Some characteristics of young sediments in Lake Yssel

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Summary

Tests on a very young and a somewhat older sediment in Lake Ysscl showed that their physical and chemical compositions differ considerably, particularly as regards water, organic matter, clay, sulphur compound and exchangeable calcium, magnesium and ammonium content. The results of the tests and sedimentation conditions largely explained the different nature of the very young material.

Introduction

The completion of the Enclosure Dam across the neck of the Zuyder Zee in 1932 stopped all tidal movements and turned the area into a lake called Lake Yssel. From the moment of closure the water gradually became fresh. During this epoch, the 'Lake Yssel phase' in the sedimentation history of the Lake Yssel polders, much of the land to be reclaimed in the southern Lake Ysscl basin was covered with a layer of mud of varying thickness. In places the granulometric composition of this young sediment differs quite appreciably from that of the youngest sediments deposited just before the completion of the Enclosure Dam (the 'Zuyder Zee phase'). The clay content (mineral particles $\langle 2 \, u \rangle$ may be greater or smaller than that of the youngest Zuyder Zee sediments underneath.

Hitherto little was known about the chemical properties of Lake Yssel mud. Van Schreven (1963a, b) found that a fair amount of adsorbed ammonium was released when young soils were shaken in a potassium chloride solution. In two plots (numbered 4 and 106) in Southern Flevoland he found 0.76 and 1.05 meq. N (ammonium nitrogen) per 100 g dry soil. The lowest content was found in plot 4, where the mud sheet was very thin. In plot 106, where there was at least 10 cm of mud, he found the N content nearly 1.4 times as high as in plot 4. When such quantities of adsorbed ammonium are present in these young sediments, the ion constitutes a not inconsiderable percentage of the adsorption complex.

Shaking soil in a potassium chloride solution as Van Schreven did is general practice when testing soil for mineralizable nitrogen, for it has been found that all the ammonium available for the plant is extracted in that manner. However, it is not certain whether the amount of ammonium thus determined tallies with the amount adsorbed. The moisture in the soil is not removed, so the ammonium dissolved in this moisture is also determined. Moreover, shaking the soil in a potassium chloride solution only produces an exchange equilibrium between the solid and the liquid phases. To determine the adsorbed ions, on the other hand, the exchange liquid should be percolated

Fig. I Situation of the plots with occurrence and thickness of the Lake Yssel mud (Ym) in the projected polder Southern Flevoland, $A = 17-25\%$ *clay, B = 25-35 % clay, C = 35-50 % clay; 0.2 : thickness (in m) of the Lake Yssel mud before emergence of the polder.*

through the soil instead of shaken so as to complete the exchange reaction. The exchange ion used also affects the result. Van Schreven used potassium, because he knew from experience that more ammonium is extracted by means of potassium than by means of sodium and that this extra quantity is also taken by the plant. However, potassium may release not only adsorbed ammonium, but also ammonium that is tied to the soil in some other way.

Consequently, there was every reason to repeat this part of the test with the same type of soil and to follow closely the methods used at the Soil Science Laboratory (Hofstee 1966a, b). The results of the second test broadly confirmed the results obtained by Van Schreven. A number of interesting supplementary data were also obtained, showing that the very recent sediments differ quite appreciably from the somewhat older Lake Yssel mud, also as regards chemical properties.

Research methods

The samples were taken in 1965 from the top strata (0-40 cm) in Southern Flevoland near plots 4 and 106 where Van Schreven took samples in 1959. The exact location is shown on the map of Southern Flevoland (Fig. 1). Plot 106 lies in an area where there have been heavy deposits of Lake Yssel mud in recent years. In plot 4, however, there is little or no recent mud.

To determine the exchangeable cations, alcohol is percolated through the soil to drive out the moisture; it is then dried at $105\degree C$, ground and percolated to exchange the adsorbed cations. The method could not be adopted in the present instance, however, because during the drying process evaporation and/or mineralization of the ammonium and oxidation of the sulphides were expected to occur. So immediately after percolation with alcohol, the soil was percolated again with a 1 N sodium chloride solution to determine the exchangeable cations and the adsorptive capacity. Percolation to determine the exchangeable calcium, magnesium and ammonium produces sometimes more or less brownish extracts from soils containing humus. Apparently the salt has a tendency to dissolve the organic matter. So in this test, too, it was advisable to use a weak base instead of a strong one when distilling the ammonium in view of the risk of the organic compounds disintegrating, which might cause ammonium to be released.

