Investigations on Marsh Soils and Wadden Sea Sediments in the Tønder Region.

By Kjeld Rasmussen.

Introduction.

Formation and properties of the Tønder marsh deposits are being studied at present by professor *Niels Nielsen* and collaborators. Their work comprises description and classification of the strata based upon direct examination of samples drawn in situ with augers. Since the examinations are made on the spot, the mechanical composition of the samples must be judged solely from plasticity and apparent fineness of the material.

During the investigations occasionally material was found which according to plasticity when wet was characterized as clay, but when dry appeared as fine sand. This phenomenon presumably was due to certain physical-chemical conditions causing the wet material to occur in a disperse stage.

Such material would show very unfavourable physical properties and its occurrence suggests impeded, insufficient drainage on the areas in question. As it is difficult to judge fineness and mechanical composition of soil materials in different degrees of dispersion, the occurrence of such material would make reliable characterization by this procedure difficult.

Laboratory investigations of samples from different localities might contribute some information on the properties of Danish marsh soils and serve as an improved basis for description and classification under field conditions. For that purpose a series of representative samples were drawn in the summer of 1954 and analysed at the Laboratory for Soils and Agricultural Chemistry, at the Royal Veterinary and Agricultural College, Copenhagen, Denmark.

In other countries, especially the Netherlands, the problems of marsh soils have been thoroughly studied and are well elucidated. The purpose of the present investigation therefore was to obtain information about local conditions and soil types in Danish marsh areas. No attempt was made to obtain a high degree of accuracy in the analyses and extensive, detailed descriptions will not be given.

Agricultural problems of the marshes with reference also to some of the present results have recently been discussed by *S. Tovborg Jensen* (1955). Such problems therefore will not be treated here. The present work was planned together with Professor *S. Tovborg Jensen*, head of the laboratory. He and amanuensis Mrs. *B. Kjær* also advised me in interpretation of the analytical data. I wish to express my thanks to Mr. *N. Kingo Jacobsen*, mag. sci. for many valuable discussions.

Description of samples.

Samples were drawn with a soil auger to a depth of 125 cm. Each profile was represented by as many as 4 samples.

The samples were from localities, selected after field studies by Mr. *Kingo Jacobsen*, who assisted me in this part of the work. One profile in each polder was investigated and care was taken to find a profile characteristic of the polder in question. Samples were also drawn on the marine foreland and from sediments at the bottom of the wadden sea.

The localities where the samples were drawn will appear from a map in the preceding paper (p. 120) by *N. Kingo Jacobsen*.

Detailed information about the samples is given in Table I. There in the last column they are characterized by the same symbols as those used by *Kingo Jacobsen* who has described them in the preceding paper. Here it is sufficient to state, that letters indicate the type of deposit and figures the judged content of fine material. Figure 1 represents the smallest content and 10 the highest.

Relation between chemical and physical soil properties.

Soil colloidal clay-humus particles are supposed to be macro anions carrying a negative electric charge. They are surrounded by or connected with a corresponding number of cations i. e. protons and metal ions which counterbalance their negative charge and make them appear electro-neutral. The sum of such closely held (adsorbed) cations expressed in milliequivalents pr. 100 g dry matter is called the adsorption capacity of the soil in question.

Table I. Description of the samples.
Tabel I. Beskrivelse af prøverne.

profile no.	*locality (polder)*	*sample no.*	*depth cm*	*designation*
profil nr.	lokalitet (kog)	prøve nr.	dybde cm	betegnelse
1)	Møgeltønder Kog	1_1	0— 35	Y
	district II, field 57.	1_2	55— 70	Z
	(diked 1555)	1_3	70— 90	X
		1_4	110—125	V
2)	Rudbøl Kog,	2_1	10— 25	
	district XVIII, field 36.	2_2	50— 65	Æ^5
	(diked 1715)	2_3	70—100	Ø^7
3)	Gammel Frederikskog,	3_1	10— 40	Æ^9
	district XVI, field 94c	3_2	50— 70	Ø^2
	(diked 1692)	3_3	95—110	Ø^5
		3_4	120—125	Ø^9
4)	Ny Frederikskog,	4_1	0— 30	
	district XVII, field 133.	4_2	50— 70	Ø^7
	(diked 1861)	4_3	85—100	Ø^2
		4_4	120—125	S
5)	Marine foreland	5_1	15— 35	Æ^7
	outmost on 2' cliff, on line	5_2	50— 75	Ø^8
	with district XVII, field 2.	5_3	120—125	V
6)	Taken on the same line 100 m from sea.	6_1	10— 30	Æ^6
7)	The same line in the Wadden about 20 m west of the border of foreland.	7_1	0— 10	S
8)	Southern side of the Rømø dam	8_1	abt. 10	
	in the sedimentation basins.	8_2	abt. 40	
9)*	Marine foreland, Ny Frederikskog, in an artificial ditch, (grøblerende).	9_1	15— 35	V
10)*	Wadden sea, Ny Frederikskog, about 25 m west of the border of foreland.	10_1	0— 15	S

* sampled by N. Kingo Jacobsen in the summer 1955.

Adsorbed metal ions are held in place by electrostatic forces and may easily be displaced by other cations which means that soils are cation exchangers. The relative proportion of different adsorbed cations is governed by mass action, but since different cations are held with different strength and show different replacing power in the same concentration, different metal ions do not occur in the same relative proportion on the surface of the colloids and in the surrounding soil solution.

Among metal ions the divalent Ca^{++} and Mg^{++} show a greater replacing power than the monovalent K^{+} and especially than Na^{+}. Hydrogen ions are held more strongly than are metal ions; hydrogen saturated soil colloids are weak acids. Therefore a partially neutralized soil acts as a buffer. The p_H of the system will chiefly be determined by the degree of base saturation. Full base saturation may not be reached in a humid climate and protons may only be fully displaced if strong bases such as $Ca(OH)_2$ or NaOH are added to soils.

According to *Hissink* (1925) the degree of base saturation is $V = 100\ S/T$. In this formula S designates milliequivalents adsorbed metal ions pr. 100 g dry soil, T the total adsorbing capacity expressed in the same way. Further $T = S + H$ where H designates milliequivalents H^{+} pr. 100 g dry soil.

Several methods have been proposed for determination of H and S values. *Hissink* (1925) determined H by titrating soils with 0.1n $Ba(OH)_2$ to complete saturation i.e. when p_H of the system lies close to 11. *Bradfield and Allison* (1933) proposed that V should be arbitrarily fixed to 100 per cent when soils are in chemical equilibrium with a surplus of $CaCO_3$ and a CO_2-pressure as normally found in the atmosphere (p_H 8.3).

