IONIC EXCHANGE INTERRELATIONSHIPS IN SOILS AND CROPS [1]

I. *Ion selectivity in soils*

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SUMMARY

The relative displacing power of the various exchangeable cations in soils depends upon the difference between the ion activity in the outside solution and the inside micellar-ion activity of the clay minerals.

Theoretical calculations on the relationships between exchange capacity and distribution of ions with different valences, as demanded by Donnan systems, are demonstrated in figure 1.

In accordance to the findings of other investigators, evidence for the presence of Donnan systems is provided by the results of chemical studies of soils in the temperate zone, of tropical soils (macro- and microcatenas) and of soils of the sub-tropics (terra rossa and rendzina).

Summarily it may be said that the ratio of divalent and monovalent exchangeable cations and the Ca/Mg ratio in natural soils depend chiefly on the degree of base saturation of the soil colloid. Earlier this has been stated experimentally with clay minerals bij MATTSON and LARSSON (1946).

Highly leached acid tropical soil types contain more monovalent cations relative to divalent cations and more Mg relative to Ca, than illuvial, base saturated soils, indicating that both a valence effect and an effect of activity coefficients are playing a part in the ion distribution problem of soils.

The relations between ion selectivity in soils and crop ecology will be published in a next paper.

INTRODUCTION

Particularly MATTSON, WIKLANDER and their associates have emphasized the Donnan equilibrium in their studies of soil colloidal behaviour.

In connection to these studies we will supply some additional aspects and consequences of ion distributions in soils and crops, regarding the plant-soil system as a Donnan-system consisting of two colloidal phases.

The relative distribution between the two phases of ions with different valences will depend upon the exchange capacity of both soil and plant, as has been pointed out by ELGABALY and WIKLANDER (1949).

Our present paper deals with the problems of Donnan distributions of ions in the soil. In fact there is no Donnan-equilibrium between the soil particles and the soil solution, because there is no membrane between both. But the thermodynamic background of this equilibrium holds also for the soil-solution system. Hence, in general, the rules of the Donnan-equilibrium apply to the distribution of ions in the colloidal soil phase.

A DONNAN-EQUILIBRIA

SCHUFFELEN (1952) calculated the following mathematical evidences to support the theoretical foundation of the concept of Donnan equilibria concerning ion selectivity in soils.

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1 *The valence effect*

Supposing a system with monovalent (M^+) and divalent (M^{++}) cations, monovalent (A^-) and divalent ($A^=$) anions (moles per litre) and the soil complex, an acidoid R^- (equivalents per litre), the following scheme and equations can be set up. The indices i and o indicate inside and outside solution respectively.

inside			outside	
R^-	M_i^+		A_o^-	M_o^+
A_i^-	$2M_i^{++}$		$2A_o^=$	$2M_o^{++}$
$2A_i^=$				
		E		

Electric neutrality makes it necessary that:

$$M_i^+ + 2\,M_i^{++} = A_i^- + 2\,A_i^= + R^- \text{ for the inside solution}$$

$$\text{and } M_o^+ + 2\,M_o^{++} = A_o^- + 2\,A_o^=$$

$$\text{or } A_o^- = M_o^+ + 2\,M_o^{++} - 2\,A_o^= \text{ for the outside solution.}$$

When we assume that the activity-coefficients amount to 1, the relative activities of the ions in the inside and outside solutions may be formulated as follows:

$$\frac{M_o^+}{M_i^+} = \frac{\sqrt{M_o^{++}}}{\sqrt{M_i^{++}}} = \frac{A_i}{A_o^-} = \frac{\sqrt{A_i^=}}{\sqrt{A_o^=}} = \frac{1}{K} \quad \left(K = e^{-\left(\frac{nF}{RT}E\right)}\right)$$

From these equations the relation between R^- and the outside ratio of ions may be deduced.

$$\frac{M_o^+}{M_i^+} = \frac{1}{K} \text{ or } M_i^+ = K \times M_o^+ \text{ and } \frac{A_i^-}{A_o^-} = \frac{1}{K} \text{ or } A_i^- = \frac{1}{K} \times A_o^-$$

$$\frac{M_o^{++}}{M_i^{++}} = \frac{1}{K^2} \text{ or } M_i^{++} = K^2 \times M_o^{++} \text{ and } \frac{A_i^=}{A_o^=} = \frac{1}{K^2} \text{ or } A_i^= = \frac{1}{K^2} \times A_o^=$$

