FOLIA GEOGRAPHICA DANICA · TOM. XIX

SOIL RESEARCH IN DENMARK

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ROSENDAHLS BOGTRYKKERI · ESBJERG

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DET KONGELIGE DANSKE GEOGRAFISKE SELSKAB

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The Royal Danish Geographical Society

congratulates

Professor, Dr.phil. *Niels Kingo Jacobsen,*
Secretary General and Vice-President of the Society,

and

Professor, Dr.agro. *Kjeld Rasmussen,*
Member of the Board,

on their 70th birthdays.

S. Thostrup

S. Thostrup
Vice-President

Contents

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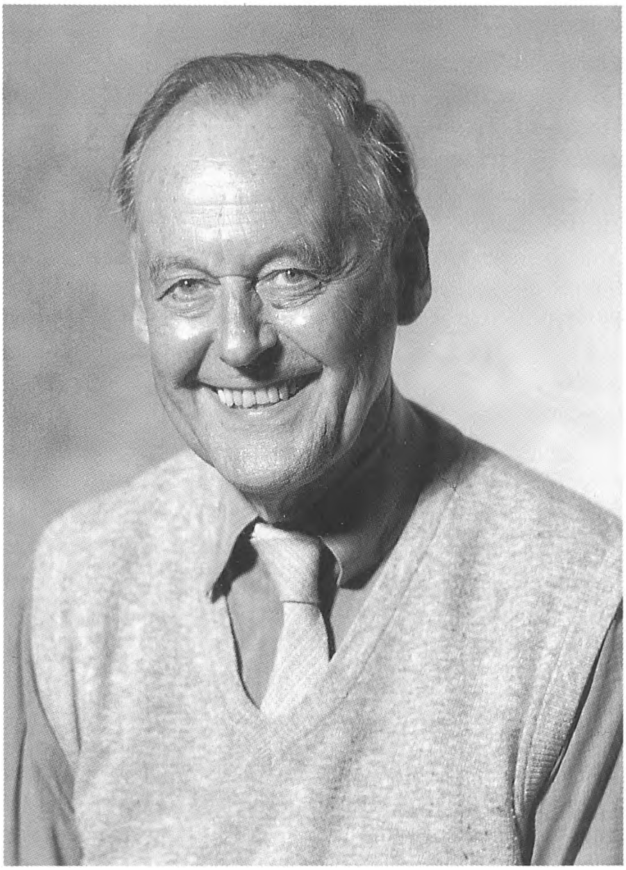

Niels Kingo Jacobsen

Niels Kingo Jacobsen was born on June 13,1921, in Copenhagen, but spent all his childhood at the west coast of Jutland, in the township of Esbjerg. Here he finished High School in 1939 and, inspired by Professor Niels Nielsen and his Wadden Sea investigations, he started to study natural sciences and geography, first in Aarhus and later in Copenhagen where he got his M.Sc. Degree in 1947. The following years N. Kingo Jacobsen developed a keen interest in two main disciplines: the arctic environment and the Wadden Sea area in western Jutland.

For 25 years he was a member of the editorial board of "Meddelelser om Grønland". In 1950 his publication on "Erhverv og Kultur langs Polarkredsen" (Economy and Culture along the Polar Circle) appeared.

From 1948 Kingo Jacobsen worked as an assistant at the Skalling Laboratory. Under the leadership of Niels Nielsen the Wadden Sea studies gradually developed into the project "The Danish Wadden and Salt-Marsh Investigations". From 1953 Kingo Jacobsen was head of the Tønder Section of this project, and he conducted numerous investigations in the Tønder salt-marsh region; his research was mainly concentrated on the geomorphology and soil of the area. The investigations resulted in maps and morphogenetic interpretations of the whole Tønder salt-marsh area, covering its surface topography, the geest surface, the extension and thickness of the single layers of silt, sand, clay, and peat, which had built up this marshland. Moreover, the land use and ownership relations were also covered.

During these years a cooperation to last for life with Kjeld Rasmussen developed, and they even stayed for quite a long time together working on their doctoral theses at the then newly established Skalling Laboratory at Ho. In 1964 Kingo Jacobsen defended his thesis entitled: "Træk af Tøndermarskens Naturgeografi med særligt Henblik på Morfogenesen" (The Natural Geographical Conditions within the Tønder Salt-Marsh). In October the same year he succeeded Niels Nielsen as professor in geography at University of Copenhagen, where he had worked as assistant professor since 1958.

Along with his activities in the Tønder salt-marsh region Kingo Jacobsen has investigated the Rejsby salt-marsh and the peninsula of Skallingen. In the mid-60s Kingo Jacobsen established the Skalling Laboratory in Esbjerg, which has since been the center for a great number of scientific investigations of waddens and marshland. During the last decade Kingo Jacobsen has been the leader of a large-scale ecological project focussing upon the west coast of Jutland, COST 647.

One of Kingo Jacobsen's greatest merits as professor has been to expand the field of geography within the disciplines: soil, hydrology and climatology. Especially the first one became his specific field of research in a close cooperation with professor Kjeld Rasmussen at the Royal Veterinary and Agricultural University. Thus Kingo Jacobsen initiated a great number of soil studies with subjects ranging from pure pedological studies over soil erosion to more stratigraphic investigations of sediment types in the Wadden Sea region.

Together with Kjeld Rasmussen he participated in the expert committee which in 1975 established the guidelines for the Danish soil classification. They submitted a minority recommendation as they wished a more pedologically oriented mapping than the majority did. Kingo Jacobsen - together with among others Kjeld Rasmussen - initiated studies of soil profiles in connection with the trench dug for the main gas pipeline system across the country. This meant the start of a nationwide pedological data base.

In the late 1970s, thanks to Kingo Jacobsen's efforts, a number of soil studies were carried out during the Danish natural science expedition to Patagonia and Tierra del Fuego.

In recent years Kingo Jacobsen has resumed his activities in Greenland and initiated various soil studies in cooperation with the Greenland Home Rule and Ministry of Greenland; to mention some, studies at Holsteinborg in West Greenland and, supported by the Knud Rasmussen Foundation, expeditions in the Thule District.

In Southern Greenland the effects of sheep-breeding on the environment has been investigated, e.g. how much the impact of grazing may aggravate erosion.

Throughout the last 25 years Kingo Jacobsen has represented the discipline geography in many boards and committees, e.g. as President of the Danish National Committee of Geography, as a member of the National Committee of International Association for Quaternary Research, and of the National Committees of Climatology, Oceanography, and Cartography. During the 1960s Kingo Jacobsen helped to establish the Section on Environment under the Nordic Soil Researchers Union where he has been the Danish representative for several periods. Moreover, he has taken great interest in nature conservation matters both in Denmark and in Greenland.

To this should be added Kingo Jacobsen's impressive personal achievements throughout the years in the Board of the Royal Danish Geographical Society, from 1972 as Secretary General and recently also as Vice President. With an unfailing optimism Kingo Jacobsen has arranged and prepared the many activities taking place in the Society, and together with the other members of the board raised funds for these activities. The greatest work load in this connection has been as chief editor of the Society's publications, especially Geografisk Tidsskrift, where so many of Kingo Jacobsen's students have presented the results of their research. In the mid-70s he resumed the publication "Atlas over Danmark" with Series II and is currently planning publication of another volume on soil conditions in Denmark in the original series I.

Kr. M. Jensen and Henrik Breuning Madsen

Kjeld Rasmussen

On June 17, 1921, Kjeld Rasmussen was born in Sønder Vissing, a village west of Skanderborg in Eastern Jutland. After finishing school in 1935, he worked on his parents' farm, and in 1939-40 he attended a course at Asmildkloster Agricultural School. In 1943 he was admitted to the Royal Veterinary and Agricultural University where he graduated in Agriculture in 1947.

He continued at the University as a postgraduate student, and in 1951 he was awarded his lie. agro. Degree with Chemistry as major subject. Following his graduation as lie. agro. he was employed as Assistant Professor at the University's Laboratory of Soils and Agricultural Chemistry. He received his dr. agro. Degree in 1962 for a dissertation on *Transformation of Inorganic Sulphur Compounds in Soil.*

In 1965 Kjeld Rasmussen was appointed Professor of Geology, Soil Science and Agricultural Chemistry at the Royal Veterinary and Agricultural University. As a Professor he has been involved in a multitude of activities within and outside the University. He has given more than 2350 scheduled lectures to students at the University and he has conducted an unknown number of laboratory classes, demonstrations and field trips. He has supervised a large number of students carrying out written assignments and been the teacher and advisor of about 40 postgraduate students. He has been a member of several academic bodies of the University, and he has taken active part in planning new developments and curricula.

Kjeld Rasmussen's research has covered a wide range of subjects with emphasis on problems encountered in soils with a content of pyrite, soil development and classification, development and improvement of analytical methods, and environmental problems. Several research projects, especially those related to the salt marsh areas and soil mapping and classification, have been carried out in cooperation with N. Kingo Jacobsen.

Outside the University he has served as chairman or member of the following commissions, committees and working groups:

- *The Ministry of Agriculture Commission supervising commercial laboratories authorized to carry out analyses of fertilizers etc. (Chairman).*
- *The Ministry of Agriculture Commission supervising commercial laboratories authorized to carry out soil analyses (Chairman).*
- *The Ministry of Agriculture Committee on methods for fertilizer analyses etc. (Chairman).*
- *The Ministry of Agriculture Committee on analyses of feeding materials.*
- *Working Group appointed by the Ministry of Agriculture to consider Denmark's relation to fertilizer trade in the European Community.*
- *Working Group on Standard Methods for Water Analyses appointed by the Danish Council on Standardization.*
- *Council on Agricultural Research and Experiments.*
- *Research Committee of the Danish Heath Society (Danish Land Development Service).*
- *Committee on Soil Classification appointed by the Ministry of Agriculture.*
- *Council on Raw Materials.*
- *The State Foundation for Technical Science, Commission for Technical Chemistry.*
- *Working Group on Pollution with Plant Nutrients appointed by the Main Soil Committee of the Environmental Pollution Council.*
- *Management Group on Acidification Research appointed by the Danish Research Council for Agricultural and Veterinary Science.*
- *Working Group appointed by the Danish Research Council for Agricultural and Veterinary Science to evaluate research on application of nitrogen, phosphorus and organic matter in agriculture and possible effects on groundwater and environment (Chairman).*
- *Working Group on Airborne Pollution and Soil Acidification appointed by the Research Planning Council (Chairman).*
- *Committee on Environmental Issues appointed by the Agricultural Commission.*
- *Environment and Pollution Committee and Working Group appointed by Danish University Rectors.*
- *Working Group and Liaison Committee appointed by the Pollution and Environment Commission of the Nature Sciences.*
- *Environmental Appeal Council (appointed by Ministry of the Environment).*
- *Working Group appointed by the Environmental Protection Agency to consider reduction of pollution of water with iron compounds.*
- *Working Group appointed by the Environmental Protection Agency to supervise mapping of areas with potential for pollution of water with iron compounds.*
- *Committee and Working Group appointed by Ringkøbing County Council to consider pollution of Ringkøbing Fjord with iron compounds.*
- *Danish Society of Soil Science (President).*
- *Danish National Geographical Committee.*
- *Council of the Royal Danish Geographical Society.*
- *Board of the Royal Danish Geographical Society.*

Kjeld Rasmussen has provided the Danish contributions to the FAO-Unesco Soil Map of the World, the Soil Map of the EEC Countries and the Soil Map of the Nordic Countries. He has been the Danish representative on an FAO project on trace elements and on an EEC project on fertilizer analyses. In connection with the 13th Congress of the International Society of Soil Science in Hamburg in 1986 he organized and guided a Post Congress Tour in Denmark and Southern Sweden.

Kjeld Rasmussen has given a large number of lectures at meetings and conferences in Denmark and abroad. He has been a member of several committees appointed to evaluate doctoral dissertations submitted to various universities, and he has served on committees for selection of candidates for professor positions at Danish, Norwegian and Swedish universities. He is a referee of papers submitted for publication in *Acta Agriculturæ Scandinavica.*

Kjeld Rasmussen is known for his extensive knowledge, integrity, thoroughness and consciousness, and these qualities have made him highly regarded by everybody who has worked with him and by his colleagues in Denmark and abroad. His dedication, positive attitude and support to staff and students have created a productive research environment and attracted a large number of graduate and postgraduate students to the fields of soil science and analytical chemistry during Kjeld Rasmussen's more than 25 years as Professor at the Royal Veterinary and Agricultural University.

Leif Petersen

Pedological Research in Denmark

Leif Petersen

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The history of Danish pedological research is suitably divided into the following periods: Prior to 1875, 1875-1920, 1920-1960, and 1960-1990.

The most remarkable soil studies prior to 1875 were carried out by G. Forchhammer, J. F. Johnstrup, and in connection with the national soil productivity survey from 1805 to 1826. Forchhammer described morphology and genesis of sandy heath soils in Jutland, and he made significant contributions to the knowledge of soil leaching, soil factors affecting plant growth, plant nutrition and clay mineralogy. J. F. Johnstrup seems to be the first author to produce a comprehensive and largely correct description of the geological origin of the surface layers in Denmark and the relationship between geology, mineralogy and soil fertility. He also described leaching of lime and clay eluviation. The national soil productivity survey carried out from 1805 to 1826 produced valuable information about the relationships between soil properties and soil productivity and about the productivity of soils in various parts of the country.

In the period from 1875 to 1920, P. E. Müller carried out his well-known studies on soil humus and development of podzols. He described the humus types mull and mor and their relation to soil properties and vegetation. An almost correct description of the podzolization process was given by P. E. Müller in 1884. Other major soil investigations in the period 1875-1920 included those by T. Westermann on the relationship between soil rating, as established by the survey carried out 1805-1826, and crop yield

The major pedological studies in the period from 1920 to 1960 included investigations on podzol soils and their productivity by F. Weis, on soil reaction by N. Bjerrum and associates, on soil acidity by S. Tovborg Jensen and associates, and on soil mineralogy by A. Tovborg Jensen, A. Unmack and others. In this period a number of pedological studies, mainly on soil genesis in relation to geology and vegetation, were made at the Danish Forest Experiment Station by A. Oppermann, C. H. Bomebusch and others.

From 1960 to 1990pedological research has been carried out at a number of institutions including the Chemistry Department of the Royal Veterinary and Agricultural University, the Geographical Institute of the University of Copenhagen, the Bureau of Land Data of the Ministry of Agriculture, the Geological Institute of the University of Aarhus, and the Danish Forest Experiment Station. The studies have covered a wide range of subjects including soil mineralogy, soil genesis, soil classification, properties of tropical and arctic soils, chemistry of humus compounds and soil environmental problems. Valuable contributions within a number of these fields have been made by Kjeld Rasmussen and N. Kingo Jacobsen.

Keywords: *History of Pedological Research, Pedology in Denmark, Danish Soil Scientists.*

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From a pedological point of view soils are considered to be natural bodies whose properties are determined by the so-called soil forming factors which include climate, organisms, parent material, topography and the passage of time. Being concerned with soils in their natural settings, pedology includes disciplines such as soil genesis, soil classification and soil mapping. Although writers have been treating pedological problems for centuries, pedology is relatively young as an independent science. The pioneer work within pedology was done about 1860-1870, mainly by American and Russian scientists, but scientists of other nationalities have also made significant contributions to the early development of pedology.

In Denmark important pedological observations were made and published in the eighteenth century, and during the nineteenth and twentieth centuries Danish scientists carried out research which greatly increased the knowledge about formation of certain types of soils. On the other hand, pedology was not really accepted as an independent science until the last few decades when a formal education in pedology has been introduced at some Danish universities. Practical applications of pedology have also been limited. Up to the present time a systematic soil classification and mapping based on pedological principles has not been carried out in Denmark.

The main pedological topics covered by Danish researchers are described in the following sections. A rather broad interpretation of pedology has been adopted in the selection of topics. In addition to works concerned directly with soil genesis, classification or mapping, works on fundamental soil properties and reactions and on development of methods for fundamental soil studies are also included.

An issue, which has received attention by scientists in practically the whole period covered in this paper, is formation of podzol soils which cover large areas of sandy melt water plains (heath plains) in Central and Western Jutland. Under natural conditions the vegetation on these plains is usually dominated by heather (*Calluna vulgaris*) and associated plants including crowberry *(Empetrum nigrum*), wavy hair-grass *(Deschampsia flexuosa),* mosses and lichens. The problems concerned with formation of the characteristic and normally well developed horizons in these soils have attracted the interest of scientists from the time when soil research started, and although the general podzolization process is now believed to be understood, many detailed questions are still to be answered, and some of these are being studied by present-day scientists.

Prior to 1875

The greatest contribution to the increase in pedological knowledge prior to 1875 was definitely made by J. G. Forchhammer who was Professor of Mineralogy at the University of Copenhagen. However, his interests also included soil development, soil leaching and even plant nutrition.

Research on genesis of sandy heath soils by J. G. Forchhammer and others

Forchhammer published a number of papers in which he described the horizon sequence in sandy heath soils and he developed a theory to explain their formation. However, he was not the first author to describe the heath soils. As early as 1758 two anonymous papers entitled "About the Heath Plains in Jutland" and "Improvement of the Cultivation of the Heath Plains" were published in Oeconomisk Journal (Anonymous, 1758a, 1758b). Detailed descriptions of the heath soil profiles were not given, but their sandy texture and infertility were noted, and methods for improved cultivation were suggested.

The first writer to provide detailed descriptions of the heath soil profiles appears to be Selmer (1802) who made thorough soil observations during his assignment for registration of land belonging to colonies established for heath land reclamation in the eighteenth century. Selmer described the layering of the soils as follows: at the surface a 3-4 inches thick layer of mor soil, under this a layer of white sand which is 3—16 inches thick, then a black layer *(al)* usually about 2 inches thick, and under this red *al* follows *(al* is a Danish term for a more or less hardened subsurface soil layer which usually has a colour differing from the colours of over- and underlying soil layers). Under the red al the soil consists of red sand more or less mixed with pebbles or gravel. In some areas the pebbles resemble those found on beaches. This is a rather precise description of the horizon sequence in soils later to become known as podzols.

Selmer further observed that the black al could be very hard, in which case it was never penetrated by plant roots. Where the black al was more loose, plant roots might even penetrate into the soil layers below.

A similar description of the heath soil profile was given be Forchhammer (1835), who considered the heath plains to be a separate geological formation of marine origin and, due to the presence of the al-layer, he termed it the *al formation.* He considered the formation of the al-layer to be a completed process and he described the al as a loose brown sandstone held together, not by iron compounds but by an organic peaty material. In a later paper Forchhammer (1850) stated that the material holding the al-layer together was organic substances combined with some iron oxides.

Forchhammer (1855) considered the heath plains to be formed from peat swamps inundated by sea water. The dark al-layer was seen as the remains of peat, and the white sand was assumed to be deposited by sea water under conditions where finer particles were washed away. The major reason for this theory was the presence of charcoal in the al-layer.

Obviously not familiar with Forchhammer's theories, J. B. Barth (1855, 1856) published a comprehensive paper on the Danish heath plains with emphasis on their vegetation history. Barth concluded that most, if not all, heath plains had been covered by forest which had degenerated due to human exploitation. Although he mentioned that the black al-layer could have formed from humus substances translocated with leaching water, he concluded that, more likely, it was the remnants of an earlier heath vegetation which had been covered by wind-blown sand.

In a strongly worded criticizm of Barth's paper, Forchhammer (1857) refused to accept that the heath plains had been covered by forests and maintained that the black al-layer was remains of peat inundated by sea water.

In what he called an "anticritical evaluation", Barth (1858) resented Forchhammer's strong criticizm but withdrew the theory concerning the formation of the black al-layer from heath vegetation covered by wind-blown sand and accepted Forchhammer's theory. However, he maintained that most heath plains had been covered with forest.

Forchhammer (1858) repeated his theory concerning the origin of the al-layer and in subsequent papers Forchhammer (1861, 1862) demonstrated that the al-material lost its coherence when treated with either strong bases, which dissolve humus compounds, or strong acids, which dissolve iron oxide, and he concluded that both kinds of compounds played a role in the cementation of the al-layer.

In his description of the heath plains in Jutland, Dalgas (1866) did not accept the existence of a separate al formation because al-layers had been observed in sandy materials belonging to other formations (morainic and tertiary materials). Based on the existence of al-layers in valleys cut by existing streams, Dalgas (1866) concluded that al was not a very old formation. Agreeing with Forchhammer he considered the cementing agent in the al-layer to be humus and iron oxide.

Other research carried out by Forchhammer

Forchhammer's pedological research was not limited to the heath soils. In two lectures presented to the Danish Natural History Society, Forchhammer (1850) gave an account of the importance of air and water for plant growth, the hydrological cycle with emphasis on soil leaching, mineral plant nutrition, the potential of certain geological formations (mainly limestone and marl) for soil amelioration, and the properties and natural fertility of the soils developed on various geological formations.

Although the cation exchange properties of soils and clays were still largely unknown, Forchhammer was aware that clay could retain certain elements and thereby prevent their leaching but not their uptake by plants. He stressed the importance of micas for supplying plant nutrients. In addition he considered lime, sodium chloride and sulphate to be important plant nutrients. He was of the opinion that all geological formations in Denmark had been covered by the sea, and he considered this sea water to be the source of the small amounts of chloride and sulphate which were always found in soils and natural waters.

To ensure an adequate supply of sulphate Forchhammer proposed the application to agricultural soils of so-called alum earth, which occurs in Tertiary formations, mainly in Jutland. In the alum earth the sulphur is present as iron pyrite which will oxidize to sulphuric acid under the influence of oxygen. Forchhammer realized that this production of sulphuric acid was harmful to plants and recommended that the alum earth be mixed with lime and left for oxidation for 2-3 years before it was used.

Forchhammer also explained the absence of calcium carbonate in the upper soil layers of calcareous morainic materials, which he called the *roundstone formation* (rullestensformationen) and considered to be formed through marine influence, as being due to leaching amplified by the vegetation and the atmosphere.

Forchhammer (ca. 1850) carried out the first thorough studies of Danish clays. He made chemical analyses of kaolinite clay from Bornholm and considered its formation from weathering products of feldspars. He also analyzed yellow and blue clays from Sealand.

Forchhammer (1865) described the formation and fertility of tidal marsh deposits, muck and peat. He had observed a relationship between the fertility of these materials and the effect on litmus paper of the gases liberated by heating of the materials. Gases causing colour change of litmus paper from red to blue were liberated from fertile materials, while infertile materials would liberate gases causing a change of colour from blue to red, and he recommended this litmus test for practical application.

National soil productivity survey 1805-1826

Early pedological work in Denmark included a country-wide soil productivity survey. The purpose of this survey was to improve the basis for land taxation. The survey was carried out in the period from 1805 to 1826. The land taxation based on the survey was introduced in 1844 and replaced systems which had been in use since the seventeenth century.

The preparation, planning and execution of the survey were described in detail by C. Rothe (1844) who was head of the Government Office responsible for the survey. The framework for the survey was worked out by a specially appointed Royal Commission including persons well-known for their contribution to rural development in Denmark at that time.

