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The Base Exchange Phenomenon of the Soil.

(from the Practical Point of View).

by

D.J.Hissink, Groningen (Holland).

Address *) read at the Plenary Meeting of the
Third International Congress of the International
Society of Soil Science,
Oxford (England),

Thursday, August 1st, 1935.

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*) This address is a resumé of my paper in German, entitled: Der Basenaustausch im Boden, included in the Proceedings of the Third International Congress; Oxford, 1935; Volume 2.

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§ 1. Introduction.

My original intention was to choose as the title of my address: Soil Adsorption. I have chosen the title: The Base Exchange Phenomenon of the Soil because this more accurately describes the material to be dealt with. I should like to add as a sub-title: from the practical point of view. On the one hand, therefore, adsorption, or perhaps better, the fixing, of anions, and also of water, is entirely disregarded; on the other hand, I shall touch as little as possible on the theoretical side of the problems, and the less so, since the treatment of this aspect is in the capable hands of Professor Wiegner.

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§ 2. Some Theoretical Considerations.

Any general lecture on the problem of Base Exchange in the soil must start from the well-known treatise of Thomas Way, in which it is shown that, when the soil is treated with solutions of neutral salts, an exchange takes place between bases from the solution and bases from the soil, especially lime. It was later found that the hydrogen also takes part in the exchange process. As is known, these exchangeable bases occur, at any rate for the greater part, in the clay-humus substance, and it is especially these exchangeable bases which play the chief part in many soil processes. The exchangeable bases may therefore obviously also be called clay-humus bases.

Way was further aware that the exchange process proceeds with great velocity, which has led to the view that it is a question of a reaction between ions of the solution and easily accessible ions in the soil, that is ions which are situated on the surface of the soil particles. The extent of the base exchange depends, then, in the first place on the specific surface of the soil; whether the soil dispersoids - the clay and humus substance - exchange only from the outer surface or also from the interior surface of their micelles, being here disregarded. In any case it is certain that the exchange capacity of the soil increases in consequence of the enlargement of the specific surface of the soil particles, that is, with the weathering both of the mineral and of the organic constituents of the soil. Since, then, the process of base-exchange is due to the surface activity, soil scientists have called the exchangeable bases adsorptively bound bases and the process of base exchange base-adsorption, and the clay-humus complex which binds these bases, the adsorbing soil complex. But they did not lose sight of the fact that it was a question of exchange adsorption.

In addition to the specific surface it is very probable that the chemical constitution of the soil dispersoids also plays a part in base adsorption. It has been found that the adsorption capacity for bases in some Dutch clay soils resides principally in the weathering silicate A (van Bemmelen), and that this silicate occurs more especially in the small clay particles (fraction smaller than 0.002 mm diameter).

Although theoretical considerations will not be treated here, I cannot refrain from adding that the exchangeable bases in the Dutch clay soils investigated are to be regarded as bound to hypothetical alumino-silicate acids, which I call clay-acids. During the leaching of the soil by water containing carbon dioxide (CO_2) in the humid climate of Holland, exchangeable bases are leached out, and replaced by hydrogen; and the soil reaction shifts in the acid direction.

Similar considerations also apply to the adsorbing organic soil complex, that is, for the humus substance; here it is the humus acids which bind the exchangeable bases.

This view may sound somewhat primitive and conservative, but it has done us good service up to the present, and fails only in one point, which I will touch on at the end.

§ 3. The Extent of the Exchangeable Capacity
of the Soil.

In comparison with other substances the clay-humus substance of the soil possesses a very great exchange capacity, or, as we soil scientists say, a very large base-binding capacity. I express this base-binding capacity by means of my T-value, which is determined with the aid of my baryta method. To obviate any misunderstanding, this value may be called the theoretical or the total base-binding capacity of the soil.

The clay substance of the Dutch clay soils possesses an average total base-binding capacity, expressed in grammes lime (CaO) per 100 gr. clay substance, of 2.24 grammes; the base binding capacity of quartz and kaoline is considerably less (less than 0.3 gr. CaO). It has been found that this base binding capacity of the Dutch clay soils resides chiefly in the weathering silicate A of van Bemmelen. The figure 2.24 gr. applies of course only to this type of soil. Soils rich in quartz powder, or whose weathering silicate possesses a more lateritic composition, will probably yield quite different figures. It is obvious that this total base binding capacity (T-value according to Hissink), calculated on small particles, may prove to be able to characterize the soil type.