As stated before, the drying of young non-aerated soils will bring about all sorts of changes, for instance in the chemical composition of the material. Since these processes also occur when the land dries on reclamation, albeit under somewhat different conditions, it is necessary to have some idea of their effects. Consequently, the exchange of cations, the adsorption capacity, the moisture and salt content and the still oxidizable sulphuric compounds were determined at various stages of desiccation. The composition of the moisture in the soil was also determined whenever possible. In addition to the adsorptively tied cations, a sometimes not inconsiderable quantity of them may be present in the soil moisture in the form of salts. The concentration of salts in the soil moisture partly determines the quantities of exchangeable cations present. The equilibrium between the two systems changes for instance when there is a change in the concentration of the soil moisture such as that brought about by the aeration of a reduced milieu. During the tests it was also possible to find out to what extent drying and aeration affect the composition of the soil moisture. An hydraulic press was used to separate the moisture from the soil (Hofstee, 1966a, b).

The usual physical quantities and the acidity were determined to get a general idea of the soils used in the test. The soils were given the following pre-treatments.

a) *Field-fresh.* The field-fresh, non-aerated soil was percolated with alcohol and examined without any drying.

b) *Partially dried at room temperature.* The field-fresh, non-aerated soil was spread thinly on a glass plate and dried until cracks appeared. The soil aggregates thus formed were aerated down to 1 mm or 2 mm below the surface. The cores still had their original bluish-black colour. The soil was then percolated with alcohol and examined without any further drying.

c) *Completely dried at room temperature and then re-moistened.* The field-fresh, nonaerated soil was dried on sheets of glass to atmospheric humidity. To remove the salts that had crystallized out during the process, the soil was ground and moistened

again till it became a paste that was easy to spread. The establishment of ion equilibrium was promoted by placing the re-moistened soil in closed pots in warm surroundings for 72 hours. It was then percolated with alcohol and examined without any further drying.

d) *Completely dried at room temperature.* The field-fresh, non-aerated soil was percolated with alcohol, dried, ground and then analysed.

e) *Completely dried at 105 °C.* The field-fresh, non-aerated soil was percolated with alcohol, dried, ground and then analysed.

f) *Completely dried at room temperature, without removing the soil moisture.* The field-fresh, non-aerated soil was dried, ground and then analysed.

g) *Completely dried at 105 °C, without removing the soil moisture.* The field-fresh, non-aerated soil was dried, ground and then analysed.

Pre-treatments a, b and c made it possible to study the changes in the exchange of cations. The composition of the soil moisture was also determined in these stages. It is thought that pre-treatments d and e might provide the answer to the question whether drying these young soils would affect the adsorptive surface. Part of the water tied to the clay minerals and organic matter may be lost due to the process of drying and subsequent hardening (Zuur, 1958). The resulting shrinkage causes these substances to form into pellets, which probably also reduces their adsorptive area. Tests were carried out to determine whether this could bring about any noticeable changes in the adsorption capacity. The effect of various drying times (pre-treatments e and f) can be judged from the sulphur compounds present before and after drying. The pre-treatments are briefly outlined in the tables, reference being made to the letters used in the foregoing.