The assumptions underlying the productivity rating were that all soils consist of mull (humus), clay, sand, lime and talc occurring in various mixtures. Talc was known to be a rare constituent of Danish soils, and lime was not assumed to be present in the surface layer. Where it did occur at the surface, the content was normally very small. Hence, mull, clay, and sand were considered to be the important constituents of Danish soils. Mull was thought to be of direct importance for plant nutrition, clay to contribute water storage properties, and sand to be important for an adequate air supply and a high soil temperature. Since all of these properties are of importance for plant growth an ideal soil should have an adequate content of all three constituents.

It is remarkable that, although the actual knowledge about soil conditions and their effects on plant growth was rather limited when these assumptions were laid down in 1805, they come very close to modern concepts of soil properties favouring plant growth and the effects of different soil constituents.

The productivity of a soil was expressed by a number indicating its productivity in proportion to that of other soils. The best agricultural soil in the country was assigned a productivity rating of 24 and the lowest rating assigned to any soil was 1/24.

It was decided that a standard soil representing the most productive soils in the country should be identified and assigned a productivity rating of 24. This soil should serve as a basis for the productivity ratings assigned to all other soils in the country. Following investigations of the soils in a number of villages in Roskilde County West of Copenhagen a soil which was considered to have qualities justifying a rating of 24 was identified in Karlslunde, about 20 km Southwest of Copenhagen. The soil was described as a mixture of 5/12 (by volume) of coarse sand and gravel, 3/12 of clay and very fine sand, and 4/12 of mull. Lime was not present in detectable amounts and the described mixture extended to a depth of more than 18 inches.

This composition was estimated from field observations since laboratory analyses were considered to be too expensive and time consuming to be employed in a country-wide survey. It is not clear how mull was defined or how the content was estimated. According to common use of the word in Danish, mull is a mixture of humus and mineral soil. Analyses made in our laboratory have shown that the present humus content in the plow layer (0-30 cm) of the standard soil at Karlslunde is 5.8% (by weight) and the weighted average humus content to a depth of 18 inches (45 cm) is about 4.3%. The soil is developed on a clayey Weichsel moraine, and the weighted average contents to a depth of 45 cm of clay (<0.002 mm), silt (0.002-0.02 mm), fine sand (0.02-0.2 mm) and coarse sand (0.2-2 mm) are 22%, 14%, 38% and 26%, respectively. However, since the soil has an argillic horizon, the clay content increases from a depth of about 40 cm to 29% in the argillic horizon. Assuming that a part of the fine inorganic material is included in mull and that "clay and very fine sand" includes the remaining clay, silt and some fine sand, the estimates from 1805 agree surprisingly well with present-day analyses.

Following the identification of the standard soil, other soils representing ratings of 20,16 and 10 were identified. All were located at Karlslunde. A rating of 20 was assigned to a soil with 11/24 (by volume) of coarse sand and a little gravel, 6/24 of clay, 7/24 of mull and no lime. The depth of the layer with this composition was 15-16 inches, at greater depth the sand and gravel contents were higher.

The soil with a rating of 16 was described as consisting of 1/2 sand with some gravel, 1/3 clay, 1/6 mull and no lime until a depth of 9-10 inches. The soil layer below consisted of 1/2 sand and 1/2 clay.

The composition of the soil with a rating of 10 was 5/12 of coarse sand with some gravel, 6/12 clay, 1/12 mull and no lime until a depth of 8-9 inches. At greater depth the clay content was higher.

A sandy soil located at Ringgive in Vejle County was selected to serve as a basis for rating of sandy soils. The soil consisted of 5/6 of sand and 1/6 of mor (poorly decomposed humus) until a depth of 9-12 inches. The underlying soil layer consisted of red to darkbrown gravel and pebbles and was characterized as al, but there was no hardpan formation. The soil was assigned a rating of 3.

Areas not subject to cultivation such as permanent pastures, meadows, heaths etc. were rated according to the production obtained, specified as the number of cows or sheep which could be grazed or the annual production of hay per unit area. The ratings assigned to such areas were generally very low.

The survey was supervised by a group of five appointed persons: Ehlers, Selmer, Ahrens, Arctander and Rothe who all had special qualifications for these duties. It is mentioned by S. Tovborg Jensen (1961,1962) that the actual rating of a soil was obtained as an average of separate ratings of 1. the depth of the layer with a mull content, 2. the composition of this layer and 3. the composition of the underlying layer. However, as noted by Dalsgaard, Hansen & Lomholt (1976) this is not mentioned by Rothe (1844) or in the protocols from the committees who prepared the guidelines for the survey.

It should be noted that although taxation based on the survey ratings was discontinued in 1905, the ratings continued to be used as a measure of land value until about 1975.

Research on soil development by J. F. Johnstrup

Properties and fertility of Danish soils in relation to geology were discussed in two papers from 1869 and 1875 by J. F. Johnstrup who in 1866 was appointed Professor of Geology at the University of Copenhagen. In his first paper Johnstrup (1869) described the deposition by glaciers of the surface layers in Eastern and Northern Denmark and the origin of the materials, partly from rocks in Norway and Sweden and partly from local formations, mainly limestone and chalk. He explained the transportation, grinding and mixing caused by the glaciers and assigned major importance for the fertility of the soils to their contents of clay and lime. He stressed that weathering of minerals present in these soils would ensure a continuous supply of plant nutrients and permit sustained plant production.

In the second paper Johnstrup (1875) described the heath plains in Jutland and their origin as melt water deposits from the glaciers. He further stated that since the soils on the heath plains consisted almost exclusively of coarse sand with a low content of weatherable minerals, sustained plant production would be possible only if practically all plant nutrients were supplied from fertilizers.

Johnstrup's paper from 1875 includes a remarkably correct description of clay eluviation in connection with leaching of lime from the surface layers of clayey soils. The description is supported by data on the sand and clay contents at various depths in soils on morainic deposits in Sealand.

1875 - 1920

The last quarter of the nineteenth century and the beginning of the twentieth century was a productive period in Danish pedology. The progress made during this period was to a very large extent due to the contributions by P. E. Müller who published a number of comprehensive papers, mainly on forest and heath soils. While the theories developed by the researches working before 1875 to a large extent have been revised as more knowledge has accumulated, many of the theories developed by P. E. Müller have been confirmed by later investigations and still remain valid.

Research on humus and podzol development by **P.** E. **Müller and associates**

P. E. Müller's field of interest was very broad and his first major publications from 1867, 1871, and 1877 were on zoological subjects (Weis, 1926). Although not published by P. E. Müller himself, the first major pedological work initiated by him was produced by C. F. A. Tuxen (1876). This work included detailed analyses of soil samples from horizons of two podzols from heath land in Jutland. The soil samples were analyzed for humus, iron, aluminum and a number of plant nutrients. The analyses showed without exception a higher content of plant nutrients in the al-layer than in the overlying bleached layer and it was concluded that the bleached layer provided very poor conditions for uptake of nutrients by plant roots.

In another paper Tuxen (1877) presented results of analyses of fresh and aerated samples of mor layers from heath soils for iron(II) compounds and tannin. Only small amounts of these compounds were identified and Tuxen therefore concluded that any adverse effects by the mor layer on the vegetation were due to factors other than contents of iron(II) or tannin. He also concluded that a few years of aeration did not cause marked changes of the important properties of the mor material.

In 1879 P. E. Müller published one of his classical works where he described in detail the characteristic properties of soils with humus types *mull* and *mor* (Müller, 1879). Some of the results of this work had already been presented in a lecture to the Royal Danish Agricultural Society and published a year earlier (Müller, 1878). The work was concerned with mull and mor occurring under beech forest vegetation and with mor under heath vegetation. The work was based on very detailed field observations carried out by P. E. Müller and on results of chemical analyses made by C. F. A Tuxen and presented in an associated paper (Tuxen, 1879).

Müller showed that beech forest soils with mull had a shallow surface cover of loose litter representing recent plant residues. The upper part of the mineral soil below the litter had a dark colour due to a content of humus. Soils with mull were, furthermore, characterized by an abundance of earthworms.

In soils with mor partly decomposed plant residues had accumulated on top of the mineral soil surface to form a rather thick cohesive layer held together by a dense network of thin roots asso-

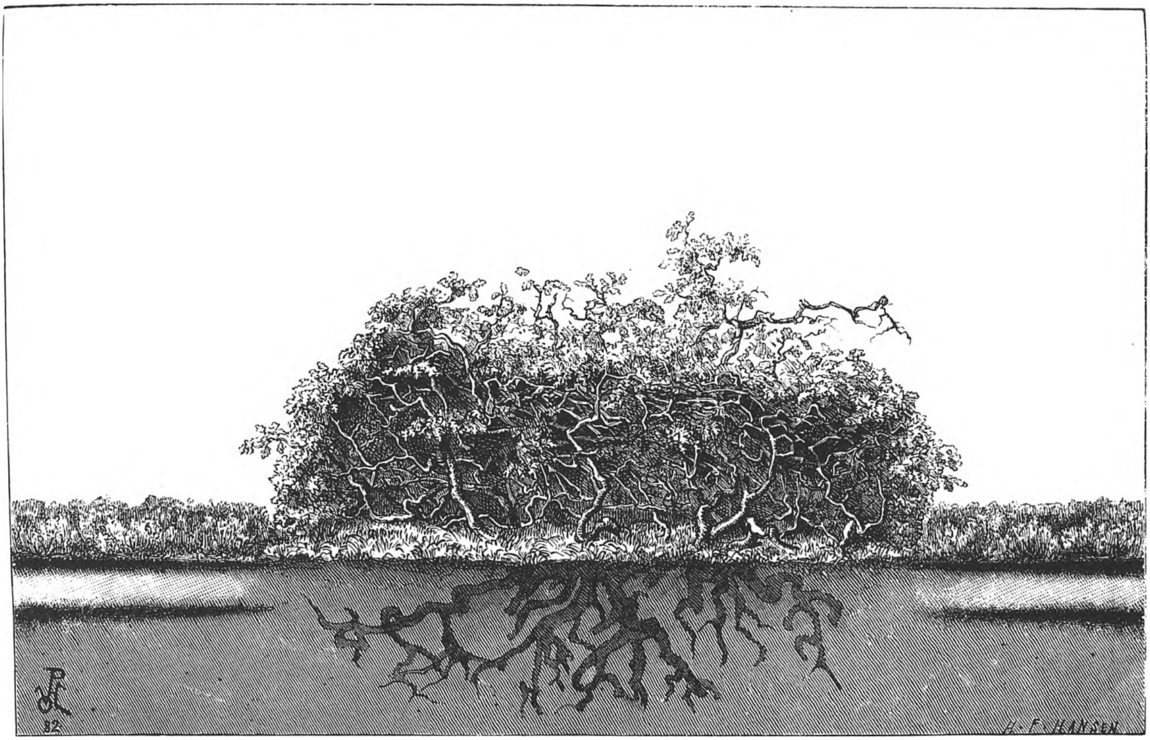

Fig. 1. The soil under oak and under surrounding *Calluna* vegetation (Müller, 1884).

ciated with fungal hyphae. Earthworms were absent from soils with mor and the mineral soil below the cohesive organic layer had a light colour due to the absence of humus compounds and bleaching of the mineral particles. Müller explained the bleaching as being due to removal of iron oxides from the surfaces of the mineral soil particles, and he believed the main reason for the bleaching to be reducing conditions resulting from the dense cohesive organic layer covering the soil.

Müller also noted that soils with mor were acid and he drew attention to the similarities between beech forest soils with mor and sandy heath soils with *Calluna vulgaris* vegetation.

In a second comprehensive work concerned with soils under oak and, mainly, with heath soils, Müller (1884) reported on continued humus and soil development studies. The work was supported by results of physical and chemical soil analyses reported by Tuxen (1884). Müller found that mor layers were more rare under oak vegetation than under beech. When a mor layer did occur under oak its structure was different from that of the mor found under beech or heather vegetation. Although the mor layer under oak could be relatively thick its structure was more amorphous and the amount of tree roots in the mor layer was smaller than in beech and heath mor layers.

Müller (1884) made detailed comparisons of the soil morphology in areas with bushy oak on heath plains and in surrounding areas with *Calluna* vegetation. The soil under *Calluna* vegetation had a thick mor layer and a well developed al-layer while both were absent under oak where the humus was described as mull (fig. 1). There were no visible differences in the parent material. In fact, P. E. Müller was not the first author to notice the absence of al-layers under oak on the heath plains since it was observed and described already by C. Lütken (1865).

A major part of Müller's (1884) work was concerned with the horizon development in podzol soils and although his analytical data were limited, he arrived at conclusions close to those established by newer studies based on more advanced methods of investigation. In agreement with the theories described in his work from 1879 he considered reducing condition to be the major cause of formation of the bleached layer through dissolution of iron oxide, and he showed that the organic compounds in the al-layer had been precipitated from solutions leached from upper soil layers. He also theorized that the bleached layer would continue to grow in thickness. Most of these observations and theories have been confirmed by results of newer investigations.

Müller's works from 1879 and 1884 were published in Danish but they were later translated into German (Müller, 1887). At about the same time the well-known German pedologist E. Ramann explained the formation of the al-layer in podzols by a mechanism similar to that proposed by P. E. Müller. Both claimed priority as to the formulation of the theory and this led to a fierce discussion started by P. E. Müller in a postscript to his German edition (Müller, 1887) and later continued by Warming (1896), Ramann (1899), Müller (1899), and Ramann (1900). Apparently, the priority issue was not resolved but P. E. Müller's works received a wide international recognition and the terms mull and mor were adopted by foreign scientists and have since been used in soil terminology in many languages.

P. E. Müller was teacher in forestry at the Royal Veterinary and Agricultural University from 1873 to 1882. Following his resignation from this position his research activities became focused on means of improving forest production, especially on acid soils with mor, and he also carried out research on nitrification potential of soils with mull and mor (Müller, 1905; Müller & Weis, 1906,1908, 1913; Müller & Helms, 1913). In connection with an investigation of growth of Norway spruce on sandy heath soils, Müller et al. (1910) described 36 soil profiles and carried out mechanical and chemical analyses on subsoil samples taken below the pedogenetic horizons. Many of the soils were strongly developed podzols.

In an honorary lecture at the Royal Veterinary and Agricultural University Müller (1918) presented some new ideas concerning podzol development on the sandy heath plains in Jutland. These theories and their background were described in detail by Müller (1924). At that time the geological origin of the heath plains as melt water deposits from the Weichsel glaciation was well understood (Johnstrup, 1875; Ussing, 1903, 1907). According to P. E. Müller's new theories the podzols on the heath plains were formed during the glaciation when the areas outside the glaciers were tundra. He interpreted the upper boundary of the al-layer to coincide with upper boundary of the permanently frozen soil and the bleached layer to be a result of cryoturbation. The tongues of al material, which often extend downwards from the al-layer into the parent material, were interpreted as being due to ice wedges formed during the tundra period.

Except for the relationship between the tongues of the al-layer and earlier ice wedges, these theories have not been confirmed by later research and the explanation of the formation of the podzol profile proposed by P. E. Müller 40-50 years earlier was definitely superior to his later theory.

Research on soil productivity by T. Westermann

The pedological research in Denmark in the period 1875-1920 included a comprehensive study by T. Westermann (1902) who analyzed 302 soil samples taken from depths down to 60 cm at 96 different locations throughout the country. All samples were from cultivated soils and all major Danish soil types were represented. The analytical results were related to the soil ratings as established by the survey carried out from 1805 to 1826 and to the grain yield based on information obtained from the owners of the land where the samples were taken. The results were used as basis for general recommendations on application of lime, fertilizes etc. to soils with different properties.

The investigation showed a rather good relationship between soil rating and grain yield although with some deviations. The most marked deviations were noted for soils with low ratings in Jutland. These soils general produced higher yields than expected from their ratings.

1920 - 1960

The major pedological studies in this period included investigations on podzols and other soils by F. Weis, on soil reaction by N. Bjerrum and associates, on soil acidity and other problems by S. Tovborg Jensen and associates, and on soil mineralogy by A. Tovborg Jensen, A. Unmack and others. A series of soil profile studies were made at the Danish Forest Experiment Station, mainly by A. Oppermann and C. H. Bornebusch.

Investigations on podzols and other soils by F. Weis

The investigations of podzols on the heath plains in Jutland were continued by F. Weis, who had worked with P. E. Müller on a number of research projects during the early twentieth century (see references in previous section). Weis (1929) made detailed profile descriptions of a number of podzols, some of which had been disturbed by plowing, and he carried out texture and chemical analyses on samples from individual horizons in the profiles. The chemical analyses included determination of pH; humus; ammonium; nitrate and total nitrogen; SiO_2, Al_2O_3 and Fe_2O_3 extracted by the method developed by Tamm (1922); hygroscopic water; loss on ignition; and total analyses of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, SO_3 and CO_2.

From the investigations Weis concluded that the pH measured in aqueous suspension increased with depth from about 4 in the mor layer to 5-5.5 in the parent material. The amount of hygroscopic water was related to the humus content and the content of SiO_2, Al_2O_3 and Fe_2O_3 as determined by Tamm's method. The organic matter in the upper horizons had a lower nitrogen content than that of the lower horizons but the nitrogen in the upper horizons could, nevertheless, be mobilized more easily than that in the lower horizons.

Weis assigned major importance to the contents of SiO_2, Al_2O_3 and Fe_2O_3, as determined by Tamm's method, for the water holding capacity and the cation exchange capacity of the soils. He considered that these compounds were leached from the upper soil horizons as colloidal solutions together with humus compounds, and he took the resulting uneven distribution of these compounds in the soil profile as an indication of soil degradation. He found no major differences between podzols developed on melt water deposits from the Weichsel glaciation and those developed on the older Saale deposits.

In his continued studies of podzols, Weis (1932) investigated in detail a number of undisturbed profiles developed on melt water plains or drifting sand. The soils were analyzed by methods similar to those used in his previous work except that measurements of particle density, bulk density and calculation of pore volume were included. The texture analyses were made by improved methods, and total chemical analyses were omitted. The results largely confirmed his earlier findings.

The pedological studies carried out by Weis also included analyses of 18 surface samples from Icelandic soils (Weis 1933). The analyses included pH, hygroscopic water, organic carbon, total nitrogen, and Fe_2O_3, Al_2O_3 and SiO_2 extracted by ammonium oxalate according to Tamm (1922). Except where the surface soil had been removed by erosion, the soils generally had high humus contents with a C/N ratio ranging from about 11 to about 19, and Weis concluded that cultivation of these soils would cause a considerable mobilization of nitrogen from the humus compounds.

Investigations on soil reaction by N. Bjerrum and associates

Another area which received attention by Danish researchers in the period starting about 1920 was soil reaction. By that time electrometric methods suitable for rapid and reliable determination of pH had become available. Fundamental studies of the factors determining soil reaction were made at the Chemistry Laboratory of Royal Veterinary and Agricultural University. The studies were initiated by N. Bjerrum, and the results were presented in a series of papers (Bjerrum and Gjaldbæk, 1919a, 1919b; Gjaldbæk, 1921; Riehm, 1932; Unmack, 1933).

In the first paper Bjerrum and Gjaldbæk (1919a) discussed acid and base properties of soils as well as definition and determination of soil pH, acidity and basicity, and they produced titration curves for soils. They concluded that although a titration curve provided information about the buffer capacity little was known about actual acid and base consuming reactions taking place in the soil. In the following paper (Bjerrum & Gjaldbæk, 1919b) studied aqueous solutions saturated with $CaCO_3$. The studies included calculations and measurements of the relationship between pH, the partial pressure of carbon dioxide and calcium concentrations.

Using different magnesium carbonates, most of which were synthesized in the laboratory, J.K. Gjaldbæk (1921) reported on studies similar to those described for calcium carbonate above.

H. Riehm (1932) carried out electrometric titrations of solutions and suspensions of various chemicals, silicate minerals and natural clays. The results showed that silicate minerals such as quartz, feldspars, hornblende, serpentine and talc had little buffer capacity. Samples of Danish Tertiary clays showed buffer action over the entire pH range from pH 4 to pH 9-10. The buffer action of the clays was found to be due to exchangeable Al^{3+}, $Al(OH)_3$ and H^+ dissociating from acid surface groups. Most clays would be subject to some decomposition in acid solution with accompanying liberation of aluminum and silicon. The clays most resistant to decomposition were those which were acid due to the conditions prevailing where they were located in nature.

A. Unmack (1933) studied problems connected with pH-measurements of poorly buffered soil extracts and concluded that the most important sources of error were contamination from glass and air and adsorption to filters and electrodes. To obtain exact pH measurements of soil extracts with low buffer capacity, precautions against these sources of error must be taken.

Investigations on soil acidity by S. Tovborg Jensen and associates

At about the same time as the studies described above were made at the Royal Veterinary and Agricultural University, a series of studies on soil reaction and soil acidity problems were carried out at the State Laboratory for Plant Research, mainly by S. Tovborg Jensen. Through these studies it was found that electrometrical methods for determination of pH and especially measurements with the quinhydrone electrode described by Biilmann and Lund (1923), were superior to colorimetric methods and tests previously employed for estimation of soil reaction. The quinhydrone electrode was furthermore well suited for routine analyses of soil samples (Christensen & Tovborg Jensen, 1923,1924; Biilmann & Tovborg Jensen, 1927).

S. Tovborg Jensen (1924a, 1924b) described a method for determination of the buffer capacity of soils. The buffer capacity was expressed as the amount of base ($Ca(OH)_2$) or acid required to change the pH of an aqueous suspension of a unit amount of soil to an arbitrary pH value in excess of the amount of $Ca(OH)_2$ or acid required for an identical pH change of a suspension of a similar amount of pure quartz sand. The determination was made by adding increasing amounts of $Ca(OH)_2$ or acid to suspensions of a series of identical soil samples and measurements of pH of the suspensions when equilibrium had been obtained. Since the buffer action against $CaCO_3$ is of a greater practical importance than the buffer action against $Ca(OH)_2$ the suspensions to which $Ca(OH)_2$ had been added were brought in equilibrium with carbon dioxide by passing atmospheric air through the suspensions prior to the pH measurements.

The method was later developed so it could be used for determination of the lime requirements of soils (Christensen & Tovborg Jensen, 1926). The increase in pH obtained in the laboratory as described above was compared with that obtained by application of $CaCO_3$ in field experiments with increasing liming rates (Tovborg Jensen, 1925). For all soils investigated it was found that the amounts of lime required for a certain pH increase in the field were about three times as high as those required for an identical pH increase in the soil suspensions used in the laboratory. The method seems to be the first real quantitative method proposed for lime requirement determination, and it proved superior to methods previously applied such as those based on titration of the acidity in a potassium chloride soil extracts. In particular, it proved satisfactory for soils with a high humus content (Tovborg Jensen, 1929c).