This definition of T and V will be used in the following, but it should be emphasized that at p_H 8.3 soil colloids still contain considerable quantities of adsorbed hydrogen. According to Hissink soils at p_H 8.3 will be only about 55 per cent base saturated.

Just as different cations are held with different strength by soil colloids they show different deflocculating or coagulating powers when added to clay-humus-water suspensions. Calcium ions are strongly adsorbed and "calcium clay" shows only a small degree of dispersion. Sodium is much less strongly adsorbed than calcium, and "sodium clay" has a pronounced tendency to appear in a highly disperse stage. It is only when sodium ion concentration in the soil solution is sufficiently high, that sodium clay appears in a deflocculated stage.

Soils containing non-disperse calcium clay will usually show a granular structure and be permeable to water, whereas similar soils containing sodium clay are non-granulated, structureless. Such soils, when moist, are pasty, nearly impermeable to water, and when drying, shrink, forming a stony crust which may be broken into hard lumps.

Thus structure and dispersity of any clayey soil depends upon ratios between the different adsorbed cations and upon salt concentration in the soil solution. In a highly disperse soil, sodium must necessarily constitute a considerable fraction of the adsorbed cations. Further, pH in the system must be high so that only small quantities of hydrogen ions are held by the colloids, and finally salt concentration in the soil solution must be low. To what extent are these requirements fullfilled i marsh soils?

Development and changes after diking.

Development and changes in diked marine deposits have been thoroughly studied by *Hissink* (1925), (1933), (1938), (1940) and by *Trilling* (1928). The fresh marine deposits form a type of soil (solonchack) which is non-stable if leaching occurs during a certain length of time. Its change and development will therefore chiefly depend upon drainage. Immediately after diking the soil always contains some $CaCO_3$, organic matter, polysulfides of iron and dissolved NaCl. In this initial stage the adsorbed cations consist of nearly equal amounts Na^+, Mg^{++}, and Ca^{++} (expressed in milliequivalents pr. 100 g dry matter).

Permeability to water in spite of the high sodium content is good, due to high salt concentration in the soil solution, which prevents dispersion of the clay colloids.

If drainage is satisfactory the surplus of dissolved NaCl will soon be carried away from surface layers by leaching. At the same time CO_2, Fe^{+++} and H_2SO_4 will appear as results from biological oxidations i.e. acids are produced and protons attack $CaCO_3$ forming Ca^{++}. These calcium ions displace Na^+ from the soils adsorbing complex and gradually give rise to a non-disperse granulated soil with nearly Ca^{++} saturated colloids. When all the $CaCO_3$ originally present has been dissolved continued production of H^+ gradually gives rise to a hydrogen saturated non-disperse soil.

If drainage is poor, oxidation and leaching will be impeded, displacement of Na^+ by Ca^{++} proceed slowly and only to a limited extent. When most of the dissolved salts originally present have been carried away by slow leaching and diffusion, conditions are favourable for the formation of disperse sodium clay.

The object of the present work has been to find out to what stage such a development has reached in soils from different polders. For that purpose $CaCO_3$-content was determined in the samples, p_H determinations were made, and amounts of various cations as well as chloride contents were also determined. To gain information on particle-size distribution, mechanical analyses were made.

Methods used for analyses.

p_H values were determined in aqueous suspensions by a glass electrode. Results from these measurements are shown in Table II.

$CaCO_3$ was determined using a Scheibler apparatus. The principle of the method is measuring the volume CO_2 developed from a definite soil quantity when treated with a surplus of hydrochloric acid. 10 g dry soil were used for each analysis. The results appear from Table II.

Chloride. A weighed quantity of soil — in most cases 20 g — was shaken in 100 c.c. of saturated $CaSO_4$-solution. After filtration 60 c.c. of the filtrate was titrated with 0.1 molar $AgNO_3$ according to Mohr. In sample 1_3 p_H was too low to permit the use of this method. The chloride contents found, expressed as milliequivalents per 100 g dry soil, are stated in Table II.

Electrical conductivity. A soil suspension was prepared in an Erlenmeyer flask from 25 g dry soil and 225 ml distilled water. After vigorous shaking the suspension was left standing during half an hour. The clay suspension was then decanted from sand at the bottom and its electric conductivity measured with a Wheatstone bridge arrangement. Results of such measurements are listed in table II under the heading L_t, which designates specific conductivity of the clay suspensions, multiplied by 10^4.

Adsorbed metal ions were displaced from the soils adsorbing complex by leaching with a 1 molar ammonium acetate solution. 125 c. c. 1 mol. ammonium acetate were added to 25 g dry soil in an Erlenmeyer flask. The flask was repeatedly shaken for several hours, the suspension filtered by suction, and the filter washed 6—8 times with ammonium acetate solution, using each time 25 c. c. The filtrate was evaporated to dryness on a steam bath. Solid ammonium acetate was removed carefully by ignition, the residue dissolved in water and the solution diluted to a volume of 250 c. c.

Calcium. To 100 c.c. of that solution 10 per cent KOH solution was added until p_H came close to 12. Then titration was made with 0.1 molar solution of E. D.T.A. (the di-sodium salt of ethylene-diamine-tetra-acetate) using murexide as an indicator. 1 mol E.D.T.A. equals 1 mol.

Table II.

p_H, $CaCO_3$ contents, chloride contents and Lt-values of the samples.

Tabel II.

Prøvernes p_H-værdi, $CaCO_3$-indhold, chloridindhold og ledningstal.

locality (polder)	*profile no.*	*sample no.*	*designation*	*depth cm*	*p_H value*	*$CaCO_3$ %*	*chloride meqv/100 g*	*Lt values*
lokalitet (kog)	profil nr.	prøve nr.	betegnelse	dybde cm	p_H-værdi	$CaCO_3$ %	chlorid mækv/100 g	Ledningstal
Møgeltønder Kog	1	1_1	Y	0— 35	7.4	0	0.1	
» »	1	1_2	Z	55— 70	7.8	0	1.2	
» »	1	1_3	X	70— 90	3.6	0		
» »	1	1_4	V	110—125	8.0	1.4	0.5	6.9
Rudbøl Kog	2	2_1		10— 25	7.5	0	0	
» »	2	2_2	Æ^5	50— 65	7.9	1.5	0.2	
» »	2	2_3	Ø^7	70—100	7.2	0.7	0.9	6.8
Gl. Frederikskog	3	3_1	Æ^9	10— 40	8.9	1.8	0.8	
» »	3	3_2	Ø^2	50— 70	8.7	1.3	2.6	4.0
» »	3	3_3	Ø^5	95—110	9.2	0.8	1.3	2.3
» »	3	3_4	Ø^9	120—125	9.1	1.3	1.4	2.9
Ny Frederikskog	4	4_1		0— 30	7.6	0		
» »	4	4_2	Ø^7	50— 70	8.1	2.6	0.5	
» »	4	4_3	Ø^2	85—100	8.7	0.9	0.2	
» »	4	4_4	S	120—125	8.3	1.6	0.2	
marine foreland	5	5_1	Æ^7	15— 35	7.2	0.9	11.9	
» »	5	5_2	Ø^8	50— 75	8.2	3,8	10.7	
» »	5	5_3	V	120—125	8.0	4.9	15.7	
marine foreland	6	6_1	Æ^6	10— 30	8.2	2.9	16.8	
wadden sea	7	7_1	S	0— 10	8.3	1.6	12.2	15.6
Rømø dam	8	8_1		abt. 10	7.9	6.3*		
» »	8	8_2		abt. 40	8.0	1.4		

