METHOD FOR ESTIMATING ADSORBED BASES IN SOILS AND THE IMPORTANCE OF THESE BASES IN SOIL ECONOMY

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TRANSLATED AND SUMMARIZED BY F. H. SMITH, GEORGIA EXPERIMENT STATION

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A part of the bases (calcium, magnesium, potassium, sodium, and ammonium) which may occur in the clay-humus complex of the soil is present in a replaceable or exchangeable form. It is possible to demonstrate this fact by treatment of the soil with a solution of a salt of one of these bases (for example with ammonium chloride). We then find a replacement of calcium, magnesium, potassium, or sodium of the soil by equivalent proportions of the ammonium from the solution. The replacement process is reversible; ammonium ions from the solution are capable of replacing Ca, Mg, K, and Na ions from the soil; but these in turn can also replace the soil ammonium to a certain extent. As soon as equilibrium is established we find in both the soil and the solution NH_4, Ca, Mg, K, and Na ions. Solutions of $NaNO_3$, $CaSO_4$, etc, behave in a similar manner.

Experiments here reported show that equilibrium is very quickly attained in this "replacing" process. This fact indicates that here we are dealing with a reaction between the solution and the easily accessible or surface particles of the clay-humus complex. If the bases on the interior of the adsorbing particles were concerned either partly or wholly in this reaction equilibrium would only be reached slowly, because diffusion occurs very slowly in solid bodies. Other phenomena would also make it appear that the particles which take part in this process are present in the ionic form. We may, therefore, consider that at the boundary surface between the soil as the solid phase and of the soil solution as the liquid phase, replaceable cations occur,—that is, replaceable cations are adsorptively bound to the adsorbing soil particles. The idea then occurs that the exchangeable cations and the adsorptively-bound cations may be identical.

Explanations of this base-adsorption are to be sought in chemical relations: chemical compounds are formed between the adsorbed bases (Ca, Mg, K, Na, and NH_4) and the clay- and humic-acids of the soil. The fact that only the molecules in the surface layer react to form these chemical combinations characterizes the reaction as an adsorption process.

[1] For original paper, tables and references, see Verslagen van Landbouwkundige Onderzoekingen der Rijkslandbouwproefstations, 1920, no. 24, p. 144–250.

Since the chemical combination only occurs at the surface of the adsorbing clay-humus particles we can well understand that, from calculations based on the mass of the whole particle, no combination occurs in simple stoichiometric proportions as is the case in ordinary chemical reactions of this kind. This difference in extent of reaction between adsorption-combinations and others of a purely chemical nature gradually becomes less as the adsorbing particles become smaller; that is, as the "specific" surface of the particles becomes greater. If the particles are so small as to approach the dimensions of a molecule the adsorption process than becomes a chemical reaction. This apparently is the case with permutite. According to Schulze, at least, every molecule in permutite particles resides on the surface of the particle. Permutites are, therefore, adsorption combinations in stoichiometric proportions. This explanation clears up the controversy between Gans, Stremme, and others. In soils, such an evolution from adsorption to chemical combination is quite possible, especially with certain of the humus-substances. Ordinarily the particles are no smaller than colloids; most of them are larger even than 0.1μ as investigation has shown. The humus constituents occur in all degrees of fineness, and some of the particles are no larger than molecules.

The adsorbed bases play important parts in the processes taking place in the soil. It is therefore desirable to ascertain the amounts of these bases present in soils. The ordinary methods of soil examination are inadequate for the purpose.

