 week, temperature 28°C. Release of K and Na determined by HCl adsorption.

The experimental evidence in this paper is based on pH and conductivity measurements. K- and Na-clays and bentonites, all of which contained 60 milliequivalents of cation per 100 gr. colloidal material, gave the following pH values:

TABLE 3.—REACTION OF K- AND Na-COLLOIDS (SUSPENSIONS)

Colloid	K- system	Na- system
Colloidal Putnam clay 5% sol_____	pH 6.51	pH 7.18
Colloidal bentonite 2% sol_____	pH 5.28	pH 5.42

The intermicellar liquid of these systems is alkaline, ranging from pH 7.10 to 7.36. Similar conditions exist in systems which are 50% saturated with bases as shown in Table 4.

TABLE 4.—pH VALUES OF 50% SATURATED K- AND Na-COLLOIDS
(pk of apparent dissociation constants)

System*	Permutit	Putnam clay	Bentonite
pH of K-colloids_____	6.92	5.52	5.15
pH of Na-colloids_____	7.16	5.93	5.51

*Time of reaction for all systems = 46 days.

In both cases the sols which contain adsorbed Na have the higher pH values (more alkaline reaction). Dilution of the systems with H_2O does not change the relative position of K and Na as seen from the following table:

TABLE 5.—EFFECT OF DILUTION UPON pH OF K- AND Na-BENTONITE.
MEASUREMENTS TAKEN 10 DAYS AFTER DILUTING

Colloid-water ratio (g)	K-bentonite	Na-bentonite
	pH	pH
9.50×10^{-3}	5.30	5.40
6.34×10^{-3}	5.35	5.63
4.75×10^{-3}	5.42	5.68
3.39×10^{-3}	5.62	5.94

Similarly all conductivity measurements show (Fig. 12, 13) that dilution is without effect upon the relative position of K and Na. The same type of curve was obtained either upon immediate conductivity measurements after dilution of the soil, or after a time elapse of ten days. The pH and conductivity methods are of particular value in this study because measurements can be taken at much lower clay concentrations than ordinary chemical methods would permit.

Magistad[52] also reports that a Na-zeolite shows a greater specific conductance than a K-zeolite. At the concentration of one M. E. zeolite per 100 cc. water, Na-zeolite hydrolyzed 24.8 per cent and K-zeolite only 11.0 per cent. *Joseph and Oakley's*[43] K-saturated clay has a pH of 9.44 while the Na-saturated clay gives a higher pH, namely 9.87. According to *Baver*[7], K and Na behave differently in regard to pH and conductivity at any degree of saturation of the colloid. Both *Aarnio's*[1] and *Perkins-King's*[64] experiments with soils from Finland and Kansas agree with the author's findings.

Summarizing the experimental results which are substantiated by data of other investigators it can be said that both pH and conductivity measurements indicate that, under various dilutions (colloid-water

ratios), *Na-clays "hydrolyze" more than K-clays; in other words, leaching of Na- and K-clays will remove more Na than K.*

Influence of Varying pH Values

Although the great soil groups have not yet been characterized by definite pH ranges, it is known that characteristic differences exist for certain climatic groups. It is, therefore, necessary to have information as to the possible effect of the hydrogen ion concentration upon the relative adsorption and release of K and Na. The following table indicates the pH ranges studied, the systems used, and the references to their graphical representation.

TABLE 6.—SUMMARY OF pH-RANGES INVESTIGATED

pH range investigated	System	Number of figures
3.30 - 3.85	H-clay	11, (18, 19)
4.10 - 5.20	H-NH_4-clay	8
4.50 - 5.70	NH_4-H-soil	5
4.90 - 6.00	NH_4-Bentonite	9
6.80 - 7.20	Ca-Permutit	10
7.70 - 8.50	NH_4-Permutit, NH_4-	
	clay, Bentonite	6, 7, 15
9 - 11	Al(OH)$_3$	14

There is no question that the relative behavior of K and Na is not affected by changes in pH; in both acid and alkaline reactions, K is always better adsorbed than Na. The same relationship is observed for the outgo of K and Na. In Figure 16 (K,Na-Permutits) the reaction is between pH 7 and 8.5; in Figure 17 (K, Na-clay) it is between pH 6 and 7. Also for K and Na-Bentonites, having pH values of 5.30 and 5.40, NH_4 Cl replaces more Na than K.

If K- and Na-clays are treated with HCl, the pH drops below 2, yet Na is always better released than K (Fig. 18, 19). These data do not support the view point of many colloid chemists (influenced by the work of Loeb) that the lyotropic series found in ionic exchange studies is due to a neglect of the hydrogen ion concentration. *Between p H 3.3 and 8.5, which includes nearly all the soil reactions found in nature, Na and K behave differently in both adsorption and release.*

Effect of Anions

In the ionic exchange experiments so far reported, the anion was usually the same, namely Cl. In soils other anions also occur, particularly OH, HCO_3, NO_3, SO_4, and phosphate anions; most common is the OH ion. It is evident from the discussion of the pH effects that OH ions do not affect the relative behavior of K and Na, since the pH range studied experimentally, pH 3.3-8.5, corresponds by definition to a pOH range of 5.5-10.7.

Ramann's data with permutits[68] demonstrate conclusively that the relative position of K and Na in his leaching experiments remains the same, whether the anion is Cl or SO_4 or NO_3. *Küllenberg*[49] studied the adsorption of K and Na by 100 g.

of soil in the presence of the following anions: Cl, NO_3, SO_4, CO_3 HPO_4, using con-
centrations from 0.01 - 0.2 normal. From the following table it is seen that always
more K than Na has been taken up by the soil, giving a K/Na ratio for the intake
of the two ions, greater than 1.

TABLE 7.—EFFECT OF ANIONS ON ADSORPTION OF K AND Na[49]

Anion	Cl	NO_3	SO_4	CO_3	HPO_4
K/Na ratio of intake	1.3 - 4.3	1.4 - 3.2	2.3 - 3.7	1.4 - 4.3	1.5 - 2.7

The ratio varies with the concentration of the salt applied and is wider for the lowest
concentrations. For instance, for the Cl-series 4.3 times more K than Na had been
taken up at the concentration 0.01 normal, while at a normality of 0.2 n, 1.3 times
more K than Na was adsorbed. *Kappen*[44] reports similar findings for the adsorption
of K and Na from acetate solutions.

*These experiments indicate that the anions commonly found in soils
do not change the relative behavior of K and Na in adsorption and release.*

Effect of Cations

Because of the well known antagonistic effect of ions, it might be
possible that certain cations reverse the normal behavior of K and Na.
The following tables demonstrate that for those cations common in
soils, namely K, Na, H, NH_4, Ca, Mg, Al, no such irregularity can be
observed.

TABLE 8.—EFFECT OF CATIONS ON ADSORPTION OF K AND Na

Cation on colloid before adsorption of K and Na	ion (K or Na) which is better adsorbed	Figure
H	K > Na	11
NH_4	K > Na	5-9
Ca	K > Na	10
Mg	K > Na	Jenny[39]

TABLE 9.—EFFECT OF CATIONS ON RELEASE OF K AND Na

Cation adsorbed in exchange for K or Na	ion (K or Na) which is better released	Figure
H	Na > K	18, 19
NH_4	Na > K	16, 17
Ca	Na > K	Table 11
Mg	Na > K	

In the system which contains large amounts of H in ihe soil solution
there are also Al ions present which have no effect on the relative position
of K and Na in intake and outgo. Also for *mixtures of salts* the relative
behavior of K and Na remains undisturbed.

Ramann[68] treated a NH_4-Permutit with 0.5 n KCl+0.5 n $CaCl_2$ and also with a
mixture of 0.5 n NaCl+0.5 n $CaCl_2$. The amount of K adsorbed was found to be
0.253 equivalents and that of Na 0.186 equivalents (per 100 g. permutit). Similar
relationships were found for adsorption of K and Na in the presence of $MgCl_2$. NH_4-
permutit took up 0.329 equivalents K, but only 0.286 equivalents Na.
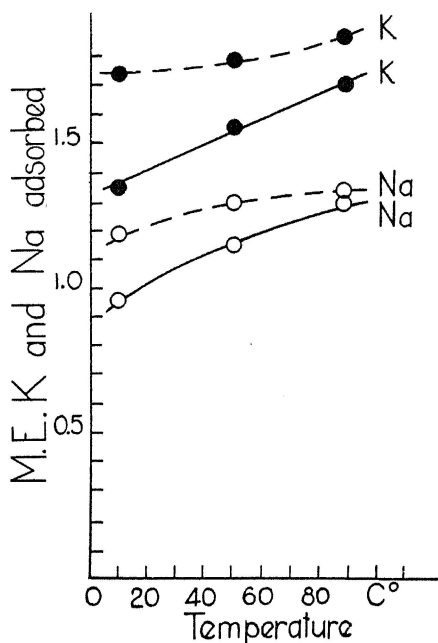
Fig. 20.—NH_4-PERMUTIT+KCl, NaCl.   0.6291g NH_4 permutit containing 2.07 milliequivalents exchangeable NH_4. Solid line: 3 M. E. KCl, NaCl added, dotted line: 10 M. E. KCl, NaCl added, total volume 250 cc. Time of reaction one week (in thermostats).
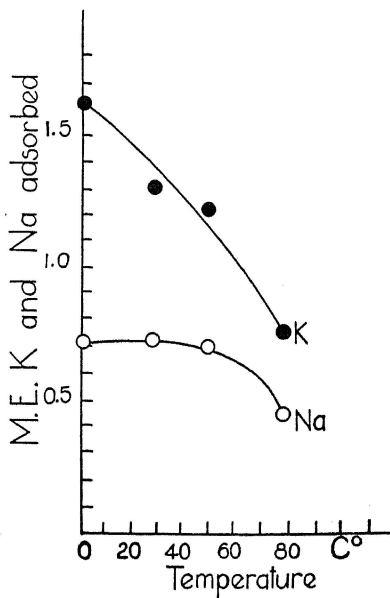
Fig. 21.—H-CLAY+KCl,   NaCl.   5.2g H-clay+25 milliequivalents KCl, NaCl; volume 500 cc. Kept for one week in thermostats.

Miyake[57] studied the effect of K and Na on the adsorption of NH_4 by a Hagerstown loam and observed that in the presence of K less NH_4 was taken up than in the presence of Na. Since this process includes "competition adsorption" the data indicate also that in the presence of NH_4, K is better adsorbed than Na.

Effect of Temperature

The effect of temperature on ionic exchange in soils is still a much disputed question, partly because only a few data are at hand. Those who believe in physical adsorption expect the intensity of ionic exchange to decrease with increasing temperature, while an observed increase is often interpreted as an evidence of a chemical reaction. From the viewpoint of soil formation under various climatic conditions, it is essential to know whether changes in temperature affect the relative behavior of K and Na. NH_4-permutit and H-clay were treated with KCl and NaCl at various temperatures (time of reaction one week). The results obtained are shown graphically in Figures 20 and 21. *It is clearly seen that the relative adsorption of K and Na is not affected by such temperature ranges as are found in soils.* K is better adsorbed than Na, at low temperature (1°C) as well as at high ones (80°C). It is of interest to note that the differential coefficient $\left(\dfrac{\text{d-adsorption}}{\text{d-temperature}}\right)$ is positive for NH_4-permutits (increasing slope of the curve) and negative for the H-clay (decreasing slope).

Influence of Lime on Base Exchange

Since the days of Way[85] and Liebig it is known that Ca CO_3 hastens ionic exchange of adsorbed ions. Recently MacIntire[50], followed by Magistad[51], have questioned the validity of this belief, arguing that $CaCO_3$ provides an alkaline medium which decreases the outgo (hydrolyses) of adsorbed cations. In view of the importance of carbonates in soil development it was found advisable to re-investigate the role of $CaCO_3$ in the liberation of cations. For the sake of accurate determination, the release of NH_4 ions in the presence or absence of carbonates was studied. In ionic exchange reactions NH_4 ions act very similarly to K ions, both ions having nearly the same ionic radii and hydration.