* 5.6 per cent Humus.

Ca^{++} (Determination of Ca^{++} and Mg^{++} by the E.D.T.A.-method has been described in detail by *H. L. Jensen* and *Aage Henriksen* (1954).

Magnesium. 100 c.c. of the above named solution was treated with a surplus of ammonia-ammonium carbonate buffer solution in order to fix its p_H value at about 10. It was then titrated with E.D.T.A.-solution, using Eriochrome black T as indicator. $Ca^{++} + Mg^{++}$ may be calculated from the amount of E. D. T. A. used in this titration. By subtracting the already determined Ca^{++}-content from the above result found by titration, the Mg^{++} quantity is found.

Sodium. The remaining 50 c.c. stock solution were filtered and Na^+-concentration in the filtrate determined with a Beckmann flame spectrofotometer, model D.U. Solutions of pure NaCl in known concentrations were used as standards.

Adsorbed hydrogen ions.

In the relatively few unsaturated soils examined, the content of adsorbed H^+ was calculated from p_H-values and total quantity of adsorbed metal ions found by analysis. Since the base saturation degree is a nearly linear function of p_H (S. Tovborg Jensen (1936)) the approximate adsorption capacity (T) may be calculated from the equation:

$$\frac{p_H - 4.1}{8.3 - 4.1} = \frac{\text{adsorbed metal ions}}{\text{adsorbed } H^+ + \text{adsorbed metal ions}}$$

By using this equation, amounts of adsorbed ions are expressed in milliequivalents.

Contents of the different adsorbed cations, adsorption capacity and percentage sodium in the adsorbing complex appear in table III.

Mechanical analysis.

Particle size and particle size distribution in the samples were determined by *Andreasen's* pipette method (1939). This method, used for soil analysis by *S. Tovborg Jensen* and *B. Kjær* (1948) is briefly described in the following:

50 g dry soil is placed in a Stohmann flask, 350 c. c. of a 0.002 molar $Na_4P_2O_7$-solution added, and the flask kept rotating for 16 hours in a revolving shaking apparatus. After this the completely disperged suspension is transferred to an ordinary medicine bottle holding 500 c. c. and closed with a stopper in which a siphon is inserted (fig. 1).

Table III. Adsorbed cations. Milliequivalents pr. 100 g soil and equivalent percentages of sodium in the adsorbing complex.

Tabel III. Adsorberede kationer i milliækvivalenter pr. 100 g jord og adsorberet natrium i ækvivalentprocent af adsorberede kationer.

locality (polder)	*profile no.*	*sample no.*	*designation*	*depth cm*	*Ca++*	*Mg++*	*Na+*	*H+*	*ads. cap.*	*Na+ equiv. %*
lokalitet (kog)	profil nr.	prøve nr.	betegnelse	dybde cm	Ca++	Mg++	Na+	H+	ads. kap.	Na+ ækv. %
Møgeltønder Kog	1	1_1	Y	0— 35	16.4	8.0	0.4	8	33	1.2
» »	1	1_2	Z	55— 70	13.6	4.4	1.2	4	23	5.2
» »	1	1_3	X	70-- 90	5.8	2.4	1.5	?	?	?
» »	1	1_4	V	110—125	34.0	4.2	0.7	0	39	1.8
Rudbøl Kog	2	2_1		10— 25	11.3	2.9	0.4	4	19	2.1
» »	2	2_2	Æ^5	50— 65						
» »	2	2_3	Ø^7	70—100	22.2	4.2	1.8	0	28	6.4
Gl. Frederikskog	3	3_1	Æ^9	10— 40	23.4	7.5	4.4	0	35	12.5
» »	3	3_2	Ø^2	50— 70	10.9	6.2	3.4	0	21	16.2
» »	3	3_3	Ø^5	95—110	3.8	0.9	1.8	0	6.5	27.6
» »	3	3_4	Ø^9	120—125	9.8	2.4	2.7	0	15	18.0
Ny Frederikskog	4	4_1		0— 30						
» »	4	4_2	Ø^7	50— 70	26.0	1.3	0.4	0	28	1.4
» »	4	4_3	Ø^2	85—100	13.8	4.4	0.1	0	18	0.6
» »	4	4_4	S	120—125						
marine foreland	5	5_1	Æ^7	15— 35	6.2	11.1	18.0			
» »	5	5_2	Ø^8	50— 75	30.2	7.8	18.5			
» »	5	5_3	V	120—125	32.8	11.5	21.5			
marine foreland	6	6_1	Æ^6	10— 30	27.0	5.8	22.0			
wadden sea	7	7_1	S	0— 10	15.1	4.7	13.5			

The suspension is filled up to a mark exactly 10 cm above the inlet of the siphon, homogenized by shaking and left standing during exactly 2 minutes for sedimentation. Then the upper 10 cm of the suspension is drawn off with the siphon. Material remaining in the flask is treated in this manner 3—4 times in succession with 0.002 molar $Na_4P_2O_7$-solution each time and the upper 10 cm is siphoned off. The operation is repeated until the liquid siphoned off is completely clear. The clay suspensions are collected.

By this procedure the soil sample is divided into two fractions 1) a sand fraction remaining in the bottle. The particles in this fraction are equal to or larger than 25 microns (μ). 2) a clay fraction drawn off as suspension containing all particles in the soil sample smaller than 25 μ.

Particle size (k) is defined as edge length of a cube having the same volume as the particle in question. k values in clay suspensions may be determined experimentally by sedimentation analysis and calculated from Stokes' formula:

$$k = 141 \sqrt{\frac{h}{t} \frac{\eta}{(d_1 - d_2)}};$$

In the formula k is expressed in μ, h designates sedimentation distance measured in cm, t sedimentation time in minutes, d_1 specific gravity of soil particles (2.61), d_2 specific gravity of the dilute $Na_4P_2O_7$-solution (1.00) and η viscosity of the same solution. η varies with temparature. At 20° C it would be 0.0102.