It is apparent that any method for estimating the adsorbed bases depends on the properties of these bases towards other bases in the solution. Since the "exchanging" process is reversible the method chosen must be based upon a leaching process. Even on digestion with a moderately strong solution of ammonium chloride (Meijer method) all the adsorbed calcium does not go into solution. Now the question arises whether by leaching soils with solutions, for example, of ammonium, potassium, or sodium chloride, only the bases from the surface of the soil particles are removed or whether they are also removed from the interior of the particles in appreciable amounts. If this were the case then the exchange process in the soil would occur in this way: at first a fairly large amount of the base elements would go into solution, while with further leaching smaller quantities go into the solution. If only the adsorbed elements are dissolved the exchange process would, for all practical purposes, soon be complete. In order to study these questions, an exact investigation was conducted with clay soils and with sandy loams, all free from calcium carbonate. The experiment showed that a point was reached very quickly at which no more bases were given up to the solution. On leaching the soil with ammonium chloride, potassium chloride, or sodium chloride, therefore, only adsorbed bases go into solution.

As further ground for this conclusion, the speed of the exchange process was investigated. If only the adsorbed bases are replaceable equilibrium should be quickly reached. For the present only the exchangeability of calcium in a clay soil and in two sandy loams will be considered. For esti-

mating this capacity for exchange of bases, a weighed quantity of soil was treated with a definite amount of the chloride solution by shaking. Determinations were than made of the amount of calcium present in the solution after periods of 5 seconds, 1 minute, 1 hour, 1 day, 1 week. With the clay soil equilibrium was reached in less than 1 minute. With a sandy loam soil only 0.01 per cent calcium went into solution after 5 minutes. From consideration of these results it was seen that of the total quantity of calcium which could go into solution under these considerations in the clay soil, 97 per cent went into solution in the first 5 seconds, and for the sandy loams 90 per cent was in solution at the end of 5 minutes. Such results could only be obtained where the exchange process is confined to the easily accessible adsorbed bases.

The solubility of $CaCO_3$ in water is low. In presence of NaCl and KCl it is not appreciably increased, but is increased to a considerable extent by NH_4Cl solution. On leaching soils containing calcium carbonate, with solutions of NH_4Cl, KCl, and NaCl, more or less of the soil carbonate of lime, in addition to adsorbed calcium, is dissolved.

It was shown in an extensive investigation that the quantity of calcium carbonate which goes into solution on leaching the soil with NH_4Cl solution decreases as leaching proceeds. In the first liter of extract, therefore, more of the $CaCO_3$ is dissolved than in the second. When using solutions of KCl or NaCl only small amounts of the carbonate dissolved. It was observed that with these two solutions this quantity is practically proportional to the quantity of the solution used for leaching (up to two liters). In the second liter there is practically as much $CaCO_3$ dissolved as in the first. On leaching with KCl or NaCl solution the difference in the calcium content of the first and of the second liter represents the amount of replaced calcium from the soil.

It was found that in the soils examined no $MgCO_3$ was present.

METHOD FOR ESTIMATING ADSORBED BASES

1. Estimation of adsorbed lime and magnesia

Twenty-five grams of soil (for mixed sandy loam soils 50 gm. may be used) were shaken in a beaker with 100 cc. of a warm normal solution of NaCl. This was occasionally shaken and allowed to stand over night. In this way the sample was thoroughly saturated with NaCl solution. The liquid was then poured through a filter into a liter flask, the mass of soil brought quantitatively on the filter and treated with successive portions of the solution. The filter was allowed to empty between each addition of NaCl solution. If the first portion of the filtrate was cloudy it was run through the filter again. When the flask was filled to the mark the funnel was placed in another liter flask and treatment continued until the second flask was also filled to the mark. The calcium content of the two filtrates was then determined. The difference in the calcium content of the first- and the second-liter portions corresponds to the replaced calcium. Adsorbed magnesium may be estimated in the same way although this is more conveniently determined as under (2).

The second liter contains only traces of magnesium; and in soils which do not contain calcium carbonate the second liter is practically free of calcium.

2. *Estimation of adsorbed magnesium, potassium, and sodium*

These elements were determined in a manner similar to (1) except that 25-gm. portions of the soil were leached out with successive portions of normal ammonium chloride and the washings were collected in two half-liter flasks.