TABLE 10.—EXPERIMENTS WITH NH_4-COLLOIDS + $CaCO_3$ in excess

Colloid	Substance added	NH_4 exchanged	pH at equilibrium sol	pH at equilibrium Supernatant liquid
NH_4-Permutit_ _ _ _ _	H_2O	4.49%	_ _ _ _	7.00
NH_4-Permutit_ _ _ _ _ _	$H_2O+CaCO_3$	36.32%	_ _ _ _	8.75
NH_4-Permutit_ _ _ _ _	H_2O+KCl	53.88%	_ _ _ _	6.90
NH_4-Permutit_ _ _ _ _ _	$H_2O+KCl+CaCO_3$	71.10%	_ _ _ _	8.37
NH_4-Putnam clay_ _	H_2O	6.98%	_ _ _ _	_ _ _ _
NH_4-Putnam clay_ _	$H_2O+CaCO_3$	65.57%	7.95	7.76
NH_4-Putnam clay_ _	$H_2O+NaCl$	50.12%	5.13	6.10
NH_4-Putnam clay_ _	$H_2O+NaCl+CaCO_3$	74.22%	7.76	8.36

The data clearly show that in every case *$CaCO_3$ has increased very considerably the outgo of the NH_4 ion* from the surface of the colloid, in spite of the strongly alkaline reaction of the intermicellar liquid. Experiments are under way to check these observations for the K ion itself.*

Arany[77] has studied the effect of lime upon exchangeable K and Na in an alkali soil of Hungary. The shift in K and Na in the surface horizons due to liming is summarized as follows:

TABLE 11.—EFFECT OF LIME ON RELEASE OF K AND NA (ARANY)

Depth	Exchangeable K (Equivalent percentage) Before liming	After liming	Difference	Exchangeable Na (Equivalent percentage) Before liming	After liming	Difference
0-20 cm	3.796	2.393	—37.0%	56.751	16.528	—72.1%
20-40 cm	2.416	1.609	—33.5%	51.790	19.968	—61.5%

Application of lime decreased the amount of exchangeable K and Na very substantially. The loss of Na is about twice that of K. This decrease in exchangeable monovalent cations is exactly equivalent to the increase in divalent exchangeable cations.

*Note During Print: Mr. Shader's experiments performed in the writer's laboratory show that $CaCO_3$ replaces also K very energetically as seen from the following figures:
 K- Putnam clay + H_2O = 4.64 % exchanged (hydrolyses).
 K- Putnam clay + H_2O + $CaCO_3$ = 40.73 % exchanged (symmetry value).
 The pH values of the sols at equilibrium are 8.00 and 8.50 respectively.

General Summary of Experimental Studies

The laboratory studies reported together with data found in the literature indicate that the relative behavior of K and Na is primarily a result of their ionic properties and is to a lesser degree affected by the substances and factors associated with the exchange reactions. All results show that K is always better adsorbed and less released than Na, and that this is independent of the nature of the colloid, the pH value of the medium, or the temperature of the system. In all experiments the Na ion exhibits a greater association with the water phase than does the K ion. Of course, it is always possible that in further experiments an abnormal case of the behavior of K and Na might be discovered. But the fact that the experimental range taken into consideration is very wide and approaches natural conditions to a great extent puts the conclusions on a very broad basis. Both theoretical background and experimental evidence may be used, therefore, as a guide in the search for K-Na relationships in natural soil systems.

Distribution of Exchangeable K and Na in the Soil Profile

What conclusions can be drawn from the K-Na behavior in colloids in regard to the distribution of exchangeable K and Na in the soil profile? For the profile as a whole it can be simply stated that in humid regions exchangeable K tends to accumulate, while, relatively speaking, exchangeable Na will be leached.

The problem becomes more complex in the study of horizon distribution of K and Na. Not only leaching but also adsorption may take place in the same horizon, depending upon many factors such as concentration of K and Na on colloids and in the soil solution, presence or absence of the replacing ions Ca, Mg and H, nature of colloidal complex, migration of soil solution, effect of living organisms, and so forth.

Confronting such a diversified condition, it seems futile to attempt any quantitative formulation for the behavior of K and Na in the various horizons of a natural profile. Yet some valuable information might be gained by analyzing a less complicated, simplified or idealized soil profile. Of course, such a profile may not be found in nature but, nevertheless, one can get a mental picture of it, the study of which might reveal significant hints for the interpretation of more complicated, natural profiles.

The laboratory experiments cited have demonstrated that release and adsorption of K and Na is determined first of all by the composition of the soil solution.* The following two cases are important:

*Soil solution as used is equivalent to supernatant liquid or ultrafiltrate.

Class I. The soil solution contains predominantly cations other than K and Na, so-called "foreign cations" such as Ca, Mg, H, NH$_4$.

Class II. The soil solution contains predominantly K and Na ions. In soils of Class I, release of adsorbed K and Na is the main reaction taking place, while in soils of Class II, adsorption becomes an important feature. The behavior of K and Na in soils belonging to Class I will be discussed first.

The Potassium—Sodium Theorem

Soils of Class I with predominantly foreign cations in the soil solution include soils that contain calcium or magnesium carbonates, which, on account of their high solubilities, furnish considerable amounts of Ca and Mg ions to the soil solution. In an attempt to deduce the behavior of K and Na for a simplified profile of this type, a series of successive steps will be discussed.

Step one: Let us assume that there exists a horizon which contains only colloidal particles of identical composition. The following picture serves to illustrate schematically the principal reaction taking place on a single particle in contact with n Ca ions (n is a large number as compared with K and Na.)*

$$
\begin{array}{|c|}
\hline
K^+ \quad K^+ \quad K^+ \\
\hline
\text{colloidal} \quad K^+ \\
\text{complex} \quad Na^+ \\
\hline
Na^+ \quad Na^+ \quad Na^+ \\
\end{array}
+ n\ Ca^{++}
\quad \rightleftharpoons \quad
\begin{array}{|c|}
\hline
K^+ \quad K^+ \quad K^+ \\
\hline
\text{colloidal} \\
\text{complex} \\
\hline
Ca^{++} \\
\end{array}
Ca^{++} + (n-2)\ Ca^{++} \\
3Na^+ \\
1\ K^+
$$
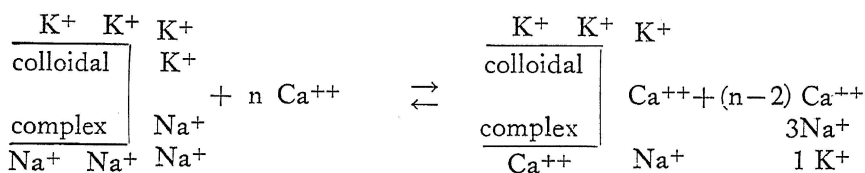
At the beginning there are 4 K and 4 Na ions present. Ca ions of the soil solution change place with these monovalent cations but replace more Na than K. At the end of the reaction there are on the surface of the colloid 2 Ca ions, but only 3 K ions and 1 Na ion. At the beginning the K/Na ratio on the clay was 1, and at the end it became 3. The result can be summarized by saying that *due to the effect of the foreign cation, the sum of K and Na on the colloid has decreased while the K/Na ratio has increased*. In other words, there exists a causal relationship between amount and ratio of K and Na on the colloidal particle.

In the above scheme the number of adsorbed K and Na ions is equal. However, this assumption is unnecessary. In view of the experimental data obtained the foreign cations will always replace more Na (on a percentage basis) than K and therefore widen the K/Na ratio,

*The minimum value of n must be great enough to give every adsorbed K and Na ion an equal probability to be "hit" by a foreign ion.

decreasing at the same time the sum of K and Na. Similarly the presence of other exchangeable cations on the colloid does not alter the conclusion drawn.

Step Two: In the next approach to the conditions of a natural soil profile the assumption is made that all horizons are identical but that the concentration of the foreign cation in the soil solution varies in different horizons. After ionic exchange has taken place one would expect to find that in every horizon the sum of K and Na has decreased while K/Na has increased, the magnitude of the change depending upon the concentration of the foreign cation in the soil solution. Not knowing the original values for the sum of K and Na, and K/Na, or the exact concentration of the foreign ion, one could nevertheless state that *the widest K/Na ratio occurs in that horizon which has the smallest sum of K and Na.* Of course, this conclusion only holds under the assumption that after equilibrium is established the soil solution itself has not moved upwards or downwards. Again the initial condition may be varied without alteration in the conclusion drawn. At the outset of step two, it is not necessary that all horizons be identical in regard to K and Na, and K/Na.

Step three: As a consequence of step two the soil solution contains beside foreign ions (Ca) some K and Na ions, although only in small amounts by definition. In nature the soil solution constantly moves upward and downward, giving the various horizons a slight chance to re-adsorb some of the released K and Na ions, thus increasing again the sum of K and Na. This increase in K and Na naturally will be accompanied by a slight change in K/Na ratio on the colloid depending upon the ratio of K and Na in the percolating soil solution.

Obviously this third step may slightly modify the conclusion drawn under step 2, as a result of migrating soil solutions. It may thus happen that the widest K/Na ratio is not found in the horizon which has the smallest sum of K and Na. In order to account for this possible disturbance, the result of step 2 may have to be modified to read as follows: *The horizon with the smallest sum of K and Na has a wider K/Na ratio than the horizon with the greatest sum of K and Na.* This conclusion is also expressed in the following equation:

$$\frac{K/Na \text{ of } (K+Na)_{\text{minimum}}}{K/Na \text{ of } (K+Na)_{\text{maximum}}} => 1$$

The experimental evidence of this theorem is limited to soil profile analyses which determine the amount and nature of exchangeable bases.*

*Of course it all depends how closely the natural profiles approach the conditions set for the theorem.

These, however, are yet scanty. The following data were found in the literature.

TABLE 12.—PROFILE OF HORTOBAGY, HUNGARY (SZIK SOIL)
(Sigmond[77], page 329)

| Depth | Milliequivalents exchangeable cations in 100 g of soil* | | | K/Na | %CaCO$_3$ in soil | %Na$_2$CO$_3$ in soil |
	K	Na	K+Na			
A$_1$ 0- 9cm	1.2	7.7	8.9	0.156	0	0
B$_1$ 9- 29	1.0	14.6	15.6	0.068	0	0
B$_2$ 29- 55	0.9	23.8	24.7	0.038	0	0
B$_3$ 55- 70	1.0	20.5	21.5	0.049	0	Trace
C$_1$ 70-100	1.8	14.6	16.4	0.123	16.36	0.14
C$_2$100-125	2.9	12.4	15.3	0.234	26.25	0.17
C$_3$125-137	2.4	14.0	16.4	0.171	24.25	0.20
D 137-150	2.0	12.8	14.8	0.156	23.77	0.09

The last two columns indicate that the soil solution contains chiefly foreign cations principally Ca. The profile belongs, therefore to Class I. The greatest value for K+Na is found in the B$_2$-horizon and the smallest in the A$_1$. In agreement with the theorem, the horizon with the smallest K+Na value (A$_1$ horizon) has a wider K/Na ratio than the horizon with the greatest K+Na value (B$_2$ horizon).

TABLE 13.—PROFILE OF KESZTHALEY (HUNGARY)
(Sigmond[75], page 471)

| Depth | Milliequivalents exchangeable bases in 100 g of soil | | | K/Na | %CaCO$_3$ in profile |
	K	Na	K+Na		
0- 25 cm	0.152	0.376	0.528	0.40	4.41
25- 50	0.134	0.408	0.542	0.33	8.27
50- 60	0.158	0.066	0.224	2.39	8.96
60- 70	0.108	0.344	0.452	0.31	23.90
70-150	0.204	0.222	0.426	0.92	49.70

The presence of much CaCO$_3$ places this profile also into Class I. Again the horizon with the smallest sum of K+Na has a wider K/Na ratio than the horizon with the greatest sum of K+Na.