The base binding capacity of the humus substance is considerably higher; the well humified organic matter of the Dutch humus soils binds on an average approximately 16 grams lime (CaO) per 100 grams humus.

This total base binding capacity (T-value according to Hissink) must be clearly distinguished from those amounts of bases which the soils contain when, from a practical point of view, they are well saturated with bases. This is the case when the soil reacts approximately neutrally. In that case 100 gr. clay substance contains about 1 gr lime (all bases calculated on CaO), and 100 gr. humus about 4.5 gr. CaO.

§ 4. Degree of Saturation of the Soil (V-value)
and the Relative Proportion of the Exchange-
able Bases.

Now there are two values which play a great part in the soil processes, the first being the degree to which the clay-humus substance is saturated with bases, and the second the relative proportion of the adsorptively bound or exchangeable bases.

a). Degree of Saturation of the Soil (value V).

In 1917/18 I introduced into soil science the value V, that is the degree of saturation of the soil with bases; and I defined this value as the relation of the amount of adsorptively bound bases present in the soil S (mE bases per 100 gr. dry matter) to the amount of bases T (likewise expressed in mE per 100 gr. dry substance) which the soil is able to bind. The degree of saturation V is therefore $100 S : T$.

The value $T-S$ represents the degree of non-saturation of the soil, and agrees in my view with the amount of exchangeable hydrogen ions.

No objections have been raised to this description of the conception of the degree of saturation of the soil (V-value). My method for the determination of the T-value, or rather, of the T-S value, has, however, encountered criticism from various quarters, which I cannot deal with here. I will confine myself to pointing out that my T-value represents the amount of the bases required for the theoretical or total saturation. It is quite in accordance with the theoretical views that theoretically saturated soils, which would therefore possess a V-value of 100 (according to Hissink), cannot occur under natural conditions. It is essential sharply to distinguish between theoretically (V according to Hissink = 100) and practically saturated soils. It is obvious that the latter must always have V-values (according to Hissink) smaller than 100.

The theoretical view of the T-value has great advantages, since it is of general application, which is not and cannot be the case with the T-values taken from practice. The so-called practical T-values must differ according to climate, type of soil and vegetation, and it is therefore obvious that there are many practical T-values; that is to say, values - (expressed in milligram equivalent bases per 100 gr. soil), with which the soil, from the practical point of view, is saturated with bases. International agreement can only be arrived at on the basis of a theoretical T-value.

b). Connection between the values V (degree of saturation) and pH (soil reaction).

It is to be concluded from my remarks that there must be a connection between the degree of saturation and the soil reaction, that is, between the V and pH-values. I have demonstrated by numerous previous investigations that this is actually the case. It may be worth while to give some statistics here also.

A series of Dutch humus soils of widely differing composition had an average V-value of about 25 with a pH-value of 6.0; with pH 6.5 the V-value was about 30; with pH 7.0, about 37. I will not omit to add here that these results point to my V-values having a certain general significance for the type of Dutch humus soils investigated and therefore being able to characterize this type of soil satisfactorily.

With the young Dutch sea-clay deposits, practically speaking well saturated with bases, which possess a slightly alkaline reaction (pH 7.5), I found quite regular V-values of about 45 on the average. With increasing age the pH-value and the V-value both decreased; the 380-year old Dollard soil (near Nieuw Beerta), which has of course long since lost its CaCO_3 , has a V-value of 32 and a pH-value of 5.9.

c). The relative proportions of the exchangeable bases.

The knowledge of the values S, T, V, and pH is not in itself sufficient to characterize the soil properly; the relative proportion of the exchangeable bases also play a large part. In the normal Dutch clay and humus soils investigated: 79 - 76 Ca, 13 Mg, 2 - 3 K, and 6 - 8 Na occur on the average to 100 equivalents of exchangeable bases. The bivalent bases, especially the lime, therefore take the chief place. It is obvious that this relative proportion is in the first place subject to the influence of manuring. The adsorbing soil complex, for instance, becomes richer in exchangeable Na ions as a result of manuring with Chili saltpetre over a period of years. More especially after an inundation with sea-water does the sodium content rise at the expense of the lime content. In countries with an arid climate the presence of salts gives rise to the formation of soils with an extremely high content of exchangeable sodium.