S. Tovborg Jensen's studies have also contributed towards clarification of a number of other soil acidity problems. Tovborg Jensen (1929b, 1932) showed that most artificial fertilizers affect the soil reaction either towards higher or lower pH values, the most notable effect being that of ammonium sulphate which causes significant acidification. The leaching of lime from agricultural soils was dealt with by Tovborg Jensen (1936, 1951b, 1952). He demonstrated that the leaching increases with the rate of lime application. Tovborg Jensen and Kjær (1948b) investigated the particle size of the lime in some Danish lime and marl deposits and found that the lime in all the deposits investigated had a sufficiently small particle size to ensure maximum reactivity in the soil. When the glass electrode had become available for pH measurements, Tovborg Jensen and Damsgaard-Sørensen (1935) tested its use for measurement of soil pH and concluded that results obtained with the glass electrode in general were superior to those obtained with the quinhydrone electrode which could be affected by chemical reactions caused by certain soil constituents.

Other investigations by S. Tovborg Jensen and associates

Although S. Tovborg Jensen published more than 30 papers on soil acidity problems his research also included a number of additional fields. Besides the methods mentioned above for measurement of soil pH, buffer capacity and lime requirements he has designed methods for determination of soil organic carbon by combustion in compressed oxygen (Tovborg Jensen, 1931c, 1931d) and determination of water content and specific gravity of soil samples by means of pyknometers (Tovborg Jensen, 1954).

In a number of laboratory experiments, Tovborg Jensen studied the factors affecting the ammonia evaporation from liquid manure and ammonium sulphate and described methods for its reduction (Tovborg Jensen, 1928, 1929a, 1930, 1931b, 1938, 1951a; Tovborg Jensen & Kjær, 1948a, 1950), and he has made contributions on cultivation of heath (Tovborg Jensen, 1931a) and marsh soils (Tovborg Jensen, 1955), amounts and properties of humus in soils (Tovborg Jensen, 1956), reactions of chlorate in soils (Tovborg Jensen & Larsen, 1957), soil mapping and classification (Tovborg Jensen, 1961,1962) and several other subjects.

Investigations on soil mineralogy by A. Tovborg Jensen, A. Unmack and others

In the period 1920-1950 clay mineralogy studies using X-ray techniques were started in Denmark. The first study was made by Clausen (1932) who investigated clays from Bornholm and Tertiary clays from other parts of Denmark. The X-ray photograph resulting from the investigation were, however, of a poor quality and difficult to interpret. The main conclusions were that the clays from Bornholm contained quartz and that calcite and minerals resembling muscovite were present in some of the Tertiary clays.

Using an improved technique, A. Unmack (1944) identified quartz, kaolinite, a "micaceous clay mineral" and, possibly, some montmorillonite in Tertiary clay from Røjle as well as quartz and a "micaceous clay mineral" in clay from Staverslund. The identification of montmorillonite was difficult because its most characteristic reflection resulting from the 14 Å layer distance could not be adequately recorded with the X-ray camera available.

In a subsequent investigation, where some improvements had been made to the X-ray equipment used, Unmack (1947) identified montmorillonite in two out of 20 clay samples from Bornholm. These samples also contained small amounts of illite but no kaolinite. The remaining 18 samples contained quartz, kaolinite and illite in various proportions.

In her continued investigations Unmack (1949) identified montmorillonite in so-called "fish clay" from the Senonian-Danian transition and in a number of Danish Tertiary clays. All clays were found to contain quartz, and calcite was identified in the "fish clay". Some of the tertiary clays contained kaolinite and various other identified or unidentified minerals. Illitic clay minerals were only identified in two samples of Tertiary clays.

A quantitative method for determination of quartz in clay materials by X-ray analysis was developed by E. Jensen (1951). The method was based on use of magnesium oxide as internal standard and measurement of the intensities of characteristic quartz and magnesium oxide reflections as recorded on a photographic film. An adaptation of the method involving use of an X-ray diffractometer equipped with a Geiger-tube was described by Jensen (1955), and the quartz content in the clay (<2 μm) and silt (2-30 μm) fractions of some Danish agricultural surface and subsoils was determined by the adapted method. The investigation included soils developed on sandy and loamy morainic materials, glacial outwash sand and late glacial marine deposits. The quartz content of the clay fractions investigated varied from 2 to about 10% while most of the silt fractions contained more than 50% quartz.

The mineralogical composition of the sand fraction (0.02 - 2.0 mm) of Danish soils, has been studied by A. Tovborg Jensen and E. Krogh Andersen (1955, 1956). The minerals were identified and their amounts estimated by microscopic examination. An etching and staining procedure was employed to facilitate separation of potassium and sodium feldspars. The identification was verified by X-ray analyses. The investigation included sand from a total of nine soils developed on materials representing all major geological deposits occurring in Denmark. As would be expected quartz was dominant in all samples, often accounting for more than 90% of the sand. Microcline and oligoclase typically accounted for 5-10% and 0-2%, respectively. The counting under the microscope was time consuming and the time required increased with increasing sample size. In order to be able to minimize the time required per sample, Jensen (1956) made a theoretical statistical study of the relationship between sample size and accuracy.

Soil investigations carried out at the Danish Forest Experiment Station

A number of soil profile studies has been carried out by the staff of the Danish Forest Experiment Station. L. Smith (1925) described 14 profiles, most of them podzols, in Skjærbæk Plantation. S. Rix (1927) investigated a number of podzol profiles in Gludsted Plantation which is located near the boundary of the maximum extension of the Weichsel glaciers. The parent material within the area studied included meltwater sand without stones, sandy materials with a content of stones and clay deposited during temporary advances of the glaciers, and drifting sand. Rix studied the wedge-shaped downward extensions of the al-layer and concluded that they were formed where big (tree) roots had penetrated weak parts of the al-layer. The weak parts could be due to ice wedges formed when the soils were permanently frozen during the glaciation as described by Muller (1924) but other causes of weakness were also considered possible. Hence, Rix (1927) did not accept the presence of wedge-shaped al-extensions as an indication that the podzolization had taken place when a tundra climate prevailed during the glaciation. The fact that two or more podzol profiles with al-layers could be found on top of each other further weakened the theory that podzolization was confined to the period with tundra climate.

A. Oppermann (1932) also considered the wedge-shaped al extensions to be due to former big tree roots and not relicts from permafrost during the glaciation.

A. Oppermann and C. H. Bornebusch (1930) compared soil profiles from areas with grass and heather in Nørholm Heath. The profile under heather was a well developed podzol with all characteristic horizons. A bleached layer and an al-layer in the profile under grass was assumed to be formed under former heath vegetation which had covered the area until 30-40 years before the profiles were studied.

C. H. Bornebusch (1931) described 13 soil profiles and provided data on texture and pH for each horizon in these profiles. Photographs of most of the profiles were also shown. The profiles were located in forests and plantations. Most profiles were podzols on sandy parent materials in Central and Western Jutland, but a well developed podzol from Falster was also included. The occurrence of podzols under oak on sandy deposits in Jutland was demonstrated, and it was stated that this did not confirm the findings of Müller (1884) showing that the soil under oak is normally a brown soil with mull. Earlier findings that roots did not penetrate the al-layer was not confirmed; on the contrary, a concentration of roots in the al-layer was observed.

Oppermann (1932) also found podzols under oak. These podzols had a rather thin mor layer, a well developed bleached layer and a weakly developed al-layer.

In a report on the effects of different degrees of thinning in a *Picea abies* plantation, Bornebusch (1933) included information on a number of soil properties. The plantation was located at Hastrup near the boundary of the maximum extension of the Weichsel glaciers, and the material consisted of alternating layers of loamy sand, sand and gravel. The soils were podzols developed to different extents. The thinning had a clear effect on the appearance of the organic matter. The plots with no thinning had a mor layer consisting to a large extent of poorly decomposed plant materials. With increasing degree of thinning the decomposition increased and the humus layer on the plots with the strongest thinning was characterized as mull. However, the effects of thinning on the total content of organic carbon, total nitrogen and pH were negligible.

E. Oksbjerg (1957) made very detailed studies of the morphological, physical, chemical and biological properties of mor layers under spruce vegetation on glacial outwash plains with podzols. He found that the voluminous structure of the mor layer depends on a superficial layer of fine spruce roots. If these roots were killed by disrupting their connection with the spruce tree or by liming, the mor layer would collapse and become less pervious to air and water, and the reducing properties of the mor would be enhanced.

H. Holstener-Jørgensen (1957) determined the so-called base mineral index in a number of forest soils, all located in Jutland. The base mineral index is the percentage of mineral particles with a specific gravity higher than 2.68 g/cm^3 in the 0.54-0.225 mm particle size fraction. The results obtained were low to very low, especially in sandy soils. For soils with low clay contents (< 6 %) a good correlation was found between the base mineral index and the content of exchangeable potassium while there was no correlation for soils with higher clay contents. There was also a positive correlation between the base mineral index and the content of phosphorus extracted with 0.1 M H_2SO_4 for soils with less than 4 % clay, but no correlation for soils with higher clay contents.

One of the major pedological works during the thirties was the compilation of a soil map of Denmark (Bornebusch & Milthers, 1935). Following a request for a contribution from Denmark to a soil map of Europe at scale 1:2 500000 it was decided to produce at the same time a soil map of Denmark at scale 1:500 000. The work included a substantial amount of field work which was carried out from 1929 through 1932. The managers of the project were K. Milthers, The Geological Survey of Denmark, and C. A. Bornebusch, The Danish Forest Experiment Station. The mapping units were combinations of geological deposits and their texture. Areas with pedological soil entities were not given separate signatures but locations with podzol profiles observed in the field and information about their stage of development were shown on the map.

Areas with strongly, medium and weakly podzolized soils, dune sand and brown soils were shown on a text map in the paper describing the general map.

1960 - 1990

The main institutions carrying out pedological research during the last 30 years include Chemistry Department, Royal Veterinary and Agricultural University; Geographical Institute, University of Copenhagen; Bureau of Land Data, Ministry of Agriculture; Geological Institute, University of Aarhus; The Danish Forest Experiment Station and others.

Chemistry Department, The Royal Veterinary and Agricultural University

At the Royal Veterinary and Agricultural University A. Tovborg Jensen and Krogh Andersen (1961) continued their studies of the mineralogical composition of sands from Danish soils described in the previous section with an investigation of the minerals present in eight samples: Three top soil samples (one from a Weichselian glacial loam and two from Saale deposits) and five subsoil samples (two from Weichselian glacial loam and three from Saale deposits). The results confirmed previous findings that all sand fractions were dominated by quartz followed by microcline and oligoclase. By comparing the mineralogical composition of the sands with that of common rocks from which the deposits could have been derived, it was concluded that the weathering resulting in the present low content of feldspars, micas and hornblende had taken place before the materials were brought to their present location by the glaciers. By comparing the mineralogical composition of sands from Weichsel and Saale deposits it was further estimated that the present rate of feldspar weathering was as low as 300 g per ha per year.

In an investigation of the content of heavy minerals in sands from Danish soils, A. Tovborg Jensen and H. Flyge (1966) found that the content of heavy minerals in the fraction investigated (250-350 μm) varied from 0.10 to 0.92%. The predominant heavy minerals were hornblende, epidote and garnets.

Jensen (1965) carried out an X-ray mineralogical investigation of the composition of a sediment from Greenland. The sediment was assumed to be deposited in a glacial lake. The sand, silt, and clay fractions accounted for 46%, 27%, and 27%, respectively. The clay fraction was dominated by oligoclase, biotite and vermiculite. The sand and silt fractions were dominated by quartz, oligoclase and biotite. The silt fraction contained some vermiculite, and 3-10 % hornblende was present in all fractions. The mineralogical composition was roughly similar to that of gneisses in the vicinity of the deposit, and the material was assumed to be formed by physical disintegration of the rock.

In another mineralogical investigation of four soils developed from gneiss and two soils developed from basalt (all from West Greenland) Jensen and Würtz (1974) found the minerals in all particle size fractions to be inherited from the parent rock with the exception of a small amount of vermiculite in the soils developed from gneiss. The soils developed from basalt were remarkable in that all particle size fractions, also the sand fraction, contained montmorillonite. The content of montmorillonite varied from 14-25% in the sand and silt fractions to 70-80% in the clay fraction. The montmorillonite was considered to be an ancient formation inherited from the parent material.

The mineralogical composition of so-called lignite clay, i.e. a clay with a content of pyrite occurring as layers alternating with layers of lignite in Miocene deposits in Central Jutland, was studied by Christensson and Jensen (1970). The sand, silt and clay fractions accounted for 22%, 34% and 44% of the material, respectively. The sand, which was almost exclusively fine sand (97.5% <250 μm), contained about 60 % glauconite, the remainder being mainly quartz. Almost half of the silt fraction and more than half of the clay fraction consisted of illite which could not be distinguished from the glauconite dominating the sand fraction.

A method for determination of the fineness and reactivity of agricultural lime was proposed by B. Kjær (1974). The fineness was determined by sieving and the reactivity by measuring the percentage of calcium carbonate dissolved by shaking for 15 minutes with a surplus of acetate buffer at pH 5.00.

Investigations on the reactivity of lime were continued by A. Tovborg Jensen and M. Brink Pedersen (1977) who studied the dissolution rate of samples of calcium carbonate and dolomite at pH 2-5 in a pH-stat maintaining pH at a preset value by addition of hydrochloric acid. It was found that the dissolution rate of calcium carbonate was several times higher than that of dolomite.

A substantial contribution to the understanding of reactions of inorganic sulphur compounds in the soil has been made by Kjeld Rasmussen. In his dissertation Rasmussen (1961) described the reactions of sulphur in soils in relation to the drainage conditions. Based on thermodynamic calculations he showed that iron(II) sulphide and pyrite could form in soils in the absence of oxygen, and by analyses of a large number of samples from water-logged soils he often found high contents of pyrite but only small amounts of iron(II) sulphide. The highest contents of pyrite were found in brackish water deposits with a high content of organic matter.

By laboratory experiments he demonstrated that oxidation of pyrite to sulphuric acid and iron compounds proceeds rapidly in the presence of oxygen and adequate moisture. He also showed that the oxidation was promoted by microorganisms having a rather low pH optimum. In the presence of $CaCO_3$, the oxidation would proceed considerably slower as a pure chemical process.

Oxidation of pyrite in soils could lead to extremely low pH-values and very large amounts of lime would be required to neutralize the acid produced. In order to reduce the amounts of lime required in connection with drainage of soils with a high content of pyrite, Rasmussen recommended that the application of lime be delayed until the major part of the oxidation products had been leached from the soil. This recommendation was tested in a field experiment with an artificial "soil" consisting of a 30-50 cm thick layer of lignite clay with an average pyrite content of 1.4% over coarse sand (Rasmussen, 1963). The material was left for oxidation and leaching and after less than two years lime was supplied. A barley crop planted on the limed soil produced a satisfactory yield.

Rasmussen (1965) reported results of lysimeter experiments with lignite clay having a pyrite content of about 3%. The lysimeters are shown in fig. 2. The results confirmed that application of lime retarded the oxidation and showed that no free sulphuric acid was leached from the lysimeters. The leachate from the lysimeter with lime was a saturated calcium sulphate solution, and in the leachate from the lysimeter without lime the ratio of iron to sulphur was close to the iron/sulphur ratio in pyrite. The excess sulphate was accompanied by an equivalent amount if aluminum originating from the soil.

In a second paper on the lysimeter experiments, Rasmussen and Willems (1981) showed that although pyrite was oxidized completely within one year in the lysimeter without lime, the soil in the lysimeter with excess lime still contained about one third of the original amount of pyrite after 8 years. As long as pyrite was still present in the lysimeter without lime, the iron was leached mainly as iron(II). Following complete oxidation of pyrite the amount of iron leached as iron(III) increased but at the same time precipitation of iron(III) compounds in the soil reduced the amount of iron leached resulting in an iron/sulphur ratio in the leachate lower than the iron/sulphur ratio in pyrite (0.5). In the lysimeter without lime the leaching of the oxidation products of pyrite was practically complete after three years.

A yellow precipitate formed in the container collecting the leachate from the lysimeter without lime was assumed to be carphosiderite, $HFe_3(SO_4)_2(OH)_6,H_2O$, by Rasmussen (1965). The assumption was based on X-ray analysis and comparison with tabulated data for carphosiderite. However, the tabulated data referred to

Fig. 2. Lysimeters used by Kjeld Rasmussen in studies of pyrite oxidation.

natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and not to carphosiderite (van Tassel, 1958). Carphosiderite had not been synthesized at room temperature and its existence in nature was considered doubtful. However, Pedersen et al. (1973) found that carphosiderite could be precipitated at room temperature from solutions containing iron(III) and sulphate provided no potassium, sodium or ammonium was present.

A survey of a former lignite strip mining area which had later been planted with coniferous trees showed low pH values and poor tree growth where the top layers consisted of lignite clay (Petersen et al., 1968).

In addition to his wide reputation as an expert on problems connected with occurrence and reactions of pyrite in soils, Kjeld Rasmussen has carried out research in several other pedological fields. Some of his earliest studies were concerned with marsh soils in the Tønder Region (Rasmussen, 1956). Through these studies relationships between soil properties, origin and development following reclamation were clarified. These problems were also discussed by Rasmussen (1982a).

Studies on potassium in soils and soil minerals were described by Rasmussen and S. Tovborg Jensen (1960) and Rasmussen (1972). In the former study electrodialysis was proposed as a method to obtain information on the ability of soils to release non-exchangeable potassium and it was shown that Danish soils exhausted for exchangeable potassium may release 20-40 kg potassium per year.

An improved method for electrical conductivity measurement of aqueous soil extracts was developed by Rasmussen and S. Tovborg Jensen (1963). By this method the contribution from calcium sulphate, which is not harmful to plants due to its rather low solubility, to the measured electrical conductivity of a soil extract is eliminated by addition of barium chloride.

Major works by Kjeld Rasmussen are concerned with soil classification and mapping and their use in development planning. He has provided the contributions from Denmark to the FAO/Unesco Soil Map of the World (FAO/Unesco, 1981) and the Soil Map of the EEC Countries (Commission of the European Communities, 1985). He has also taken part in the production of a soil map of the Nordic Countries and produced a soil map of Denmark and a chapter on soils in Landbrugsatlas Danmark (Rasmussen, 1986).

Rasmussen (1973a) showed how geological and soil conditions should be taken into account in land use planning and Rasmussen (1974,1976) reviewed existing Danish soil maps and soil evaluation schemes and stressed the importance of future soil mapping being based on permanent soil properties of direct importance for potential land use. Rasmussen (1979) considered practical applications of pedological maps and reviewed soil conditions and contemporary soil mapping projects in the Nordic Countries.

As members of a committee appointed by the Ministry of Agriculture to establish quidelines for a country-wide classification of agricultural soils, Rasmussen and Kingo Jacobsen (1975) described principles for soil classification and evaluation and a plan for execution of a soil survey covering Denmark. The proposed classification was to a large extent based on complete descriptions of soil profiles with their genetic horizons. However, the scheme was not adopted by the Ministry of Agriculture who opted for a rapid survey proposed by a majority of the members of the committee mentioned above. This scheme was mainly based on routine collection and analyses of soil samples from the plow layer and some samples from the subsoil without consideration being paid to pedological development.

Kjeld Rasmussen's research has also included a number of clay mineralogical investigations. Lindgreen and Rasmussen (1978) isolated a fine clay (<0.3 μm) from a Weichselian glacial till and subjected it to a number of studies by chemical methods, X-ray and electron diffraction, Mossbauer and infrared spectroscopy, differential thermal analyses, and electron microscopy. Based on the results of these investigations it was proposed that the clay isolate had been formed from weathering of mica entailing practically complete potassium depletion from some interlayers and almost no depletion from other interlayers. Formation by clay neosynthesis was considered unlikely.

A mineralogical investigation of the clay fraction in samples of two recent fluvio-glacial sediments from East Greenland was carried out by Petersen and Rasmussen (1980). The majority of the clay size material in both sediments consisted of primary minerals including feldspars, quartz and micas. However, X-ray diffractograms showed clear evidence of presence of vermiculite and smectite and these minerals were estimated to account for 10-20% of the materials. The minerals were assumed to be weathering products of biotite.

In 1981 Kjeld Rasmussen and N. Kingo Jacobsen initiated systematic soil investigations in connection with establishment of a pipe line system for natural gas in Denmark. The field and laboratory work which was completed in 1985 included description and analyses of almost 900 profiles covering most typical soils occurring in Denmark (Rasmussen 1987b). Clay mineralogical investigations made on selected profiles showed a definite relationship between the mineralogical composition of the clay fraction and the classification according to Soil Taxonomy (Møberg, Petersen & Rasmussen, 1988). The main differences between taxonomic entities were lower contents of illite, vermiculite, chlorite and kaolinite in the clay fraction of the upper horizons of Spodosols developed on Saale deposits and Weichselian fluvio-glacial deposits than in the corresponding horizons of Alfisols developed on Weichselian glacial till.

In recent years Kjeld Rasmussen has been actively engaged in the solution of environmental problems. Some of his contributions within this field are related to his studies on pyrite oxidation in soils and leaching of the oxidation products. He has contributed to reports and papers concerning pollution of Ringkøbing Fjord in Western Jutland caused by oxidation products of pyrite in the reclaimed Skjern Å area (Betænkning I, 1975; Betænkning II, 1978; Beredskabsplan, 1978; Rasmussen, 1982b, 1984a, 1984b, 1985a). The reports and papers contain information about the amounts of iron leached from the soils and transferred to Ringkøbing Fjord, experiments conducted in order to design suitable methods for reducing the iron deposition, and planned future activities.

The contents and reactions of plant nutrients in the soil and risk of ground water pollution, especially with nitrate, have been evaluated by Christensen et al. (1971), Rasmussen (1973b, 1980, 1981, 1984a, 1987a) and Rasmussen et al. (1985).

Kjeld Rasmussen has also contributed to the solution of problems concerned with deposition of highly radioactive waste products from nuclear plants and possibilities of waste deposition in geological formations occurring in Denmark (Atomenergikommissionen, 1976), and he has described possibilities and risks connected with application to agricultural soils of fly-ash from electrical power plants operating on coal (Rasmussen, 1983). He pointed out that the major risk connected with application of the fly-ash is caused by its content of cadmium.

An account of acid producing processes in soil and the effects of acid precipitation was given by Rasmussen (1985b). It was concluded that the effects of the acid precipitation depend on the composition and conditions of the soils as well as on their use and vegetation.

Kjeld Rasmussen's scientific activities are not fully described by the review of his major pedological publications given above. Many of the research projects carried out by the staff working with him have been suggested by him, and he has provided assistance and advice during the progress of the research. In the following, the major projects conducted by the staff working with pedological research of the Chemistry Department of the Royal Veterinary and Agricultural University will be summarized.

The soil development in three Danish profiles on glacial till from the Weichsel and Saale glaciations was studied by S.A. Faizy (1973). Clay illuviation was shown to have taken place in one of the profiles on a Weichselian deposit. In the two other profiles evidence of clay illuviation was doubtful. The clay fraction was investigated by X-ray and chemical methods. Micaceous clay minerals, vermiculite, montmorillonite, kaolinite and quartz were identified in the clay in all soil horizons studied, but feldspars were not identified in any horizon of the three profiles.