Results

Of the various pre-treatments only the partial drying and the drying and re-moistening of one of the two samples, viz. the one taken in plot 106, have any noticeable effect on the exchange of cations (Table 1). The quantity of adsorbed ammonium drops steeply after drying and increases again after re-moistening. For the samples taken from plot 4, the quantity remains the same and only increases very slightly after re-moistening. This indicates that the material from plot 106 is of an entirely different nature from that from plot 4. Van Schreven found that the sample from plot 106 contained nearly 1.4 times as much adsorbed ammonium as that from plot 4. Now, six years later, the difference has become much greater. Plot 106 now contains more than 4 times as much adsorbed ammonium as plot 4. Bacterial activity (ammonification) in plot 106 must therefore be considerable. This requires large quantities of fresh proteins. Its presence is evident from the humus content, which is twice as high in plot 106 (Table 2). The fact that this large quantity of organic matter is young is evident from the rise in humus content since 1959, viz. from 3.1% to 6.3 %. It is therefore reasonable to assume that the sample taken by Van Schreven from this plot in 1959 must have been of an entirely different nature. The humus content he found corresponds with that of the sediment deposited during the Zuyder Zee phase; the present content with that of the Lake Yssel phase (Hissink, 1954). The adsorbed ammonium in Lake Yssel mud is apparently so loosely tied that it escapes under aerobic conditions through nitrification and possibly even through evaporation. When the soil has been partially dried, i.e. after aeration at room temperature, only about one-sixth of the original percentage remains. After re-moistening

 6.5

 3.6

 3.3

13.4

 73.2

29.20

1.90

 1.04

0.97

3.92

21.37

 31.35

106

94391

Table 1 Exchangeable cations after various pre-treatments of soil samples

the soil dried at room temperature, ammonification occurs again, increasing the percentage of exchangeable ammonium to 70% of the quantity present in the fresh material. Bacterial activity was encouraged by leaving the moistened soil in closed pots for 72 hours at a temperature of about 30° C. It is obvious that humus disintegration occurs, since the humus content drops from 6.3 % to 5.7 % (Table 2).

If there is little or no albuminous material, little or no ammonium is formed, even under favourable conditions. A clear example of this is the sample taken from plot 4, which hardly loses any ammonium when partially dried in the air and in which very little ammonium is produced when it is re-moistened. The humus content, already lower originally, also drops very little, viz. from 2.9 % to 2.7 %.

When the exchangeable ammonium content is relatively high, the soil moisture, too, is bound to have a clearly demonstrable ammonium content. The ammonium soluble in water, i.e. 'very loosely tied', found by Van Schreven (1963a) will have been ammonium partially or perhaps even entirely dissolved in the soil moisture. In soils from Southern Flevoland Van Schreven finds 0.13-0.56 meq. ammonium nitrogen soluble in water per 100 g dry soil, but the soil moisture of the soils now examined has 0.03 and 0.43 meq. (calculated from Table 3). In the light of these figures it would seem advisable to drive out the soil moisture before determining the quantity of adsorbed ammonium.

Drying the soil at room temperature hardly affects the exchangeable ammonium content when the soil moisture has been removed (Table 1). The content found in plot 4 is the same as that found in field-fresh material and only slightly more is found in plot 106. Percolation with alcohol will render the bacteria largely inactive, thus halting mineralization. Drying at 105 °C clearly gives lower ammonium contents, which is not surprising in view of the fairly high temperature and the volatility of ammonium.

The changes in moisture content also bring about great changes in the composition of the soil moisture (Table 3). The sulphidic sulphur compounds oxidize during the drying process and become sulphates, and the quantities of calcium and sulphate in solution increase considerably. The ammonium content of the soil moisture in plot 106 displays the same tendency as adsorbed ammonium. Partial drying of the soil causes it to drop through nitrification and when the soil is re-moistened it increases again through renewed ammonification. The occurrence of nitrification is demonstrated by the increasing nitrate $+$ nitrite content. The absence or presence of oxygen obviously determines the quantity produced. This is once again confirmed by the steep increase after drying in the air and the very slight increase in soils kept in closed pots and left for some time at about 30 °C.

Compared with the foregoing the soil moisture in plot 4 shows only little alteration. After partial drying of the soil the ammonium content remains nearly the same. The small increase is probably due to analytical errors. Drying at room temperature, followed by remoistening also causes some ammonification. Nitrification occurs too, but much less than in plot 106, in which ammonification and nitrification activities are more important, due to the presence of fresh proteins.