The first equation for the inside solution may, after several substitutions, be converted to:

$$KM_o^+ + 2\,K^2M_o^{++} = \frac{1}{K}\,A_o^- + \frac{2}{K}\,2\,A_o^= + R^- \text{ or}$$

$$R^- = KM_o^+ + 2\,K^2M_o^{++} - \frac{1}{K}\,M_o^+ - \frac{2}{K}\,M_o^{++} + \frac{2}{K}\,A_o^= - \frac{2}{K^2}\,A_o^= \text{ or}$$

$$R^- = (K - \frac{1}{K})\,M_o^+ + 2\,(K^2 - \frac{1}{K})\,M_o^{++} + 2\,(\frac{1}{K} - \frac{1}{K^2})\,A_o^=.$$

Partly by mathematical and partly by graphical calculations the graph in figure 1 was computed.

It appears that the influence of the term with $A_o^=$ in the last equation is slight. Only under special conditions there will be an influence of the valence of the anions on the distribution of the cations between solution and complex. Therefore, figure 1 is calculated for a system with monovalent anions, but qualitatively it holds also for systems with monovalent and divalent anions.

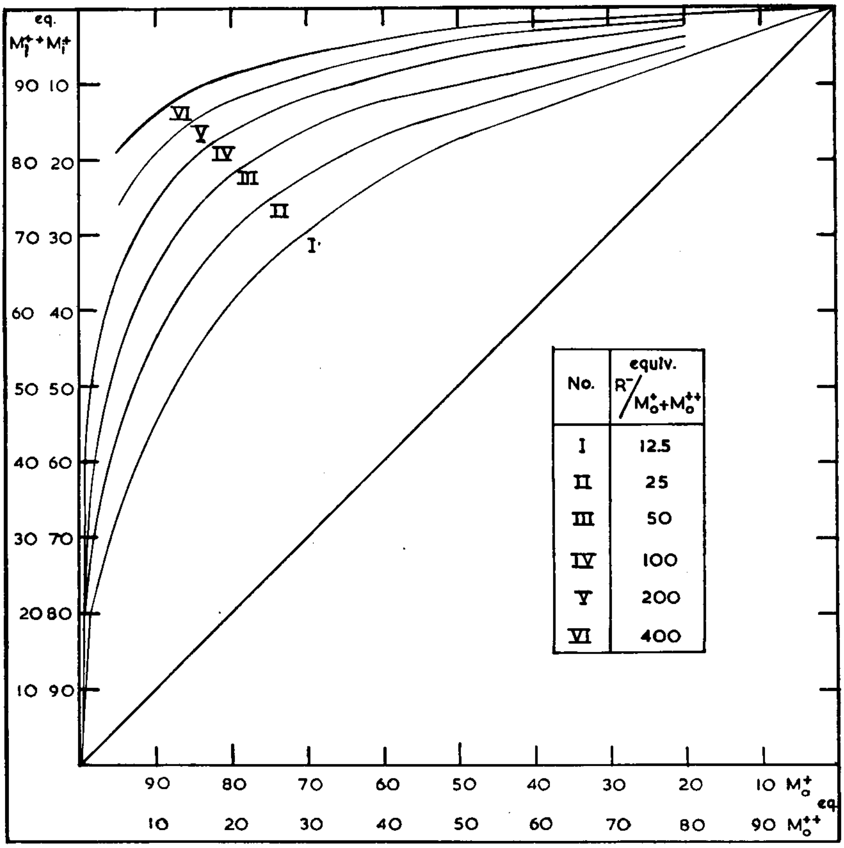

Fig. 1.

R^- is a function of the exchange capacity of the soil, viz.

$$\frac{\text{exchange capacity}}{\text{volume of double layer}}.$$

It is clear that there is a great influence of the ratio R^- to the concentration of the outside solution $\left(\frac{R^-}{M_o^+ + 2M_o^{++}}\right)$ on the ratio of monovalent and divalent cations in the outside solution.

Dilution of the solution or increasing the ratio $R^-/(M_o^+ + 2\ M_o^{++})$ has the result that more monovalent cations relative to divalent cations will go into solution.

A second important fact is that a soil with a high exchange capacity will have a higher $R^-/(M_o^+ + 2\ M_o^{++})$ ratio than a soil with a low exchange capacity. Figure 1 shows that by dilution in the former soils the solution will be richer in monovalent ions than in the latter.

Therefore in a humid climate leaching may be expected to result in the lowest content of exchangeable monovalent cations in the soil complex with the highest exchange capacity.