H. P. Lindgreen (1976) made a comprehensive study of instrumental and chemical methods for characterization of soil clays. The clays were isolated from a loamy morainic soil and were found to contain a variety of primary and clay minerals. The methods applied included X-ray analysis, differential thermal analysis, total elemental analysis and selective dissolution analysis. All methods proved to have severe shortcomings when applied to the complicated mineral mixtures encountered in soil clays, and it was concluded that reliable information on the composition of soil clays can only be obtained when several independent methods were applied.

S. Storgaard Jørgensen has studied acid-base properties of quartz suspensions (Storgaard Jørgensen and A. Tovborg Jensen, 1967) and carried out a series of solubility and dissolution studies on amorphous silica (Storgaard Jørgensen, 1968), flints (Storgaard Jørgensen, 1970), aluminum hydroxides and oxyhydroxides (Storgaard Jørgensen & Mitchell, 1970) and silicate minerals (Storgaard Jørgensen, 1976). Together with M. Willems and B. Pedersen he has studied the leaching of elements from soils mixed with large amounts of sewage sludge or sludge ash (Willems, Pedersen & Storgaard Jørgensen, 1981).

The structure of soil humic compounds extracted with ethanol and pyridine has been studied by B. Pedersen et al. (1985) using UV-, IR- and ^{1}H-NMR-spectroscopy. Storgaard Jørgensen and Willems (1987a, 1987b) studied the transformation of lead in soils on shooting ranges and lead originating from lead roofs.

Studies on humic acids have also been carried out by O. K. Borggaard (1974) who determined acidity and pK values by potentiometric titrations. Borggaard (1976a, 1976b, 1981) applied EDTA as a general extractant for metals from soil samples and as a selective extractant for amorphous iron oxides. Following these studies Borggaard has carried out extensive investigation of iron oxides and hydroxides in soils, their reactions and effects on soil properties.

The investigations have included influence of iron oxides on the surface area of soils (Borggaard, 1982) and the effects of surface area and mineralogy of iron oxides on their surface charge and anion adsorption properties (Borggaard, 1983a). Borggaard has also studied the influence of iron oxides on adsorption by soils of phosphate (Borggaard, 1983b, 1986), chloride and cobalt (Borggaard, 1984,1987). Recently the importance of iron oxides and, in particular, aluminium oxides as phosphate adsorbents has been pointed out (Borggaard et al., 1990). A number of other factors related to iron oxides and their effects on soil properties and reactions have been studied by Borggaard and reported in a number of publications. A summary of these studies as well as those mentioned above is given by Borggaard (1990).

Borggaard's scientific work has also included a number of studies on the adsorption of herbicides by soils and soil constituents (Borggaard & Streibig, 1988a, 1988b, 1989).

Most of the research carried out by J. P. Møberg has been concerned with tropical African soils but investigations relating to Danish soils have also been included in his research. Møberg's research on tropical soils covers a wide range of chemical and mineralogical soil properties and fertility problems. Chemical and mineralogical properties of some Tanzanian soils are described by Møberg (1972, 1973) and the formation, mineralogy and fertility of some tropical highland soils are dealt with by Møberg (1974). Møberg (1979) gave an outline of soil conditions, land use and soil problems in Tanzania.

Pedological and edaphological properties of two soil associations in the Morogoro area of Tanzania were studied by Møberg, Msanya and Kilasara (1982), and Mrema, Møberg and Urigo (1984) studied phosphate retention in soils commonly occurring in Tanzania.

In a number of publications Møberg has reported on the properties, composition and clay mineralogy of soils from Nigeria, f.ex. Esu and Møberg (1990).

Møberg's research on Danish soils has mainly included clay mineralogical investigations (Møberg, 1975,1976,1982; Møberg & Dissing Nielsen, 1983, 1986; Dissing Nielsen & Møberg, 1984; Møberg, Petersen & Rasmussen, 1988), and classification of Danish soils according to international soil classification systems (Dissing Nielsen & Møberg, 1985).

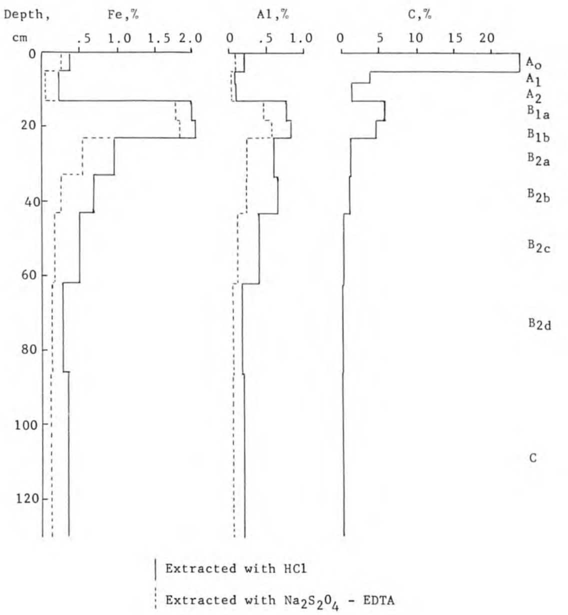

Fig. 3. Iron, aluminium and organic carbon in a podzol profile (Petersen, 1976).

The scientific studies carried out by L. Petersen have included investigations of ochreous precipitates in tile drains (Petersen, 1966). The investigations showed that the precipitates had a varying composition and always a significant organic matter content. They were hardly formed by a simple oxidation of iron (II) compounds. Petersen (1969) described a method for chemical determination of pyrite in soils. Problems connected with alkali soil reclamation are described by Petersen and Oad (1974), and structural properties of lowland soils in Thailand by Petersen (1975) and Alva & Petersen (1979).

In his work on podzolization Petersen (1976) showed that podzol profiles are developed by a mechanism involving dissolution of aluminum and iron compounds by soluble organic compounds in the upper soil horizons. The dissolved materials are transported with leaching water to deeper horizons where the organic compounds are made insoluble due to further uptake of aluminum and iron. The distribution of iron, aluminium and organic carbon in a podzol profile is shown in fig. 3. Other papers on podzolization were published by Petersen (1978, 1980a, 1984).

Effects of ground water lowering on peat soils have been studied by Petersen and Breuning Madsen (1978) and the mineralogical composition of the clay fraction of soils in Thailand by Petersen (1977,1983). Petersen (1987) described soil and other constraints to agricultural development in the province of Central Kalimantan, Indonesia. In some parts of the province the land is unsuitable for agriculture due to flooding, poor drainage, steep slopes or sandy soils. In areas where these constraints are less serious, the soils are usually acid and very low in plant nutrients, and sustained agriculture will require liming and continuous fertilizer applications.

In the last decade L. Petersen has made a number of studies on the effects of acid precipitation on soils (Petersen, 1980a, 1980b, 1984b, 1986; Hovmand & Petersen, 1984a, 1984b). The general conclusion from these studies was that acid precipitation has little effect on neutral soils with a high buffer capacity and on very acid soils. The most sensitive soils are those with a low buffer capacity and near neutral pH values.

A comparative study of soil development on arable land and under coniferous forest was described by K. Raulund-Rasmussen and Petersen (1987) and Petersen and Raulund-Rasmussen (1987). The study showed that lime and fertilizers applied to arable soils had affected the horizons below the plow layer, and it was concluded that planting of trees on agricultural land will cause soil acidification.

Comprehensive studies on effects of acid precipitation on soils have been carried out by Raulund-Rasmussen (1989b, 1989c). The studies have included application of artificial acid rain to a Typic Haplohumod with a vegetation of *Picea abies* and analyses of soil solution from different horizons. The sulphuric acid applied with the artificial acid rain to the unlimed plot was neutralized quantitatively in the O horizon, mainly by cation exchange with calcium and magnesium. Sulphate was not retained in the soil. Acidification of forest soils is also described by Raulund-Rasmussen, Mor sing and Leth (1990) and Raulund-Rasmussen and Larsen (1990).

Raulund-Rasmussen (1989a, 1989d) found that ceramic filters commonly used for extraction of soil solution are unsuitable because they release aluminum to the extracted solution.

In order to increase the understanding of the formation of certain double metal-hydroxy carbonate minerals in soils and their importance as intermediates in the formation and transformation reaction of oxides and oxidhydroxides of iron, H. C. B. Hansen (1989) reported on the properties of synthetic Fe(II)Fe(III)-hydroxy-carbonate and Hansen and Taylor (1990) studied the conditions for formation of pyroaurite and reevesite under controlled conditions in the laboratory.

Other pedological investigations carried out at the Chemistry Department of the Royal Veterinary and Agricultural University include a study of soil development on a late glacial fluvial deposit in South Sealand by N. J. Christoffersen (1975). A soil profile described in the area was classified as a Eutric Fluvisol.

A. Skjoldager (1978) studied the composition of adsorbed cations in a number of salt-marsh soils and found no relation between the adsorbed cations and the conditions prevailing during the deposition of the sediments. The composition of the adsorbed cations was controlled by the composition of the present soil solution.

Soils with placic horizons have been studied by C. J. W. Koch (1987) who employed a number of chemical and physical methods including X-ray diffraction, Mössbauer spectroscopy and transmission electron microscopy. A definite conclusion as to the formation of placic horizons was not arrived at, but it was indicated that redox processes was the main reason for accumulation of iron compounds in the placic horizons while the accumulation of aluminium compounds was due to complexation by organic matter.

M. Styczen and K. Høgh-Schmidt (1986) developed a model for calculation of splash erosion based on the assumption that splash detachment of soil particles is proportional to the squared momenta of the rain drops. The results produced

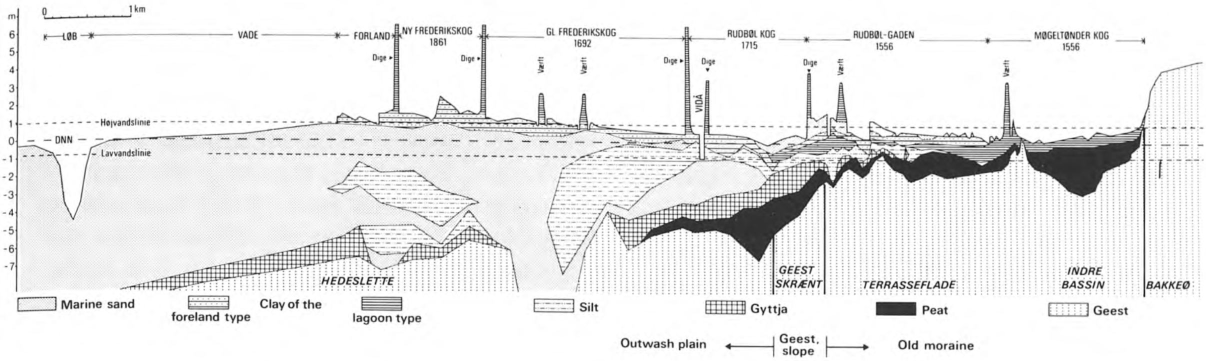

Fig. 4. Cross section of the Tønder salt marsh (Kingo Jacobsen, 1964).

by the model were in better agreement with experimental data than results obtained from earlier models based on the kinetic energy or the intensity of the rainfall.

Styczen (1987) described soil erosion problems and prospects of existing and future soil conservation programmes in some African countries.

Geographical Institute, University of Copenhagen

At the Geographical Institute, University of Copenhagen, pedological research was started as part of studies of landscape elements in Western Jutland which have been under way since 1930 (Nielsen, 1960). Comprehensive and detailed pedological studies were made by N. Kingo Jacobsen in the period 1953-1958 when he was the head of an integrated investigation of the salt-marsh area at Tønder. The methodology and preliminary results of the investigations in the salt-marsh area were described by Kingo Jacobsen (1956), and Kingo Jacobsen (1959) described the topography and previous soil development in the layers of glacio-fluvial and aeolian sand underlying the post-glacial marsh deposits. The nature of the post-glacial deposits in different parts of the Tønder salt-marsh area was described by Kingo Jacobsen (1960a, 1960b).

In his dissertation Kingo Jacobsen (1964) presented a comprehensive account of the results of the investigation in the Tønder salt-marsh area including not only pedology but also history, topography and a detailed description of the formation and the age of the post-glacial deposits. Large-scaled maps showing topography, land use, land ownership and nature of the deposits as well as cross-sections of the entire area were also presented (fig. 4). A description of the sediments in the Tønder salt-marsh area and their formation is also given by Kingo Jacobsen (1969).

From an investigation of the sediments in the Stadil Fjord area, Kingo Jacobsen (1961) concluded that salt-marshes occur along the west coast of Jutland as far north as Nissum Fjord. The natural conditions in the salt-marsh area at Rejsby were described by Kingo Jacobsen (1972). The soil conditions were compared with those in the salt-marsh at Tønder.

A description of sedimentation and sediments, including data on the particle size distribution of the sediments, in various parts of Wadden Sea area was given by Kingo Jacobsen (1986).

Kingo Jacobsen (1976) described natural-geographical regions of Denmark with their characteristic soils, and he made a substantial contribution to the publication "Naturgeografisk Regionindelning av Norden" (1977). His contribution included descriptions of the natural-geographical regions of Denmark, descriptions of soils occurring in the Nordic Countries, and other items.

A soil map of Denmark based on the FAO-Unesco soil classification system was presented by Kingo Jacobsen (1984). The map includes 14 mapping units, each representing associations of soil units.

Kingo Jacobsen has been engaged in a number of activities in Greenland. *The Knud Rasmussen Memorial Expedition* in 1979, which is described by Kingo Jacobsen (1980), included pedological investigations in the Tugtuligssuaq Peninsula extending from 75° 20' to 75° 27' N and from 58° 14' to 58° 42' W. The pedological investigations included profile studies of soils characterized as *Arctic Brown Soils* and *Tundra Soils* (Holm Jakobsen, Gylling Mortensen & Thingvad, 1980). The main factors causing variation in soil properties were considered to be differences in relief, depth of permafrost table, soil drainage and age. A more detailed account af the soils in the Tugtuligssuaq area, partly based on results of chemical analyses, was given by Holm Jakobsen (1988b). Weathering, humus accumulation, leaching, podzolization and gleying were observed, and differences in stage of soil development were attributed to age and, possibly, climatic differences. Buried A horizons in some of the profiles studied were suggested to be formed during a warmer climate prevailing 8500-9000 years ago.

In a report on natural resources and culture in the Holsteinsborg area (Ministeriet for Grønland, 1980) Kingo Jacobsen described results of investigations of the soil conditions in the area.

From 1983 to 1987 Kingo Jacbsen was a member of a *Committee on Environment and Sheep Raising in South Greenland.* The Committee conducted a number of geo-ecological investigations which are described by Holm Jakobsen (1984b, 1986), Frederiksen (1986a, 1986b) and in the Committee’s concluding report (Arbejdsgruppen vedrørende Miljø og Fåreavl, 1988). The work initiated by the Committee included an investigation by Kingo Jacobsen and Holm Jakobsen (1986) of a buried podzol soil in the area of Greenland which was inhabited by Norsemen from about 985 to about 1450 a.c. C^{14}-dating of the organic material in the surface horizon of the buried soil indicated an age of about 1000 years, and it was concluded that the layer of aeolian material covering the buried surface horizon was due to erosion caused by land clearing and grazing during the Norsemen period. Prior to the settling by the Norsemen, the soil was protected from erosion by vegetation facilitating podzol development as found in the buried soil.

The problems of soil erosion in the area inhabited by Norsemen were further discussed by Kingo Jacobsen (1987) who indicated that the extinction of the Norse settlements late in the 15th Century could be due to climatic oscillations related to overgrazing and soil erosion.

Working both at the Geographical Institute, University of Copenhagen and at the Bureau of Land Data (see next section), H. Breuning Madsen has carried out a large number of studies covering a wide field of pedological subjects.

Classification of Danish soils has been considered by Breuning Madsen (1979a, 1979b, 1983a, 1983b). Breuning Madsen (1979a) proposed classification of Danish soils by a coding based on texture, pedological development, drainage, thickness and humus content of the A horizon and content of stones. Later, he added a number of secondary characteristics such as geological origin, hardpans, pH in the subsoil and occurrence of horizons with sulphides or sodium to be included in the code (Breuning Madsen, 1979b). Since, the soil characteristics included in the soil coding affect plant growth, a productivity rating could be derived from the code.

A hierarchical soil classification system with four levels was proposed by Breuning Madsen (1983a, 1983b). The classification was based on diagnostic horizons and profile characteristics in the upper 120 cm of the soil profile. The diagnostic horizons used in the system are not identical to those used in the Soil Taxonomy or FAO-Unesco systems. The nomenclature used in the system was partly taken from other systems and was partly new. It was stated that the system was more suitable for classification of Danish soils, for classification of soils in the field, and for computer handling than the existing Soil Taxonomy and FAO-Unesco systems which are accepted and used at an international level. A soil toposequence studied by Breuning Madsen (1983b) is shown in fig. 5.

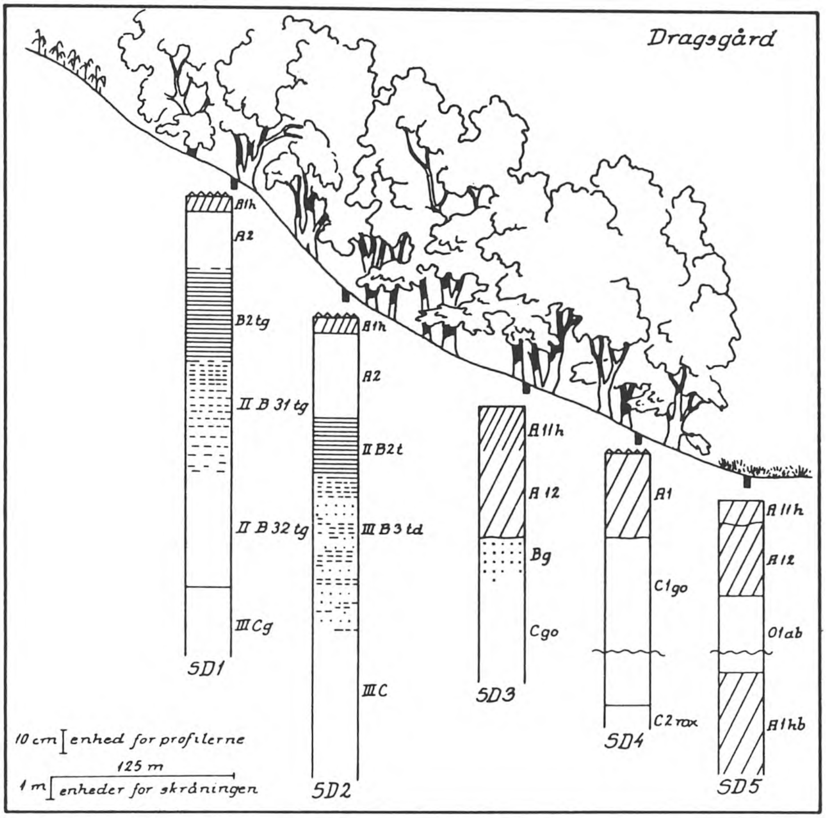

Fig. 5. Soil toposequence in Himmerland (Breuning Madsen, 1983b).

Use of aerial photographs of agricultural soils without vegetation in soil surveys was investigated by Breuning Madsen (1978b, 1979a). It was concluded that air photographs were useful for establishing soil boundaries provided sufficient data on the soils had been collected by field observations.

Root development of agricultural crops, especially barley, has been the subject of several investigations carried out by Breuning Madsen. In a paper on the development of barley roots in relation to texture, pedological development, pH, bulk density and air content in the soil, Breuning Madsen (1978a) showed that low pH values hampered root development while the effect of compact soil layers were comparatively small provided the compact layers had cracks due to a developed soil structure. Breuning Madsen (1979a) found shallow root development in soils dominated by coarse sand and pronounced effects on the root development of pedogenic horizons. A podzol B horizon with a high content of organic matter promoted root development while a B horizon with low organic matter content hampered the root development. The development of barley and potato roots in relation to pedological features was studied by Breuning Madsen (1980 b). It was found that roots did not penetrate placic horizons, and argillic horizons with high bulk density and few vertical cracks hampered root development.

Breuning Madsen (1983b) studied root development of several agricultural crops in a variety of soils and calculated average rooting depths for each crop in relation to soil texture and parent material. The distribution of barley roots in relation to texture and climatic conditions was studied by Breuning Madsen (1985).

Problems connected with plant available water in soils have been studied by Breuning Madsen (1976,1979a, 1983b, 1986) and Breuning Madsen et al. (1986). Results of computer simulation of crop production are given by Breuning Madsen (1979a, 1983b) and Kjær Hansen and Breuning Madsen (1984).

Mapping of areas with a content of pyrite in the soil has been described by Breuning Madsen (1980a, 1984b) and Breuning Madsen et al. (1984, 1985). The mapping was carried out in order to identify areas from which iron and sulphur compounds could be liberated and cause water pollution following artificial drainage. The mapping covered lowland areas in five counties located in Jutland. The combined area of the five counties is about half of the total area of Denmark. It was found that a total area of 255 000 ha lowlands in the five counties contains soils with potential for water pollution with sulphur and iron compounds. Breuning Madsen and Jensen (1988) showed that pyrite could be found in wetland soils of both marine and non-marine origin.

Breuning Madsen has also made contributions within a number of additional pedological fields including determination of size and stability of soil aggregates (Breuning Madsen, 1975), description and interpretation of a soil profile with a well developed, eluvial horizon and an argillic horizon showing signs of degradation (Breuning Madsen & Holm Jakobsen, 1980), description of a soil profile in which clay migration had been followed by podzolization in the coarse material above the argillic horizon (Breuning Madsen, 1984a), factors affecting pH in agricultural soils (Breuning Madsen and Munk, 1987) and mapping of Danish soils with low capacity for available water (Breuning Madsen & Aagaard Holst, 1988). The mapping was based on texture, humus content and estimated rooting depth.

Breuning Madsen and Jensen (1985) described investigations of 835 soil profiles carried out in connection with construction of pipelines for natural gas in Denmark and storage of the data obtained in a computer data base at the Ministry of Agriculture, Bureau of Land Data. N. Jensen and Breuning Madsen (1988) described a systematic investigation of 875 soil profiles from all parts of Denmark. The investigation was carried out in connection with a country-wide investigation of nitrate leaching from soils. Breuning Madsen (1989c) estimated that about 20% of the cultivated area in Denmark is marginal for agricultural production due to a low water holding capacity of the soils, 10% of the area is marginal due to wetness and 1% due to steepness. The estimates were based on data available in the soil data bases of the Ministry of Agriculture, Bureau of Land Data.

The data in these data bases were also used by Breuning Madsen (1989b) in an investigation of pH and the occurrence of lime in Danish soils. The results showed that although most agricultural soils have been limed, soil pH is generally higher in Eastern Denmark than in the Western parts of the country. Lime is frequently present in the plow layer of agricultural soils in areas where chalk occurs close to the present surface, i.e. in the Southeastern part of the country and in Northern Jutland. In these areas there is also a high frequency of soils with a content of lime at a depth of 1 m.