TABLE 14.—SOUTHERN CHERNOZEM (RUSSIA)
(Gedroiz[28], page 218)

| Horizon | Milliequivalent exchangeable cations in 100 g of soil | | | K/Na |
	K	Na	K+Na	
A$_1$ 0- 6 cm	1.508	0.309	1.817	4.88
B$_1$ 20- 29 cm	0.614	0.174	0.788	3.53
C$_1$ 75- 83 cm	0.537	6.73	7.267	0.08
C$_3$ 175-183 cm	1.203	11.05	12.253	0.11

*For certain profiles it might be of advantage to express K and Na in percentage of saturation capacity.

The analytical data do not show whether this profile contains $CaCO_3$. Since, however, chernozems belong to the pedocals (soils with $CaCO_3$ horizons), this profile was grouped under Class I. The correlation between small K+Na and wide K/Na ratio is also manifested.

TABLE 15.—CHESTNUT SOIL FROM HUNGARY (CSORVAS)
(Sigmond[66]: page 305)

Horizon	Milliequivalents exchangeable cations in 100 g of soil*			K/Na	%CO₂
	K	Na	K+Na		
A₁ 0- 18 cm	1.02	0.80	1.82	1.28	0.46
A₂ 60- 80 cm	1.25	1.10	2.35	1.14	2.11
A₃ 100-120 cm	1.00	3.50	4.50	0.29	6.62

The A₁ horizon with the smallest K+Na value has a much wider K+Na ratio than the A₃ horizon with the greatest K+Na value.

All soil analyses so far discussed indicate that the K/Na theorem seems to be a working principle which regulates the distribution of exchangeable K and Na in profiles belonging to soils of Class I.

Soil Profiles with K and Na Predominating in the Solution. (Class II)

Soils belonging to this group include many soils from arid regions, particularly the alkali soils. Soils in humid regions, derived from parent material low in Ca and Mg (many igneous rocks) and soils which are under the influence of ground water rich in K and Na are also to be classified under this group.

The problem is more complicated in that adsorption of K and Na occupies a prominent place in the exchange reactions. Two main types of profiles have to be distinguished:

    a.   those in which K=Na, or K>Na in the soil solution;
    b.   those in which K<Na in the soil solution;

At present, no scheme can be formulated in this case because it is not yet definitely known whether K or Ca is better exchanged by Na, particularly under high pH values. Unless laboratory experiments clarify the mutual exchange of monovalent and divalent cations in various soils, —as has been done by the author for permutits—no definite predictions can be made.

Relationships Between K and Na in Total Analysis of Soil Profiles

Total K and Na determinations in soils include both the exchangeable and non-exchangeable ions in weathered and unweathered material, (including organic substances). Although it is possible that the outgo of K and Na from the same surface of unweathered mineral follows similar ionic exchange principles as in colloids, it must be kept in mind that in all probability K and Na in unweathered materials, are bound

in different crystal frames, thereby disturbing the normal outgo of each. For example, data indicate that K bound in glauconite is more easily exchanged than Na bound in plagioclase. Such variations and further irregularities brought about by actions of micro-organisms will necessarily violate any conclusions drawn on the base exchange experiments cited. The main thing, to look for in the total soil analyses is whether or not they will *reflect the same trend of K and Na behavior* as is found in the colloidal exchange complex. This should be most pronounced in well weathered soils in which the colloidal fraction dominates over the unweathered Al-silicates.

Terminology

For the interpretation of total analyses it is best to relate K+Na to some soil compound which is not affected by weathering. Real changes in K+Na could then be easily traced. Such inert substances would be, for instance, platinum, gold, silver and possibly quartz. Most soil analyses, however, do not include these constituents. A relatively stable substance, as compared with K and Na, is Al_2O_3 although it is known that Al sometimes migrates, particularly in podsolized soils. Instead of simply using K+Na, the ratio $\dfrac{K_2O+Na_2O}{Al_2O_3}$ was preferred which is designated throughout the paper by ba_1 (*ba* derived from *ba*ses, the index referring to monovalent). The index is used in order to distinguish ba_1 from the value "ba" which is used by Harrassowitz[32] to express the ratio $\dfrac{CaO+K_2O+Na_2O}{Al_2O_3}$. These values receive also some theoretical justification from Pauling's[63] studies on Al-Si-structures.* The K/Na ratio refers to the value $K_2O : Na_2O$, all expressed in molecular values.

In order to become independent of the frequent minor changes in atomic weights, Washington and Niggli[31] suggest (for international use) the following molecular values:

$$Al_2O_3 = 102$$
$$K_2O = 94$$
$$Na_2O = 62$$

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*Pauling thinks that in silicates the cations K and Na are surrounded by eight oxygen ions with a corresponding electrostatic bond strength of ⅛. Such crystals should have a tendency to a 1:1 ratio for the alkali and the aluminum ion. This ratio is observed in a large number of silicates, especially in the important felspars.

The ba_1 and K/Na Values of Parent Material

Interesting conclusions can be drawn from a survey of ba_1 and K/Na of parent materials. From the data of Clarke[16] the following table was calculated:

TABLE 16.—K-Na RELATIONSHIPS IN VARIOUS TYPES OF PARENT MATERIALS

Type of Rocks	Igneous rocks	Shales	Sandstones	Limestones
Number of analyses	1252-1703	78	253	345
$ba_1 = \dfrac{K_2O + Na_2O}{Al_2O_3}$	0.589	0.433	0.454	0.544
$K/Na = \dfrac{K_2O}{Na_2O}$	0.596	2.114	1.935	4.351

It will be noticed that all average ba_1 values of the sedimentary rocks are smaller than those of the igneous rocks, indicating a loss of monovalent bases (on the assumption that Al remained constant) during the process of transformation of igneous material. At the same time the K/Na ratio increased, demonstrating that Na has been more affected than K. If one considers igneous rocks as parent material and sedimentary rocks as the weathered horizon, the whole system represents a huge soil profile, in which the differential leaching of K and Na is the same as that observed in soil colloid investigations. The Na lost should be found in the groundwater, in rivers, and in the ocean. Hevesy[37] states that 35 million tons of Na are annually carried by the rivers into the ocean. At present the K/Na ratio in the ocean is 0.0212 (Clarke[16]) or, for every K ion there are 47 Na ions present. The following scheme illustrates convincingly the shift in the relationship between K and Na. The quotients indicate number of Na ions per K ion present:

$$\text{Igneous rocks} \xrightarrow{\text{weathering}} \text{Sedimentary rocks}$$

$$\frac{Na}{K} = \frac{1.68}{1} \qquad\qquad \frac{Na}{K} = \frac{1}{3.18}$$

leaching

Rivers and lakes

$$\frac{Na}{K} = \frac{4.63}{1}$$

Ocean

$$\frac{Na}{K} = \frac{47.18}{1}$$
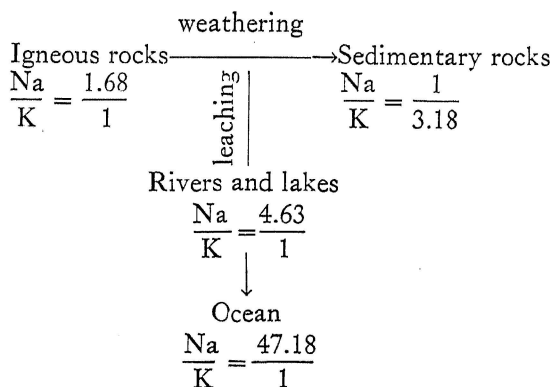
In igneous rocks Na predominates, while in sedimentary rocks K is present in larger quantities. In the extracted "soil solution" (rivers) this original predominance of Na over K is intensified by about 175 per cent. In the ocean the Na/K ratio is more than 10 times wider than in rivers which demonstrates the easier replaceability of Na over K. *Summarizing*, it can be said that in sedimentary rocks the K/Na ratio is narrower than in igneous rocks while in rivers, lakes and oceans it is much wider.

COMPARISON BETWEEN "LEACHED" HORIZON AND PARENT MATERIAL IN SOIL PROFILES

From the viewpoint of ionic exchange one would expect to find that the soil horizons (Solum) would have smaller ba_1-values $\frac{(K_2O+Na_2O)}{Al_2O_3}$ and wider K/Na ratios than the parent material; this would only be expected however, in regions where the downward migration of water exceeds the upward movement. In other words, the relationship between ba_1 of the parent material and ba_1 of the soil horizons will be affected by climatic conditions. It might also be possible to find a correlation between the magnitudes of K/Na and the various ba_1 values (compare page 26). This should be particularly the case for soils of Class I which contain Ca- or Mg- carbonates.

From the profile data at hand, the ba_1 value and the K/Na ratio were calculated for every analyzed horizon. That horizon in the solum (the "solum" means all horizons except the parent material) which had the lowest value of ba_1 was called the "leached horizon" with respect to K and Na. This ba_1 value was then compared with ba_1 of the parent material by forming the following quotient, called *leaching value*,

$$leaching\ value\ \beta = \frac{ba_1\ of\ leached\ horizon}{ba_1\ of\ parent\ material\ (C\text{-}horizon)}$$

which was designated by β (beta). Similarly for the K/Na ratio the following *shifting value* was formed:

$$Shifting\ value\ \mu = \frac{K/Na\ of\ leached\ horizon}{K/Na\ of\ parent\ material\ (C\text{-}horizon)}$$

"K/Na of leached horizon" means the K/Na ratio of that horizon in the solum (excluding C-horizon) which has the lowest ba_1 value. The ratio was called μ (mu—from first letter of *m*onovalent bases). With these leaching and shifting values the behavior of K and Na in various soil profiles can be easily described in an exact way.

A profile in which K, Na and Al have not undergone any change, evidently has a β and μ value of 1.

All analyzed profiles were grouped according to parent materials and climatic soil types. Following the reasoning developed in the

discussion on exchangeable bases, all soils were divided into the two main classes: *I. Soils containing carbonates (Ca, Mg) and II. Soils not containing carbonates.* The arrangement of the profiles is shown in the following tabulation:

A. *Groups of parent material*

Class I. Soils containing carbonates (more than 1%).
a. sedimentary rocks (shales, sands, moraines, loess)
b. limestones

Class II. Soils containing no carbonates:
a. igneous and metamorphic rocks
b. sedimentary rocks (shales, alluvial sands, moraines)*

B. *Groups of climatic soil types*[29, 40]

Podsolized soils (including arctic soils, podsols, brown timber soils, Ramann's brown earth, prairie soils, rendzina, wiesenböden)

Yellow-red soils (only those of humid regions mainly from America.)

Laterites

Chernozems (including a few chestnut soils)

Effect of Parent Material on Leaching (β) and Shifting (μ) Values in Podsolized Soils

Most of the profiles in which parent material has been analyzed belong to the podsolized group. Table 17 contains a summary of the calculated β-values and μ-values. The column under "β<1" gives the number of cases in percentage which have a leaching value smaller than 1. Similarly the column "μ>1" contains the number of profiles, expressed in percentage, than have a shifting value greater than 1.

TABLE 17.—Effect of Parent Material on Leaching (β) and Shifting (μ) Values of K and Na in Podsolized Soils

Nature of parent material	Number of Analyses	Leaching value (β)		Shifting value (μ)	
		Average	β<1	Average	μ>1
Limestones	9	0.488±0.141	90%	2.272±0.500	90%
Sedimentary rocks with CaCO₃	12	0.719±0.053	92%	>1.516±0.208*	75%
Igneous rocks	19	0.822±0.073	74%	1.805±0.245	84%
Sedimentary rocks without CaCO₃	28	0.934±0.068	72%	1.347±0.201	68%

*The sign > means "greater than".

The mean error of the average was calculated according to the common formula

$$m = \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

*This class includes a few profiles with less than 1 per cent CaCO₃.

Owing to the fact that in some instances the average values were computed from a limited number of analyses, "Students" tables must be consulted in judging the reliability of the means (Compare M. Ezekiel, Methods of Correlation Analyses, p. 392, 1930). Both β and μ values reveal a number of very interesting features in regard to K-Na relationships in soil profiles as influenced by the type of parent material.

    a) **Effect of parent material on leaching of K and Na (β-values).—** It is clearly seen that for all types of parent material the average β-value is smaller than 1, indicating that K and Na have been leached out in the process of profile development.* (Table 17).