Particle-size and — distribution in the sand fraction is determined after drying by sifting using 5 different sieves with mesh sizes 63 — 105 — 149 — 250 and 350 μ and by weighing the fractions held back on each of them and that passing the smallest meshes (63 μ). When sand contents have been determined, the content of silt + clay in the collected suspensions may be calculated.

In the clay fraction particle-size distribution is determined by sedimentation analysis using the Andreasen pipette apparatus. It consists of a 30 cm. tall glass cylinder containing 500—600 c. c. and with an internal diameter of 6 cm. It is closed at the top by a glass stopper, supplied with a 10 c. c. pipette by means of which suspension samples may be drawn at intervals during the sedimentation period from a layer exactly 20 cm below the initial liquid surface (fig. 2). For analysis a representative portion of the collected suspensions is transferred to the apparatus The suspension is homogenized by shaking and the apparatus left standing for sedimenta-

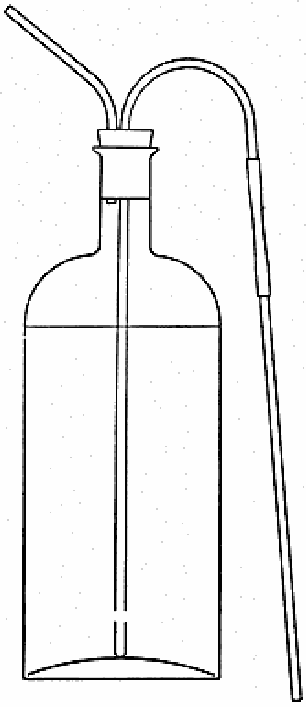


Fig. 1. Bottle with siphon.

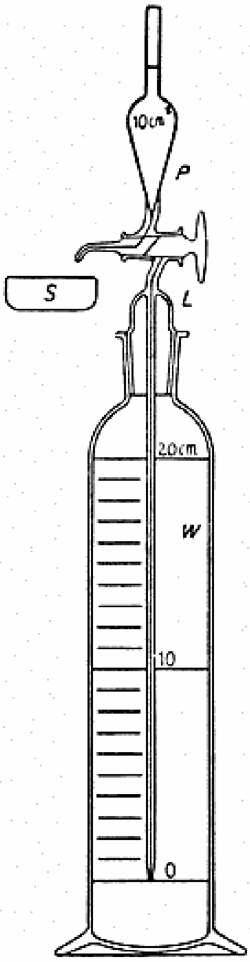


Fig. 2. Andreasens pipette apparatus.

tion and sample drawing. The first pipette sample (zero sample) is drawn immediately after shaking, the following 5, 15, 45, 150, 405 and 1440 minutes later than the zero sample.

While standing sedimentation takes place continuously and the settling rate will differ for different particles, depending upon their size. Particles of the same size will settle with the same constant velocity. When a certain time (t minutes) has elapsed all particles above a corresponding size k_t will have fallen from the surface below the inlet of the pipette.

Some particles smaller than k_t have also sunk below the inlet, but they are constantly replaced by other particles of the same size and in the same concentration from the layers above. Thus in the horizontal layer around the pipettes inlet suspended particles having $k < k_t$ will occur in the same concentration as in the initial suspension, while coarser particles ($k > k_t$) do not occur at all.

Table IV.

Percentages of material with particle-sizes smaller than 2, 20 and 200 μ.

Tabel IV.

Procent materiale med partikelstørrelse mindre end 2, 20 og 200 μ.

locality (polder)	*profile no.*	*sample no.*	*desig-nation*	*depth cm*	*% < 2 μ*	*% < 20 μ*	*% < 200 μ*
lokalitet (kog)	profil nr.	prøve nr.	beteg-nelse	dybde cm	% < 2 μ	% < 20 μ	% < 200 μ
Møgeltønder Kog	1	1_1	Y	0— 35	60	88	n. d.
» »	1	1_2	Z	55— 70	62	95	—
» »	1	1_3	X	70— 90	43	91	—
» »	1	1_4	V	110—125	43	88	—
Rudbøl Kog	2	2_1		10— 25			
» »	2	2_2	Æ^5	50— 65	21	32	98
» »	2	2_3	Ø^7	70—100	19	30	99
Gl. Frederikskog	3	3_1	Æ^9	10— 40	38	64	96
» »	3	3_2	Ø^2	50— 70	15	22	98
» »	3	3_3	Ø^5	95—110	9.5	14	99
» »	3	3_4	Ø^9	120—125	12	16	98
Ny Frederikskog	4	4_1		0— 30	20	40	94
» »	4	4_2	Ø^7	50— 70	29	46	96
» »	4	4_3	Ø^2	85—100	8.5	12	98
» »	4	4_4	S	120—125	8	11	97
marine foreland	5	5_1	Æ^7	15— 35	31	52	96
» »	5	5_2	Ø^8	50— 75	45	67	97
» »	5	5_3	V	120—125	40	60	97
marine foreland	6	6_1	Æ^6	10— 30	30	47	95
wadden sea	7	7_1	S	0— 10	10.5	15	98
Rømø dam	8	8_1		abt. 10	38	80	n. d.
» »	8	8_2		abt. 40	9.5	16	96
marine foreland	9	9_1	V		42.3 (43.9)	64.4 (64.4)	98
wadden sea	10	10_1	S		4.7 (5.2)	6.5 (6.5)	98

Under fixed conditions k_t values depend only on sedimentation time and may for each sample be calculated from Stokes' formula, since this, also as demonstrated by *Andreasen* (1939), is valid for suspensions containing non-spherical particles.

The six successive samples drawn after the zero sample correspond to k_t values about 22 — 13 — 7 — 4 — 2 and 1 μ. They, and the zero sample are all collected in small silver bowls evaporated to dryness and weighed. The amount of dry matter is corrected for the (small) content of $Na_4P_2O_7$.

By comparing the amounts of clay found in each of the six samples with the amount found in the zero sample, percentage of the particles smaller than indicated by the respective k_t values may be calculated. Since sand content is already known, this may be included in the calculation and results stated as contents of particles below definite sizes (k_t) in per cent of total solids.