A proposal for a soil profile and analytical data base connected with the Soil Map of the European Community was outlined by Breuning Madsen (1989a).

As described by Breuning Madsen, Schmidt Nielsen and Ødum (1980), Breuning Madsen and P. Frederiksen have carried out soil investigations in Argentina. The investigations were made in three areas dominated by volcanic ashes, glacial and glacio-fluvial deposits and loess, respectively.

The application of LANDSAT images and aerial photographs to mapping of Argentine soils was discussed by P. Frederiksen (1981) who concluded that LANDSAT images were suitable for identification of large land systems and general vegetation pattern. When knowledge on the relationship between topography, vegetation and soil development had been obtained from field observations, information about general soil characteristics could be derived from aerial photographs. Frederiksen (1984) found that, provided the relationship between geomorphological and botanical units on the one hand, and the occurrence of soil associations on the other hand, were known from field studies, information about a number of soil properties could be derived from LANDSAT false colour composite images.

Frederiksen (1982a) found that differences in the cambic horizon observed in a climatic sequence of nine soils developed on loess in Argentina did not result in different classification of the soils according to the Soil Taxonomy or FAO-Unesco soil classification systems. The soils shoved variations in occurrence of horizons, thickness of horizons and solum, colour, base saturation percentage, humus content and distribution, and C/N-ratio, all of which could be related to processes depending on climate (Frederiksen, 1982b).

A detailed account of a number of soils occurring in Tierra del Fuego in Argentina was given by Frederiksen (1988). The discussion included interpretation of the soil forming processes in relation to climate, parent material and other soil forming factors.

B. Holm Jakobsen (1981) studied the origin of the parent material and soil development in an area bordering the salt-marsh area at Tønder. The geological formations and the conditions for soil development in the area were very complex. Maps showing parent materials, drainage conditions and soil productivity were presented. Formation of pyrite in some Danish lowland soils was studied by Holm Jakobsen (1984a, 1985, 1987,1988a). In soils, located in the Tønder saltmarsh area and consisting of loam overlying gyttja, pyritic sulphur originated from sea water. In other lowland soils, located in depressions in pre-Weichselian landscapes, the pyritic sulphur originates from the groundwater and has probably been dissolved from Tertiary deposits.

Holm Jakobsen (1989) studied soil development in a subarctic podzol in Southern Greenland. Distinct cutans in the B horizon were analyzed by energy dispersive X-ray techniques on thin sections. It was found that the cutans had a high content of Si in the interior parts whereas the outer parts were predominantly Al and organic matter. From this it was concluded that the translocation processes involved in the podzolization were complex and had changed from a dominating translocation of Si during the early stages of podzolization to a translocation of Al-organic matter complexes during later stages.

K. Dalsgaard (1970) investigated 8 soil profiles from Bellona, one of the Solomon Islands. Bellona is an emerged atoll and the soils investigated were developed on limestone or deposits of phosphatic clay. The soil profiles developed on limestone were shallow and even the top soil contained significant amounts of calcium carbonate.

S. Vedby (1978) made detailed descriptions and analyses of some hydromorphic soils in South Sealand. In most of the profiles studied the present rate of peat formation was reduced due to improved drainage.

Ministry of Agriculture, Bureau of Land Data

The Bureau of Land Data was established in 1975 and its first task was to conduct a countrywide classification and mapping of agricultural soils (Landbrugsministeriet, 1976). The methodology applied was similar to that used earlier by Duus Mathiesen (1974, 1975) for classification and mapping of soils on the island of Bornholm and in Northern Jutland. The soils were classified according to the texture of the plow layer, and the survey was based on texture analyses of approx. 35 000 soil samples taken throughout the country. The work, which was completed in 1980, involved production of about 400 map sheets at scale 1: 50 000 showing soil texture, slope and geological origin. All data were stored in national data base system (Platou, 1984). The classification and its application to land use planning is described by Duus Mathiesen (1980,1981, 1982, 1983).

During 1981-1984 additional maps showing landforms, wetlands and subsoil texture were produced (Breuning Madsen, 1984c). These maps have been digitized an are stored in a data base.

In the 1980'es the Bureau of Land Data has participated in two major soil survey projects:

The pedological investigations carried out in connection with establishment of the main gas pipeline as described on page ** (Breuning Madsen & Jensen, 1985) and pedological investigations following a 7 km grid covering the whole country and established for monitoring nitrogen leaching (Jensen & Breuning Madsen, 1988). In both projects complete profile descriptions were made, and soil samples were collected and analyzed by standard methods. All data were stored in data bases.

The Bureau's data bases have been applied to land use, water and irrigation planning (Breuning Madsen & Platou, 1983; Aagaard Holst & Breuning Madsen, 1986, 1988; Breuning Madsen & Aagaard Holst, 1990), mapping of soil erodibility by wind and water (Breuning Madsen et al., 1986a, 1986b; Hasholt et al., 1989), estimation of nitrate leaching from agricultural soils (Landbrugsministeriet, 1984), mapping of areas with a content of pyrite in the soil (Breuning Madsen et al., 1985; Breuning Madsen & Jensen, 1988), and mapping of land with marginal soils (Breuning Madsen & Aagaard Holst, 1987; Breuning Madsen, 1989; Breuning Madsen et al., 1990; Svendsen & Pedini, 1987).

The work carried out at the Bureau of Land Data has also included digitizing of the Soil Map of the European Community (Platou et al., 1989) and use of the digitized map in modelling and mapping of rootzone water capacity and irrigation requirement (Breuning Madsen et al., 1989).

Geological Institute, University of Aarhus

Since about 1975 pedological research has been carried out at the Geological Institute, University of Aarhus, mainly by K. Dalsgaard and P. Nørnberg. These studies have been concerned with soil development in relation to different soil forming factors, evaluation of earlier soil conditions in different parts of Denmark based on the survey carried out from 1805 to 1826 (this survey is in the following referred to as the 1844 survey because the taxation based on the survey was started in 1844), and application of pedological investigations to archaeology.

E. Baastrup et al. (1977) described soil profiles developed on Saale deposits in Central Jutland and found that soil development (podzolization) was strongly dependent on the iron content in the parent material which included glaciofluvial sand and wind-blown sand. Soil development in sands of different age in Northern Denmark was investigated by Nørnberg (1977,1986), who found that the clay and silt contents were generally higher in the topsoil than in the subsoil of the same profile. This was attributed to weathering in situ. The upper boundary of the B horizon in podzols was located higher in the profile in old than in young soils, and this was taken to confirm older theories that the B horizon moves upward during podzolization. Investigations by Nørnberg (1980,1986) confirmed that the higher silt and clay content in the upper horizons of a podzol, as compared with the clay content in deeper horizons, was due to weathering in situ of rock fragments containing chlorite and mica. Once these minerals are released from rock fragments they rapidly break down into silt and clay size particles.

Soil development on a Weichselian till deposit in relation to the topography was studied by Dalsgaard et al. (1981). Field observations, standard laboratory methods and micromorphological technique were applied in the investigation which included six Alfisols and one Mollisol. The profiles were located in different positions on a slope, and the strongest profile development, indicated by thickness of eluvial and argillic horizons and the extent of clay translocation, was observed in two profiles located on the steepest part of the slope. The strong soil development in these profiles was attributed to lateral water movement.

Nørnberg et al. (1985) studied soil development in profiles overlying limestone from lower Danian in Jutland. It was concluded that the solum had not been derived from the limestone but was formed on Quaternary glacial till. However, the lower part of the B horizon and the C horizon in one of the profiles investigated had been formed in residue from limestone and these horizons were assumed to be remnants of a soil profile developed prior to the Weichsel glaciation. The origin of the lower B horizon as a residue from the limestone was confirmed by Nørnberg and Dalsgaard (1985) who found textural and mineralogical similarities between the lower B horizons and residuum from the limestone. In the fine silt fraction from the C horizon of this soil Nørnberg (1990) identified a zeolite which he classified as a heulandite and he considered that it was formed in situ in the limestone.

Effects of vegetation on the properties of podzols have been described by K. E. Nielsen (1986), Nielsen et al. (1987a, 1987b), Nielsen et al. (1987), and Nørnberg (1989). In these papers it was shown that invasion of oak on a Calluna-heath causes depodzolization, i.e. the pedogenetic horizons become less pronounced, the accumulation of mor stops, the distribution of iron and aluminium oxidhydroxides in the profile is changed, the amount of organic matter in the Bh horizon is reduced and the composition of the organic matter is changed.

Dalsgaard (1988a) described a paleosol developed on sandy Saalian till and covered by fluviatile sand of Weichselian age. The paleosol was a well developed podzol with an underlying argillic horizon, and both the argillic horizon and the spodosol were assumed to be formed during the Eemian Interglacial. The podzol was very similar to present-day podzols, while the argillic horizon was considered to be developed more strongly than argillic horizons under present-day podzols.

An overview of the environment, occurrence, formation, and properties of podzol soils in Denmark, as well as problems connected with their identification and classification was presented by Dalsgaard (1988b).

Soil ripening following reclamation of gyttja soils in Kolindsund, Eastern Jutland, was studied by P. Larsen (1973). The most important ripening processes were a considerable vertical and horizontal shrinking of the soil material and oxidation of iron(II) sulphides to iron(III) and sulphate.

Occurrence and weathering of minerals, especially phyllosilicates, in different soil environments have been studied by de Coninck et al. (1983) and de Coninck et al. (1987). It was found that during initial weathering stages, trioctahedral chlorite and micas may change into vermiculite intergrades by removal of interlayer hydroxy sheets and interlayer potassium, respectively.

Dalsgaard et al. (1976) compared soil ratings from the 1844 survey with present soil productivity estimated from modern field and laboratory investigations. In general the results showed a good agreement for soils with high ratings according to the 1844 survey. For soils with low ratings according to the 1844 survey the present productivity was estimated to be considerably higher. This was due to soil improvements, mainly artificial drainage and liming, carried out after the 1844 survey and the fact that meadows, pastures and other soils not used for usual arable agriculture at that time were assigned low ratings in the 1844 survey.

Dalsgaard (1984, 1986, 1989) analyzed soil rating maps produced from 1844 survey and compared land use shown on these maps with present land use. The main results were that large areas shown as wetland on the maps from the 1844 survey later have been artificially drained and brought under cultivation. Also, large areas covered with *Calluna* heath in the first half of the nineteenth century have later been reclaimed and are now cultivated.

Dalsgaard et al. (1990) considered an ecological mapping system used in Lower Saxony, Germany, for mapping of forest sites, and concluded that, in general, the system was suitable for Danish forests. However, some problems were connected with estimation of rooting depth, available water and nutrients, and the system should be made compatible with current Danish soil classification principles.

Pedological studies in relation to archaeology are described by Dalsgaard and Nørnberg (1982, 1985), Courty and Nørnberg (1985), Nørnberg and Courty (1985) and Nørnberg and Dalsgaard (1988). Dalsgaard and Nørnberg (1982) compared a soil profile below a burial mound from Roman Iron Age with a soil profile located outside the mound. The A horizon of the buried soil had a higher content of organic matter than the Ap horizon of the profile outside the mound. A greyish appearance of the A horizon and accumulation of iron oxidhydroxides as nodules and cutans in the argillic B horizon was taken as evidence of iron translocation in the soil under the mound. These features were absent in the profile outside the mound. Dalsgaard and Nørnberg (1985) concluded from investigations including X-ray and electron diffraction methods that the cutans consisted of amorphous iron oxidhydroxides. The translocation of iron in the buried soil was assumed to be due to more constant moisture conditions in the soil below the burial mound than in the soil outside the mound where no iron translocation was observed.

Courty and Nørnberg (1985) compared soils cultivated during the Iron Age and later covered by wind-blown sand with soils, also covered by wind-blown sand, but never cultivated. The soil parent material was also wind-blown sand dominated by particles in the range 0.125 mm to 0.5 mm. The uncultivated soil was a rather well developed podzol with a thick buried O horizon. It was found that, in addition to disturbance of the upper soil horizons, cultivation had caused an increase in the silt and clay content in the cultivated layer, a change in the distribution of organic matter and organic phosphorus, and a decrease in the C/N ratio. The increase in the content of fine particles was attributed to disintegration of coarse particles.

Nørnberg and Courty (1985) showed that methods commonly used for pedological studies, including micromorphological methods, could be applied successfully to establish the origin of materials encountered in archaeological excavations.

A number of other studies where cooperation between archaeologists and pedologists has led to successful interpretation of field observations was described by Nørnberg and Dalsgaard (1988).

Danish Forest Experiment Station

At the Danish Forest Experiment Station, E. Holmsgaard et al. (1961) studied soil development under first and second generation Picea abies but found no significant differences.

Holstener-Jørgensen (1965b) carried out an investigation of texture and pH in 18 soil profiles developed on glacial till in Sealand. The general trend was an increase in pH with depth. In the surface soil there was a tendency towards an increase in pH with increasing clay content. Although not mentioned by Holstener-Jørgensen, the results indicate that most profiles have an argillic horizon but the interpretation of the results is complicated by the facts that the analytical results do not refer to specific horizons and that lime, which is definitely present in some of the deep soil layers analyzed, seems not to have been removed before the texture analyses were made.

From a laboratory experiment involving leaching of the upper part of a moraine sand column with 4.7 normal hydrochloric acid Holstener-Jørgensen (1965a) concluded that leaching could also affect soil layers below the ground water level.

In order to establish whether clay migration has occurred in Danish soils on calcareous glacial till, Holstener-Jørgensen (1973) made texture analyses of the horizons in 15 profiles. The results showed large variations due to heterogeneity of the glacial till, but it was concluded that clay migration was likely to have occurred in the area which is located in the eastern part of Sealand.

An investigation of the effects of wood production on soil pH was described by Holstener-Jørgensen et al. (1988). There was a clear negative relationship between soil pH and wood production expressed as annual basal-area increment in m^3/ha. The relationship was explained as being due to increasing uptake of plant nutrients, including cations, with increasing wood production. The investigation was based on an experiment including 12 different tree species and carried out at 13 different locations covering a wide range of soil conditions. No specific effects of individual tree species on soil pH were demonstrated. This was interpreted to indicate that the pH change was determined solely by the increment achieved.

Other Institutions

Studies of properties of the organic matter in B horizons of podzols have been carried out by E. H. Hansen of the Technical University of Denmark. The studies were made at the Soil Research Institute, Canada Department of Agriculture, in cooperation with M. Schnitzer. Oxidative degradation of the organic matter with alkaline permanganate was carried out by Hansen and Schnitzer (1966) and a number of aliphatic and aromatic carboxylic acids were identified among the oxidation products. However, the compounds identified accounted for only a small fraction of the original amount of organic matter. Among the compounds produced by oxidation of illuvial organic matter with nitric acid, Hansen and Schnitzer (1967) identified a number of phenols and benzene carboxylic acids, and it was concluded that the organic matter consisted primarily of heavily substituted isolated aromatic rings linked together by aliphalic chains or saturated cyclic or hydroaromatic structures.

Organic matter extracted from a Canadian podzol was subjected to Zn-dust distillation and fusion by Hansen and Schnitzer (1969b). The main reaction products were condensed aromatic compounds and it was concluded that soil humic compounds contain significant amounts of polycyclic aromatic ring structures or structures yielding such compounds. Molecular weights of extracted organic matter were determined by vapour pressure osmometry in water by Hansen and Schnitzer (1969a). The results showed a range in molecular weights of fractions obtained by gel filtration from 275 to 2110. Schnitzer and Hansen (1970) studied properties and stabilities of a number of metal-soil organic matter complexes prepared in the laboratory.

Working with the Mineralogical-Geological Institute, University of Copenhagen and Institute of Technical Geology, Technical University of Denmark, A. Fobian has carried out pedological investigations including a study of the horizon development in three profiles on calcareous glacial till in Eastern Sealand (Fobian, 1966), use of aerial photographs in soil mapping (Fobian, 1976), micromorphological features in a soil classified as a Mollic Hapludalf (Fobian, 1981) and soil mapping and land suitability evaluation of an area located West of Copenhagen (Fobian, 1984). The profiles studied by Fobian (1966) had an argillic horizon above the boundary of lime leaching which was found at depths 1-1.5 m. From X-ray analyses it was concluded that, in soil layers with low pH, illite had lost some interlayer potassium and attained a capacity for limited swelling. In the profile studied by Fobian (1981) clay cutans, frequently in connection with iron oxide and/or humus cutans, were observed in the argillic horizon. Lime cutans were found in the upper part of the C horizon.

An area located West of Copenhagen and covering about 60 km^2 was mapped by Fobian (1984). A total of about 1400 soil observations were made in the area. The dominant soils observed in well drained sites were Inceptisols and Alfisols while peat and mineral soils with gley characteristics were mapped in poorly drained sites.

At the Geological Survey of Denmark, S. T. Andersen (1979) and B. Aaby (1983) have studied soil genesis by a method based on the content of pollen and fungal hypha fragments in the soil. The method is based on the fact that pollen and hypha are decomposed in neutral soils but survive more or less intact in acid soils. By relating the content and species of pollen found in the soil to vegetation changes, the age of podzols in Eldrup and Draved Forests, located in Eastern and Southwestern Jutland respectively, were established. It was found that podzolization can take place in less than 100 years when conditions for podzolization are adequate.

Soils developed on morainic material from the Saale glaciation at Emmerlev were studied by P. Klix-Henningsen (1981) who found a deeper and more intensive development than on corresponding Weichselian till. This was attributed to weathering in Eemian interglacial, Weichselian interstadial and periglacial periods.

Concluding remarks

Many of the studies quoted above have contributed significantly to the development of pedology at an international level. The international impact of P. E. Müller's works on humus has already been mentioned above, and his works on podzol development published in the 1870's and 1880's were comparable or even superior to those of well-known researchers working about the same time.

The works on soil reaction and acidity by Bjerrum and associates and by S. Tovborg Jensen also represent major developments in an international context.

The investigations by Kjeld Rasmussen on the factors affecting oxidation of pyrite in soils and leaching of the oxidation products and by Kingo Jacobsen on the tidal marsh soils and their formation have also been utilized by pedologists at an international level.

It is too early to evaluate the importance of more recent Danish pedological research. However, there is no doubt that many of the more recent findings quoted above have contributed significantly to increased pedological knowledge and will serve as a basis for future research.

The most important results produced by Danish soil scientists have been concerned with fundamental soil problems. Unfortunately, the trend in recent years has been towards research which can be applied immediately to the solution of practical problems.

Although this research may lead to the desired results, there is no doubt that the most suitable permanent solutions to practical problems can be designed when they are based on a thorough knowledge of fundamental soil properties. Hence, research on fundamental pedological problems should be extended, improved and encouraged.

References

Aaby, B. (1983): Forest development, soil genesis and human activity illustrated by pollen and hypha analysis of two neighbouring podzols in Draved Forest, Denmark. Danmarks Geologiske Undersøgelse, II. Række, Nr. 114.

Alva, A.K. & Petersen, L. (1979): Soil physical properties in relation to rice yield and water consumption under flooded and unflooded conditions. Plant and Soil, 52: 353-63.

Andersen, S.T. (1979): Brown earth and podzol: soil genesis illuminated by microfossil analysis. Boreas, 8: 59-73.

Anonymous (1758a): Om Hederne i Jylland. Oeconomisk Journal: 20-38.

Anonymous (1758b): Hedens Dyrknings Forbedring. Oeconomisk Journal: 39-56.

Arbejdsgruppen vedrørende Miljø og Fåreavl (1988): Beretning med vurdering af arbejdsresultater 1983-87. Grønlands Hjemmestyre og Ministeriet for Grønland. København.

Atomenergikommissionen (1976): Geologisk deponering i Danmark af højaktivt affald fra kernekraftværker. København.

Baastrup, E., Dalsgaard, K. & Petersen, T.H. (1977): Jorde på Bording Bakkeø. Rapport Nr. 4. Geologisk Institut, Aarhus Universitet.

Barth, J.B. (1855): De danske Heder og deres Dannelse, en forstvidenskabelig Udvikling. Nordisk Universitets-Tidskrift, 1:3: 16-56.

Barth, J.B. (1856): De danske Heder og deres Dannelse, en forstvidenskabelig Udvikling (continued). Nordisk Universitets-Tidskrift, 2:3: 1-22.

Barth, J.B. (1858): Antikritisk Bedømmelse af Conferentsraad Forchhammers "Barth om de danske Heder og deres Dannelse". Nordisk Universitets-Tidskrift, 3:4: 131-36.

Beredskabsplan (1978). Forslag udarbejdet af teknikergruppen tilknyttet det af Ringkøbing Amtsråd nedsatte okkerudvalg vedrørende forureningsproblemerne omkring Ringkøbing Fjord - Skjernå systemet. Ringkøbing Amtsråd.

Betænkning I (1975). Afgivet af teknikergruppen tilknyttet det af Ringkøbing Amtsråd nedsatte udvalg vedrørende forureningsproblemerne omkring Ringkøbing Fjord. Ringkøbing Amtsråd.

Betænkning II (1978). Afgivet af teknikergruppen tilknyttet det af Ringkøbing Amtsråd nedsatte udvalg vedrørende forureningsproblemerne omkring Ringkøbing Fjord - Skjernå systemet. Ringkøbing Amtsråd.

Biilmann, E. & Jensen, S. Tovborg (1927): On the determination of the reaction of soils by means of the quinhydrone electrode. Transactions of the Second Commission of the International Society of Soil Science, Vol. B: 236-74.

Biilmann, E. & Lund, H. (1921): Sur l'électrode a quinhydrone. Annales de Chimie, 9^{e} série, 14: 321-40.

Bjerrum, N. & Gjaldbæk, J.K. (1919a): Undersøgelser over de Faktorer, som bestemmer Jordbundens Reaktion. I. Om Bestemmelse af en Jords sure eller basiske Egenskaber. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 48-64.

Bjerrum, N. & Gjaldbæk, J.K. (1919b): Undersøgelser over de Faktorer, som bestemmer Jordbundens Reaktion. II. Om Reaktion af Vædsker, som er mættet med Kalciumkarbonat. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 64-91.

Borggaard, O.K. (1974): Experimental conditions concerning potentiometric titration of humic acid. Journal of Soil Science, 25: 189-95.

Borggaard, O.K. (1976a): Selective extraction of amorphous iron oxides by EDTA from a mixture of amorphous iron oxide, goethite, and hematite. Journal of Soil Science, 27: 478-86.

Borggaard, O.K. (1976b): The use of EDTA in soil analysis. Acta Agriculturæ Scandinavica, 26: 144-50.

Borggaard, O.K. (1981): Selective extraction of amorphous iron oxides by EDTA from soils from Denmark and Tanzania. Journal of Soil Science, 32: 427-32.

Borggaard, O.K. (1982): The influence of iron oxides on the surface area of soil. Journal of Soil Science, 33: 443-49.

Borggaard, O.K. (1983a): Effect of surface area and mineralogy of iron oxides on their surface charge and anion adsorption properties. Clays and Clay Minerals, 31: 230-32.