    But this "leaching" is different for various kinds of parent material. Limestone soils are outstanding in that they have the lowest β-value of all groups of parent material, indicating a great loss in K and Na; next come the sedimentary rocks containing carbonates, then the carbonate-free sedimentary rocks and finally the igneous rocks. The mean errors, however, are too large to establish statistically these differences in the form of simple β averages. A better way of showing the significance of the various β-values is in the form of frequency distribution curves as given in Figure 22 in which class averages of .20 units were used. The *modes*, corresponding to the peaks in the curves, exhibit the same trend as the average values as seen from the following table:

TABLE 18.—RELATION BETWEEN LEACHING VALUE AND PARENT MATERIAL AS EXPRESSED IN MODES. (Podsolized soils).

Parent material	β-value of mode
Limestones	0.30
Sedimentary rocks with carbonates	0.70
Igneous rocks	0.80
Sedimentary rocks without carbonates	0.90

    The limestone soils again exhibit the greatest leaching of K and Na.

    From the viewpoint of the ionic exchange principle, it is of particular interest to compare the two classes—*soils with carbonates, and soils without carbonates*, as a whole. This is done in Table 19.

TABLE 19.—β-VALUES AND μ-VALUES OF SOILS "WITH" AND "WITHOUT" CARBONATES (Podsolized soils).

Soil class	Number of analyses	Leaching value		Shifting value	
		Average	$\beta < 1$	Average	$\mu > 1$
Class I: Soils with $CaCO_3$	21	0.620 ± 0.071	91%	1.857 ± 0.252	82%
Class II: Soils without $CaCO_3$	47	0.888 ± 0.047	72%	1.532 ± 0.163	75%

*Always assuming that Al remained stable.

The data show that the two classes differ markedly in their leaching values. Soils with $CaCO_3$ in the profile have an average β-value which is 30% lower than the one for $CaCO_3$—free soils. From a statistic standpoint, the difference is significant, being greater than the three-fold mean error of the difference. According to Table 19 the displacement of K and Na is hastened in the presence of $CaCO_3$ and $MgCO_3$. This may be partly due to ionic exchange reactions, and partly due to the fact that the total amount of K and Na in pure limestone soils is very small at the beginning of the process of soil development. The few low β-values of igneous rocks refer to basalts which are very rich in Ca. These profiles, apparently on account of the abundance of Ca in the soil solution, behave as soils of Class I.
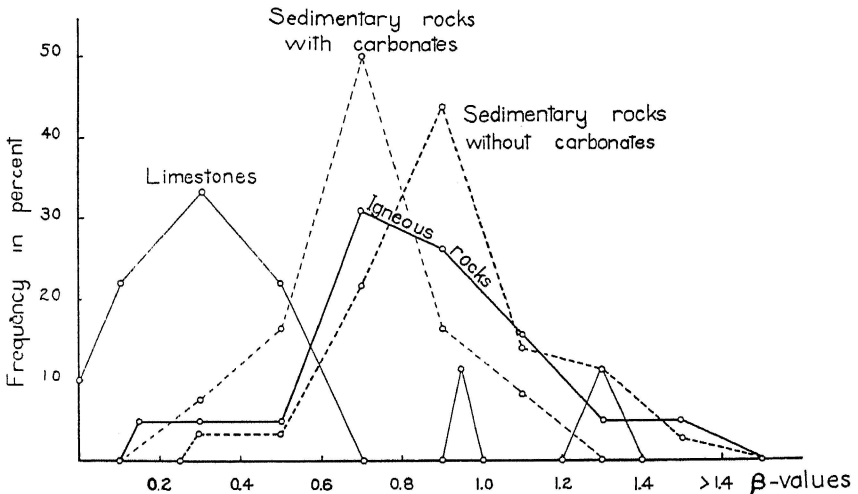
Fig. 22.—Frequency distribution of leaching values (β) of podsolized soils as affected by parent material.

Although all β-value-averages are smaller than 1, it can be seen under the column "$\beta < 1$" that β has not become smaller in every case. In fact, about 10% of the lime-containing rocks and nearly 30% of the profiles containing no carbonates have β-values greater than 1. It means that all horizons in these profiles have higher ba_1 values than the parent material. If one assumes that Al_2O_3 is stable the conclusion would follow that K and Na have accumulated in such a profile even in its most leached horizon. This, however, is hardly acceptable because the profiles were all developed in humid regions, some under extremely high moisture conditions. The proper explanation—so far as can be seen— is that Al_2O_3 has also been leached in those profiles, in fact more strongly than K and Na.
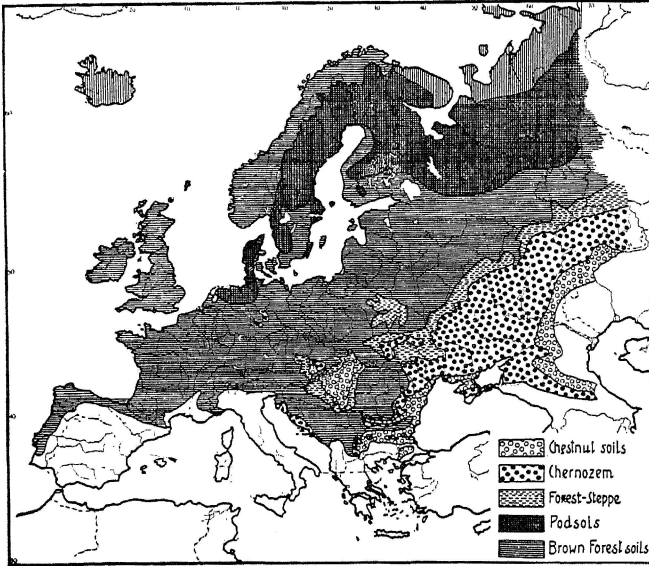
Fig. 23.—Climatic soil types of Europe investigated for the K-Na-relationship (after Stremme and Coll).
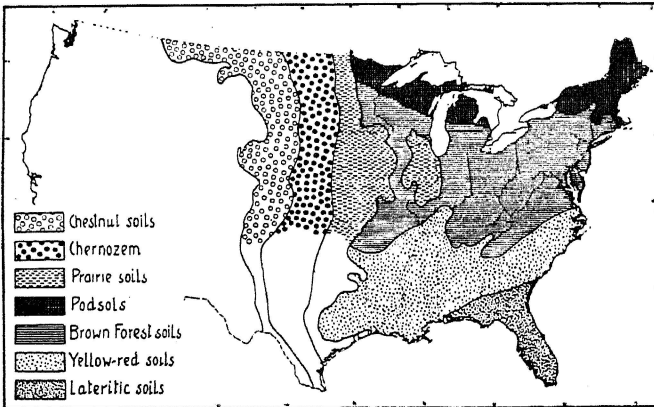
Fig. 24.—Climatic soil types of the United States of America investigated for the K-Na-relationship (after C. F. Marbut).

Migration of Al_2O_3 is typical for podsols and has been explained by the protective action of acid humus, which prevents flocculation of the positively charged $Al(OH)_3$ sols.[88] It is characteristic for soils of Class I (containing carbonates) to have a much smaller percentage of β values > 1. Neutral or alkaline reactions are not favorable to the migration of Al_2O_3. In such soils the podsolization process which is characterized by migration of sesquioxides is retarded.

b) **Effect of parent material on shifting of K and Na (μ-values).—**
By definition the μ-value stands for a quotient in which the K/Na ratio
of leached horizons is compared with the K/Na ratio of the parent
material. From Table 17 it is seen that all μ-value-averages of the various
parent materials are greater than 1, indicating that in general more Na
was lost than K. Limestone soils have the highest μ-value, namely 2.272,
and sedimentary rocks without carbonates the lowest ($\mu = 1.347$). A simi-
lar relationship is observed for the two soil classes as a whole. Soils con-
taining carbonates (Table 19) average 1.857 for the μ-value, while
soils without carbonates average only 1.532. The mean errors, however,
are too large to establish the difference on a statistical basis. The in-
creasing trend of the μ-value is also supported by the percentage figures
"$\mu > 1$" (Tables 17-19.) More soils of Class I than of Class II have μ-
values greater than 1. The tendency that wide K/Na ratios are asso-
ciated with pronounced leaching is clearly manifested in these profiles.

Summary: The effect of parent material on the K-Na relationship
in podsolized soils is very pronounced. It justifies, in particular the
separation of the profiles into those having carbonates, (Class 1) and
those having no carbonates (Class II). In soils of Class I, especially
in limestone soils, the leaching of K and Na as compared with Al_2O_3
is more advanced than in soils of Class II as judged from the magnitudes
of the leaching values (β). The difference is statistically established and
amounts to 30%. Apparently the presence of $CaCO_3$ or $MgCO_3$ hastens the
translocation of K and Na and retards that of Al in the soil profile. Inspec-
tion of the number of profiles having β-values greater than 1 reveals that
in a considerable number of these podsolized soils Al disappears faster than
K and Na which is probably due to the migration of colloidal Al-sols
under the protective influence of humus. This effect is much more
pronounced in soils of Class II than in soils derived from parent material
containing carbonates. The average μ-value, illustrating the shift in
the K/Na ratio, is beyond doubt "greater than one" for all soil groups,
indicating that more Na than K has been lost during the process of
horizon development. There is the observed tendency that soils of Class
I have a wider K/Na ratio in the leached horizon than soils of Class II,
and furthermore, that low β-values are associated with high μ-values,
although these findings cannot yet be established on a statistical basis.

*Generally speaking the average leaching and shifting values conspicuous-
ly reflect the presence of ionic exchange reactions in soil formation.*

Effect of Climate on Leaching and Shifting Values

(Discussion on the basis of climatic soil types)

The conclusion arrived at in the basic exchange studies that parent material, or more precisely the nature of the soil solution, is more important than temperature and water in affecting the behavior of K and Na, makes it necessary to keep the parent material constant in discussions of K-Na relationships in climatic soil types.

1) **Podsolized soils and Chernozems.**—Podsolized soils and chernozems are mainly found in temperate and cold regions of Eurasia and North America.[29, 40] The main difference between the two types is one of humidity, the chernozems being developed in semiarid and semi-humid regions, while the podsolized soils are mainly found under humid and perhumid climates. According to Marbut the chernozems belong to the group of pedocals, while the podsolized soils are typical for pedalfers. The calculation of β and μ-values has been restricted to soils derived from sedimentary rocks containing carbonates (Class Ia).

In Table 20 the leaching and shifting values of the two groups are listed and it is evident that the figures are very characteristic for the two climatic soil types.

TABLE 20.—EFFECT OF CLIMATE ON LEACHING AND SHIFTING VALUES OF SOILS CONTAINING CARBONATES. (CLASS Ia)

Soil groups	Number of analyses	Leaching value		Shifting value	
		Average	$\beta<1$	Average	$\mu>1$
Podsolized Soils (humid region)	12	$0.719\pm.053$	92%	$1.516\pm.208$	75%
Chernozems (Semi-humid to semi-arid region)	15	$0.981\pm.059$	60%	$1.066\pm.070$	67%

The average *leaching value* (β) of podsolized soils is considerably smaller than that for chernozems. The difference 0.262 ± 0.0798 is significant from a statistical point of view in that the difference exceeds

the three-fold mean error. The β-figure may thus become of value as an exact numerical expression for the group separation of chernozems and podsolized soils.* The observation that the β-value for chernozems is about 36% higher than the β-value of podsolized soils is very instructive in regard to climatic influences and can be safely interpreted as being due to less leaching. Chernozems are known as those soils in which leaching and accumulation of mineral matter approximately balance each other. The fact that the β-value of this group of soils, approaches the magnitude of 1 (0.981) quantitatively supports this belief.