Some of the analysed samples consisted chiefly of clay. Of these samples only 5 — 10 g material were used for analysis. After disperging with 350 c.c. $Na_4P_2O_7$-solution, the entire sample was transferred to the Andreasen apparatus without previous separation of sand, and particle-size distribution determined directly. The initial concentration of suspended material was calculated from weight of solid material and volume of the Andreasen apparatus. In such cases no zero sampling was used. Sample number 1 was drawn after a settling period of 1 minute corresponding to a k_t value about 45 μ. Soil samples 9 and 10 were analysed by using both procedures.

The small quantities of solid material used in analyses as described above, secure complete dispersion of clay particles in the pyrophosphate solution. If larger quantities for instance 50 g of heavy clay soils are used, a complete dispersion is hardly obtainable, especially if such soils also contain appreciable quantities of soluble salts.

The analysed samples contained some organic matter which, if very accurate results are desired, must be destroyed prior to sedimentation. Since organic matter content was small in comparison with clay content, and since no high degree of accuracy seemed necessary in this case, organic matter (and $CaCO_3$) was not destroyed.

Results from mechanical analyses of representative samples are shown graphically as summation curves in figs. 3—10.

The ordinate, at any point of such curves, shows percentage material having particle-sizes equal to or smaller than that read from the abscissa (k).

Per cent material with particle-sizes smaller than read from the abscissa (k)

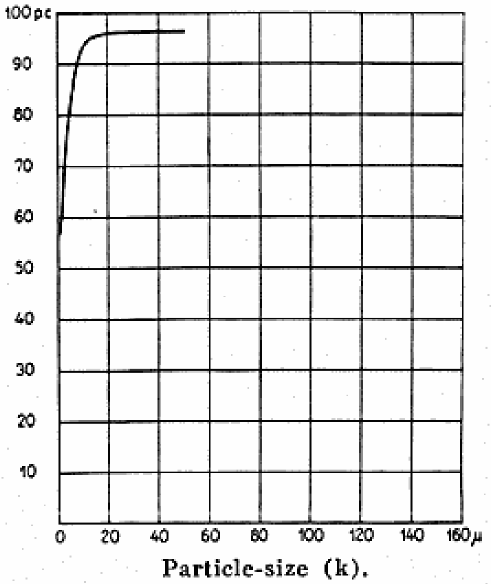


Fig. 3. Sample 1_2, Z, Møgeltønder Kog.

Per cent material with particle-sizes smaller than read from the abscissa (k)

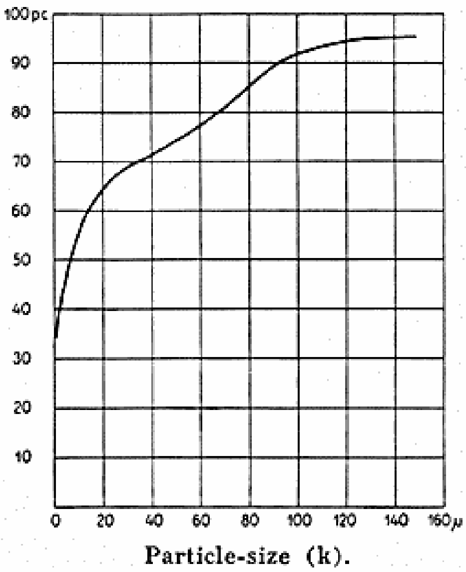


Fig. 4. Sample 3_1, Æ^9, Gl. Frederiks-kog.

Per cent material with particle-sizes smaller than read from the abscissa (k)

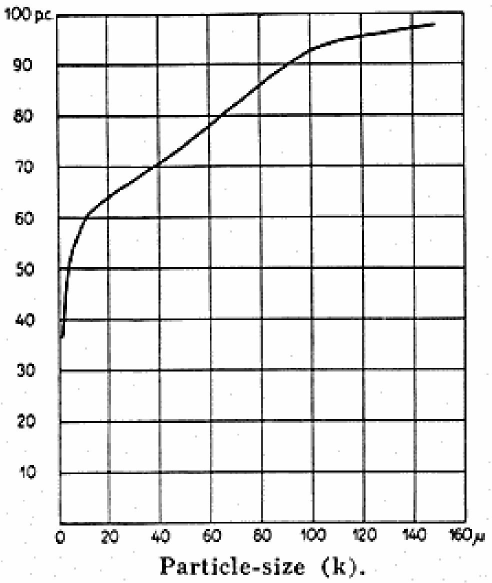


Fig. 5. Sample 9_1, V, marine foreland.

Per cent material with particle-sizes smaller than read from the abscissa (k)

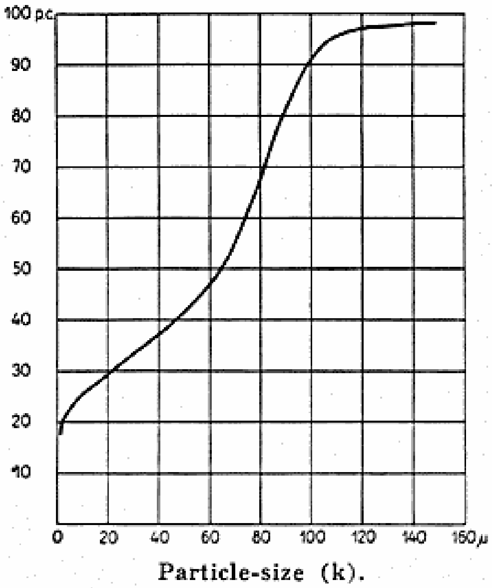
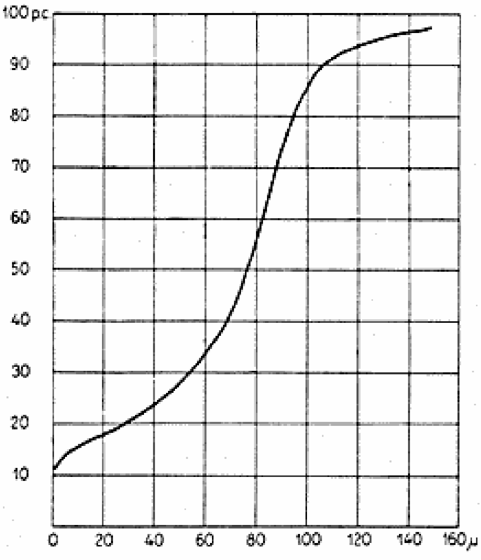


Fig. 6. Sample 2_3, Ø^7, Rudbøl Kog.