Borggaard, O.K. (1983b): The influence of iron oxides on phosphate adsorption by soil. Journal of Soil Science, 34: 333-41.

Borggaard, O.K. (1984): Influence of iron oxides on the non-specific anion (chloride) adsorption by soil. Journal of Soil Science, 38: 71-78.

Borggaard, O.K. (1986): Iron oxides in relation to phosphate adsorption by soils. Acta Agriculturæ Scandinavica, 36: 107-18.

Borggaard, O.K. (1987): Influence of iron oxides on cobalt adsorption by soils. Journal of Soil Science, 38:229-38.

Borggaard, O.K. (1990): Dissolution and adsorption properties of soil iron oxides. Chemistry Department, Royal Veterinary and Agricultural University, Copenhagen.

Borggaard, O.K., Jørgensen, S. Storgaard, Møberg, J.P. & Raben-Lange, B. (1990): Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils. Journal of Soil Science, 41: 443-49.

Borggaard, O.K. & Streibig, J.C. (1988a): Atrazine adsorption by some soil samples in relation to their constituents. Acta Agriculturæ Scandinavica, 38: 293-301.

Borggaard, O.K. & Streibig, J.C. (1988b): Chlorsulfuron adsorption by humic acid, iron oxides, and montmorillonite. Weed Science, 36: 530-34.

Borggaard, O.K. & Streibig, J.C. (1989): Chlorsulfuron adsorption by selected soil samples. Acta Agriculturæ Scandinavica, 39: 351-60.

Bornebusch, C.H. (1931): Hedeskovenes Foryngelse. III. Dybtgående Jordbundsundersøgelser. Det Forstlige Forsøgsvæsen i Danmark, 13: 1-50.

Bornebusch, C.H. (1933): Et Udhugningsforsøg i Rødgran. Det Forstlige Forsøgsvæsen i Danmark, 13: 117-214.

Bornebusch, C.H. & Milthers, K. (1935): Jordbundskort over Danmark. Danmarks Geologiske Undersøgelse, III. Række, Nr. 24.

Christensen, H.R. & Jensen, S. Tovborg (1923): Undersøgelser vedrørende elektrometriske Metoder til Bestemmelse af Jordreaktionen. Tidsskrift for Planteavl, 29: 783-816.

Christensen, H.R. & Jensen, S. Tovborg (1924): Untersuchungen bezuglich der zur Bestimmung der Bodenreaktion benutzten elektrometrischen Methoden. Internationale Mitteilungen für Bodenkunde, 14: 1-26.

Christensen, H.R. & Jensen, S. Tovborg (1926): On the quantitative determination of the lime requirement of the soil. Transactions of the Second Commission of the International Society of Soil Science, Vol. A: 94-115.

Christensen, W., Frederiksen, J., Hansen, L., Henriksen, Aa., Juel, O., Kofoed, A. Dam, Lindhard, J. & Rasmussen, K. (1971): Plantenæringsstoffer. Publikation Nr. 16. Forureningsrådet - Sekretariatet. København.

Christensson, F. & Jensen, E. (1970): The mineralogical composition of the pyrite-bearing lignite clay from Southwest Jutland. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 123-43.

Christoffersen, N.J. (1975): En fluvisol i Sydsjælland. Studier omkring et mindre vandløbs terrasse. Geografisk Tidsskrift, 74: 79-85.

Clausen, H. (1932): Røntgenografiske Undersøgelser af danske Lerarter. Meddelelser fra Dansk Geologisk Forening, 8: 167-74.

Commission of the European Communities (1985). Soil map of the European Communities 1:1 000 000. Directorate-General for Agriculture. Coordination of Agricultural Research. Luxembourg.

Coninck, F. de, Jensen, W. & Kimpe, C. de (1987): Evolution of silicates, especially phyllosilicates, during podzolization. In: Podzols et Podzolisation. Ed. D. Righi and A. Chauvd. INRA-FES: 147-62.

Coninck, F. de, Ranst, E. van & Jensen, W. (1983): Trio-ctahedral and dioctahedral chlorite in soils; examples of a Dystrochrept (Corsica), a Cryorthod (Norway) and a Haplaqualf (France). In: Pétrologie des altérations et des sols. Ed. D. Nahon and Y. Noach. Sciences Geologiques, Memoire, 73: 74-84. Strasbourg.

Courty, MA. & Nørnberg, P. (1985): Comparison between buried uncultivated and cultivated iron age soils on the West Coast of Jutland, Denmark. ISKOS, 5: 57-69.

Dalgas, E. (1866): En Oversigt over Hederne i Jylland. Aarhus.

Dalsgaard, K. (1970): Description of some highly porous soil profiles on the island of Bellona, an emerged atoll in the Solomon Islands. Geografisk Tidsskrift, 69: 93-114.

Dalsgaard, K. (1984): Matrikelkortet fra 1844 anvendt til rekonstruktion af det udrænede landskab. Aarbøger for Nordisk Oldkyndighed og Historie: 282-302.

Dalsgaard, K. (1986): Soil fertility distribution as shown by taxation maps from about 1800 and the effect of later drainage works on the present day landscape. Transactions XIII. Congress of the International Society of Soil Science, Hamburg, Vol. Ill: 1086-87.

Dalsgaard, K. (1988a): Comparison of soils from the last interglacial and holocene in Denmark. International Working Meeting on Soil Micromorphology, San Antonio, Texas: 57.

Dalsgaard, K. (1988b): Spodosols of Denmark. Proceedings V. International Soil Correlating Meeting: 133-41.

Dalsgaard, K. (1989): Udviklingen i landbrugslandskabet fra Stavnsbåndets tid til i dag. In: Bondefrigørelse. Dansk Landbrug i Fortid, Nutid og Fremtid. Ed. J. Andersen, T. Bekker-Nielsen and O. Fenger. Acta Jutlandica LXV:3. Naturvidenskabelig Serie 8: 87-101. Århus.

Dalsgaard, K., Baastrup, E. & Bunting, B.T. (1981): The influence of topography on the development of alfisols on calcareous clayey till in Denmark. Catena 8: 111-36.

Dalsgaard, K., Greve, M.H. & Sørensen, P. (1990): Den niedersachsiske Standortskartierungs anvendelighed under danske forhold. Ugeskrift for Jordbrug, 135: 54-57.

Dalsgaard, K., Hansen, K. & Lomholt, S. (1976): 1844 boniteringen anvendt til at belyse jordbundsforholdene i ældre tider. Intern Rapport Nr. 1. Laboratoriet for Fysisk Geografi, Geologisk Institut, Aarhus Universitet.

Dalsgaard, K. & Nørnberg, P. (1982): A comparative study of present and ancient dark-coloured topsoil for the purpose of evaluating soil fertility in the past. PACT, 7: 247-56.

Dalsgaard, K. & Nørnberg, P. (1985): Formation of structurized 'amorphous' ironoxide cutans in a soil below a Roman Iron Age barrow. 5th Meeting of the European Clay Groups Prague 1983: 585-89. Univerzita Karlova Praha.

Esu, I.E. & Møberg, J.P. (1991): Clay mineralogical composition of three vertisol pedons developed on different parent materials in NE Nigeria. Journal of Soil Science (accepted for publication).

Faizy, SA. (1973): Profile development in Danish loamy soils. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 49-63.

FAO-Unesco (1981): Soil map of the World 1: 5 000 000. Volume V. Europe. Unesco, Paris.

Fobian, A. (1966): Studie über Parabraunerden in Danemark. Pedologie, 16: 183-98.

Fobian, A. (1976): Flyvebilleders anvendelse ved jordbundskortlægning. Dansk Geologisk Forening, Årsskrift:7-21.

Fobian, A. (1981): Mikromorfologiske træk af et jordbundsprofil i moræneler. Dansk Geologisk Forening, Årsskrift: 29-44.

Fobian, A. (1984): Jordbundskortlægning og arealklassificering. Pedologisk kort over et område vest for København og dets anvendelse for praktiske formål. Instituttet for Teknisk Geologi, Danmarks Tekniske Højskole.

Forchhammer, G. (1835): Danmarks geognostiske Forhold forsaavidt som de ere afhængige af Dannelser, der ere afsluttede, Kjøbenhavn.

Forchhammer, G. (1850): Danmarks Jordbund i Forhold til Plantevæxten. Tidskrift for Landoekonomie, II. Række, 12: 481-518.

Forchhammer, G. (ca. 1850): Undersøgelse om Oprindelsen og de nærmere Bestanddele af nogle af de vigtigste Leerarter, Kjøbenhavn.

Forchhammer, G. (1855): De jydske Heder. Steenstrup, Dansk Maanedsskrift, 1: 161-80.

Forchhammer, G. (1857): Barth om de danske Heder og deres Dannelse. Nordisk Universitets-Tidskrift, 3:2:74-83.

Forchhammer, G. (1858): Bidrag til Skildringen af Danmarks geographiske Forhold i deres Afhængighed af Landets indre geognostiske Bygning, Kjøbenhavn.

Forchhammer, G. (1861): Den jydske Hedeslettes physiske og geognostiske Forhold. Tidskrift for Landoekonomie, III. Række, 9: 143-59.

Forchhammer, G. (1862): Ahlformationen og Campinesandet. Oversigt over det Kongelige danske Videnskabernes Selskabs Forhandlinger og dets Medlemmers Arbejder: 152-65.

Forchhammer, G. (1865): Om Marsk, Dynd og Tørv. Tidskrift for Landoekonomie, III. Række, 13: 321-39.

Frederiksen, P. (1981): Landsat, aerial photography and state factors in soil survey of arid and humid Patagonia, Argentina. Geografisk Tidsskrift, 81: 39-48.

Frederiksen, P. (1982a): Evaluation of Soil Taxonomy and FAO-Unesco in relation to nine climo-sequence soils, Argentine. Geografisk Tidsskrift, 82: 11-15.

Frederiksen, P. (1982b): Climatic influence on morphology and chemistry of nine loess-profiles, Argentine. Geografisk Tidsskrift, 82: 16-24.

Frederiksen, P. (1984): The Third Danish Scientific Expedition to Patagonia and Tierra del Fuego. Geografisk Tidsskrift, 84: 1-5.

Frederiksen, P. (1986a): Sydgrønlands naturforhold. Nanortalik området. Geografisk Institut. København.

Frederiksen, P. (1986b): Sydgrønlands naturforhold. Saarloq - Vatnaverfi - Qassiarsuk området. Geografisk Institut. København.

Frederiksen, P. (1988): Soils of Tierra del Fuego. A satellite-based land survey approach. Folia Geographica Danica, Tom. XVIII. København.

Gjaldbæk, J.K. (1921): Undersøgelser over de Faktorer, som bestemmer Jordbundens Reaktion. III. Magnesiumkarbonatets forskellige Former og om Reaktionen af Vædsker, som er mættet dermed. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 245-296.

Hansen, E.H. & Schnitzer, M. (1966): The alkaline permanganate oxidation of Danish illuvial organic matter. Soil Science Society of America Proceedings, 30: 745-48.

Hansen, E.H. & Schnitzer, M. (1967): Nitric acid oxidation of illuvial organic matter. Soil Science Society of America Proceedings, 31: 79-85.

Hansen, E.H. & Schnitzer, M. (1969a): Molecular weight measurements of polycarboxylic acids in water by vapor pressure osmometry. Analytica Chimica Acta, 46: 257-64.

Hansen, E.H. & Schnitzer, M. (1969b): Zn-dust distillation and fusion of a soil humic and fulvic acid. Soil Science Society of America Proceedings, 33: 29-36.

Hansen, G. Kjær & Madsen, H. Breuning (1984): Soil evaluation based on simulation by a model. Acta Agriculturæ Scandinavica, 34: 9-16.

Hansen, H.C.B. (1989): Composition, stabilization, and light absorption of Fe(II)Fe(III)hydroxycarbonate ('green rust'). Clay Minerals, 24: 663-69.

Hansen, H.C.B. & Taylor, RM. (1990): Formation of synthetic analogues of double metal-hydroxy carbonate minerals under controlled pFt conditions: I. The synthesis of pyroaurite and reevesite. Clay Minerals, 25: 161-79.

Hasholt, B., Madsen, H. Breuning & Platou, S.W. (1989): Evaluation of soil erosion risk and sources of suspended load in Denmark. Proceedings of International Symposium on Erosion and Volcanic Debris Flow Technology: 12.1-12.16. Yogyakarta.

Holmsgaard, E., Holstener-Jørgensen, H. & Yde-Andersen, A. (1961): Bodenbildung, Zuwachs und Gesundheitszustand von Fichtenbeständen erster und zweiter Generation. 1. Nord-Seeland. Det Forstlige Forsøgsvæsen i Danmark, 27: 1-167.

Holst, K. Aagaard & Madsen, H. Breuning (1986): The elaboration of drainage class maps covering Denmark. Landscape and Urban Planning, 13: 199-218.

Holst, K. Aagaard & Madsen, H. Breuning (1988): Modelling the irrigation need. Acta Agriculturæ Scandinavica, 38: 261-69.

Holstener-Jørgensen, H. (1957): Danske skov- og plantagejorders mineralogiske sammensætning. Meddelelser fra Det norske Skogforsøksvesen, 48: 203-13.

Holstener-Jørgensen, H. (1965a): An investigation of the podsolation processes in soils with a high groundwater-table. Det Forstlige Forsøgsvæsen i Danmark, 29: 299-308.

Holstener-Jørgensen, H. (1965b): Tekstur og pH i fedt moræneler på Bregentved. Det Forstlige Forsøgsvæsen i Danmark, 29: 245-81.

Holstener-Jørgensen, H. (1973): Om lemedslemningpå dansk moræne. Det Forstlige Forsøgsvæsen i Danmark, 33: 327-44.

Holstener-Jørgensen, H., Krag, M. & Olsen, H.C. (1988): The influence of 12 tree species on the acidification of the upper soil horizons. Det Forstlige Forsøgsvæsen i Danmark, 42: 15-25.

Hovmand, M. & Petersen, L. (1984a): Forsuringsprojektet: Jordforsuring. Miljøstyrelsen, København.

Hovmand, M.F. & Petersen, L. (1984b): Udvaskningstab fra agerjord som følge af syredeposition. Nordforsk, Miljovårdsserien, Publikation 1984:2: 89-98.

Jacobsen, N. Kingo (1956): Jordbundsundersøgelser i Tøndermarsken. Geografisk Tidsskrift, 55: 106-46.

Jacobsen, N. Kingo (1959): Geest-topografi under Tøndermarsken. Geestoverfladens morfologi i Møgeltønder Kog, beskrivelse og forsøgsvis tolkning. Geografisk Tidsskrift, 58: 141-81.

Jacobsen, N. Kingo (1960a): Types of sedimentation in a drowned delta region. Examples from the salt-marsh area at Tønder. Geografisk Tidsskrift, 59: 58-69.

Jacobsen, N. Kingo (1960b): Agricultural geography and regional planning in a marine foreland. Geografisk Tidsskrift, 59: 145-62.

Jacobsen, N. Kingo (1961): Iagttagelser fra Stadil Fjord området. En foreløbig meddelelse. Geografisk Tidsskrift, 60: 54-73.

Jacobsen, N. Kingo (1964): Træk af Tøndermarskens naturgeografi med særligt henblik på morfogenesen. Folia Geographica Danica, Tom. VII, No.l. København.

Jacobsen, N. Kingo (1969): Landskabsformerne. Meddelelser fra Skallinglaboratoriet, 22.

Jacobsen, N. Kingo (1972): Rejsbymarsken. Folia Geographica Danica, Tom. XII, No. 1. København.

Jacobsen, N. Kingo (1976): Natural-geographical regions of Denmark. Geografisk Tidsskrift, 75: 1-7.

Jacobsen, N. Kingo (1980): The Knud Rasmussen Memorial Expedition. Introduction. Geografisk Tidsskrift, 80: 29-32.

Jacobsen, N. Kingo (1984): Soil map of Denmark according to the FAO-Unesco Legend. Geografisk Tidsskrift, 84: 93-98.

Jacobsen, N. Kingo (1986): The intertidal sediments. Geografisk Tidsskrift, 86: 46-62.

Jacobsen, N. Kingo (1987): Studies on soils and potential for soil erosion in the sheep farming area of South Greenland. Arctic and Alpine Research, 19: 498-507.

Jacobsen, N. Kingo & Jakobsen, B. Holm (1986): datering af en fossil overfladehorisont ved Igaliku Kujalleq, Sydgrønland, set i relation til nordboernes landnam. Geografisk Tidsskrift, 86: 74-77.

Jakobsen, B. Holm (1981): Pedologisk kortlægning og jordbundsbonitering i et geestrandområde ved Tønder. Geografisk Tidsskrift, 81: 17-32.

Jakobsen, B. Holm (1984a): En beskrivelse og tolkning af nogle sedimentkemiske forhold i en række forskellige lavbundsområder vest for hovedstilstandslinien. Redegørelse om den tre-årige forsøgsordning til nedbringelse af okkergener i vandløb. Bilag 20. Miljøministeriet, Miljøstyrelsen. København.

Jakobsen, B. Holm (1984b): Jordbundsgeografiske undersøgelser i SV-Grønland, sommeren 1984. Geografisk Institut. København.

Jakobsen, B. Hobn (1985): An interpretation of the occurrence of pyrite at two localities in Western Jutland, Denmark. Geografisk Tidsskrift, 85: 9-14.

Jakobsen, B. Holm (1986): Jordbundsgeografiske undersøgelser i Sydvestgrønland. Foreløbig rapport. Geografisk Institut. København.

Jakobsen, B. Holm (1987): Occurrence of pyrite and carbonate minerals in a lowland moor area. Journal of Sedimentary Petrology, 57: 530-36.

Jakobsen, B. Holm (1988a): Accumulation of pyrite and Fe-rich carbonate and phosphate minerals in a lowland moor area. Journal of Soil Science, 39: 447-55.

Jakobsen, B. Holm (1988b): Soil formation on the peninsula Tugtuligssuaq, Melville Bay, North West Greenland. Geografisk Tidsskrift, 88: 86-93.

Jakobsen, B. Holm (1989): Evidence for translocation into the B horizon of a subarctic podzol in Greenland. Geoderma, 45: 3-17.

Jakobsen, B. Holm, Mortensen, N. Gylling & Thingvad, N. (1980): Report of activities at Tugtuligssuaq, Melville Bay, 1979 - Geographical investigations. Geografisk Tidsskrift, 80: 32-38.

Jensen, A. Tovborg & Andersen, E. Krogh (1955): The minerals present in sands from Danish soils and subsoils. I. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 1-12.

Jensen, A. Tovborg & Andersen, E. Krogh (1956): The minerals present in sands from Danish soils and subsoils. II. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 1-12.

Jensen, A. Tovborg & Andersen, E. Krogh (1961): The minerals present in sands from Danish soils and subsoils. III. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 1-30.

Jensen, A. Tovborg & Flyge, H. (1966): The minerals present in sands from Danish soils and subsoils. IV. Heavy minerals in the sand fraction. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 118-28.

Jensen, A. Tovborg & Pedersen, M. *Brink* (1977): Om kalkvirkningens grundproces. En sammenlignende laboratorieundersøgelse af reaktiviteten af en blød og en hård dansk jordbrugskalk og tre dolomiter. Ugeskrift for Agronomer, Hortonomer, Forstkandidater og Licentiater, 122: 647-51.

Jensen, E. (1951): Quantitative determination of quartz by X-ray analysis in clay materials. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 65-80.

Jensen, E. (1955): The mineralogical composition of the fine-grained fractions of some typical Danish agricultural soils. I. Quartz. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 13-32.

Jensen, E. (1956): Sample size requirements for accurate mineralogical analyses of sand. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 13-29.

Jensen, E. (1965): The low-plastic clay from Godthåb, Greenland. An X-ray mineralogical investigation. Meddelelser om Grønland, 165:4: 1-15.

Jensen, E. & Würtz, L. (1974): Soil weathering in West Greenland. An X-ray mineralogical investigation. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 1-11.

Jensen, N.H. & Madsen, H. Breuning (1988): Jordprofilundersøgelser. Ugeskrift for Jordbrug, 133: 599-602.

Jensen, S. Tovborg (1924a): Om Bestemmelse af Jordens Stødpudevirkning. Tidsskrift for Planteavl, 30: 565-85.

Jensen,S. Tovborg (1924b): Ueber die Bestimmung der Pufferwirknung des Bodens. Internationale Mitteilungen für Bodenkunde, 14: 112-30.

Jensen, S. Tovborg (1925): Undersøgelser over Kalciumkarbonats reaktionsændrede Virkning i Jordbunden. Tidsskrift for Planteavl, 31: 744-78.

Jensen, S. Tovborg (1928): Undersøgelser over Ammoniakfordampning i Forbindelse med Kvælstoftab ved Udbringning af naturlige Gødninger. I: Ajle. Tidsskrift for Planteavl, 34: 117-47.

Jensen, S. Tovborg (1929a): Undersøgelser over Ammoniakfordampning i Forbindelse med Kvælstoftab ved Udbringning af naturlige Gødninger. II. Ajle. Tidsskrift for Planteavl, 35: 59-80.

Jensen, S. Tovborg (1929b): Om Kunstgødningers Indvirkning på Jordens Reaktion. Tidsskrift for Planteavl, 35: 390-419.

Jensen, S. Tovborg (1929c): On the quantitative determination of the lime requirements of soils and lime absorption in acid humus soils. Transactions of the Second Commission of the International Society of Soil Science, Vol. A: 47-58.

Jensen, S. Tovborg (1930): Untersuchungen über Ammoniakentbindung und Stickstoffverluste bei der Düngung mit Jauche. Wissenschaftlicher Archiv für Landwirtschaft, Abteilung A: Archiv für Pfanzenbau, 3: 161-80.

Jensen, S. Tovborg (1931a): Heden og dens Dyrkning. Tilskueren, 48: 57-68.

Jensen, S. Tovborg (1931b): Om Ajlens Opbevaring og Anvendelse. Ugeskrift for Landmænd, 76: 243-46.

Jensen, S. Tovborg (1931c): Om Bestemmelse af Jords Kulstofindhold ved Forbrænding i komprimeret Ilt. Tidsskrift for Planteavl, 37: 151-64.

Jensen, S. Tovborg (1931d): Über die Bestimmung des Kohlenstoffgehaltes des Bodens durch Verbrennen in komprimiertem Sauerstoff. Wissenschaftliches Archiv für Landwirtschaft, Abteilung A: Archiv für Pfanzenbau, 6: 299-310.

Jensen, S. Tovborg (1932): Kvælstofgødninger Indvirkning på Jordens Reaktion. Nordisk Jordbrugsforskning: 313-23.

Jensen, S. Tovborg (1936): Kalkens Omsætninger i Jordbunden, teoretisk og eksperimentelt belyst. Tidsskrift for Planteavl, 41: 571-649.

Jensen, S. Tovborg (1938): Om Kvælstoftab ved Ammoniakfordampning fra Ajle. Tidsskrift for Planteavl, 43: 177-88**.**

Jensen, S. Tovborg (1951a): Ammoniakfordampning fra Jord og dens Betydning for Landbrugets Kvælstoføkonomi. Akademiet for de Tekniske Videnskaber. Meddelelser: 117-36.