In podsolized soils derived from lime-containing parent material, nearly all profiles (except 8%) have a β-value <1, indicating that K and Na are more leached than Al_2O_3. In chernozems, however, a surprisingly high number of cases (40%) have β-values, greater than 1, showing that every soil horizon contains more K and Na than the parent material. In other words, on the basis of the β-value, K and Na have moved upwards in these profiles. Of course, there remains the possibility that the high β-values are due to losses of Al_2O_3. But various pedological reasons speak against this argument. The soil reaction of chernozems fluctuates closely around the neutral point which, according to colloid chemical investigations, permit little chance for migration of Al_2O_3.[15, 88] The stability of Al_2O_3 is also manifested in the relatively constant $SiO_2:Al_2O_3$ ratio of the various soil horizons. Figure 25 shows that the β-value differences of chernozems and podsols are also pronounced in frequency diagrams.

The shifting values (μ) indicate the same trend in the soil formation process. The average μ-value of the chernozems differs little from 1, as does the β-value; in other words, the K/Na ratio of the most leached *horizons is only slightly higher than that of the parent material.* This also indicates that leaching and accumulation of K and Na in chernozems are well balanced. The μ-value of the more humid, podsolized soils is considerably higher corresponding to the smaller β-value of that soil group on account of more pronounced leaching.

Summarizing the data found in comparing chernozems with podsolized soils it can be said that the K-Na relation is manifested in both soil groups. Taken as a whole Na is more leached than K. Furthermore, the magnitude of the leaching and shifting-values seems to be a sensitive indicator for the climatic factors active during the formation

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*Also arid soils may have β-values smaller than one, but the position of the leached horizon within the profile is different from soils of humid regions.
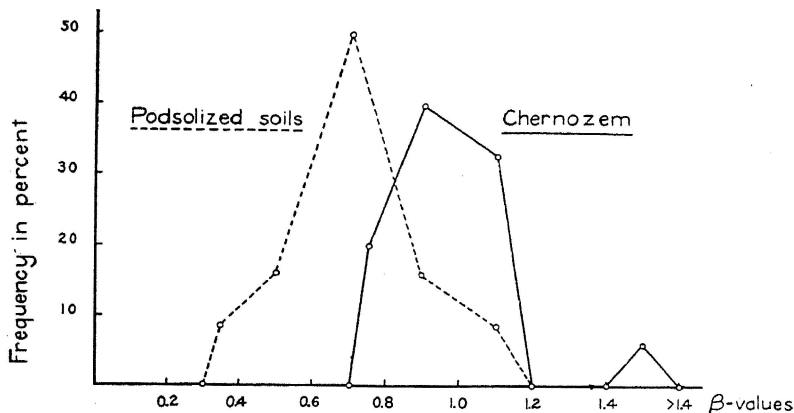
Fig. 25.—Frequency distribution curve of leaching values of podsolized soils and chernozems derived from sedimentary rocks containing carbonates.

of these two soil groups. Under higher humidity conditions, the leaching of the K and Na is very pronounced which exhibits itself in a low β-value of the podsolized soils. Chernozems which lay at the boundary of arid and humid climates have leaching and shifting values approaching the magnitude 1 which indicate that little translocation of K and Na during soil formation has taken place.*

2) **Comparison between podsolized soils, yellow-red soils and lateritic soils.**—These climatic soil groups are all found in humid regions, the main differences being due to temperature. Podsolized soils are mainly found in cold and temperate regions, yellow-red soils in sub-tropical regions and laterites in certain tropical districts.[29, 40] This grouping is a very broad one and exceptions are known. The study of these soils is restricted to such profiles as are derived from igneous and metamorphic rocks; in other words, the parent material is kept constant

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Note During Print.
Hopper, Nesbitt and Pinckney have published 29 total analyses of "chernozem-like" soils of North Dakota. Computation of β and μ results in the following average values:

leaching value $\beta = 0.915$
shifting value $\mu = 1.201$
per cent $\mu_a > 1 = 80\%$

Well drained upland soils (Barnes, Bearden) have somewhat lower β values, namely 0.881, while the poorly drained soils (Fargo, Valentine, Lamoure) with little leaching average $\beta = 1.039$. See:
Hopper, T. H., Nesbitt, L. L., and Pinckney, A. J.: The chemical composition of some chernozem-like soils of North Dakota. North Dakota Agr. Exp. Station, Technical Bulletin 246, 72 pages, 1931.
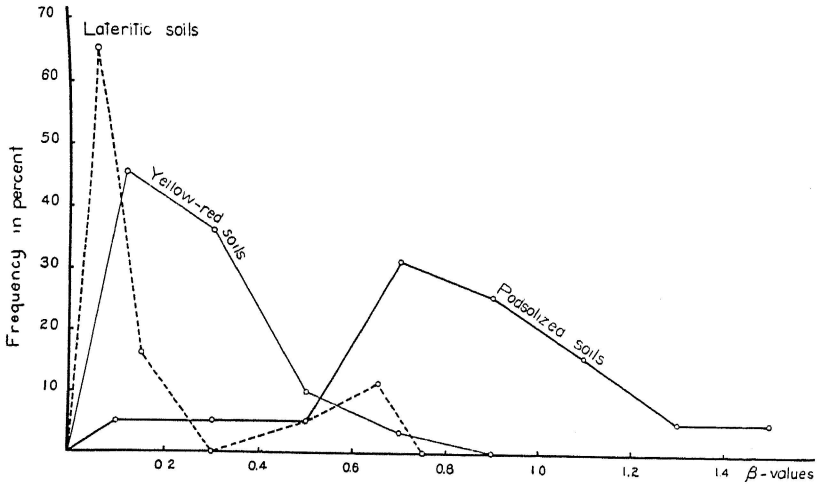
Fig. 26.—Frequency distribution of leaching values (β) of climatic soil types derived from igneous and metamorphic rocks.

and the soils belong to the general Class II_a, which includes parent materials and profiles having no carbonates. As seen from Table 30 in many profiles only the parent material and surface horizon were analyzed and apparently no attention was given to intermediate horizons. This restricts, somewhat, the possibilities for interpreting the differences in greater detail. In Table 21 the various data are arranged according to the climatic soil types mentioned.

Leaching values. The average β-values decrease consistently from the podsolized soils to the yellow-red soils and laterites, indicating an increase in stage of weathering from north to south. For instance, the average β-value of laterites is 83% lower than that of podsolized soils. The table also shows the significant fact that for the yellow-red and lateritic soils all β-values are smaller than one, indicating that in every profile K and Na are more leached than Al_2O_3. This is in agreement with the general observation that in southern soils Al_2O_3 is relatively more stable than in northern soils.

TABLE 21.—LEACHING AND SHIFTING VALUES FOR PODSOLIZED, YELLOW-RED AND LATERITIC SOILS, (DERIVED FROM IGNEOUS AND METAMORPHIC ROCKS)

Soil group	Number of analyses	Leaching values (β)		Shifting values (μ)	
		Average	$\beta < 1$	Average	$\mu > 1$
Podsolized soils	19	$0.822 \pm .073$	74%	$1.805 \pm .245$	84%
Yellow-red soils	25	$0.278 \pm .035$	100%	$2.767 \pm .590$	72%
Lateritic soils	18	$0.141 \pm .050$	100%	3.206 ± 1.099	87%

The differences between the β-values of podsolized soils on the one hand and yellow-red and lateritic soils on the other, are beyond question because they exceed many times the mean error of the difference. The observed change in β from yellow-red to laterites, however, cannot yet be established statistically because both groups contain a few β-values which are abnormally high. A good illustration of the trend of the leaching values from north to south is presented in Figure 26, which shows a frequency distribution diagram based on β-class averages of 0.2 units. The curves are unsymmetrical distribution curves and the peaks lean against the lower β-values.*

Shifting values: The average μ-values increase from podsolized soils to the laterites, from 1.805 to >3.206. The sign $>$ indicates that in a number of cases the K/Na ratio of the soils is infinite, that is, all Na is lost and K is the only monovalent base left. The infinite value could, of course, not be included in the average. The variation of the μ-values within the various groups is great, thereby not permitting a definite statement as to the validity of the shifting value as an exact criterion for characterizing quantitatively the three soil groups. The simultaneous trend of the μ-values and β-values, however, is obvious. β decreases from north to south, while μ increases. The number of profiles having μ-values greater than one is highest in laterites. This is to be expected since the ratio of colloidal-Al-silicates to unweathered Al-silicates is greater, the more intense and advanced the weathering process. The greater this ratio, however, the more will the behavior of K and Na in soils be governed by the relationships found in the study of pure soil colloids.

Summarizing the effect of climate, it can be said that the K−Na relationship exhibits characteristic magnitudes in various climatic soil types. In semi-arid to semi-humid regions (Chernozems) with limited leaching, both leaching and shifting values are approaching the value one, indicating little change in the absolute and relative translocation of K and Na. In humid regions, the "leached horizon" shows a decided loss in monovalent bases accompanied by a significant increase in the K/Na ratio. This behavior of K and Na is intensified as one goes from north to south passing through the climatic soil types: podsols, yellow-red soils, and laterites. Higher temperature, more rainfall, and longer time of weathering are some of the factors responsible for low β-values and high μ-values in soils of southern latitudes.

*The few low β-values of the podsolized soils belong to profiles developed on basaltic rocks rich in calcium. It might have been appropriate to exclude these samples since the high Ca-content gives them the characteristics of soils of Class I (compare page 35).

TABLE 22.—SHIFTING VALUES OF K AND Na ON THE BASIS OF PARENT MATERIAL (μ) AND ACCUMULATION HORIZON (μ_a)

Soil groups	Shifting values		Trend of change	Number of analyses
	Percentage of soils having $\mu > 1$ (parent material)	Percentage of soils having $\mu_a > 1$ (accumulation horizon)		
Class I: Soils containing $CaCO_3$				
a. *podsolized soils*				
limestones_____	89%	100%	increase	19
sedimentary rocks_____	75%	83%	increase	12
b. *chernozems* _____	67%	73%	increase	15
Class II: Soils without $CaCO_3$				
a. *podsolized soils*				
igneous rocks_____	84%	53%	decrease	19
sedimentary rocks_____	68%	57%	decrease	28
b. *yellow-red soils*_____	72%	64%	decrease	25
c. *lateritic soils*_____	87%	87%	no change	15

THE TREND OF THE SHIFTING VALUE (μ) OF K AND NA IN LEACHED AND ACCUMULATION HORIZONS

In the study described thus far the leached horizon of the profile has been compared with the parent material. In agreement with the K-Na relationship observed in colloids, the average K/Na ratio was found to be wider in the leached horizon than in the unweathered rock. But there are a considerable number of individual profiles in which for some reason this relationship does not hold. From the viewpoint of ionic exchange it is advisable to compare the K/Na ratio of the leached horizon not only with the parent material but also with the K/Na ratio of the accumulation horizons. This is done in Table 22. The "accumulation horizon" is that horizon in the profile—including the parent material—which has the highest ba- value. In order to distinguish between the two shifting values, the new factor is called μ_a the superscript "a" designating "accumulation horizon".

The comparison between the two shifting values throws very interesting light upon the behavior of the two soil classes. All soils which contain carbonates (class I) show an increase in the number of profiles having shifting values "greater than 1" while for the soils of Class II (no carbonates) the percentage decreases with the exception of laterites which exhibit no change. In soil of Class I, ($Ca\ CO_3$) 84 out of a hundred have a wider K/Na ratio in the leached horizon than in the accumulation horizon. The average for soil of Class II is only 65%

In the search for soil analyses in the literature it was noticed that the parent material often had not been analyzed. Furthermore, in a great number of soil analyses, particularly those from the United States, it is not evident whether the C horizon has been included, since only the depth of the various layers is mentioned. For these soils the behavior of K and Na can only be studied on the basis of leached and accumulation horizon (lowest and highest ba_1-value in the profile). These soils were grouped according to the following procedure: Whenever a CO_2-content of over 1% $Ca\ CO_3$ was found in one of the horizons the soil was brought into Class I. When no CO_2 was given, but the profile description indicated that the parent material contains or contained carbonates, the profile was also grouped under Class I. All other profiles were assembled into Class II. The results are summarized in Table 23.