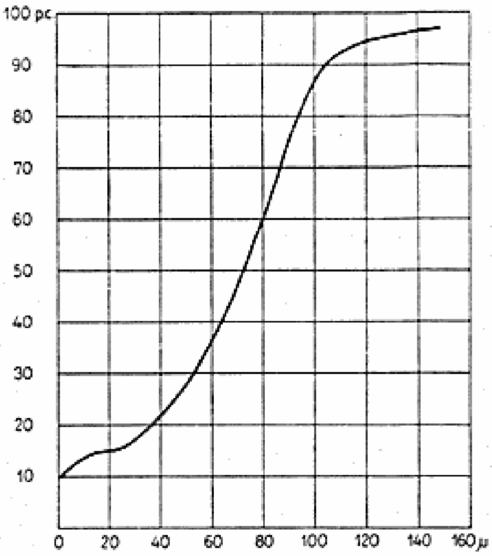
Per cent material with particle-sizes smaller than read from the abscissa (k)



Particle-size (k).

Fig. 7. Sample 3_4, Ø^{9}, Gl. Frederiks-kog.

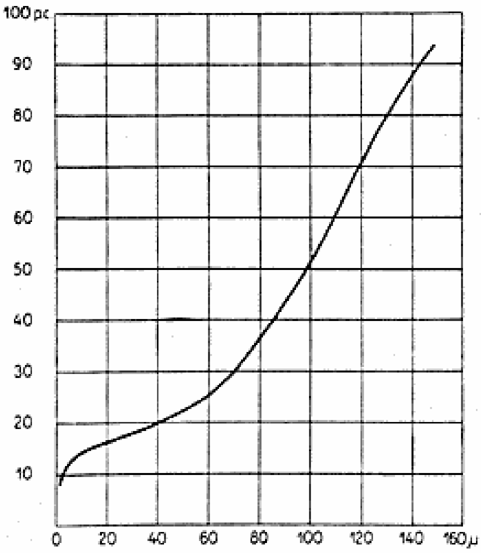
Per cent material with particle-sizes smaller than read from the abscissa (k)



Particle-size (k).

Fig. 8. Sample 7_1, S, wadden sand.

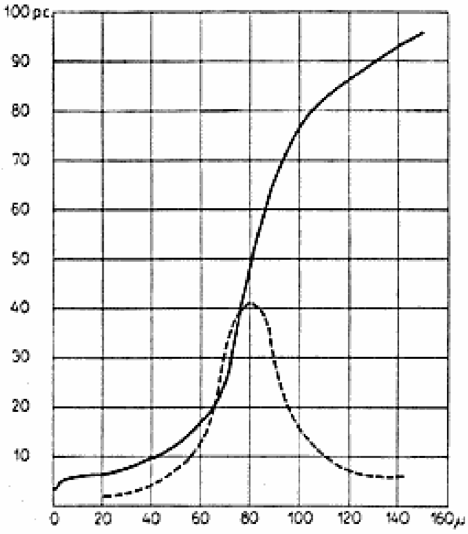
Per cent material with particle-sizes smaller than read from the abscissa (k)



Particle-size (k).

Fig. 9. Sample 8_2, Rømø dam.

Full line: per cent material with particle-sizes smaller than read from the abscissa (k)
Dotted line: per cent material with particle-sizes differing less than 10 μ from that read from the abscissa (k)



Particle-size (k).

Fig. 10. Sample 10_1, S, wadden sand.

In fig. 10 the dotted curve shows the distribution of material between particle-size intervals. The ordinate, at any point of this curve, shows percentage material having particle-sizes which differ less than 10 μ from that read from the abscissa (k).

In Table IV percentages material smaller than 2, 20 and 200 μ are stated. For samples 9 and 10, the first figures show results from the full mechanical analyses and figures in brackets results found when only the Andreasen apparatus was used.

Discussion.

In drawing conclusions from the experimental data we shall first consider the content of $CaCO_3$ in the samples. This content will depend partly on initial content and partly on rate and degree of leaching. Rate and degree of leaching again depend largely upon local drainage conditions.

The initial $CaCO_3$ content seems closely related to the clay content of the samples. Thus fresh deposits close to the Rømø dam contain 6.3 per cent $CaCO_3$ in the clay surface layer, but only 1.4 per cent in deeper sandy layers. Similarly, fresh clay deposits from profile 6 contain more $CaCO_3$ than does wadden sand from profile 7.

Young deposits on the marine foreland contain $CaCO_3$ throughout the entire profile, whereas in polders this substance is found only in the layers some distance below surface. This shows that $CaCO_3$-content is related to age and depth of strata. Ordinarily soils from young polders, such as Ny Frederikskog diked one century ago, contain more $CaCO_3$ than soils in polders diked several centuries ago. Gl. Frederikskog, diked 1692, is an exception from this rule. Here the soil still contains $CaCO_3$ at the surface.

The samples 2_2, 3_2 and 4_2 contain more $CaCO_3$ than the samples 2_3, 3_3 and 4_3 respectively. This may be explained by the higher clay content in the upper layers than in the lower more sandy layers.

At a depth of 120 cm, $CaCO_3$ contents again increase. We are here close to the ground water table and leaching has not affected this horizon appreciably. It has been stated that dissolution of $CaCO_3$ and subsequent leaching proceed with nearly constant velocity and that ordinarily it will take several centuries before the entire $CaCO_3$-content has disappeared from diked marsh soils. This statement however, should not be generalized since initial content and rate of leaching in many cases largely depend upon local conditions.

Thus in Gl. Frederikskog where drainage has been poor, soils may still contain nearly 2 per cent $CaCO_3$ at the surface, whereas soil from profile 5 on the marine foreland only contains 0.9 per cent although this is a very young deposit.

Presumably the free permeability to water so characteristic of recently deposited clay in the marine stage, together with biological activity in the mud may cause a rapid dissolution and disappearance of $CaCO_3$.

Nearly all samples containing $CaCO_3$ showed p_H-values around 8. Higher p_H were found only in soil from Gl. Frederikskog. This will be discussed later in the present paper. Acid soils (p_H 3.6) were found in profile 1 but only in the horizon 70 — 90 cm below surface. This may be due either to a recent application of marl to the surface layer or to different origin of layers and different initial $CaCO_3$-contents.

The chloride content is not related to the solid soil particles, but depends only upon composition of the soil solution. Therefore chloride percentage depends upon water movements, moisture content and — distribution in soil profile.

On the marine foreland chloride content is high, 0.3—0.5 per cent in soil dry matter. Behind the dikes the highest Cl-content was found in soil from profile 3 Gl. Frederikskog indicating impeded drainage in this locality.

The highest specific conductivity was found in the sample 7_1 from the wadden sea. The L_t-value found was 15.6. In ordinary tilled soil the L_t value will rarely exceed 1 (Steenbjerg 1946). Many crops are injured from salinity if L_t values lie higher than 3.