DISCUSSION

In this method the adsorbed bases are represented by the difference in quantities removed in the first and the second liter or half-liter portions. Even if further study should show that besides the adsorbed bases small quantities of that class of bases which I have designated as "acid-soluble" are also removed, the method would still permit the satisfactory determination of the adsorbed bases. The small quantities of acid-soluble bases removed would be proportional to the amount of leaching liquid. Thus if sodium chloride removed small quantities of acid-soluble calcium and magnesium the amounts removed in the first- and second-liter portions would be equal. Therefore the difference in calcium or magnesium content of the first and second liters would represent the exchangeable calcium or magnesium. The same considerations apply to ammonium chloride except that we deal with half-liter portions. From the same line of reasoning we need expect no serious difficulty due to impurities in the sodium chloride or ammonium chloride.

The adsorbed calcium was estimated in a large number of clay soils as described above, while for a part of these soils the adsorbed magnesium, potassium, and sodium was also estimated. The results are stated as the content of exchangeable bases, in percentages. From these percentages are calculated the content of exchangeable bases expressed in milligram-equivalents per 100 gm. of air-dry soil, and per hundred adsorbed ions. Thus, an average of the soils examined contained per 100 gm. of soil: 30.0 m.e. Ca, 5.0 m.e. Mg, 0.8 m.e. K, and 2.5 m.e. Na,—a total of 38.3 milligram-equivalents in 100 gm. of soil. Then in one hundred adsorbed cations there are 79 Ca, 13 Mg, 2 K, and 6 Na ions. The divalent ions predominate, calcium being the most prominent one.

Two sandy loam soils were examined for adsorbed bases. In the humus, there were 76.3 Ca ions, 13.1 Mg ions, 3.0 K ions, and 7.6 Na ions for each hundred adsorbed cations. In these soils the divalent ions also predominate.

The term "acid-soluble bases" designates the portion of Ca, Mg, K, and Na which goes into solution when the soil is treated with strong HCl, after deducting the adsorbed bases and the water-soluble chlorides, carbonates, etc. All clay soils examined have a low acid-soluble Ca and Na content (averaging 0.251 and 0.270 per cent) as compared with a high acid-soluble K and Mg content (1.340 and 0.826 per cent). Of the total calcium (adsorbed

and acid-soluble), 76.9 per cent was in the adsorbed condition. Of the total Mg, K, and Na contents only 5.6, 2.6, and 10.9 per cent respectively, were adsorbed. These bases occur for the greater part in the acid-soluble form, as contrasted with calcium, which is for the greater part adsorbed.

Two sandy loams were examined for acid-soluble bases. These differed from the clay soils in that the calcium ranked highest as the acid-soluble base. In the clay the greater part of the bases was in the acid-soluble form with the exception of calcium. With the sandy loams, the opposite relations were observed. For a fair comparison the *sum* of the total bases, should be compared with the sum of the adsorbed bases (both expressed in equivalents). Thus 100 gm. of a clay soil contained 137.7 m.e. of total bases and only 35.4 m.e. of adsorbed bases. Of the total bases (soluble in strong HCl) present in the clay soil about 25 per cent occurred as adsorbed bases. The sandy loam soils contained 36.9 m.e. of total bases, and 21.8 m.e. (or 59 per cent) of adsorbed bases. In the humus the major part of the bases occurred in the adsorbed form, while in the weathered mineral-complex (clay) the greater part occurred in the acid-soluble form. It is evident that the reason for this distinction is to be found in the variation in size of the particles in the mineral and in the organic weathered-complex. The smaller the particles the greater the ratio of surface to mass and naturally the greater the amount of adsorbed substances present.

The great importance of adsorbed bases in the soil processes is recognized both from the standpoint of clay soils and of sandy loams.

The amounts of adsorbed bases in milligram-equivalents designated as S varied in the clay soils examined from 23.3 to 48.9 (with the exception of a very low value of 12.4 for a soil B38) and with the loam soils examined, from 8.4 to 21.8. These values depend primarily on the content of adsorbing substance in the soil (clay-humus), and further, they decrease in the course of years due to action of plants and the percolating action of rain water.