The general impression of this table is very similar to the one given for soils including parent material analyses (Table 22). Soils of Class I, have a high percentage of cases with μ_a values greater than one (88% of all), while for Class II only 52% have μ_a values above one. The two soil classes are, therefore, sharply distinguished on the basis of frequency

TABLE 23.—SHIFTING VALUES (μ_a) OF SOIL PROFILES WITHOUT ANALYSES OF
PARENT MATERIAL
(Comparison of K/Na ratio of leached and accumulation horizons)

Soil Groups	Percentage of profiles having $\mu_a > 1$	Number of analyses
Class I: Soils containing $CaCO_3$ or derived from parent material with carbonates		
a. *podsolized soils*		
limestone		
sedimentary rocks	82%	22
b. *chernozems*	100%	11
Class II. Soils without carbonates.		
a. *podsolized soils*		
igneous	75%	6
sedimentary	57%	14
b. *yellow-red soils*		
igneous and metamorphic	46%	13
sedimentary	45%	11

value for μ_a. This class difference based on the carbonate content of parent material is more pronounced than the effect of the climate.

Uniting all soils of Tables 22 and 23 into the two classes and neglecting the influence of climate, the following results were obtained:

TABLE 24.—K/NA RELATIONSHIP IN LEACHED AND ACCUMULATION HORIZONS OF
190 SOIL PROFILES

Classes	Percentage of soils having shifting values $\mu_a > 1$	Number of analyses
Class I: soils with $CaCO_3$	86%	69
Class II: soils without $CaCO_3$	64%	121

This table summarizes two significant things. First, there is a tendency in all profiles for the K/Na ratio of the leached horizon to be wider than that of the accumulation horizon; secondly, this trend is particularly pronounced in soils containing carbonates.

In 86% of all soils of Class I, the K/Na ratio has been widened in the leached horizon, that is to say Na was more washed out than K. There seems to be no question that the presence of foreign ions, such as Ca and Mg intensifies the shift in the K/Na as evidenced from the magnitude of $\mu_a > 1$ of the two classes of soils. This is easiest explained by ionic exchange according to the K-Na-theorem advanced on page 26. *Generally speaking, the behavior of K and Na in soils of Class I as evidenced from total analyses is in accordance with what might be expected if K and Na relations in soil formation follow the laws of base exchange of colloidal clays.*

General Discussion on the Different Leaching of K and Na in Soils.

This investigation sheds a new light upon the old problem of why Na accumulates in the ocean. The well known observation that sedimen-

tary rocks have a wider K/Na ratio than igneous rocks is substantiated in this study by the variation of the K/Na ratio during soil formation. An analysis of a large number of soil profile analyses has revealed the unquestionable tendency for the K/Na ratio to be wider in the leached horizon than in the parent material. This is particularly the case for soils developed in humid regions and it is intensified in subtropical and tropical districts (Tables 17-20).

Various explanations have been put forward, as to the causes of this different behavior of K and Na in the weathering process. The statement is often made in textbooks that this difference is due to variations in the solubility of the alumino-silicates, and that the Na-compounds are more soluble than the K-compounds. However, insufficient experimental evidence[23] is presented to support this hypothesis.

Furthermore, "solubility" is hardly the proper term to be used since the solubility of alumino-silicates is not a simple and reversible process as, for instance, the dissolution of sugar in water. The extraction of a powdered orthoclase with water and subsequent evaporation of the liquid does not result in a new orthoclase crystal. The entire process is much more complicated than a mere solubility process in its common physico-chemical meaning.

Many writers—apparently conscious of the misnomer "solubility"—use the expression *"decomposition* of alumino-silicates" which is more general and does not imply any assumption as to the mechanism of the reaction taking place.[82] In more recent times, and especially as the result of laboratory investigations, the viewpoint: *"hydrolysis* of alumino-silicates" has taken a most prominent place in textbooks discussing weathering. *Ramann*[67] states that the hydroxyl ions are the dominating agencies in bringing about decomposition of silicates. Ramann does not discuss the differences in release of K and Na, but some investigators explain it on the basis that "Na-clay is more hydrolyzed than K-clay". It should be emphasized, however, that this statement can hardly be called an explanation; it is merely a description in a different terminology.* No mechanical reason is given why Na-clay hydrolyzes more than K-clay. In fact, on the basis of hydrolysis equilibria there should be no difference in the behavior of K and Na, since in the chemical hydrolysis equations of a salt of a weak acid (clay acid) and a strong base (K, Na) only the dissociation constant of the acid enters the formula. It follows then that the classical hydrolysis viewpoint used in chemistry is not broad enough to account for differences in the leaching of K and Na in soils.

*The same holds for the phrase "Na-clay is more ionized than K-clay." Just what is meant by degree of surface dissociation on a crystal which is 100% ionized is not clear. More accurate definitions are needed.

The experimental data presented, together with the results of other investigators, clearly show that the hydroxyl ion is in no way essential in bringing about a differential release of K and Na. The effect takes place in the presence of any common anion. Furthermore, any cation (at least those found in soil solutions) will replace K and Na in such a way that under comparable conditions more Na than K is exchanged. The most effective cation in replacing K and Na is the hydrogen ion— as demonstrated in previous papers—and it is by virtue of this fact that water "hydrolyzes" alumino-silicates. Hydrolysis is only a special case of the more general process of ionic exchange, in that it involves the hydrogen ions of the water. From the viewpoint of ionic exchange it does not matter whether the hydrogen ions come from the dissociation of water or from any other source, such as carbonic acid and organic acids.

The cause of the better release of Na has been explained (in its physical meaning) in this paper on the basis of the inherent ionic properties of K and Na, especially on their difference in ionic radii. Equal electric charges coupled with a difference in size of the ions brings about a great difference in the electric field strength of the two ions, which is the direct cause for the great affinity of the Na ion for water molecules. The mechanism discussed on page 11 illustrates the principle that owing to its strong hydration, Na is likely to be leached better than K, if bound on the same type of surface.

This latter restriction suggests the idea that soil colloids may act as an important regulator in determining the magnitude of the K/Na ratio in rivers, lakes and oceans. In a great majority of igneous rocks, K and Na are not bound in the same crystal lattice and no plausible reason exists why K could not be easier replaced than Na, since the forces of fixation may be weaker for the K-system. Were it not for the fact that the released ions from weathering minerals are partly adsorbed and again released by soil colloids which regulate the K/Na ratio during soil formation, it could be easily conceived that rivers and oceans might contain more K than Na. In other words soil colloids may be largely responsible for the observed conditions that rivers and oceans are richer in Na than in K.

General Summary

1. An attempt has been made to approach the important but complex problem of soil formation from a systematic and *quantitative* angle. Two constituents—K and Na—have been selected, and their behavior during soil development is studied from a theoretical and experimental viewpoint.

2. On the basis of the inherent properties of the K and Na ions, which bring about a difference in their hydration, it has been suggested that *under comparable conditions K is better adsorbed than Na, while Na is better released than K.*

3. Elaborate experimental studies on ionic exchange with K and Na furnish convincing evidence that the above principle applies to all soil colloids so far investigated.

4. In applying these results to the study of K and Na in natural soil profiles, soils were divided into two main classes:

    Class I, soils having predominantly foreign cations (Ca, Mg) in the soil solution,

    Class II, soils having considerable amounts of K and Na in the soil solution.

5. For the distribution of *exchangeable K and Na* in the various horizons of soils belonging to Class I, the following theorem was advanced: *the horizon with the smallest amount of K and Na has a wider K⁄Na ratio than the horizon having the largest amount of K and Na.* The profile analyses (exchangeable bases) found in the literature support this theorem.

6. About 200 total soil profile analyses from all parts of the world were inspected as to the existence of quantitative K-Na relationships using the K-Na theorem as a guide.

7. For the study of these profiles the sum of $K_2O + Na_2O$ was related to Al_2O_3, calling the quotient ba_1. A *leaching factor* (β) was formed by comparing the lowest ba_1 value in the profile (leached horizon) with the ba_1 value of the parent material. Similarly, a *shifting factor* (μ) was calculated by comparing the K⁄Na ratio of the leached horizon with that of the parent material.

8. The nature of the parent material decidedly affects the rate of leaching and shift of K and Na in the profile. Soils of Class I (containing carbonates) have lower β-values and higher μ-values than soils of Class II (without carbonates). In other words, *the leaching of K and Na and the widening of the K⁄Na ratio is most pronounced in soils containing $CaCO_3$.*

9. *Both leaching and shifting values are sensitive indicators of the climatic factors operating during soil formation.*

    a. In podsolized soils and chernozems both values differ distinctly. The chernozems have β values which approach the magnitude one, indicating little loss and translocation of K and Na. In podsolized soils leaching and widening of the K⁄Na ratio is much more pronounced.

   b.   Analysis of the climatic soil types—podsol, yellow-red soil, and laterite shows distinctly that β becomes smaller as one goes from north to south, while μ has the tendency to become greater. The intensified weathering of subtropical and tropical regions results in greater losses of K and Na, and in a more pronounced widening of the K/Na ratio in the leached horizon.

10.   Comparison of the K/Na ratio of leached and accumulation horizons reveals a marked tendency for the K/Na ratio of the leached horizon to be wider. This behavior of K and Na is most pronounced is soils of Class I (carbonate soils) and is in line with what might be expected if ionic exchange reactions play an important role in soil formation.

11.   The old observation that K accumulates in sedimentary rocks while Na is washed out and concentrates in the ocean is shown to be valid also for the horizons in soil profiles. This behavior is explained on the basis of differences in ionic properties of the two ions which dominate the various factors acting during weathering.

Table 25.—Summary of Data for Podsolized Soils Derived from Limestones

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of accumulation horizon	Number of horizons analyzed	Parent material	Locality	Soil type	References[1]
1	0.246	2.195	B$_2$	2.195	C	4	limestone	Germany	Rendzina	Stremme,[81] p. 521
2	0.496	5.038	soil	5.038	C	2	chalk sandstone	Spitzbergen	Arctic	Meinardus,[55] p. 57
3	0.558	1.444	soil	1.444	C	2	marl limestone	Switzerland	Rendzina	Jenny,[41] p. 104
4	0.123	3.760	soil	3.760	C	2	limestone	Switzerland	Rendzina	Jenny,[41] p. 104
5	0.304	2.120	soil	2.120	C	2	limestone	Switzerland	Rendzina	Jenny,[41] p. 104
6	1.376	0.161	A+B	6.210	A+B	2	limestone	France	Brown earth	Agafonoff,[3] p. 77
7	0.260	1.110	A −B	1.110	C	4	limestone	Germany	Rendzina	Aarnio-Stremme,[2] p. 104
8	0.093	2.031	A −B	2.031	C	4	limestone	Germany	Rendzina	Aarnio-Stremme,[2] p. 103
9	0.938	2.594	subsoil	1.045	surface	3	limestone	Germany	Rendzina	Aarnio-Stremme,[2] p. 102

[1]This list refers to easily available publications which contain the analyses quoted. From the viewpoint of scientific interpretation it would have been better—and also more just—to give the names of both collector of samples and analyst.