2 *The effect of the activity coefficients*

Using activity-coefficients (f) the relation between R^- and the ion concentration (c) in the outside solution becomes:

$$R^- = \left(K\frac{1}{(f_{Na})_i} - \frac{1}{K}\frac{(f_{Cl})_o}{(f_{Cl})_i}\right)(f_{Na})_o\,(c_{Na})_o + \left(K\frac{1}{(f_K)_i} - \frac{1}{K}\frac{(f_{Cl})_o}{(f_{Cl})_i}\right)(f_K)_o\,(c_K)_o +$$

$$+ \left(K^2\frac{1}{(f_{Mg})_i} - \frac{1}{K}\frac{(f_{Cl})_o}{(f_{Cl})_i}\right)(f_{Mg})_o\,(c_{Mg})_o +$$

$$+ \left(K^2\frac{1}{(f_{Ca})_i} - \frac{1}{K}\frac{(f_{Cl})_o}{(f_{Cl})_i}\right)(f_{Ca})_o \cdot (c_{Ca})_o$$

According to SCHUFFELEN and BARENDREGT (1946) the activity-coefficients of the adsorbed ions in first approximation are for each kind independent on the adsorbed quantity and approximatively constant. As a consequence, clay minerals and humus being similar, the distribution of ions of the same valence depends chiefly upon the activity coefficients in the outside solution.

MATTSON and LARSSON (1946) stated that the order of activity of the single ions is Na^+ K^+ and Mg^{++} Ca^{++} which is the same as the order of hydration. It is supposed that the less hydrated and the more loaded a cation the closer it will get to the surface and therefore the greater will be its polarizing effect on the surface ions.

SCHACHTSCHABEL (1952) gives a series of activity coefficients (in relation to concentration) of the chlorides of Na, K, Mg and Ca. In case of decreasing concentration, the activity coefficients of Ca and K chlorides are increasing at higher rate than those of Mg and Na chloride respectively. As a consequence of the Donnan equilibrium SCHACHTSCHABEL (1952) states that those cations, the activity coefficient of which is changed less by dilution, must accumulate in the diluted phase. So when an outside chloride solution is diluted, it is expected that Ca displaces Mg and K displaces Na from the complex.

3 *Theoretical summary*

From a theoretical point of view there can be distinguished three rules, viz.:

A Decreasing the concentration of the soil solution increases

$$R^-/(M_o^+ + 2\ M_o^{++}) \text{ and the ratio } \frac{2M_i^{++}}{M_i^+}.$$

Increasing the concentration of the soil solution decreases

$$R^-/(M_o^+ + 2\ M_o^{++}) \text{ and the ratio } \frac{2M_i^{++}}{M_i^+}.$$

B Decreasing the exchange capacity of the soil decreases

$$R^-/(M_o^+ + 2\ M_o^{++}) \text{ and the ratio } \frac{2M_i^{++}}{M_i^+}.$$

Increasing the exchange capacity of the soil increases

$$R^-/(M_o^+ + 2\ M_o^{++}) \text{ and the ratio } \frac{2M_i^{++}}{M_i^+}.$$

C Decreasing the concentration of the soil solution increases the ratios of the activities of $\frac{Ca_o^{++}}{Mg_o^{++}}$ and $\frac{K_o^+}{Na_o^+}$ and increases the ratios of $\frac{Ca_i^{++}}{Mg_i^{++}}$ and $\frac{K_i^+}{Na_i^+}$.

Increasing the concentration of the soil solution decreases the ratios of the activities of $\frac{Ca_o^{++}}{Mg_o^{++}}$ and $\frac{K_o^+}{Na_o^+}$ and decreases the ratios of $\frac{Ca_i^{++}}{Mg_i^{++}}$ and $\frac{K_i^+}{Na_i^+}$.

B APPLICATION TO SOILS

Experiments with soils lead to the conception of a polyphase soil colloidal system. Each microsystem establishes its own equilibrium, even though the outside solution is common to every system.

Therefore chemical determinations only can provide average results of heterogeneous mixtures of microsystems in the soil.

MATTSON and LARSSON (1946) pointed out that under natural conditions leaching is accompanied by an increase in acidity, lowering the dissociation of the acidoid. The undissociated acidoid doet not participate in the Donnan-equilibrium. A highly unsaturated soil has therefore a greatly reduced micellar-ion concentration.

According to the above mentioned authors two opposite effects are playing a part in ion distribution of soils. Dilution of the outside solution leads to replacement of monovalent by divalent cations, whereas dilution of the inside or micellar solution (brought about by lowering the base saturation) leads to an increase of the proportion of monovalent ions in the exchange complex.