Determination of adsorbed metal ions by the method used in this investigation will be subject to certain minor errors. First: cations from dissolved salts will be registered among adsorbed cations. Chloride contents and conductivity measurements show, that this error will only be of importance when analysing samples from the marine foreland. Therefore for such samples adsorption capacity and amounts of adsorbed metal ions may not be stated. Second: small quantities of $CaCO_3$ will disolve in the neutral ammonium acetate solution and be registered as adsorbed Ca^{++}. Finally small quantities of Fe^{+++} and Al^{+++} may be taken for Ca^{++} when titrating with E.D.T.A. *(H. L. Jensen,* and *Aa. Henriksen* (1954)*)*.

The adsorption capacity T increases with increasing clay content. In samples characterized as clay it was about 30—40 milliequivalents per 100 g dry matter. In samples characterized as sand, T-values were 10—15.

Adsorbed magnesium was about 20 equivalent per cent of the total quantity adsorbed metal ions. Similar amounts were found by *Hissink* in Dutch soils of marine origin, (1933, 1938, 1940) and by Aslyng (1955) in Danish marsh soils. Danish arable soils developed from glacial drift contained, in most cases, less than 10 equivalent per cent magnesium (S. Tovborg Jensen, 1936).

Considerable amounts adsorbed sodium were found only in samples from the marine foreland and from Gl. Frederikskog. Samples from other localities contained less than 7 equivalent per cent adsorbed sodium. Even if this is considerably more than in most Danish soils of non-marine origin it is insufficient to cause high dispersity and impermeability to water. In marsh soils wich such low sodium percentages, clay contents judged from field observations agree well with these found in the laboratory by mechanical analyses.

Clay content in samples from the marine foreland was also judged fairly accurately by direct observation even if such material must contain high percentages adsorbed sodium. This undoubtedly is due to high salt concentration in the soil solution, which prevents dispersion of colloidal clay particles.

Samples from one locality in Gl. Frederikskog contained 15 — 25 equivalent per cent adsorbed sodium and showed p_H values around 9. Salt content in the soil solution here was only $^1/_{10}$ of that found in samples from the marine foreland. Samples from profile 3 are of the alkaline soil type mentioned in the introduction and should be highly disperse.

This apparently is also the case. Clay contents in the samples judged from plasticity were entirely too high when compared with the corresponding contents determined by mechanical analyses. In this locality we find an alkali soil with properties characteristic for such soils i. e. alkaline reaction, high plasticity and impermeabilily to water. This soil type has developed under the influence of poor drainage.

p_H-values above 9 cannot be caused by $CaCO_3$ but require presence of a more „effective" base. Such a base is sodium carbonate Na_2CO_3 which as studies in true alkali soils have shown, may be produced by interaction between sodium clay and pure water containing CO_2.

The nature of such an interaction, which may also take place by soil formation processes on marine clay deposits, is not well known. Presumably the total and relative amounts of adsorbed metal ions will change under influence of changes in composition of the soil solution. The base saturation degree of soil colloids depends primarily upon the p_H of the system, colloid-soil solution, but also to some extent on salt concentration. At a fixed p_H, base saturation degree will increase with increasing salt concentration in the soil solution.

In the marine stage, clay colloids are in chemical equilibrium with a 3 per cent NaCl-solution and finely divided $CaCO_3$ particles: Base saturation degree in this stage is high. When NaCl is removed by leaching and diffusion, the soil colloids are subjected to hydrolysis. Adsorbed sodium ions are replaced by hydrogen ions, H^+ (from HCO_3^-) and reaction changes in an alkaline direction i.e., p_H of the system, increases. At the same time sodium carbonate Na_2CO_3 is formed. This may be explained as follows:

The ratios $\frac{\text{adsorbed } Ca^{++}}{\text{free } Ca^{++}}$ and $\frac{\text{adsorbed } Na^{+}}{\text{free } Na^{+}}$ will

not show the same variation, when the soil solution is diluted by leaching. During the dilution process percentage of adsorbed Ca^{++} increases, while that of adsorbed Na^+ decreases. Therefore chiefly free sodium ions will be produced by hydrolysis and leached away.

Results from the mechanical analyses show, that marine deposits in Danish marsh areas consist only of fine material. This material may be divided into two distinctly different fractions according to particle-size distribution. One of these fractions consists of fine sand having a rather uniform particle size, around 80 μ. The other consists of silt + clay having particle sizes $k < 20\ \mu$. In the silt-clay fraction about $^2/_3$ is usually clay ($k < 2\ \mu$) and $^1/_3$ silt ($2\mu < k < 20\mu$).

The definition used by Dutch authors for marine clay deposits is: a material consisting of particles smaller than 16 μ (*Hissink* 1940). Using this figure instead of 20 μ as upper limit for the clay-silt fraction would not mean any great difference in percentages, as the content of material having particle-sizes around 20 μ is usually small.

Differences in particle-size distribution from one sample to another are chiefly due to differences in the ratio silt+clay/sand. The figures in Table IV show great variations in this ratio. They show that most Danish marsh „clay“ contains various amounts of sand, probably deposited on the marine foreland under the combined influence of wind and high water. Only material from profile 1 does not contain wadden sand.

The deeper strata in the three youngest polders show nearly the same particle-size distribution as wadden sea sediments. The upper layers however in this respect are much similar to soils from profiles 5 and 6.

The sandy material found in deeper layers was presumably deposited under ordinary wadden sea conditions, and the upper clayey material during a period when the surface was vegetation covered

(*Niels Nielsen* 1935, *Børge Jakobsen* 1954) i. e. under marine foreland conditions resembling those of to-day.

Particle-size distributions in clay from the samples 4_1, 1_3, 1_4 and 8_1 are different from those in other samples. Here the particles smaller than 2 μ only amount to about 50 per cent of the clay-silt fraction.

Profile 8 is not typical for the marine foreland. It is situated close to the Rømø dam. The sample 8_2 consists of relatively coarse sand which has not been sorted to the same degree as sand from other localities.

It is already mentioned that the samples 3 and 4 from profile 1 show unusual variations in pH and $CaCO_3$ content. This fact and particle-size distribution determined by analysis suggest that sedimentation conditions in this locality differed from those on marsh foreland of to-day. The available data however do not permit definite conclusions on that subject.

The samples of wadden sea sand consist chiefly of well assorted material very uniform in particle-size. This has earlier been shown by *H. Gry* (1942) and by *K. Hansen* (1951 and 1954). Even if this well assorted material seems rather uniform with most particles around 80 μ, it contains 6—15 per cent silt+clay. This peculiar fact is probably due to the high salt concentration of sea water which flocculates clay particles into aggregates (secondary particles) much larger than the primary particles.