The influence of the relative proportion of the bases on the structure, especially of heavy clay soils, is well-known. Even a slight increase of the exchangeable sodium at the expense of the lime manifests itself in a deterioration of the structure of the clay soils.

§ 5. The Changes in the Exchangeable Bases in
the Dutch Kwelder Soils after Endiking.
The Exchangeable Magnesia.

The study of the weathering processes of the marine clay deposits of Holland after their endiking forms a good example of the changes which may occur in the two important values, viz. the V-value and the relative proportion of the exchangeable bases.

The Dutch kwelder soils, that is the soils before their endiking, which are thus regularly flooded with sea-water, contain approximately

30 to 40 Ca, 45 to 35 Mg, 6 K and 15 Na per 100 equivalents of exchangeable bases; these soils are therefore to be regarded as magnesia - sodium clay soils.

After the endiking the calcium of the calcium carbonate first replaces the exchangeable sodium of the soil, and then the exchangeable magnesium, so that after at the most 70 years (soil of the Reiderwolderpolder endiked in 1862) the soil is converted into a true calcium clay soil, with a relative proportion of $85 + 10 + 4 + 1 = 100$. This soil still contained about 9 % CaCO_3 , and had a V-value of 45 and a pH-value of about 7.5. As long as the Dollard soil still contains calcium carbonate, that is for about 250 years after endiking, no changes occur in these values; only the CaCO_3 disappears, but both the pH- and V-values and also the relative proportion of the bases remains unchanged. It has further been found that after the washing out of the CaCO_3 - and even in the period when only very small amounts of CaCO_3 (of a few tenths per cent) are still present in the soil - the content of the exchangeable CaO also decreases; but that this loss of CaO is at first compensated by a rise of the content of exchangeable magnesia. About 50 years after the disappearance of the CaCO_3 the pH and V-values are still unchanged (pH = approx. 7.5 and V = approx. 45), but the relative proportion has now become $80 + 16 + 3 + 1 = 100$ (more MgO). In still older soils the content of exchangeable magnesia increases still a little further, but the loss of exchangeable lime is greater, so that the pH and V values now decrease (380 year old soil, pH = 5.9, V = 32; relative proportion = $71 + 24 + 2 + 3 = 100$).

It is necessary to inquire where the exchangeable magnesia comes from. I would here refer to my speculations of the year 1920 (two causes, a : diffusion, and b : grinding); further to the investigations of Kelley, who found an increase of exchangeable magnesia when the mineral particles were ground. I am, however, inclined in this

case to think rather of a slow diffusion of the magnesium from the interior of the soil particles towards the surface. Finally there is also the possibility that the larger content of exchangeable MgO dates from as early as the kwelder-period.

§ 6. The relation between the properties of the adsorbing soil complex and the growth of plants in relation to soil types and climate.

The chief object of many investigations into the question of base exchange is to give some indication as to the degree of acidity (pH) or the degree of saturation (V-value) at which the various crops grow best, or as to what rotations are to be considered in the case of a soil of known V and pH values. Besides this, the influence of the type of soil and of the climate should be studied.

I can here give only a few general remarks on Dutch soils.

With regard to the Dutch heavy clay soils it seems to me best to lime them in such a way that the soils retain some lime in the form of CaCO_3 as a reserve. The soil will then attain a V-value (according to Hissink) of about 45 and a pH-value of from about 7 to 7.5. Very large amounts of lime, from 10.000 to 12.000 kg. CaO per hectare, may be given at a time to these heavy clay soils without any ill-effects.

With regard to the Dutch humus soils and humus sandy soils, my impression is that it is best to try gradually to obtain a slightly acid reaction with a pH of about 6.5, with the aid of not too large amounts of lime at a time. As already stated, the Dutch humus soils hitherto investigated in this respect have a degree of saturation (according to Hissink) of about 30, with a reaction of $\text{pH} = 6.5$.