In the end in highly developed and leached soils the latter effect predominates, with the result that the ratio M^+/M^{++} in the exchange complex will increase as the solution becomes more acid.

1 *In the temperate zones*

An example of the effect of diluting the outside solution can be found in the data of the Zuiderzee Reclamation Works on inundated marine soils in the Netherlands (3), some of which are shown in table 1.

Table 1. Directie Wieringermeer 1945.

Sea clay soils of the Netherlands	Exchangeable % of total bases				Ratio $\frac{Ca + Mg}{K + Na}$	Ratio $\frac{Ca}{Mg}$	Ratio $\frac{K}{Na}$
	Ca	Mg	K	Na			
Immediately after inundation	15	36	10	39	1.0	0.4	0.3
After leaching	60	23	5	12	6.1	2.6	0.4
Normal sea clay	87	8	4	1	19.0	10.9	4.0

The influence of leaching saline soils compared with the base status of normal sea clay soils, demonstrates the valence effect (rule A) and the effect of activity coefficients (rule C) on cation ratios as well.

Desalinization results in an increased $\frac{Ca + Mg}{K + Na}$ ratio, whereas Mg is displaced by Ca and Na by K, all as demanded by the concept of Donnan equilibria.

The effect of diluted micellar solutions may be demonstrated by comparing soils with various base saturation.

Evidence for the influence of both base saturation and acidoid content is provided by recent analyses of the Plant Nutrition Research Laboratory of the Chilean Nitrate Agricultural Service in Wageningen (1952).

Some results of analyses of exchangeable bases in Dutch soils without undissolved Ca-salts, are recalculated, averaged and summarized in table 2.

Table 2. Chilean Nitrate Educational Bureau 1952.

Dutch soil types	pH	Exchange capacity	% Base saturation	$\frac{Ca + Mg}{K + Na}$
5 sandy soils	5.5	4.9	69	7.0
5 sandy soils	6.3	7.2	78	11.5
1 loam soil	5.9	8.5	88	12.6
1 river clay soil	6.4	13.8	87	28.3

The $\frac{Ca + Mg}{K + Na}$ ratio gradually increases simultaneously with exchange capacity and base saturation (rule B).

Evidence is found also in the results of MATTSON and LARSSON (1946) from their studies of hydrologic soil series in Sweden. In a podzol with very low base saturation, as expressed by the Ca content of about 0.1 m.e./100 g soil, the Ca/K ratio is about 1, whereas in a brown earth with a Ca-content of 5–10 m.e./100 g soil, the Ca/K ratio is about 20 (rule B).

Data collected in Nebraska U.S.A. by FOX, OLSON and MAZURAK (1952) summarized in table 3 show the same relationship (rule B).

Table 3. FOX, OLSON and MAZURAK 1952.

Fertilization rate in lb/acre of N as NH_4	pH	Exchangeable m.e./100 g of soil						Ratio $\frac{Ca + Mg}{K + Na}$
		H	Ca	Mg	K	Na	NH_4	
20	5.6	2.0	14.7	5.1	1.0	0.15	0.04	17.1
80	5.2	3.5	11.6	3.1	0.9	0.04	0.04	15.6

2 *In the tropics and sub-tropics*

The influence of Donnan distribution of ions is expected to be of significance particularly under tropical conditions, where intensive weathering takes place.

In the tropics silicic acid is mobilized and iron and aluminium accumulates in relation to it (laterization). The leached silicic acid and mobilized bases (particularly calcium) are infiltrated into lower lying areas and give rise to grey or black siliceous clay soils.

The result of the anionic eluviation of silica is a colloidal complex with a lower acidoid content and thus a reduced cation-exchange capacity.

When due to climatic conditions, illuviation or eluviation predominates, the two types of weathering occur kilometres apart, giving rise to distinct differences between kaolinitic red soils having low ion exchange capacities and heavy bentonitic black soils with high ion adsorption capacities.

In accidented terrain with uneven topography however, leached brown-red higher ridges or hilltops may alternate regularly with grey-black valleys. Such chains of soil associations were called "catenas" by the English soil scientist Milne. They can be regarded as weathering profiles differentiating in horizontal direction, under identical climatic conditions.

Besides loss of silica, there occurs at the same time a decrease of base saturation, which leads also to lower exchange capacity of the complex in the upper soil types.

Mattson and Larsson (1946) confirmed experimentally that kaolin and laterite adsorb relatively more NH_4 ions than was adsorbed by bentonite from solutions of NH_4Cl and $CaCl_2$.