Jensen, S. Tovborg (1951b): Calcium adsorption and lime loss from leaching in soils. United Nations Scientific Conference on the Conservation and Utilization of Resources VI: 213-25.

Jensen, S. Tovborg (1952): The liming problem. Transactions of Commission II and Commission IV International Society of Soil Science, Vol. I: 93-106.

Jensen, S. Tovborg (1954): Determination of water content and specific gravity in soil samples by means of pyknometers. Transactions Fifth International Congress of Soil Science, Leopoldville, Vol. II: 118-22.

Jensen, S. Tovborg (1955): Om Nordsømarsken og dens landøkonomiske udnyttelse. Tidsskrift for Planteavl, 59: 291-327.

Jensen, S. Tovborg (1956): Humusproblemet. Ugeskrift for Landmænd, 101: 307-10 and 327-28.

Jensen, S. Tovborg (1961): Jordbundsklassificering og Jordbonitering. En Oversigt. In; Om Jord og Planter, Festskrift til K. A. Bondorff: 139-59. København.

Jensen, S. Tovborg (1962): Soil classification and soil mapping Denmark. Transactions Commission IV and Commission V, International Society of Soil Science: 349-54.

Jensen, S. Tovborg & Damsgaard-Sørensen, P. (1935): Om Glaselektroden og dens Anvendelse til Bestemmelse af Jordopslemningers Brintionkoncentration. Tidsskrift for Planteavl, 40: 687-708.

Jensen, S. Tovborg & Kjær, B. (1948a): Kvælstoftab ved Ammoniakfordampning efter Gødskning med svovlsur Ammoniak. Tidsskrift for Planteavl, 51: 666-711.

Jensen, S. Tovborg & Kjær, B. (1948b): Undersøgelser over Kornstørrelsesfordelingen i en Række danske Kalk- og Mergelforekomster. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 148-65.

Jensen, S. Tovborg & Kjær, B. (1950): Stickstoffverluste aus Boden durch Ammoniakverdampfung bei Düngung mit schwefelsaurem Ammoniak. Zeitschrift für Pflanzenernährung, Düngung und Bodenkunde 50 (95): 25-38.

Jensen, S. Tovborg & Larsen, S. (1957): Reduktion og udvaskning af chlorat i jordbunden. Tidsskrift for Planteavl, 61: 103-18.

Johnstrup, J.F. (1869): Om Jordbundens Dannelse i Danmark. Tidsskrift for Landøkonomi, IV. Række, 3: 541—62.

Johnstrup, J.F. (1875): Om de geognostiske Forhold i Jylland. Tidsskrift for Landøkonomi, IV. Række, 9:457-85.

Jørgensen, S. Storgaard (1968): Solubility and dissolution kinetics of precipitated amorphous silica in 1 M $NaClO_4$ at 25°C. Acta Chemica Scandinavica, 22: 335-41.

Jørgensen, S. Storgaard (1970): The application of alkali dissolution techniques in the study of Cretaceous flints. Chemical Geology, 6: 153-63.

Jørgensen, S. Storgaard (1976): Dissolution kinetics of silicate minerals in aqueous catechol solutions. Journal of Soil Science, 27: 183-95.

Jørgensen, S. Storgaard & Jensen, A. Tovborg (1967): Acid-base properties of quartz suspensions. Journal of Physical Chemistry, 71: 745-50.

Jørgensen, S. Storgaard & Mitchell, B.D. (1970): The application of alkali dissolution techniques in the study of aluminium hydroxides and oxyhydroxides. Israel Journal of Chemistry, 8: 343-56.

Jørgensen, S. Storgaard & Willems, M. (1987a): The fate of lead in soils: The transformation of lead pellets in shooting-range soils. AMBIO 16: 11-15.

Jørgensen, S. Storgaard & Willems, M. (1987b): The fate of lead in soils: Lead originating from roofs of ancient churches. AMBIO 16: 16-19.

Kjær, B. (1974): A laboratory method for estimating relative dissolution rates of lime. Revised by A.Tovborg Jensen. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 12-28.

Klix-Henriksen, P. (1981): Soils from Warthe till at the Emmerlev Kiev in Southern Denmark. Stratigraphy and paleopedology. Geografisk Tidsskrift, 81: 33-38.

Koch, C.J.W. (1987): A study of placic horizons in spodosols. Chemistry Department, Royal Veterinary and Agricultural University.

Landbrugsministeriet (1976): Den danske jordklassificering. Teknisk redegørelse. København.

Landbrugsministeriet (1984): Kvælstoftilførselogkvælstofudvaskning i dansk planteproduktion. Gennemsnitsopgørelser 1978-1982. Arealdatakontoret, Vejle.

Larsen, P. (1973): Initial development (ripening) of some reclaimed gyttja soils in Kolindsund, Denmark. Catena, 5: 285-304.

Lindgreen, H.B. (1976): Instrumental and chemical methods for characterization of soil clays. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 133-54.

Lindgreen, H. & Rasmussen, K. (1978): A microcrystalline Danish soil clay investigated by diffraction, spectroscopic, thermal, chemical dissolution and adsorption methods. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 103-37.

Lütken, C. (1865): Om Skovdyrkning i det vestlige Jylland. Tidskrift for Landeconomie, III. Række, 13: 367-406.

Madsen, H. Breuning (1975): Aggregatstabilitetsanalyse. Geografisk Tidsskrift, 74: 70-78.

Madsen, H. Breuning (1976): Nogle jyske jordes vandindhold. Folia Geographica Danica, Tom. X, No. 4. København.

Madsen, H. Breuning (1978a): Bygs rodudvikling i relation til fysiske parametre i naturligt lejret jord. Tidsskrift for Planteavl, 82: 335-42.

Madsen, H. Breuning (1978b): Possibilities and limitations of black-and-white aerial photographs in soil surveying. Geografisk Tidsskrift, 77: 43-48.

Madsen, H. Breuning (1979a): Jordbundskartering og bonitering. Belyst ved hjælp af jordens vandretention, bygs rodudvikling og simuleret planteproduktion. Folia Geographica Danica, Tom. X, No. 5. København.

Madsen, H. Breuning (1979b): Opbygning af et jordbundsklassificeringssystem med særlig henblik på bonitering. Geografisk Tidsskrift, 78: 20-27.

Madsen, H. Breuning (1980a): Fastlæggelse af højokkerpotentielle områder i Himmerland. Landbrugsministeriet. Arealdatakontoret. Beretning nr. A-01.

Madsen, H. Breuning (1980b): Jordbundsforhold og rodudvikling på Tylstrup forsøgsstation. Tidsskrift for Planteavl, 84: 5-14.

Madsen, H. Breuning (1983a): A pedological classification system for Danish soils. Pedologie, 33: 171-97.

Madsen, H. Breuning (1983b): Himmerlands jordbundsforhold. Et regionalt studie omhandlende jordbundsudvikling, -klassifikation, afgrøders rodudvikling og jordens plantetilgængeligevandmængde. Folia Geographica Danica, Tom. XVI. København.

Madsen, H. Breuning (1984a): Clay migration and podzolization in a Danish soil. Geografisk Tidsskrift, 84: 6-9.

Madsen, H. Breuning (1984b): Omfattende kortlægning af okkerholdige områder. Vækst. Hedeselskabets Tidsskrift, Nr. 5: 6-7.

Madsen, H. Breuning (1984c): Soil mapping in Denmark. Soil Survey and Land Evaluation, 4,3: 57-82.

Madsen, H. Breuning (1985): Distribution of spring barley roots in Danish soils of different texture and under different climatic conditions. Plant and Soil, 88: 31-43.

Madsen, H. Breuning (1986): The construction of root zone capacity maps based on computerized soil maps and pedological data. Pedologie, 36: 133-54.

Madsen, H. Breuning (1989a): Elaboration of a soil profile and analytical database connected to the EC-soil map. In: Application of Computerized EC Soil Map and Climate Data. Proceedings of a Workshop in the Community Programme for Coordination of Agricultural Research. Ed. H.A.J. van Lanen and A.K. Bregt: 119-32. Wageningen 1988. Luxembourg.

Madsen, H. Breuning (1989b): Kalk og pH i danske jorde. Grøn Viden, nr. 41.

Madsen, H. Breuning (1989c): Potentielle marginaljorder bestemt ud fra naturgivne faktorer. Geografisk Tidsskrift, 89: 25-30.

Madsen, H. Breuning, Hasholt, B. & Platou, S. W. (1986a): Soil erodibility map covering an area of Southern Zealand. In: Partikulært Bundet Stoftransport i Vand og Jorderosion. Ed. B. Hasholt. NHP-Rapport Nr. 14: 273-83. København.

Madsen, H. Breuning, Hasholt, B. & Platou, S.W. (1986b): The development of a computerized erodibility map covering Denmark. In: Soil Erosion in the European Community - Impact of Changing Agriculture. Ed. G. Chisci and R.P.C. Morgan: 143-54. Rotterdam.

Madsen, H. Breuning & Holst, K. Aagaard (1987): Potentielle marginaljorde - Landsdækkende kortlægning af jordbundsfysiske og -kemiske forhold, der har indflydelse på jordens dyrkningsværdi. Skov- og Naturstyrelsen/ Miljøstyrelsen. København.

Madsen, H. Breuning & Holst, K. Aagaard (1988): A nationwide mapping of dry soils for plant production - A case study from Denmark. Geografisk Tidsskrift, 88: 1-8.

Madsen, H. Breuning & Holst, K. Aagaard (1990): Mapping of irrigation need based on computerized soil and climatic data. Agricultural Water Management, 17: 391—407.

Madsen, H. Breuning, Holst, K. Aagaard & Mikkeben, S. Aggergård (1989): The use of the EC-soil map in modelling and mapping the root zone capacity and irrigation need. - A case study from Denmark. In: Computerization of Land Use Data. Proceedings of a Symposium in the Community Programme for Coordination of Agricultural Research. Ed. R.J.A. Jones and B. Biagi: 74-84. Pisa 1987. Luxembourg.

Madsen, H. Breuning & Jakobsen, B. Holm (1980): A Danish podzoluvisol. Geografisk Tidsskrift, 80: 78-80.

Madsen, H. Breuning & Jensen, N.H. (1985): The establishment of pedological soil data bases in Denmark. Geografisk Tidsskrift, 85: 1-8.

Madsen, H. Breuning & Jensen, N.H. (1988): Potentially acid sulfate soils in relation to landforms and geology. Catena, 15: 137-45.

Madsen, H. Breuning, Jensen, C.R. & Boysen, T. (1986): A comparison of the thermocouple psychrometer and the pressure plate methods for determination of soil water characteristic curves. Journal of Soil Science, 37:357-62.

Madsen, H. Breuning, Jensen, N.H., Jakobsen, B. Holm & Platou, S.W. (1984): Potentielt svovlsure jorde i Nordjyllands, Viborg, Ringkøbing, Ribe og Sønderjyllands amtskommuner. Redegørelse om den tre-årige forsøgsordning til nedbringelse af okkergener i vandløb. Bilag 1. Miljøministeriet, Miljøstyrelsen. København.

Madsen, H. Breuning, Jensen, N.H., Jakobsen, B. Holm & Platou, S.W. (1985): A method for identication and mapping potentially acid sulfate soils in Jutland, Denmark. Catena, 12: 363-71.

Madsen, H. Breuning & Munk, I. (1987): The influence of texture, soil depth and geology on pH in farmland soils - A case study from Southern Denmark. Acta Agriculturæ Scandinavica, 37: 407-18.

Madsen, H. Breuning, Nieben, E. Schmidt & Ødum, S. (1980): The Danish scientific expedition to Patagonia and Tierra del Fuego 1978-1979. Geografisk Tidsskrift, 80: 1-28.

Madsen, H. Breuning & Platou, S. W. (1983): Land use planning in Denmark. Nordic Hydrology, 14: 267-76.

Madsen, H. Breuning, Reenberg, A. & Holst, K. Aagaard (1990): Mapping potentially marginal land in Denmark. Soil Use and Management, 6: 114-20.

Mathiesen, F. Duus (1974): Bonitetsanalyse af landbrugsjord. Landboorganisationernes Kontaktudvalg for Landskabsplanlægning. Rønne.

Mathiesen, F. Duus (1975): Klassificering af landbrugsjord i Nordjyllands Amt. Landboorganisationernes Kontaktudvalg for Landskabsplanlægning. Ålborg.

Mathiesen, F. Duus (1980): Soil classification in Denmark. Its result and applicability. EEC-Seminar on Land Resource Evaluation. Wexford, Ireland, 1978.

Mathiesen, F. Duus (1981): Landbrugsplanlægningens sammenhæng med vandplanlægningen. NHP-Rapport Nr. 1. Nordisk Symposium. Åbenrå.

Mathiesen, F. Duus (1982): Land classification as a data source in relation to physical planning. NATO Seminar. Land and Its Uses, Actual and Potential, an Environmental Appraisal. Edinburgh.

Mathiesen, F. Duus (1983): Soil classification in Denmark and its adjustment in relation to land-use planning. Progress in Land Evaluation. Seminar on Soil Survey and Land Evaluation. Wageningen.

Ministeriet for Grønland (1980): Holsteinsborg. Sisimiut kommune. Natur- og kulturforhold. København.

Mrema, J.P., Møberg, J.P. & Uriyo, A.P. (1984): The effect of cations, anions, and the destruction of organic matter on phosphate retention by soils from four soil orders commonly occurring in Tanzania. East African Agricultural and Forestry Journal, 49: 91-101.

Müller, P.E. (1878): Nogle Undersøgelser af Skovjord. Tidsskrift for Landøkonomi, IV. Række, 12: 259-83.

Müller, P.E. (1879): Studier over Skovjord, som Bidrag til Skovdyrkningens Theori. I. Om Bøgemuld og Bøgemor på Sand og Ler. Tidsskrift for Skovbrug, 3: 1-124.

Müller, P.E. (1884): Studier over Skovjord, som Bidrag til Skovdyrkningens Theori. II. Om Muld og Mor i Egeskove og paa Heder. Tidsskrift for Skovbrug, 7: 1-232.

Müller, PE. (1887): Studien über die natürlichen Humusformen und deren Einwirkung auf Vegetation und Boden. Berlin

Müller, P.E. (1899): Zur Theorie der Ortsteinbildung, eine Antwort an Herrn Prof. Dr. Ramann. Engler's botanischen Jahrbüchern 27:3, Beiblatt Nr. 63.

Müller, PE. (1905): Om nogle Bælgplanters Udvikling i bearbejdet jydsk Hedejord. Det Forstlige Forsøgsvæsen, 1: 97-112.

Müller, P.E. (1918): Fortsatte Iagttagelser over Muld og Mor i Egeskove og på Heder. Dansk Skovforenings Tidsskrift, 3: 477-95.

Müller, P.E. (1924): Bidrag til de jydske Hedesletters Naturhistorie. Karup Hedeslette og beslægtede Dannelser. En pedologisk Undersøgelser. Det Kgl. Danske Videnskabernes Selskab. Biologiske meddelelser. IV, 2.

Müller, PE. & Helms, J. (1913): Forsøg med Anvendelse af Kunstgødning til Grankultur i Midtjydsk Hedebund. Med Bidrag til Hedebundens Naturhistorie. Det Forstlige Forsøgsvæsen i Danmark, 3: 271-403.

Müller, P.E., Rørdam, K., Helms, J. & Wøldike, E.H. (1910): Bidrag til Kundskab om Rødgranens Vækstforhold i Midtjydsk Hedebund. Det Forstlige Forsøgsvæsen i Danmark, 3: 1-270.

Müller, P.E. & Weiss, F. (1906): Studier over Skov- og Hedejord. I. Om Kalkens Indvirkning paa Bøgemor. Det Forstlige Forsøgsvæsen, 1: 235-320.

Müller, P.E. & Weiss, F. (1908): Studier over Skov- og Hedejord II. Om Salpetersyrens Forekomst og Dannelse i Muld og Mor. Det Forstlige Forsøgsvæsen, 2: 257-96.

Müller, P.E. & Weiss, F. (1913): Studier over Skov- og Hedejord. III. Forsøg over forskellige Kalkmængders Indflydelse paa Bøgens Udvikling paa Morbund. Det Forstlige Forsøgsvæsen i Danmark, 3: 404-37.

Møberg, J.P. (1972): Some soil fertility problems in the West Lake region of Tanzania, including the effects of different forms of cultivation on the fertility of some ferralsols. East African Agricultural and Forestry Journal, 38: 35-46.

Møberg, J.P. (1973): Some chemical and mineralogical properties of four soils of the West Lake region of Tanzania. East African Agricultural and Forestry Journal, 39: 46-56.

Møberg, J.P. (1974): Formation, mineralogy and fertility of some tropical highland soils. DSR Forlag, København.

Møberg, J.P. (1975): Mineralogical composition of a Danish soil developed on young morainic material. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 91-110.

Møberg, J.P. (1976): A chemical and physicochemical investigation of two Danish podzol profiles. Kgl. Veterinaer- og Landbohøjskole, Årsskrift: 112-32.

Møberg, J.P. (1979): Jordbrugsproblemer i Tanzania. Geografisk Tidsskrift, 78: 10-19.

Møberg, J.P. (1982): Mineralogical composition and some physicochemical properties of two clay soils developed in material deposited during the Saalian glacial phase. Acta Agriculturæ Scandinavica, 32: 289-98.

Møberg, J.P., Msanya, B.M. & Kilasara, M. (1982): Pedological and edaphological properties of the soils of two soil associations in the Morogoro area. Tropical Agriculture (Trinidad), 59: 139-48.

Møberg, J.P. & Nielsen, J. Dissing (1983): Mineralogical changes in soils used for potassium-depletion experiments for some years in pots and in the field. Acta Agriculturæ Scandinavica, 33: 21-27.

Møberg, J.P. & Nielsen, J. Dissing (1986): Den mineralske sammensætning af jorde fra danske forsøgsstationer. Tidsskrift for Planteavl, særnummer 1870.

Møberg, J.P., Petersen, L. & Rasmussen, K. (1988): Constituents of some widely distributed soils in Denmark. Geoderma, 42: 295-316.

Naturgeografisk Regionindelning av Norden (1977). Nordisk Ministerråd, NU B 1977:34.

Nielsen, J. Dissing & Møberg, J.P. (1984): The influence of K depletion on mineralogical changes in pedons from two field experiments and in soils from four pot experiments. Acta Agriculturæ Scandinavica, 34: 391-99.

Nielsen, J. Dissing & Møberg, J.P. (1985): Klassificering af jordprofiler fra forsøgsstationer i Danmark. Tidsskrift for Planteavl, 89: 157-67.

Nielsen, K.E. (1986): Depodzolization caused by oak invasion on a Calluna-heath. Transactions XIII. Congress of the International Society of Soil Science, Hamburg, Vol. III: 1226-27.

Nielsen, K.E., Dalsgaard, K. & Nørnberg, P. (1987a): Effects on soils of an oak invasion of a Calluna heath, Denmark, I. Morphology and chemistry. Geoderma, 41: 79-95.

Nielsen, K.E., Dalsgaard, K. & Nørnberg, P. (1987b): Effects on soils of an oak invasion of a Calluna heath, Denmark, II. Changes in organic matter and cellulose decomposition. Geoderma, 41: 97-105.

Nielsen, K.E., Nørnberg, P. & Dalsgaard, K. (1987): Egeskoven ændrer jordbunden. Vækst. Hedeselskabets Tidsskrift, Nr. 3: 16-17.

Nielsen, N. (1960): The organization of research work in South-West Jutland. Geografisk Tidsskrift, 59: 1-9.

Nørnberg, P. (1977): Soil profile development in sands of varying age in Vendsyssel, Denmark. Catena, 4:165-79.

Nørnberg, P. (1980): Mineralogy of a podzol formed in sandy materials in Northern Denmark. Geoderma, 24: 25-43.

Nørnberg, P. (1986): Weathering processes and the accumulation of silt and clay size material in the top horizons of sandy soils in Denmark. Transactions XIII. Congress of the International Society of Soil Science, Hamburg, Vol. Ill: 1228.

Nørnberg, P. (1989): Vegetationens betydning for forsuring af jordbunden. In: Bondefrigørelse. Dansk Landbrug i Fortid, Nutid og Fremtid. Ed. J. Andersen, T. Bekker-Nielsen and O. Fenger. Acta Jutlandica LXV:3. Naturvidenskabelig Serie 8: 103-14. Århus.

Nørnberg, P. (1990): A potassium-rich zeolite in soil development on Danian chalk. Mineralogical Magazine, 54: 91-94.

Nørnberg, P. & Courty, MA. (1985): Standard geological methods used on archaeological problems. ISKOS, 5: 107-17.

Nørnberg, P. & Dalsgaard, K. (1985): The origin of clay minerals in soils on Danian chalk. 5th Meeting of the European Clay Groups, Prague 1983:553-61. Univerzita Karlova, Praha.

Nørnberg, P. & Dalsgaard, K. (1988): Pedologi/arkæologi. Fælles mål og fælles metoder, et tilbageblik over otte års samarbejde. In: Arkæologiske Udgravninger i Danmark 1987: 44-53.

Nørnberg, P., Dalsgaard, K. & Skammelsen, E. (1985): Morphology and composition of three mollisol profiles over chalk, Denmark. Geoderma, 36: 317-42.

Oksbjerg, E. (1957): Rødgranens og nogle andre nåletræers jordbundsdannelse på fattig jord. Det Forstlige Forsøgsvæsen i Danmark, 23: 125-279.

Oppermann, A. (1932): Egens Træformer og Racer. Det Forstlige Forsøgsvæsen i Danmark, 12: 1-400.

Oppermann, A. & Bornebusch, C.H. (1930): Nørholm Skov og Hede. Det Forstlige Forsøgsvæsen i Danmark, 11: 257-360.

Pedersen, B., Larsen, P. & Rasmussen, K. (1973): The formation of carphosiderite and jarosites at room temperature. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 71-85.

Pedersen, B., Willems, M, *Olsen, C.E. & Jørgensen, S. Storgaard* (1985): UV-, IR-, ^{1}H-NMR spectroscopy of soil organic matter extracted with ethanol and pyridine. Symposium Humus et Planta VIII, Prague, Volume I: 83-86.

Pedini, M. & Svendsen, T.B. (1987): Sammenhængen mellem jordtype og vedproduktion. Miljøministeriets Projektundersøgelser 1986, Teknikerrapport nr. 4. Skov- og Naturstyrelsen, København.

Petersen, L. (1966): Ochreous deposits in drain-pipes. Acta Agriculturæ Scandinavica, 16: 120-28.

Petersen, L. (1969): Chemical determination of pyrite in soils. Acta Agriculturæ Scandinavica, 19: 40-44.

Petersen, L. (1975): Hydraulic conductivity and structural properties of some lowland soils in Thailand. Asian Instistitute of Technology, Bangkok. Research Report No. 52.