That also the relative amounts of exchangeable bases may have a great influence on the yield of the crops was recently stated in a

posthumous work of Gedroiz. Gedroiz points out inter alia that the calcium occupies a very special position with regard to the influence it exerts on the vegetation (and in all probability also on the microflora); calcium is the only kation that is able to provide favourable conditions for the development of vegetation in the absence of other exchangeable kations in the soil. On the other hand soils containing exchangeable calcium kations alone are far from yielding the largest crops. Gedroiz draws especial attention to the great influence which the relative proportion of the exchangeable calcium to the exchangeable magnesium exerts on the amount of the yield.

I will content myself with these brief remarks, and would merely add that they form a proof of the great importance of the adsorptively bound bases in the nutrition processes of the plants. In this connection I would refer to the following pronouncement made in 1860 by my fellow-countryman G.J.Mulder : The plants in good, fertile soils obtain chiefly exchanged constituents, for in good soils which contain sufficient zeolithic material, it is not the plants, but the soil, that is manured.

Mulder's pronouncement implies that the object of manuring is, at least partly, to provide the adsorbing soil complex with the necessary plant-food constituents. This applies in the first place to a manuring with lime. The object of liming is primarily to bring CaO into the clay-humus substance of the soil, so as to increase the values S and V, and also pH.

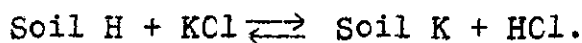
It must be taken into account that, when the soil is limed, the soil carbonic acid competes with the soil acids for the possession of the lime. The result of this is that only part of this lime is adsorbed by the clay humus substance, whilst the other part remains behind in the soil as CaCO_3 . My experiments have shown that soils with low V and pH values adsorb the largest amounts of lime in the shortest

time. Another consequence of the influence of the soil carbonic acid is that - to reach a particular V or pH value in the field - more lime must be applied than is indicated by laboratory experiments in vitro.

§ 7. The peculiar position of the hydrogen ion
in the soil.

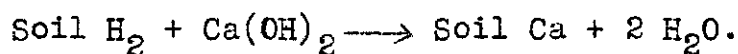
This practical problem, to provide the adsorbing soil complex with the required plant foods, brings me back to the theoretical considerations with which I started. I mean the question of the enrichment of the clay-humus substance with potassium.

Manuring with potassium is almost always done with neutral potassium salts soluble in water, chiefly KCl and K₂SO₄. Manuring experiments have shown that in this way no supply of potassium is formed in the soil in strongly acid soils. It is not until the soil reaction of these strongly acid soils has been made less acid by means of liming that a stock of potassium is formed in the soil with potassium fertilization. This phenomenon may be explained in the following manner. In slightly acid to slightly alkaline humus-clay soils the potassium of the potassium salts finds enough lime in the soil for exchange. In strongly acid soils, however, the potassium of the potassium salts has to exchange itself against the hydrogen of the soil, and the soil hydrogen can only be replaced to a slight extent by treatment with solutions of neutral salts. The following reaction is what takes place :



Theoretically speaking, it is easy to understand that - owing to the strength of the hydrochloric acid formed - this equilibrium shifts only slightly to the right. If, however, the test is carried out in such a way that a solution of KCl is poured over the soil, so that the

HCl formed is leached out, there is no apparent reason why this process should not continue. Yet this is not the case. Experiments were made by Ramann in which he leached out the soil with a few hundred litres of KCl solution, without succeeding in replacing more than a very slight amount of hydrogen with potassium. With this process, that is, the soil reaction shifts only slightly in the alkaline direction (for instance from a pH of 4.2 to one of 4.6). The remarkable point is further that the same, but less acid soil (say, with a pH of 5.0), leached out in the same way with KCl solution, again exchanges a little hydrogen against potassium, again shifting at the same time somewhat in the alkaline direction (from the pH of 5.0 to, say, one of 5.4). And according to the investigations of van der Spek this is repeated even with weak alkaline soils. There is only one way to bring about an immediate and complete replacement of the soil hydrogen, and that is the treatment of the soil with hydroxides or basic salts, in other words, the application of OH-ions. The soil hydrogen combines in this case with the OH group to form water, in accordance with the following equation :



As far as I am aware there is no theory up to date which explains this behaviour of the soil hydrogen.