The bentonite adsorbs relatively more of the monovalent ions, the more unsaturated it becomes, as is demonstrated in table 4 (rule B).

Table 4. Mattson and Larsson 1946.

pH of bentonite suspension	Exchangeable		$\frac{Ca}{NH_4}$
	NH_4	Ca	
4.7	6.71	53.65	7.9
3.8	5.91	45.10	7.5
3.0	4.86	32.80	6.7

Analytical data of Prillwitz (1932) show that there exists a fairly good correlation between the decrease in the ratio of divalent/monovalent cations and the base saturation, after acidifying Java soils artificially by means of increasing quantities of sulfur (rule B). The results of two soils are given in table 5.

Table 5. Prillwitz 1932.

Soil types of Java	pH	Exchange capacity m.e./100 g	% Base saturation	Exchangeable m.e./100 g of soil		$\frac{Ca + Mg}{K+Na+NH_4}$	$\frac{Ca}{Mg}$
				Ca + Mg	$K+Na+NH_4$		
Bogor	6.6	29.7	79	17.5	6.1	2.9	4.6
	4.0	24.2	25	4.1	1.9	2.0	3.1
	3.6	24.0	12	1.1	1.8	0.6	1.8
Mount Gedeh	5.9	38.7	73	18.8	9.6	2.0	8.4
	3.8	34.8	25	3.3	5.3	0.6	3.7
	3.7	34.9	18	1.7	4.7	0.4	2.4

The effect of the activity coefficients is also reflected in the shifted Ca/Mg ratios shown in table 5 (rule C).

Another example is given by figures of Bonnet and his co-workers (1952) in Puerto Rico. Some of their results are summarized in table 6 and figure 2. Shifted Ca/Mg and K/Na ratios indicate, that the soil solution is less concentrated in the Coloso clay soils with the lowest content of exchangeable bases (rule C).

The highest (Ca + Mg)/(K + Na) ratio is found in the soil with the highest amount of exchangeable bases and the lowest (Ca + Mg)/(K + Na) ratio occurs in the soil with the lowest exchange capacity, as is illustrated in the graph of figure 2 (rule B).

Table 6. Bonnet, Lugo-López and Abruna 1952.

Top soils of Puerto Rico	Exchangeable m.e./100 g of soil				Total exchangeable bases	$\frac{Ca + Mg}{K + Na}$
	Ca	Mg	K	Na		
Alluvial Coloso clay	18.08	3.20	0.26	0.74	22.28	21.3
	12.97	1.10	0.92	0.52	15.51	9.8
	9.03	0.41	1.94	0.35	11.73	4.1
	9.27	0.66	0.76	0.38	11.07	8.7
	6.45	0.25	1.61	0.26	8.57	3.5

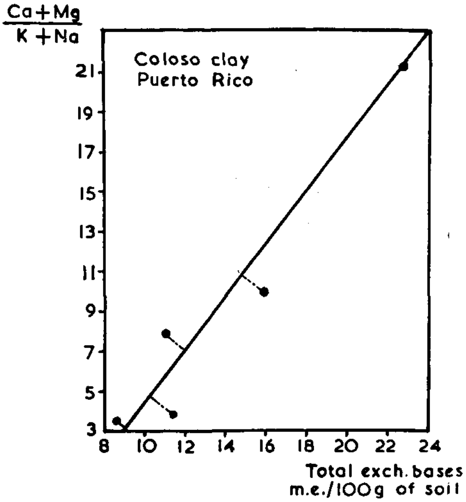

Fig. 2.

As for the K/Na ratio it is difficult to find more data which confirm the influence of activity coefficients, in relation to the concentration of the soil solution (rule C). Probably the slight alterations of the activity coefficients at the usually low level of K and Na concentrations in soil solutions, do not show a measurable effect.

a Macro-catenas

The sum total of catenary conditions covers a fair proportion of the land surface in tropical and subtropical regions of the world, resulting from climatic differences and from varying soil drainage and aeration as well.

If we regard the climatogenic soil types, with different clay minerals as *macro-catenas*, the rhythmic soil patterns under identical climate brought about by different drainage conditions and soil climate within small areas, may be called *micro-catenas*, as has been suggested by Thorp (1941).

A good example of differentiating macro-catenas is found in the studies of Albrecht (1943) in the United States of America : he describes four silt loam profiles developed from similar loessial parent materials in different locations (from Iowa to Mississippi) extending through rainfall increase from 27 to 55 inches, and a temperature increase of 8.72 to 17.66° C.