TABLE 26.—SUMMARY OF DATA FOR PODSOLIZED SOILS DERIVED FROM SEDIMENTARY ROCKS CONTAINING CARBONATES

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of ac-cumula-tion horizon	Num-ber of hori-zons an-alyzed	Parent material	Locality	Soil type	Reference
1	0.368	0.945	A₂	0.945	C	7	Loess	U. S. S. R.	Podsol	Glinka,[29] p. 98
2	0.562	1.083	B₂	1.083	C	6	Moraine	U. S. A.	Brown timber	Baldwin,[5] p. 280
3	0.588	1.618	B₂	1.618	C	7	Moraine	U. S. A.	Brown timber	Baldwin,[5] p. 281
4	0.971	2.465	C	2.465	C	2	Loess	Germany	Gelblehm	Harrassowitz,[33] p. 193
5	0.627	∞	B₂	1.305	B₁	3	Moraine	Germany	Gelblehm	Harrassowitz,[33] p. 193
6	0.740	2.545	soil (29e)	2.545	C	3	Shale	Spitzbergen	Arctic	Meinardus,[55] p. 60
7	0.602	1.018	No. 4	1.276	No. 1	4	Glacial	U. S. A.	Brown timber	McCool,[54] p. 100
8	0.709	2.155	No. 4	1.748	No. 1	4	Glacial	U. S. A.	Podsol	McCool,[54] p. 98
9	0.937	1.086	No. 4	1.202	No. 1	4	Glacial	U. S. A.	Podsol	McCool,[54] p. 99
10	0.722	0.793	B₃	1.036	A₁	3	Moraine	U. S. A.	Podsol	Denison,[22] p. 474
11	0.710	2.298	lower B	1.744	No. 2	4	Clay	U. S. A.	Podsol	Veatch,[83] p. 354
12	1.097	0.814	B	0.865	A₂	4	Loam	U. S. S. R.	Wiesenboden	Glinka,[29] p. 166

TABLE 27.—SUMMARY OF DATA FOR PODSOLIZED SOILS DERIVED FROM SEDIMENTARY ROCKS WITHOUT CARBONATES

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of accumulation horizon	Number of horizons analyzed	Parent material	Locality	Soil type	Reference
1	0.935	0.647	B_2	0.826	B_1	4	Moraine	Finland	Brown earth	tremme,[79] p. 169
2	1.078	0.930	B	1.254	A	3	Moraine	Finland	Brown earth	tremme,[79] p. 168
3	0.802	1.502	B_2	1.398	A_2	4	Moraine	Finland	Podsol	Stremme,[79] p. 168
4	0.912	1.043	B	1.083	A	3	Sand	Finland	Podsol	Stremme,[78] p. 146
5	0.848	0.971	A_2	0.971	C	2	Moraine	Finland	Podsol	Stremme,[78] p. 149
6	0.808	1.265	B	1.182	A_2	4	Moraine	Sweden	Podsol	Aarnio-Stremme,[2] p. 75
7	0.830	1.182	B	1.142	A_2	3	Moraine	Sweden	Podsol	Aarnio-Stremme,[2] p. 75
8	0.773	0.964	B	1.004	A_2	4	Moraine	Sweden	Podsol	Aarnio-Stremme,[2] p. 76
9	1.018	1.126	B_2	0.769	A_2	4	Sand	Sweden	Podsol	Aarnio-Stremme,[2] p. 78
10	0.710	1.811	B	1.811	C	3	Moraine	Sweden	Podsol	Aarnio-Stremme,[2] p. 79
11	0.702	1.157	B	1.157	C	3	Moraine	Germany	Podsol	Aarnio-Stremme,[2] p. 79
12	0.381	1.782	B	1.422	A_2	4	Moraine	Germany	Podsol	Aarnio-Stremme,[2] p. 80
13	1.191	1.024	B	0.684	A	4	Sand	Germany	Podsol	Aarnio-Stremme,[2] p. 81
14	0.616	0.304	B	0.304	C	3	Sandstone	Germany	Brown earth	Aarnio-Stremme,[2] p. 81
15	0.762	0.870	A	0.870	C	3	Flugsand	Germany	Brown earth	Aarnio-Stremme,[2] p. 82
16	0.946	0.763	B	0.763	C	3	Sand	Finland	Podsol	Aarnio-Stremme,[2] p. 86
17	0.873	1.296	B_1	2.070	A_2	4	Clay	Finland	Brown earth	Aarnio-Stremme,[2] p. 88
18	1.224	6.465	B	0.863	A	3	Sand	Germany	Podsol	Harrassowitz,[32] p. 309
19	1.230	1.281	B	0.862	A	3	Sand	Germany	Podsol	Harrassowitz,[32] p. 309
20	1.003	1.023	B	0.921	A_2	3	Moraine	Sweden	Podsol	Harrassowitz,[32] p. 309
21	0.955	1.088	B	0.978	A_0	5	--------	U. S. S. R.	Wiesenboden	Glinka,[29] p. 166
22	0.695	1.536	No. 2	1.536	C	4	Sand	U. S. A.	Podsol	McCool,[54] p. 99
23	0.865	1.833	B	3.180	A	3	Limon	France	Brown earth	Agafonoff,[3] p. 77, No. 10
24	0.963	0.800	B	1.290	A	3	Limon	France	Brown earth	Agafonoff,[3] p. 77, No. 1
25	0.910	1.328	soil 22	1.328	C	4	Sandstone	Spitzbergen	Arctic	Meinardus,[55] p. 56
26	2.182	1.584	A_3	0.384	A_1	5	Sand	Denmark	Podsol	Weis,[87] Table V
27	0.600	1.405	A_3	1.405	C	5	Sand	Denmark	Podsol	Weis,[87] Table VI
28	1.340	0.745	A_3	1.516	A_1	5	Sand	Denmark	Podsol	Weis,[87] Table VII

TABLE 28.—SUMMARY OF DATA FOR PODSOLIZED SOILS DERIVED FROM IGNEOUS AND METAMORPHIC ROCKS

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of accumulation horizon	Number of horizons analyzed	Parent material	Locality	Soil type	Reference
1	1.148	2.188	soil	0.435	soil	3	Diabase	Spitzbergen	Arctic	Meinardus,[55] p. 61
2	0.650	1.854	weathered	1.854	C	2	Granite	Germany	Brown earth	Mortensen,[58] p. 459
3	0.959	1.654	crust	1.654	C	2	Gneiss	Russia	Podsol	Harrassowitz,[32] p. 313
4	1.021	1.148	decomposed	0.870	decomposed	2	Gneiss	Switzerland	Podsolized	Jenny,[41] p. 106
5	1.057	1.313	desintegrated	0.762	desintegrated	2	Gneiss	Switzerland	Podsolized	Jenny,[41] p. 106
6	0.766	0.828	soil	0.828	C	2	Verrucano	Switzerland	Podsolized	Jenny,[41] p. 106
7	0.862	0.578	desintegrated	0.578	C	2	Schist	Switzerland	Podsolized	Jenny,[41] p. 106
8	0.871	1.496	soil	1.496	C	2	Amphibolite	Switzerland	Podsolized	Jenny,[41] p. 106
9	1.308	1.032	soil	0.969	soil	2	Gneiss	Switzerland	Podsolized	Jenny,[41] p. 106
10	0.351	2.840	clay	2.840	C	2	Basalt	Germany	Anmoorig	Aarnio-Stremme,[2] p. 113
11	0.684	1.016	B	0.887	A₂	3	Granite	Germany	Podsol	Aarnio-Stremme,[2] p. 80
12	0.868	4.696	weath red	4.696	C	2	Granite	Germany	Brown earth	Blanck,[8] p. 218
13	0.616	1.000	A₁	1.000	C	4	Granite	U. S. S. R.	Podsol	Glinka,[29] p. 77
14	1.525	2.710	B	0.319	A₂	3	Diorite	U. S. S. R.	Podsol	Glinka,[29] p. 79
15	0.697	1.438	B	1.438	C	2	Gneiss	Germany	Gelblehm	Harrassowitz,[33] p. 192
16	0.648	3.622	siallite	3.622	C	2	Labradorite	Norway	--------------	Harrassowitz,[32] p. 259
17	0.585	3.025	decomposed	3.025	C	2	Phonolite	Czecho-Slovakia	Brown earth	Merrill,[56] p. 198
18	0.830	0.812	desintegrated	0.812	C	2	Diabase	U. S. A.	Brown earth	Merrill,[56] p. 200
19	0.163	1.045	decomposed	1.045	C	2	Basalt	France	Brown earth	Merrill,[56] p. 206

Table 29.—Summary of Data for Chernozems

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of accumulation horizon	Number of horizons analyzed	Parent material	Locality	Soil type	Reference
1	1.103	1.022	A_2C	0.978	A_2C	4	Loess	U. S. S. R.	Chernozem	Stremme,[80] p. 270
2	1.652	0.555	A_3	1.203	A_2	4	Loess	Germany	Chernozem	Stremme,[80] p. 269
3	1.161	0.916	A	1.091	A	2	Loess	Hungary	Chernozem	Stremme,[80] p. 266
4	1.018	0.652	A	2.590	C_{40}	3	Marl	Germany	Chernozem	Aarnio-Stremme,[2] p. 100
5	0.857	1.094	A	1.094	C	2	Marl	Germany	Chernozem	Aarnio-Stremme,[2] p. 99
6	0.973	0.885	A	0.885	C	2	Loess	Germany	Chernozem	Aarnio-Stremme,[2] p. 99
7	0.948	0.833	A_2	0.844	A_1	3	-----	U. S. S. R.	Chernozem	Aarnio-Stremme,[2] p. 98
8	0.716	1.356	0-30	1.356	C	5	Loess	U. S. S. R.	Chernozem	Glinka,[29] p. 126
9	0.736	1.490	A	1.490	C	2	Loess	U. S. S. R.	Chernozem	Glinka,[29] p. 127
10	0.937	1.192	loess	1.192	C	2	Loess	U. S. S. R.	Chernozem	Krokos,[48] p. 7
11	1.068	1.055	No. 3	1.306	No. 2	4	Loess	U. S. S. R.	Chernozem	Krokos,[48] p. 5
12	0.953	1.150	No. 2	1.150	C	3	Loess	U. S. S. R.	Chernozem	Krokos,[48] p. 5
13	0.802	1.172	No. 2	1.172	C	3	Loess	U. S. S. R.	Chernozem	Krokos,[48] p. 4
14	0.785	1.352	B_2	1.167	A_0	3	Glacial deposit	U. S. A.	Chernozem	Denison,[22] p. 473
15	1.012	1.160	5-12 cm	0.438	11-17cm	4	Loess	Hungary	Chestnut	Sigmond,[76] p. 299

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of accumulation horizon	Number of horizons analyzed	Parent material	Locality	Soil type	Reference
1	0.532	0.952	sand	0.952	C	3	Granite	U. S. A.	Yellow-red	Merrill,[56] p. 186
2	0.106	3.205	decomposed	3.205	C	2	Gneiss	U. S. A.	Yellow-red	Merrill,[56] p. 194
3	0.143	1.061	"B"	1.061	C	2	Biotite	U. S. A.	Yellow-red	Merrill,[56] p. 195
4	0.131	3.255	decomposed III	3.255	C	4	Syenite	U. S. A.	Yellow-red	Merrill,[56] p. 196
5	0.567	1.298	decomposed	1.298	C	2	Diabase	U. S. A.	Yellow-red	Merrill,[56] p. 204
6	0.260	4.065	decomposed	4.065	C	2	Diorite	U. S. A.	Yellow-red	Merrill,[56] p. 207
7	0.164	0.638	soil	0.638	C	2	Andesite	U. S. A.	Yellow-red	Merrill,[56] p. 208
8	0.763	0.521	soil	0.521	C	2	Soapstone	U. S. A.	Yellow-red	Merrill,[56] p. 211
9	0.239	0.630	clay	0.630	C	2	Argillite	U. S. A.	Yellow-red	Merrill,[56] p. 214
10	0.556	1.572	dust	1.572	C	3	Oligoclase	U. S. A.	Yellow-red	Merrill,[56] p. 228
11	0.115	2.845	soil	2.845	C	2	Gneiss	U. S. A.	Yellow-red	Merrill,[56] p. 347
12	0.282	0.613	B2	0.613	C	5	Gneiss	Brazil	Immature laterite	Harrassowitz,[34] p. 376
13	0.258	0.789	B	0.789	C	3	Gneiss	Switzerland	Yellow loam	Harrassowitz,[33] p. 192
14	0.412	2.632	A	2.632	C	3	Gneiss	Switzerland	Yellow loam	Harrassowitz,[33] p. 191
15	0.385	1.652	B	1.652	C	3	Acid rock	U. S. A.	Yellow-red	Cobb,[17] p. 458
16	0.271	1.310	B	0.905	A	3	Acid rock	U. S. A.	Yellow-red	Cobb,[17] p. 458
17	0.074	0.108	B	0.108	C	3	Acid rock	U. S. A.	Yellow-red	Cobb,[17] p. 458
18	0.187	3.838	B	3.838	C	3	Basic rock	U. S. A.	Yellow-red	Cobb,[17] p. 459
19	0.167	8.210	B	8.210	C	3	Basic rock	U. S. A.	Yellow-red	Cobb,[17] p. 459
20	0.080	7.410	B	7.410	C	3	Basic rock	U. S. A.	Yellow-red	Cobb,[17] p. 459
21	0.199	1.252	B1	1.252	C	4	Gneiss	U. S. A.	Yellow-red	Denison,[22] p. 473
22	0.193	1.071	B2	0.955	A1	4	Schist	U. S. A.	Yellow-red	Denison,[22] p. 473
23	0.308	3.282	B1	3.282	C	4	Gneiss	U. S. A.	Yellow-red	Denison,[22] p. 473
24	0.396	12.940	C4	12.960	rock	5	Granite	U. S. A.	Yellow-red	Denison,[22] p. 473