It is at any rate obvious that, owing to this peculiar position of the hydrogen in the soil, the degree of saturation of the soil cannot be determined by treating the soil with solutions of neutral salts

§ 8. The destruction of the adsorbing soil complex
(Decrease of the T value).

All the properties of the soil - physical, chemical, and biological, - are closely connected with the amount of exchangeable kations of the adsorbing soil complex, which is expressed in the values S, T, V, and pH and the relative proportions of bases. All factors which play an essential part in the life of the plants, are directly dependent on the amount of the adsorbing soil complex, that is, on the T value and its content of exchangeable kations.

Our efforts must therefore be directed primarily to keeping this valuable soil complex in good condition; that is, to preserving it from destruction (unchanged T value) and to seeing that the V and pH values, and further the relative proportions of bases, remain as close as possible to the values required for the best possible plant-growth. Although, in view of the changing demands made by the various plants and types of soil and climate, no figures of general application can be given, it may be taken that the slightly acid to slightly alkaline soil reaction and the corresponding saturation values, and further a marked predominance of lime among the exchangeable bases, are the general conditions sine qua non for a good plant-growth; and that at the same time they give the greatest stability to the adsorbing soil complex (unchanged T value).

Of the factors which bring about a change in this ideal condition of the adsorbing soil complex, the climate undoubtedly plays the chief part, and in this regard the climatic influences always amount to the removal of constituents by means of rain-water.

In cold and temperate humid climates it is the acid humus substances which attack the mineral soil building. As a result of the leaching of the soil by water containing acid humus, this mineral soil

building breaks down; the separate bricks (Al_2O_3 , SiO_2 , Fe_2O_3) are carried off, and only the practically unweatherable minerals - quartz and mica - remain. According to Atterberg the soils in the central and northern parts of the Scandinavian peninsula consist chiefly of sand and humus; the mineral adsorbing soil complex has completely disappeared.

In countries with a tropical humid climate the disintegration and ultimate disappearance of the adsorbing soil complex may lead to the formation of completely sterile, purely lateritic soils.

In a semi-arid climate, where leaching out by rain water still takes place, even if only to a slight extent, it is the exchangeable sodium that plays the principal part in the destruction of the adsorbing soil complex. The adsorbing soil complex of soils which contain adsorbed sodium in fairly large quantities offers the least resistance; it is, as a matter of fact, more easily attacked by water than any other soil complexes found in natural conditions. Its instability is perhaps directly connected with the looseness with which the exchangeable sodium is bound by the adsorbing soil complex, and owing to which an alkaline reaction is produced in the soil solution, which may dissolve SiO_2 , Al_2O_3 , Fe_2O_3 , and humus. According to the results of Gedroiz' investigations the adsorbing complex in sodium-clay soils is very greatly affected by rain-water and carried off in large quantities. This process is called "solodizing", and a soil formed in this way is called a "solodj". When the sodium soil was originally quite saturated with sodium and the solodizing process has gone on to the very end, the solodj soil produced is entirely free from any adsorbing complex ($T = 0$).

§ 9. Concluding Remarks.

When the soil, this living organism, which is able to render plant-growth possible, has lost the adsorbing soil complex, it becomes a completely sterile thing, a dead body, which is of no further value to plant-life. It is, therefore, one of the most important tasks of agriculture to prevent the disintegration and ultimately the complete destruction of the adsorbing soil complex. Although perhaps other measures, such as, for instance, rational ploughing, may be appropriate. I will only point out in this address that an ample application of lime to the adsorbing soil complex is the measure par excellence, for the reason that the adsorbed calcium does most to check the destructive activity of the water, or in other words, gives the greatest stability to the adsorbing soil complex. And so I may best conclude this address by repeating in a slightly altered form Tacke's pronouncement, with which I began a treatise on the soil lime question 20 years ago:

"The lime question is by far the most difficult and at the same time by far the most important problem of the theory of manuring.

GRONINGEN, February-March, 1935.