In the moist climate of Holland the soils are adsorptively unsaturated.

The loss of a part of the adsorbed bases is partly caused by physiological agencies and partly by colloidal-chemical means. If a sufficient amount of adsorbed bases is lacking, the soil is in such a condition of unsaturation that the adsorbing soil complex can not efficiently function as the pH regulator. The soils then become acid. Besides, a change in the colloidal equilibrium of the soil occurs following such a desaturation of the soil, and this causes considerable modification of its physical nature (formation of hard-pans). With clay soils the effects of this desaturation on the colloidal-chemical processes are more noticeable. With loam soils the physiological effects are noticed to a greater or lesser extent. With these there is as much probability of a strongly alkaline as a strongly acid reaction. in the soil solution. The range of optimum acidity of the soil solution, the acidity being expressed by the value pH, is more quickly changed in either direction with soils high in humus than is the case with clay soils. This difference may be due to the difference in strength of the clay- and the humic-acids.

The value of S (sum of adsorbed bases expressed as milligram-equivalents per 100 gm. of soil) gives us no positive insight into the real character of the soil. To fully understand this a knowledge of the degree of saturation of the soil is necessary. This term is used by the author to designate the ratio of the actual quantity of adsorbed bases in the soil S to the possible degree to which this might be extended; that is, to the amount of bases which the soil is capable of adsorbing T. A satisfactory procedure for the determination of T has not yet been worked out. A relation evidently exists between the value T and the clay-humus content, or, T varies with the content of clay humus substance. The values calculated on this assumption, which do not give the actual saturation capacities but are only proportional to them, were determined for a series of clays and for one sandy loam soil. With clay soils, the degree of saturation varied from 67 with the younger peat soils to 20 with older soils and "Katteklei"; in sandy loams it ran from 193 with calcareous valley soil to 64 with an old valley soil.

The colloidal chemical equilibrium depends not only upon the degree of saturation of the soil but also on the relation of the adsorbed bases one to another. For practical purposes, to these various relations of adsorbed cations may be ascribed that well known agricultural fact that calcic fertilizer materials act favorably on soil structure while sodium compounds have the opposite effect, and make the soil "sticky." Theoretically, the difference in effect of lime fertilization on the soil structure on the one hand, and the effect of fertilization with sodium compounds, on the other, is due to formation of gels in the first case and sols in the latter. Then the great variation in the deflocculating power of the di- and mono-valent cations on clay suspensions and humus fluids is due to the colloidal chemical effects of the adsorbed monovalent and divalent cations in the soil. Changes in these relations lead to changes in the equilibrium and influence changes in the soil structure.

The Rothamsted experiments have shown the unfortunate results of continued yearly applications of nitrate of soda on the soil structure. Likewise the ill effects of flooding fields with sea water is well known. Examination of such soils shows that they differ markedly from normal soils. As a rule they contain per 100 adsorbed cations only 56.9 Ca ions and 20.2 Mg. ions, or 77 divalent cations, against 23 monovalent cations. In normal soils the figures are 92 divalent to 8 monovalent cations.

Salts in sea water not only affect the adsorbing substances of mineral nature but also those of organic or humus nature. The effects are mainly on the calcium (gels) and sodium (sols) humates. The presence of the humus sols in soils treated with sea water is shown by extraction of such soils with water. Normal calcium-clay soils give bright yellow colored extracts; the extracts from the sodium-clay soils are yellow to brown in color.

It is evident that variations occur in the relations of adsorbed cations of water-borne soils according to whether the soil was deposited by fresh or salt water. In the latter instance, such as the so-called "Kwelder" soils, the soils

are distinguished by their high content of adsorbed monovalent cations (50 divalent and 50 monovalent, generally) while the fresh water action on soils leaves them with much smaller amounts of the monovalent cations. As the content of exchangeable calcium increases, the content of exchangeable sodium and of calcium carbonate decreases. One experiment seems to show that salt water clays always contain considerable exchangeable sodium. In this way soils which have been in contact with fresh water may be distinguished from those which have been in contact with salt water.