In order to prove the correctness of that theory, sedimentation analyses were made of the samples 9_1 and 10_1 using sea water as disperging agent instead of the usual very dilute pyro-phosphate solution. Under such conditions the samples apparently contained no particles at all smaller than 2 μ.

These analyses therefore do not give a true picture of (primary) particle-size and particle-size distribution in wadden sea sand, nor do they show the true particle-size and -distribution of the (secondary) particles under wadden sea conditions, but they demonstrate clearly the coagulating power of sea water and its influence upon clay sedimentation.

The particle-size and -distribution is only determinable after the material has been fully disperged in $Na_4P_2O_7$-solution or in another suitable medium.

Conclusions.

The investigations show that soils in the two youngest polders, Ny Frederikskog and Rudbøl Kog, have changed from the initial marine stage into the present non marine stage. Leaching has been sufficient to prevent formation of sodium clay, and the soils show physical properties favourable for agriculture.

In one locality in Gl. Frederikskog, too high ground water level has apparently impeded leaching and biological oxidation processes necessary for the ion exchanges with ultimately cause formation of non-disperse granular calcium clay. Highly disperse sodium clay was found in layers slightly below the surface and the soils physico-chemical properties are at present very unfavourable for agriculture.

The analytical data do not permit definite conclusions about formation processes in Møgeltønder Kog. Here sedimentation seems to have taken place under conditions somewhat different from those in the other polders. Inhomogeneity of strata in this marsh section makes generalizations impossible.

SUMMARY

Orientation analyses were made on samples from profiles representing soils in 4 polders in Tønder marsh, the marine foreland and bottom material in the wadden sea. In the samples, contents of $CaCO_3$, chloride, adsorbed Ca^{++}, Mg^{++} and Na^{+}, p_H-values and particle-size distribution were determined. The results were used for physico-chemical characterization of soils in the polders. The analytical data show, that disperse sodium clay occurred in one locality.

Undersøgelser af marskjord og vadehavssedimenter fra Tønderområdet

Sammenfatning.

For at supplere de undersøgelser over Tøndermarskens dannelsesforhold og egenskaber, som for tiden foretages af professor Niels Nielsen og medarbejdere, blev der i sommeren 1954 udtaget jordprøver til analyse på Landbohøjskolens Agrikulturkemiske Laboratorium. Formålet var at opnå en orientering om jordernes fysiske og kemiske tilstand.

Hvert kog i Tøndermarsken er repræsenteret med 1 profil, som er placeret på et for det pågældende område karakteristisk sted. Desuden er der taget prøver på det marine forland og af vadehavssedimenter.

Hver profil repræsenteres af indtil 4 prøver.

En nærmere beskrivelse af prøverne vil fremgå af tabel 1, hvor prøverne er karakteriseret ved de symboler, der anvendes ved arbejdet i marken og hvis forklaring er givet af N. Kingo Jacobsen i den foregående artikel. Af et kort, side 120, i denne afhandling fremgår desuden prøveudtagningsstedernes beliggenhed.

Marskjorderne fysiske egenskaber vil afhænge dels af deres lerindhold, dels af deres kemiske tilstand, idet de vil påvirkes af saltindholdet, reaktionstallet (pH-værdien) og mængdeforholdet mellem de adsorbtivt bundne metalioner.

Hvis natrium udgør en væsentlig del af de adsorberede metalioner og reaktionstallet er højt, vil den pågældende jord have tendens til at foreligge i dispers form og have uheldige fysiske egenskaber.

En sådan tilstand skyldes under vort klima utilstrækkelig afvanding efter inddigning, hvorved udviklingen fra det saltholdige stadium kun kan forløbe delvis. Mangelfuld afvanding af marsken vil også kunne påvises gennem et højt kloridindhold, ligesom indholdet af calciumcarbonat vil være afhængigt af den udvaskning, som har fundet sted.

Arbejdet har derfor bestået i at karakterisere jordernes kemiske tilstand og den udvikling, de hidtil har gennemgået ved hjælp af bestemmelser af prøvernes indhold af calciumcarbonat og chlorid, deres reaktionstal og mængdeforholdene af de adsorberede metalioner. Resultaterne af disse undersøgelser er vist i tabellerne 2 og 3.

Desuden bestemtes prøvernes kornstørrelsesfordeling. Resultaterne er gengivet i tabel 4 og i fig. 3—10, hvor hvert punkt på kurverne angiver hvor mange procent af materialet, der har kornstørrelser, som er mindre end abscissen angiver.

Resultaterne giver oplysning om prøvernes lerindhold og derigennem om de forhold, hvorunder materialet er aflejret. Resultaterne kan også i nogen grad tjene som grundlag for karakteriseringen i marken.

Undersøgelserne viser, at jorderne i Ny Frederikskog og Rudbøl Kog har gennemgået en fuldstændig udvikling fra det oprindelige, saltholdige stadium til deres nuværende tilstand. Chloridindholdet er ringe og reaktionstallene og sammensætningen af de adsorberede ioner viser, at dispers natriumler ikke findes på disse lokaliteter. Fra cirka en halv meters dybde indeholder jorden endnu kendelige mængder calciumcarbonat.

I den undersøgte lokalitet i Gl. Frederikskog synes en høj grundvandstand at have vanskeliggjort den udludning og iltning, som er en betingelse for de ionbytningsprocesser, der sluttelig fører til dannelsen af ikke-dispers calciumler. Selv om jorden har været inddiget i cirka 300 år, er chloridindholdet ret højt og calciumcarbonat findes endnu helt op i overfladelaget. Reaktionstallene og mængdeforholdene af de adsorberede metalioner viser, at højdispers natriumler forekommer tæt op til overfladen. Jordens nuværende fysisk-kemiske tilstand er meget uheldig for dens dyrkning.

I disse 3 kog bestod de dybere lag af et materiale med samme mekaniske sammensætning som vadehavssandet, medens det øverste lag i så henseende viste stor lighed med forlandsklægen.

Man må derfor antage, at de dybere lag er tidligere vadehavsbund, medens det øverste lag sandsynligvis er afsat på bevokset grund under lignende forhold som de, der karakteriserer aflejringen af det nuværende forlandsklæg.

For Møgeltønder Kog tillader analyseresultaterne ikke bestemte slutninger angående lagenes oprindelse eller deres senere udvikling. I dette område synes aflejringen at have fundet sted under noget afvigende betingelser.

Lagdannelserne i dette kog er meget varierende, hvorfor resultaterne fra undersøgelsen af en enkelt profil kun kan karakterisere den pågældende lokalitet.

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