Table 7. Albrecht 1943.

U.S.A. topsoils	Annual rainfall in inches	$\frac{SiO_2}{R_2O_3}$ of soil	Exchange capacity of clay in m.e./100 g	Ca/K ratio	Ca/Mg ratio
Mississippi	55	2.6	44	16	1
Kentucky	48	3.2	50	24	1
Missouri	40	4.0	66	33	2
Iowa	27	5.1	73	133	8

The highly developed soil in Mississippi is an anionic eluviated type with low exchange capacity, low Ca/K ratio and low Ca/Mg ratio, whereas the properties of the soil formed in the dry climate of Iowa suggest that these siallitic soil may be looked upon as an illuvial type having high exchange capacity, high Ca/K ratio and high Ca/Mg ratio. These data demonstrate the valence effect and an effect of activity coefficients as well (rules B and C).

Results of Van der Merwe (1950) show the same relationships (table 8).

Table 8. Van der Merwe 1950.

Soil types of South-Africa	$\frac{SiO_2}{R_2O_3}$ of lutum fraction	Exchangeable m.e./100 g of soil				$\frac{Ca + Mg}{K + Na}$	$\frac{Ca}{K}$	$\frac{Ca}{Mg}$
		Ca	Mg	K	Na			
Red soil No. 1	0.5	0.09	0.13	0.04	0.04	2.8	2.2	0.6
No. 2	1.0	1.26	1.07	0.26	0.14	5.8	5.0	1.1
No. 3	1.1	3.78	1.01	0.20	0.30	9.6	18.9	3.7
Black soil	3.3	58.80	7.60	1.00	0.90	34.9	58.8	7.7

Venema (1952) averaged analytical results of 22 tropical red soils and of 15 tropical grey and black soils with the following results (table 9).

Table 9. Venema 1952.

Tropical soil types	Exchange capacity in m.e./100 g of soil	H	Ca + Mg	K	Na	$\frac{Ca + Mg}{K + Na}$
22 red soils	18.1	9.9	1.8	2.3	4.1	0.3
15 grey-black soils	53.3	1.3	50.3	0.7	1.0	29.6

The figures for hydrogen in table 9 show the great difference in base saturation between red and black earths, which is partly the cause of the great difference in exchange capacity.

The tropical soils with low exchange capacity always show a lower ratio of divalent/monovalent ions than soils with high exchange capacities (rule B).

b Micro-catenas

For agricultural practice with a view to the assessment of nutrient requirement and fertilization policy, the differences between the associated members of micro-catenas in soil formation are of special interest.

Middelburg (1952) assembled some chemical data of micro-catenas from different estates in Indonesia which are summarized in table 10; they show shifted ion selectivity in dependence on the degree of leaching.

Table 10. Middelburg 1952.

Soil types of Indonesia	Origine	Crop	Ratio of $\frac{\text{divalent}}{\text{monovalent}}$ bases
Eluvial	Mount Malabar,	cinchona	0.2
Illuvial	Java		2.0
Eluvial	East coast	oilpalm	1.6
Illuvial	Sumatra		6.0
Eluvial	Principalities,	tobacco	1.1
Illuvial	Java	and rice	34.0

The M^{++}/M^{+} is always lowest in the upper part of the catena (rule B).

Recently in our laboratory a more systematic study of catenary development in the soils of the rubber estate Danau Salak, in the district Marta-Pura of South-East Borneo was carried out. A plan of site of the samples from 4 different profiles is given in figure 3.

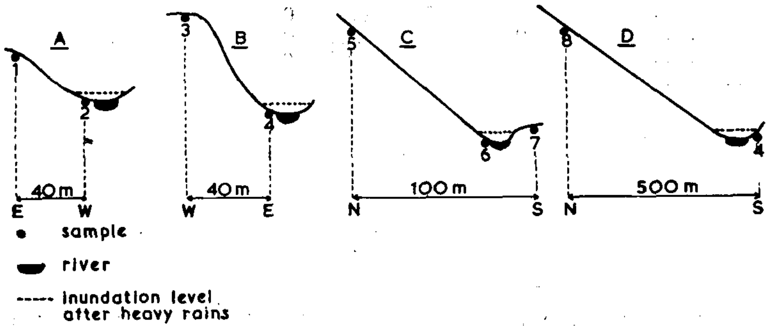

Fig. 3.

The numbers 1, 3, 5, 7 and 8 represent eluvial red-brown lateritic soil types and the numbers 2, 4 and 6 the illuvial grey-brown members of these micro-catenas.