At the present it is generally assumed that plant nutrients are distributed through the soil in a slightly water-soluble form, so that neither a complete removal by leaching on the one hand or too strong a concentration of the soil solution on the other, can occur. But water, and especially carbonated water can always take up small quantities. As plants withdraw the dissolved materials from this dilute solution they are replaced to a greater or lesser extent by weathering of silicates or humus materials. It is worthy of note that this explanation of withdrawing of nutrients from the soil by the chemical changes taking place between adsorbing material of the soil and the substances dissolved in the soil water has not been elaborated before. The investigations of Prianischnikow have directed attention to these changes. From his investigations it was shown that potassium absorbed in potash-permutite could not be utilized by plants without the action of the other salts of the soil solution. The author has shown, moreover, that adsorbed potash is just as available for the plants' needs as the water-soluble potash. The same conclusion was also drawn as regards the ammonia of ammonium permutite. It does not matter if *only* the adsorbed bases are assimilated. Kellner has made a study of this and concludes that potash and calcium in the dissolved or absorbed condition can serve as nutrients for legumes but cannot be taken up from difficultly-soluble compounds by the roots.

From evidence presented we cannot say that it is principally the adsorded substances which are adsorbed. Perhaps the opinion of Adolph Meyer may well be considered, i.e., that the substances in the adsorbed condition are *not* the only ones available. But it seems that the adsorbed bases are of fundamental importance in absorption through the roots of plants. From this standpoint the determination of these bases deserves thorough attention.

In this connection it is well to give attention to the experiment and observations of Ehrenberg who has studied the "calcium-potassium-ratio." This ratio concerns to a great extent the great differences in content of adsorbed calcium and potassium in clay soils, and considers the general relation of the adsorbed bases with one another. "Kwelder" soils which are high in sodium and poor in calcium are spoken of as of the "calcium-sodium-type."

The question arises as to whether there is a reciprocal transfer between the adsorbed and acid-soluble bases. This cannot possibly occur to any great extent. If it were the case then we could not explain why the content of adsorbed and of acid-soluble bases in a soil had not become equalized after

existing so closely together for these hundreds of years. There should, for example, not be such great difference between the adsorbed magnesium (0.08 per cent) and potassium (0.024 per cent) and the acid-soluble magnesium (1.34 per cent) and potassium (0.826 per cent). Then also the lowering of the degree of saturation of soil, which actually occurs and to a considerale extent, could not be explained so long as these soils have such an excess of acid-soluble bases. From these considerations we must consider two forms of bases, the exchangeable or adsorbed bases, and the acid-soluble bases. Between these two classes no appreciable exchange occurs.

The influence of adsorbed bases on the soil processes, as previously mentioned is remarkable. The small amount of adsorbed potassium found in the soils examined, and averaging only 0.024 per cent is of greater importance for plant nutrition than the 0.826 per cent acid-soluble potassium. The degree of saturation of soils depends on the content of adsorbed bases. While this content in the course of years might decline only a little in comparison with the total-base content, yet even a small decrease has a great effect on the processes, physiological as well as colloidal-chemical, which take place in the soil. There is further the relation between the monovalent and the divalent cations which is also involved in governing the colloid-chemical equilibrium in the soil. In normal soils the adsorbed monovalent cations are outnumbered by the total number of adsorbed cations. The proportion of acid-soluble divalent cations to monovalent acid-soluble cations is not of any significance.

Even if it should be shown by future investigations that in my discussion the importance of adsorbed or exchangeable bases has been given too much emphasis and the acid-soluble bases undervalued, enough has been shown to indicate that the former are of greater importance to soil properties than the latter. At any rate the estimation of exchangeable or adsorbed bases should have a place in any extensive scheme of soil examination.