The tests did not reveal that drying affected the adsorptive area in any way. At all events, the adsorption capacity, which is the parameter available for the purpose, gave no indication of any reduction in the adsorptive area. It is quite likely, however, that the method of determining the adsorption capacity is not sufficiently accurate for the purpose. Testing a larger number of samples might provide more definite information.

So, judging by these tests, the various pre-treatments of the soil samples of the somewhat older sediments in Lake Yssel (plot 4) have little effect on the exchange of cations. Even the contents of exchangeable ammonium are comparable and are at the same level as those found by Van Schreven. Zuur (1954) says that on becoming dry a loamy soil from the North East Polder had a cation ratio that differed little from that in plot 4. But he did not measure the exchangeable ammonium. In the light of the results since obtained, the ratio he gives, viz. Ca : $Mg : K : Na$ $= 53 : 34 : 6 : 7$, will probably be Ca : Mg : K : Na ; NH₄ $= 51 : 33 : 6 : 7 : 3$. Through aeration and natural percolation with rain-water the ratio changes towards the ultimate cation ratio Ca : Mg : K : Na $= 87:8:4:1$. The exchangeable ammonium has then disappeared altogether. It probably continues to affect reclaimed land for a short time only. Percolation removes large quantities of nitrogen (20–30) kg/ha from the soil every year) (Van Schreven, 1963b). The easily soluble and rapidly nitrifiable ammonium will be one of the first nitrogenous compounds to go in the process. If reeds are sown immediately after the land has been reclaimed, the ammonium nitrate in the top 20 cm will be consumed almost entirely by the plants in one year. The first generation of *Senecio congestus* (R.Br./DC.) has the same effect on the top 60 cm (Bakker, 1958, 1960),

The behaviour of the very young sediment in plot 106 differs completely from that at plot 4. The moisture content is abnormally high compared with that of the somewhat older sediments of the Lake Yssel phase. The water factor *n,* which can be calculated from the relation between moisture and humus content $\{$ moisture content $= 20 + n \times$ (clay (mineral particles $\lt 2 \mu$) + 3 \times humus) } and which is normal in plot 4 (2.2), is as high as 4.3 in plot 106. The humus content is higher, too. The quantity of sulphur compounds, however, is abnormally low. As was to be expected, aeration clearly affects the watersoluble sulphate content (Table 2). After drying at room temperature, i.e. after prolonged exposure to the air, the sulphate content is higher than after quick drying at a high temperature. It is our experience that after quick drying at high temperature the quantity of soluble sulphates differs only little from that in fresh soil, so that the production of sulphate may be calculated from the difference between the two figures found by drying at low and high temperature. In plot 106, where the total quantity of sulphur compounds is much smaller than in plot 4, the production of sulphate after slow drying is more than three times as much as it is in plot 4. Since bacteria accelerate the oxidation of sulphidic sulphur compounds, the considerable bacterial activity in plot 106 is very probably the cause of the difference.

As regards the exchangeable cations (Table 1), it is remarkable that the calcium content should be higher and the magnesium, potassium and sodium contents lower than normal. Attention has already been drawn to the exceedingly high percentage of ammonium.

Discussion

The experiments have revealed that the very young Lake Yssel sediment differs greatly from the somewhat older sediment. Apparently, considerable changes take place after sedimentation, when both organic matter and water are lost. The higher humus content in the young material is accompanied by higher adsorbed calcium and ammonium contents and a lower adsorbed magnesium content. This might indicate that the humus adsorbs calcium and ammonium more readily.

Table 3 Composition of soil moisture after various pre-treatments of soil samples

* Not demonstrable

This young material has been in prolonged and intensive contact with the fresh water of Lake Yssel, one might say the water has more or less percolated through it, and this may be one of the causes of the difference between the very young and the somewhat older sediments whose cation exchange is still being slightly affected by the former marine milieu. The adsorbed magnesium, potassium and sodium will have been exchanged for the calcium in Lake Yssel water. This may also explain its lower sulphur compounds content. The sulphur compounds oxidized into sulphate in the young material which is rich in oxygen and bacterially active are percolated by the Lake Yssel water and thus removed. Moreover, fewer new insoluble compounds are formed in fresh water than in seawater rich in sulphates.

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