TABLE 31.—SUMMARY OF DATA FOR LATERITIC SOILS DERIVED FROM IGNEOUS AND METAMORPHIC ROCKS

No.	β-value	μ-value	Nature of leached horizon	μ_a-value	Nature of accumulation horizon	Number of horizons analyzed	Parent material	Locality	Soil type	Reference
1	0.0361	∞	laterite	∞	C	2	Amphibolite	Yap	laterite	Harrassowitz,[32] p. 335
2	0.0231	1.511	spotted zone	1.154	No. 9	13	Gneiss	India	laterite	Harrassowitz,[32] p. 338
3	0.0562	1.860	Zersatz	1.860	C	7	Gneiss	India	laterite	Harrassowitz,[32] p. 340
4	0.451	14.560	weathered	14.560	C	2	Phyllade	Africa	laterite	Harrassowitz,[32] p. 374
5	0.0166	2.121	A	2.121	C	4	Syenite	Guinea	laterite	Aarnio-Stremme,[2] p. 91
6	0	-----	crust	-----	C	3	Diabase	Guinea	laterite	Aarnio-Stremme,[2] p. 92
7	0.134	1.669	laterite	1.669	C	2	Diabase	Tabouna	laterite	Aarnio-Stremme,[2] p. 92
8	0.0480	0.155	laterite	0.155	C	2	Diabase	Tabouna	laterite	Aarnio-Stremme,[2] p. 93
9	0.106	8.090	laterite	8.090	C	2	Diabase	Songueta		Aarnio-Stremme,[2] p. 93
10	0.0357	∞	B_2	∞	C	4	Diabase	Songueta	laterite	Aarnio-Stremme,[2] p. 94
11	0.632	2.665	siallite	2.665	C	2	Syenite	U. S. A.	fossil	Harrassowitz,[32] p. 488
12	0.0951	1.608	soil	1.608	C	2	Andesite	U. S. S. R.	laterite	Glinka,[29] p. 225
13	0.0566	4.255	weathered	4.255	C	3	Basalt	U. S. S. R.	laterite	Glinka,[29] p. 228
14	0.133	0.574	loam	0.574	C	5	Serpentine	Cuba	laterite	Harrassowitz,[35] p. 417
15	0.680	1.081	Zersatz	1.081	C	6	Gneiss	Ettakot	laterite	Harrassowitz,[35] p. 413
16	0.0274	1.523	Zersatz	1.523	C	6	Gneiss	Colombo	laterite	Harrassowitz,[35] p. 412
17	0	-----	Zersatz	-----	C	3	Peridolit	Guinea	laterite	Harrassowitz,[35] p. 412
18	0	-----	No. 1	-----	C	3	Schist	Fataya	laterite	Aarnio-Stremme,[2] p. 95

TABLE 32.—SHIFTING VALUES (μ_a) OF SOIL PROFILES WITHOUT ANALYSES OF PARENT MATERIAL

(Comparison of K/Na ratio of leached and accumulation horizons)

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference

CLASS I: SOILS WITH CARBONATES
Podsolized soils derived from limestones and sedimentary rocks

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
1	1.66	Hagerstown	U. S. A.	Brown timber soil	Emerson,[25] p. 355
2	2.05	Miami	U. S. A.	Brown timber soil	Emerson,[25] p. 362
3	1.22	Miami	U. S. A.	Brown timber soil	Emerson,[25] p. 362
4	1.03	Loess	U. S. A.	Prairie soil	Alway,[4] p. 428
4	1.03	Loess	U. S. A.	Prairie soil	Alway,[4] p. 429
6	1.35	Glacial till	U. S. A.	Podsol	McCool,[54] p. 99
7	1.17	Glacial till	U. S. A.	Brown timber	McCool[54] p. 98
8	0.89	Carrington	U. S. A.	Prairie and Br. timber	Rost,[71] p. 177
9	0.94	Carrington	U. S. A.	Prairie and Br. timber	Rost,[71] p. 177
10	0.96	Carrington	U. S. A.	Prairie and Br. timber	Rost,[71] p. 178
11	1.19	Carrington	U. S. A.	Prairie and Br. timber	Rost,[71] p. 178
12	1.14	Fargo	U. S. A.	Prairie and Br. timber	Rost,[71] p. 179
13	1.05	Fargo	U. S. A.	Prairie and Br. timber	Rost,[71] p. 179
14	1.78	Hagerstown	U. S. A.	Brown timber soil	Thomas, p.
15	1.01	Limestone	France	Brown earth	Agafonoff,[3] p. 76
16	1.49	Hagerstown	U. S. A.	Brown timber	Rob.-Hol.[70] p. 11
17	1.22	Clarksville	U. S. A.	Brown timber	Rob.-Hol[70] p. 11
18	1.28	Miami	U. S. A.	Brown timber	Rob.-Hol.,[70] p. 11
19	0.77	Marshall	U. S. A.	Prairie	Rob.-Hol.,[70] p. 11
20	1.05	Grundy	U. S. A.	Prairie	Emerson,[25] p. 357
21	1.24	Grundy	U. S. A.	Prairie	Emerson,[25] p. 357
22	1.66	Limestone	Germany	Terra Rossa	Aarnio-Str.[2] p. 95

Chernozems

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
1	1.12	------------	U. S. A.	Chernozem	Emerson,[25] p. 358
2	1.13	------------	U. S. A.	Chernozem	Emerson,[25] p. 358
3	1.01	Colby	U. S. A.	Chestnut	Emerson,[25] p. 359
4	1.04	------------	Canada	Chernozem	Emerson,[25] p. 360
5	1.24	Colorado soil	U. S. A.	Chestnut	Emerson,[25] p. 360
6	1.37	------------	Canada	Chernozems	Emerson,[25] p. 361
7	1.31	------------	Canada	Chernozems	Emerson,[25] p. 361
8	1.08	Wanneta	U. S. A.	Chestnut	Alway,[4] p. 424
9	1.07	McCook	U. S. A.	Chestnut	Alway,[4] p. 425
10	1.07	Holdrege	U. S. A.	Chernozems	Alway,[4] p. 426
11	1.10	Hastings	U. S. A.	Chernozems	Alway,[4] p. 427

CLASS II: SOILS WITHOUT CARBONATES
Podsolized soils derived from igneous rocks

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
1	1.65	Granite	France	Skelett-soil	Agafonoff[3] p. 88
2	1.12	Granite	France	Skelett-soil	Agafonoff,[3] p. 88
3	1.78	Volcanic	France	Brown timber	Agafonoff,[3] p. 87
4	0.73	Volcanic	East Indies	Podsol	Senstius,[74] p. 38
5	∞	Volcanic	East Indies	Podsol	Senstius,[74] p. 43
6	0.86	Volcanic	Philippines	Podsol	Senstius,[74] p. 43

Podsolized soils derived from sedimentary parent material

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
1	0.92	------------	U. S. A.	Prairie	Rob.-Hol.[70] p. 11
2	0.96	------------	U. S. A.	Brown timber soil	Rob.-Hol.,[70] p.11
3	1.52	Pecherde	Finnland	Brown timber soil	Aarnia-Str.[2]p.110

TABLE 32.—SHIFTING VALUE (μ_a) OF SOIL PROFILES WITHOUT ANALYSES OF PARENT MATERIAL (Continued)

(Comparison of K/Na ratio of leached and accumulation horizons)

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
4	1.04	Lebanon	U. S. A.	Prairie	Emerson,[25] p. 356
5	1.25	Cherokee	U. S. A.	Prairie	Emerson,[25] p. 356
6	8	Sand	U. S. A.	Podsol	McCool,[54] p. 98
7	0	Clay	U. S. A.	Podsol	McCool,[54] p. 98
8	4.28	Sand	U. S. A.	Podsol	McCool,[54] p. 98
9	1.01	Sand	U. S. A.	Podsol	McCool,[54] p. 98
10	0	Sand	U. S. A.	Podsol	McCool,[54] p. 99
11	1.54	Sand	U. S. A.	Podsol	McCool,[54] p. 99
12	7.71	Sand	U. S. A.	Podsol	McCool,[54] p. 100
13	0.11	Sand	U. S. A.	Podsol	McCool,[54] p. 100
14	0.63	Sand	U. S. A.	Podsol	McCool,[54] p. 100

Yellow-red soils derived from igneous and metamorphic rocks

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
1	3.30	Iredell	U. S. A.	Yellow-red	Cobb,[18] p. 155
2	3.49	Mecklenburg	U. S. A.	Yellow-red	Cobb,[18] p. 155
3	0.54	Davidson	U. S. A.	Yellow-red	Cobb,[18] p. 155
4	0.91	Chester	U. S. A.	Yellow-red	Emerson,[25] p. 349
5	1.41	Chester	U. S. A.	Yellow-red	Emerson,[25] p. 350
6	0.59	Cecil	U. S. A.	Yellow-red	Emerson,[25] p. 350
7	0.90	Cecil	U. S. A.	Yellow-red	Emerson,[25] p. 351
8	0.41	Georgeville	U. S. A.	Yellow-red	Emerson,[25] p. 351
9	1.16	Cecil	U. S. A.	Yellow-red	Emerson,[25] p. 352
10	4.42	Iredell	U. S. A.	Yellow-red	Emerson,[25] p. 352
11	0.29	Manor	U. S. A.	Yellow-red	Rob.-Hol.[70] p. 11
12	1.66	Cecil	U. S. A.	Yellow-red	Rob.-Hol.[70] p. 11
13	0.20	Chester	U. S. A.	Yellow-red	Rob.-Hol.[70] p. 11

Yellow-red soils derived from sedimentary parent material

No.	μ_a-value	Parent material or local name of profile	Locality	Climatic soil type	Reference
1	1.52	Collington	U. S. A.	Yellow-red	Emerson,[25] p. 347
2	0.43	Collington	U. S. A.	Yellow-red	Emerson,[25] p. 347
3	2.60	Sassafras	U. S. A.	Yellow-red	Emerson,[25] p. 348
4	0.44	Sassafras	U. S. A.	Yellow-red	Emerson,[25] p. 348
5	1.30	Leonardtown	U. S. A.	Yellow-red	Emerson,[25] p. 349
6	0.97	Norfolk	U. S. A.	Yellow-red	Emerson,[25] p. 353
7	1.01	Tipton	U. S. A.	Yellow-red	Emerson,[25] p. 354
8	1.80	Huntington	U. S. A.	Yellow-red	Rob.-Hol.,[70] p. 11
9	0.35	Norfolk	U. S. A.	Yellow-red	Rob.-Hol.,[70] p. 11
10	0.08	Orangeburg	U. S. A.	Yellow-red	Rob.-Hol.,[70] p. 11
11	0.91	Sassafras	U. S. A.	Yellow-red	Rob.-Hol.,[70] p. 11

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