Chemical data (supplied by J. G. de Zwaan and A. Poyck) are presented in the tables 11 and 12.

Silica and aluminium were determined by the Gedroiz method (1929), treating the samples with 5% KOH solution. Assuming that kaolinite has a molecular ratio of 2 SiO_2 : 1 Al_2O_3, the surplus of Al_2O_3 or SiO_2 is calculated, indicating the degree of eluvial or illuvial weathering of the soil.

Exchangeable bases were percolated with 0.05 n HCl and exchangeable H by the Riehm method (1946), whereas humus was determined by the Istscherekow method.

Table 11.

Borneo catenas	Sample No.	% Humus	% Lutum < 2 μ	% SiO_2	% Al_2O_3	% SiO_2 + % Al_2O_3	% "Kaolinite" (2 $SiO_2.Al_2O_3$)	% Surplus	
								SiO_2	Al_2O_3
A	1	3.8	36	1.97	2.82	4.79	3.64	–	1.15
	2	3.9	28	1.84	2.21	4.05	3.40	–	0.65
B	3	3.4	52	1.24	1.83	3.07	2.29	–	0.78
	4	4.4	42	0.71	0.97	1.68	1.31	–	0.37
C_1	5	4.6	49	0.71	1.64	2.35	1.31	–	1.04
	6	4.6	37	1.18	0.88	2.06	1.93	0.13	–
C_2	7	3.0	40	1.68	1.72	3.40	3.10	–	0.30
	6	4.6	37	1.18	0.88	2.06	1.93	0.13	–
D	8	4.1	53	0.91	1.96	2.87	1.68	–	1.19
	4	4.4	42	0.71	0.97	1.68	1.31	–	0.37

The figures in table 11 show that the humus content mostly is somewhat lower, and the lutum content markedly higher in the laterized oxidative zones than in the lower lying illuvial soil types of the micro-catenas.

From the surplus of Al_2O_3 it can be concluded that there are considerable differences in degree of eluviation (laterization) between the upper and lower parts of the profiles. In No. 6 even a surplus of SiO_2 is found.

A remarkable thing in this connexion is the fact, that though the $\frac{SiO_2}{Al_2O_3}$ ratios are markedly lowered in the leached sites, differential thermal analyses (carried out in our laboratory by R. Arnold Bik) merely show kaolinite curves in all the samples. If the intensity of the reaction temperatures in the D.T.A. curves is regarded as an indication for the degree of crystallization, we may conclude that well crystallized kaolinite is found in the upper parts of the laterized catenas only.

The relations between the above mentioned properties and ion selectivity in these tropical Borneo soils are demonstrated in table 12.

Marked differences in cation distributions are found within short distances of 40 m.

From the data in table 12 it is obvious that leaching in noncalcareous tropical red earths takes place chiefly at the expense of the divalent cations (rule B), just as has been stated by Mattson and Larsson (1946) in hydrologic soil series of Sweden.

Besides this valence effect we find indications of an effect of the activity coefficients in the Ca/Mg ratio which, in most cases, is highest in the low lying members of the catenas. Thus the more acid the soil solution the stronger Mg relative to Ca appears to be adsorbed (rule C).

Apparently in this case the base saturation and not the nature of the clay minerals or the ratio $\frac{SiO_2}{Al_2O_3}$ is the major factor, that is responsible for variations in ion selectivity of soils.

Table 12.

Borneo catenas	Sample No.	Site	$\frac{SiO_2}{Al_2O_3}$	pH	Exchangeable m.e. per 100 g of soil					Exchange capacity	$\frac{Ca + Mg}{K + Na}$	$\frac{Ca}{Mg}$	$\frac{Ca + Mg}{H + K + Na}$
					H	Ca	Mg	K	Na				
A	1	high	1.2	5.3	5.00	1.21	1.78	0.20	0.38	8.56	5.2	0.9	0.5
	2	low	1.4	6.4	4.00	7.03	8.24	0.10	0.15	19.52	63.6	0.9	3.6
B	3	high	1.1	4.8	15.00	0.80	1.98	0.25	0.39	18.42	4.3	0.4	0.2
	4	low	1.2	6.0	8.30	8.05	7.83	0.13	0.16	24.47	54.7	0.9	1.9
C_1	5	high	0.7	4.5	15.00	0.78	1.03	0.23	0.18	17.23	4.3	0.8	0.1
	6	low	2.3	6.2	4.70	20.73	8.18	0.12	0.11	33.85	120.5	2.5	5.9
C_2	7	high	1.7	5.2	6.90	2.77	2.86	0.11	0.18	12.82	19.4	1.0	0.8
	6	low	2.3	6.2	4.70	20.73	8.18	0.12	0.11	33.85	120.5	2.5	5.9
D	8	high	0.8	4.7	14.00	0.54	0.79	0.06	tr.	15.40	22.3	0.7	0.1
	4	low	1.2	6.0	8.30	8.05	7.83	0.13	0.16	24.47	54.7	0.9	1.9

Table 13. LIATSIKAS 1934.

Terra rossa of Greece	% Lutum	% Humus + H_2O	pH	Exchangeable m.e. per 100 g of soil					Exchange[1] capacity	$\frac{Ca + Mg}{K + Na}$	$\frac{Ca + Mg}{H + K + Na}$
				H	Ca	Mg	K	Na			
Forest soil No. 1	45	16	7.9	1.82	30.62	1.32	0.90	0.29	34.95	26.8	10.6
,, ,, No. 2	40	21	7.7	3.90	34.68	1.20	1.10	0.24	41.12	26.6	6.8

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1) Determined by the KAPPEN method (1929).

Further evidence to support this conception is found by comparing the acid tropical red soils with alkaline calcareous red soils from the Mediterranean zone.

Liatsikas (1934/35) analysed red soils, called terra rossa, derived from limestone in Greece and found (determined by the Gedroiz method) a ratio $\frac{SiO_2}{Al_2O_3}$ of 1.5, which is about the same as those of the Borneo soils. Some of the properties of the terra rossa from Greece are demonstrated in table 13.

As a consequence of the high pH and base saturation and probably also of the high humus content, the exchange capacity is very high in these calcareous red-brown forest soils from Greece. Therefore the ratios of divalent to monovalent cations are also high (rule B).

In addition some results of analyses of terra rossa from Israël, recently carried out in our laboratory, are presented in table 14. These soils contain large quantities of $CaCO_3$ and are low in humus content due to the absence of vegetation. The lower lying grey limestone soils are called rendzina in Israël.

Table 14.

Limestone soils of Israël	Altitude	Origine	% Lutum $< 2\ \mu$	% Humus	% $CaCO_3$
Terra rossa eluvial ..	600 m	Safed	44	3.9	3.1
Terra rossa illuvial ..	400 m	Gardosj	56	2.9	2.9
Rendzina eluvial	175 m	Neveh Yaar	64	5.3	0.8
Rendzina illuvial	100 m	Neveh Yaar	52	1.1	10.4

Shifted ion selectivity as related to catenary conditions in these sub-tropical calcareous soils are illustrated by the chemical data in table 15 (supplied by W. C. Hulsbos and L. v. d. Hoonaard).

Table 15.

Limestone soils of Israël	Altitude	pH	Exchangeable m.e. per 100 g of soil					Exchange capacity	$\frac{Ca + Mg}{H+Na+K}$	$\frac{Ca}{H}$
			H	Ca	Mg	Na	K			
Terra rossa eluvial	600 m	8.0	6.55	6.38	5.00	0.04	tr.	17.97	1.7	1.0
Terra rossa illuvial	400 m	7.8	6.55	12.00	6.05	0.07	tr.	24.67	2.7	1.8
Rendzina eluvial	175 m	7.5	3.50	15.90	3.85	0.07	tr.	23.32	5.3	4.6
Rendzina illuvial	100 m	7.8	0.58	19.88	5.39	0.25	tr.	26.10	30.4	34.3

Because of the presence of $CaCO_3$ exchange capacity, exchangeable H, and exchangeable bases were determined by the Mehlich method (1942), extracting the soil with triethanolamine of pH 8.1 and $BaCl_2$. In the extracts Ca and Na were determined with the spectrograph. These extracts contained only traces of K, which could not be estimated by the applied spectrographical technique.

Although the exchange capacity of the terra rossa is of the same order of magnitude as those of the illuvial Borneo soil types, the ratio of divalent : monovalent bases is very much higher in the former than in the latter. The presence of much undissolved $CaCO_3$ keeps the terra rossa saturated with Ca and no clear alteration in base selectivity is observed. Nevertheless, marked differences in the ratio $\frac{Ca + Mg}{H + Na + K}$ are found and the gradually increasing Ca/H ratios, descending from 600 to 100 m, indicate that though Ca predominates, a general trend in the Ca saturation of the clay complex is established. We therefore believe that the rendzinas may be looked upon as catenary associates and lower lying horizons of the terra rossa.

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