Petersen, L. (1976): Podzols and podzolization. DSR Forlag, Copenhagen.

Petersen, L. (1977): Mineralogical composition of the clay fraction of some soils in the Central Plain of Thailand. Proceedings of the Fifth Southeast Asian Conference on Soil Engineering, Bangkok: 313-26.

Petersen, L. (1978): Solubility interactions between iron/aluminium and soil organic matter during podzolization. 11th Congress of the International Society of Soil Science, Edmonton. Abstracts for Commission Papers, Vol. I: 385-86.

Petersen, L. (1980a): Podzolization: Mechanism and possible effects of acid precipitation. In: Effects of Acid Precipitation on Terrestrial Ecosystems. Ed. T.C. Hutchinson and M. Havas: 223-37. New York.

Petersen, L. (1980b): Sensitivity of different soils to acid precipitation. In: Effects of Acid Precipitation on Terrestrial Ecosystems. Ed. T.C. Hutchinson and M. Havas: 573-77. New York.

Petersen, L. (1983): Mineralogical composition of the clay fraction of two soils in Northeast Thailand. Thai Journal of Agricultural Science, 16: 73-94.

Petersen, L. (1984a): Om jordbundsforsuring. Dansk Kemi, 65: 68-70.

Petersen, L. (1984b): The podzol concept. In: Podzols. Ed. P. Buurman: 12-20. New York.

Petersen, L. (1986): Effects of acid deposition on soil and sensitivity of the soil to acidification. Experientia, 42: 340-44.

Petersen, L. (1987): Conditions for agricultural development in Central Kalimantan, Indonesia. Geografisk Tidsskrift 87: 49-56.

Petersen, L. & Madsen, H. Breuning (1978): Possible effects of ground water lowering on some peat soils in Sjælland. Geografisk Tidsskrift, 77: 25-35.

Petersen, L. & Oad, R.N. (1974): Alkali soil reclamation with concentrated solutions. Thai Journal of Agricultural Science, 7: 145-59.

Petersen, L. & Rasmussen, K. (1980): Mineralogical composition of the clay fraction of two fluvio-glacial sediments from East Greenland. Clay Minerals, 15: 135-45.

Petersen, L., Rasmussen, K. & Jensen, A. Tovborg (1968): Soil problems and tree growth after lignite strip mining. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 35-48.

Petersen, L. & Raulund-Rasmussen, K. (1987): Jordbundsudvikling under ager og nåleskov. Geografisk Tidsskrift, 87: 65-67.

Platou, S.W. (1984): The ADK database systems (PDS and LADS). In: Soil Information Systems. Proceedings of the Sixth Meeting of the ISSS Working Group on Soil Information Systems. Ed. P.A. Borrough & S.W. Bie. Bolkesjø, Norway. Wageningen.

Platou, S.W., Nørr, A.H. & Madsen, H. Breuning (1989): Digitisation of the EC-soil map. In: Computerization of Land Use Data. Proceedings of a Symposium in the Community Programme for Coordination of Agricultural Research. Ed. R.J.A. Jones & B. Biagi: 12-24. Pisa 1987. Luxembourg.

Ramann, E. (1899): Zur Theorie der Ortsteinbildung. Engler's botanischen Jahrbüchern 27:1, Beiblatt nr. 62.

Ramann, E. (1900): Über Ortsteinbildung. Abschliessende Erklärung betr. Dr. P. E. Müller. Engler's botanischen Jahrbüchern 27:5, Beiblatt nr. 64.

Rasmussen, K. (1956): Investigations on marsh soils and wadden sea sediments in the Tønder region. Geografisk Tidsskrift, 55: 147-70.

Rasmussen, K. (1961): Uorganiske svovlforbindelsers omsætninger i jordbunden. DSR Forlag, København.

Rasmussen, K. (1963): Foreløbig beretning om markforsøg med sulfidholdig brunkulsklæg. Ugeskrift for Landmænd, 108: 211-15.

Rasmussen, K. (1965): Foreløbige resultater af lysimeterforsøg med pyritholdig brunkulsklæg. In: Festskrift til S. Tovborg Jensen: 93-111. DSR Forlag, København.

Rasmussen, K. (1972): Potash in feldspars. Potassium in soil. Proceeding of the 9th Colloquium of the International Potash Institute held in Landshut/Federal Republic of Germany: 57-60.

Rasmussen, K. (1973a): Kvartärgeologi som underlag for samhällsplanering. Nordisk Jordbrugsforskning, 55: 342-45.

Rasmussen, K. (1973b): Plantenæringsstoffernes jordbundskemiske forhold. Nordisk Jordbrugsforskning, 55: 173-75.

Rasmussen, K. (1974): Jordbonitering og planlægning. Ugeskrift for Agronomer og Hortonomer, 3: 530-33.

Rasmussen, K. (1976): Danske jordbundskort. Nordisk Jordbrugsforskning, 58: 300-01.

Rasmussen, K. (1979): Jordbundskortlægning. Nordisk Jordbrugsforskning, 61: 225-26.

Rasmussen, K. (1980): Fertilizer application and ground water pollution. Annales Agriculturae Fenniae, 19: 71-80.

Rasmussen, K. (1981): Kvælstofbalancen i dansk landbrugsjord. Tidsskrift for Landøkonomi, 168: 57-63.

Rasmussen, K. (1982a): Landvinding. Nordisk Jordbrugsforskning, 64: 577-80.

Rasmussen, K. (1982b): Skjernådalens afvanding. Okkerproblemer. Nordisk Jordbrugsforskning, 64: 560-62.

Rasmussen, K. (1983): Deponering af flyveaske på landbrugsjord. Tidsskrift for Landøkonomi, 170: 279-88.

Rasmussen, K. (1984a): Fra jern i jorden til okker i vandløb. Vækst. Hedeselskabets Tidsskrift, Nr. 5: 4-5.

Rasmussen, K. (1984b): Landbrugets forureningsproblemer. Tidsskrift for Landøkonomi, 171: 211-17.

Rasmussen, K. (1985a): Okkerdannelse og vandløbsforurening i Danmark. Jord og Myr, 9: 205-11.

Rasmussen, K. (1985b): Sur nedbørs virkning på jord. Ugeskrift for Jordbrug, 130: 128-33.

Rasmussen, K. (1986): Jordbund. In: Landbrugsatlas Danmark. Ed. Kr.M. Jensen and A. Reenberg: 4-9. Det Kongelige Danske Geografiske Selskab, København.

Rasmussen, K. (1987a): Begrænsning af landbrugets udledning af kvælstof og fosfor. In: Kvælstof og Forsfor i Vandmiljøet. Konsensusrapport: 102-10. Planlægningsrådet for Forskningen.

Rasmussen, K. (1987b): Pedologiske undersøgelser langs naturgasledningen. In: Danmarks længste Udgravning. Arkæologi på Naturgassens Vej 1979-86. Ed. Rigsantikvarens Arkæologiske sekretariat: 31-36. København.

Rasmussen, K. & Jacobsen, N. Kingo (1975): Om retningslinier for en landsomfattende jordbonitering med henblik på en registrering af de jordbrugsmæssige resourcer i Danmark. Ugeskrift for Agronomer og Hortonomer, 4: 779-85.

Rasmussen, K., Jensen, A., Johnsen, I. & Gissel-Nielsen, G. (1985): Kvælstofomsætningen i dansk landbrugsjord. Statens Jordbrugs- og Veterinærvidenskabelige Forskningsråd, København.

Rasmussen, K. & Jensen, S. Tovborg (1960): Investigations on potash and potash release in Danish soils. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 88-122.

Rasmussen, K. & Jensen, S. Tovborg (1963): Om påvisning af et skadeligt saltindhold i jord ved hjælp af ledningsevnemåling. Tidsskrift for Planteavl, 67: 143-62.

Rasmussen, K. & Willems, M. (1981): Pyrite oxidation and leaching in excavated lignite soil. Acta Agriculturæ Scandinavica, 31: 107-15.

Raulund-Rasmussen, K. (1989a): Aluminium contamination and other changes of acid soil solution isolated by means of porcelain suction-cups. Journal of Soil Science, 40: 95-101.

Raulund-Rasmussen, K. (1989b): Effect of artificial acid rain and liming on the base status in an acid forest (Picea abies (L.), Karst.) soil (Typic Haplohumod). Scandinavian Journal of Forest Research, 4: 417-25.

Raulund-Rasmussen, K. (1989c): Effects of artificial acid rain and liming on the base status in an acid forest soil. Meddelser fra Norsk Institut for Skogforskning, 42: 177-78.

Raulund-Rasmussen, K. (1989d): Porcelain cups as a source of error in soil acidification studies. Meddelelser fra Norsk Institut for Skogforskning, 42: 95-100.

Raulund-Rasmussen, K., Morsing, M. & Leth, S. (1990): Vekselvirkning mellem jordbund og skovbevoksning. Ugeskrift for Jordbrug, 135: 49-53.

Raulund-Rasmussen, K. & Larsen, J.B. (1990): Jordbundsforsuringens årsager og virkninger i skove - med særlig henblik på effekten af luftforurening og skovdyrkningspraksis. Dansk Skovbrugs Tidsskrift, 75:1-41.

Raulund-Rasmussen, K. & Petersen, L. (1987): Arealanvendelse og jordbundsudvikling. - Jordbundsudvikling ved marginalisering af sandede jorde. Miljøministeriets Projektundersøgelser 1986, Teknikerrapport nr. 10. Skov- og Naturstyrelsen, København.

Riehm, H. (1932): Untersuchungen über die Faktoren, die die Reaktion des Erdbodens bestimmen. IV. Ein Beitrag zur Klärung der Frage über das Wesen der Silikatpufferung des Ackerbodens. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 21-80.

Rix, S. (1927): Undersøgelser over jydsk hedejord. Gludsted plantage. Dansk Skovforenings Tidsskrift, 12: 97-132.

Rothe, C. (1844): Beretning om den i Aaret 1844, for Kongeriget indførte nye Jordskyldsætnings Væsen og Historie, samt Oversigt af de ældre Matrikuler af 1644 og 1690. Kjøbenhavn.

Schnitzer, M. & Hansen, E.H. (1970): Organo-metallic interactions in soils: 8. An evaluation of methods for the determination of stability constants of metal-fulvic acid complexes. Soil Science, 109: 333-40.

Selmer (1802): Efterretninger om Ahlheden og Randbølleheden i Nørrejylland. Oeconomiske Annaler, 3:123-51.

Skjoldager, A. (1978): Die postsedimentäre Verteilung der adsorbierten Kationen im Marshboden. Geografisk Tidsskrift, 77: 48-58.

Smith, L. (1925): Gødningsforsøg ved Nyanlæg af Skov på midtjydsk Hedejord. Det Forstlige Forsøgsvæsen i Danmark, 9: 1-160.

Styczen, M. (1987): Soil conservation programmes: Some strategies, constraints and effects. Der Tropenlandwirt, Beiheft, Nr. 31: 63-77.

Styczen, M. & Høgh-Schmidt, K. (1986): A new description of the relation between drop sizes, vegetation, and splash erosion. In: Partikulært Bundet Stoftransport i Vand og Jorderosion. Ed. B. Hasholt. NHP-Rapport Nr. 14: 255-71. København.

Tamm, O. (1922): Om bestämning av de oorganiske komponentema i markens gelkomplex. Meddelanden från Statens Skogförsöksanstalt, 19: 385-404.

Tassel, R. van (1958): On carphosiderite. Mineralogical Magazine, 31: 818-19.

Tuxen, C.F.A. (1876): Nogle Analyser af jydsk Hedejord. Tidsskrift for Skovbrug, 1: 262-99.

Tuxen, C.F.A. (1877): Om Lyngskjoldens Udluftning. Tidsskrift for Skovbrug, 2: 187-98.

Tuxen, C.F.A. (1879): Nogle kemiske Undersøgelser af Jordbunden i Bøgeskove. Tidsskrift for Skovbrug, 3:125-47.

Tuxen, C.F.A. (1884): Nogle kemiske og fysiske Undersøgelser af Jordbunden i Skove og Heder. Tidsskrift for Skovbrug, 7: 233-47.

Unmack, A. (1933): Untersuchungen über die Fatoren, die die Reaktion des Erdbodens bestimmen. V. pH-Bestimmung in schwach gepufferten Losungen. Kgl- Veterinær- og Landbohøjskole, Årsskrift: 19-43.

Unmack, A. (1944): Resultater af nyere Lerundersøgelser. Den røntgenografiske Metodes Anvendelse på 2 danske Lerarter. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 33-59.

Unmack, A. (1947): X-ray investigation of some Danish clays. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 1-30.

Unmack, A. (1949): X-ray investigation of some Danish clays. II. Montmorillonitic clays. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 192-204.

Ussing, N.V. (1903): Om Jyllands Hedesletter og Teorierne for deres Dannelse. Oversigt over Det Kgl. Danske Videnskabernes Selskabs Forhandlinger: 99-165.

Ussing, N.V. (1907): Om Floddale og Randmoræner i Jylland. Oversigt over Det Kgl. Danske Videnskabernes Selskabs Forhandlinger: 161-213.

Vedby, S. (1978): Jordbundsgeografiske undersøgelser i Herlufmagle-Kirkelyng Mose i relation til grundvandsstanden. Geografisk Tidsskrift, 77: 36-42.

Warming, E. (1896): P.E. Müller, nicht E. Ramann, hat die Entstehung des Ortsteins entdeckt. Engler's botanischen Jahrbüchern 21:4, Beiblatt nr. 53.

Weis, F. (1926): Peter Erasmus Müller. 25 Okt. 1840 - 5. Okt. 1926. Botanisk Tidsskrift, 39: 375-84.

Weis, F. (1929): Fysiske og kemiske Undersøgelser over Danske Hedejorder med særligt Henblik paa deres Indhold af Kolloider og Kvælstof. Det Kgl. Danske Videnskabernes Selskab. Biologiske Meddelelser. VII, 9.

Weis, F. (1932): Fortsatte fysiske og kemiske Undersøgelser over Danske Hedejorder og andre Podzoldannelser. Det Kgl. Danske Videnskabernes Selskab. Biologiske Meddelelser. X, 3.

Weis, F. (1933): Some investigations on Icelandic soil types. Kgl. Veterinær- og Landbohøjskole, Årsskrift: 1-18.

Westermann, T. (1902): Undersøgelser over Typer af Danske Jorder. København.

Willems, M., Pedersen, B. & Jørgensen, S. Storgaard (1981): Accelerated leaching of some common and trace elements from soil mixed with sewage sludge and sludge ash. Acta Agriculturæ Scandinavica, 31: 323-42.

Formation and Development of the Clay Fraction in Danish Soils

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Investigations of formation of the day fraction in Danish soils and the changes which seem to have taken place in them indicate that a substantial proportion of the clay fraction consists of primary minerals such as quartz, microcline and plagioclase. In the less weathered soils hornblende is also present in some cases. The dominant layer silicate clay mineral is illite. Smectite and/or chlorite/vermiculite are also present together with kaolinite in larger or smaller amounts. The A and B horizons contain in some cases some hydroxy interlayered layer silicate clay minerals (HICM) and some randomly interstratified clay minerals. Of other constituents the clay fraction in Danish soils contains Fe-oxyhydroxides (sometimes Al-containing). In the more strongly weathered soils gibbsite and poorly crystalline oxyhydroxides of Al and Al-Si may also be present.

The processes involved in the development which has taken place in the clay fraction since the end of the last glacial stage are evaluated.

Keywords: *Clay Formation, Clay Composition of Danish Soils, Clay Development Processes.*

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Although most of constituents present in the clay fraction of Danish soils are inherited from the unconsolidated materials on which they have developed (Møberg, 1991) recent investigations indicate that changes in composition have occurred since deposition and/or redeposition of most of these materials took place during the Weichselian Glaciation (WG). A period which came to a close about 10,000 years ago. Materials left over from the Saale Glaciation (SG) and the Eemian Interglaciation (EIG) are here considered parent material for the soil developed during these periods.

The composition of the clay fraction present in these unconsolidated materials varies greatly. It is not only related to geology and geomorphology (Møberg et al., 1988) but also to the kinds of material brought by the glaciers from outside. Either $CaCO_3$-rich marine deposits together with substantial amounts of weatherable minerals, or $CaCO_3$-depleted material low in weatherable minerals picked up by the glaciers locally.

Selective analytical techniques such as sequental extractions, total elemental analysis, and magnetic separation together with XRD-analysis with computer treatment of the diffraction data have made it possible to get a good qualitative to semiquantitative picture of the composition of the clay fraction in Danish soils. The techniques have also made it possible to observe changes in the clay constituents during the approx.10.000-12,000 years since the last major disturbance of the landscape took place.

Most of the methods used for the analyses have been presented by Møberg et al. (1988) and Møberg and Nielsen (1987). Analyses not described in these papers include selective extractions. The procedures for these selective extractions are as follows: Shaking with Na_2CO_3-solution followed by treatment with acid NH_4-oxalate, then by citrate-bicarbonate-dithionite (CBD), and finally with NaOH. XRD diffraction analysis was carried out before the extractions and after the CBD and NaOH treatments. In the following only resent results will be included to illustrate the development of the clay constituents and the explanations offered.

More detailed information on the clay fraction in Danish soils is presented (Møberg 1991). In the present paper the abbrevation HICM will be

Location	Classification
Vang	Fine sandy, mixed, mesic Fluvaquentic Flumaquept
Fire Huse	Sandy, mixed, mesic Typic Haplumbrept
Bjeverskov	Fine loamy, mixed, mesic Mollic Hapludalf
Tystofte	Fine loamy, mixed, mesic Aquic Argiudoll
Dyrvig	Coarse sandy, mixed, mesic Typic Haplorthod
Jyndevad	Coarse sandy, mixed, mesic Orthic Haplohumod
Galtlund	Sandy, mixed, mesic Humic Haplorthod
Troldholm	Fine loamy, mixed, mesic Typic Paleudult
Lintrup	Clayey, mixed, mesic Typic Paleudult

Table 1. Location of the soils dealt with in this paper and their classification according to Soil Taxonomy.

used for Hydroxy Interlayered Clay Minerals. The term covers all types of 2:1 layer silicate clay minerals having a hydroxy interlayer except primary trioctahedral chlorite and Al-hydroxy interlayered chlorite, which is also commonly called secondary chlorite (Schachtschabel et al., 1989). Hence, HICM includes also HIV (hydroxy interlayered vermiculite) and HIS (hydroxy interlayered smectite) (Barnhisel and Bertsch, 1989).

Classification, parent materials and location of soils

The location and classification of each soil referred to in this paper are presented in table 1. Their geomorphological setting is outlined in table 2. The soils have been selected to illustrate some of the main features related to changes observed in the clay fraction of Danish soils.

Composition of the clay fraction in the C horizon of some representative soils

Fig. 1 contains the XRD-diagrams and table 3 contains the results of the total elemental analysis (TEA) and of sequential extractions of the clay fraction of the C horizon in soils from four common suborders, classified according to Soil Taxonomy, in Denmark.

Profile site	Geology and Geomorphology
Vang	Postglacial, fine sandy, marine deposits - 5000-6000 years old and more - composed of weakly weathered material.
Fire Huse	Sandy glacifluvial deposits from the main phase of the WGS, composed mainly of weathered, calcite-free material from the SGS and EIGS.
Bjeverskov	Loamy to clayey morainic deposits from the latest phase of the WGS. composed mainly of weakly weathered, calcite-rich material.
Tystofte	Loamy to clayey morainic material from a later Baltic phase of the WGS. composed mainly of unweathered, calcite-rich material.
Dyrvig	Sandy, glacifluvial material from the main phase of the WGS.
Jyndevad	Sandy glacifluvial sediments from the WGS. It is mainly composed of weakly to more strongly weathered, calcite-free material.
Galtlund	Sandy to gravelly sediments from the SGS composed of weathered glacial and interglacial material.
Troldholm	Loamy morainic material from the SGS, composed of weathered, calcite-free material.
Lintrup	Clayey, glacial deposits from the SGS, composed mainly of weath-ered, calcite-free material.

Table 2. The geology and geomorphology of the profile sites dealt with in this paper.

The clay fraction of all the soils contains a substantial proportion of primary minerals such as quartz, K-feldspars (microcline), Ca-Na-feldspars (plagioclase), and hornblende in some of the more weakly weathered soils (fig. 2). Milling of the transported materials and the exposure to frost and thaw during the glaciation periods may be the main causes of the presence of the substantial amounts of these minerals in the clay fraction. Illite is the dominant layer silicate clay mineral in the clay fraction of the parent material of all the soils, but kaolinite is

Element	*Tystofte*	*Bjeverskov*	*Fire Huse*	*Galtlund*	*Troldholm*
TEA					
SiO_2	55.2	52.4	54.9	50.6	52.3
Al_2O_3	22.6	17.9	15.9	23.7	21.3
Fe_2O_3	7.04	10.8	9.80	5.79	7.74
MgO	2.68	2.50	2.50	1.78	2.23
CaO	0.63	0.35	0.19	0.10	0.05
K_2O	5.29	4.42	3.14	2.53	2.95
Na_2O	0.83	0.51	0.84	0.18	0.46
TiO_2	-	0.86	1.55	1.01	1.33
MnO_2	-	0.12	0.04	0.04	0.04
Sequential extractions					
Na_2CO_3					
Al_2O_3			0.00	0.05	0.05
SiO_2	-	-	0.10	0.05	0.13
Oxalate					
Al_2O_3	-	-	3.55	0.77	0.74
Fe_2O_3	-	-	4.07	1.31	1.05
SiO_2	-	-	1.88	0.24	0.22
CBD					
Al_2O_3	0.28	0.32	0.39	0.30	0.28
Fe_2O_3	2.43	3.04	4.93	4.37	1.93
SiO_2	-	0.43	0.46	0.20	0.63
NaOH					
Al_2O_3	-	-	2.66	3.85	2.52
SiO_2	-	-	13.8	4.88	4.90

Table 3. Results of total elemental and sequential analyses of the C horizons of Tystofte, Bjeverskov, Fire Huse, Galtlund, and Troldholm soil profiles (%).

TEA				
Tystofte	Ap	Bt	Btg	Ck
SiO_2	56.2	58.3	53.8	55.2
Al_2O_3	23.3	24.1	23.2	22.6
Fe_2O_3	6.32	7.00	7.29	7.04
MgO	2.06	2.12	2.99	2.68
CaO	0.32	0.21	0.35	0.63
K_2O	3.55	4.12	4.49	5.29
Na_2O	0.67	0.53	0.68	0.83
TiO_2	0.83	1.09	0.54	-
MnO_2	0.05	0.06	0.07	-
Bjeverskov	Ap	Btg1	Btg2	Ckg
SiO_2	53.1	52.6	52.9	52.4
Al_2O_3	19.4	20.8	19.4	17.9
Fe_2O_3	9.36	10.5	10.5	10.9
MgO	1.90	2.21	2.35	2.58
CaO	0.20	0.20	0.30	0.40
K_2O	3.49	3.79	4.12	4.54
Na_2O	0.47	0.38	0.47	0.55
TiO_2	0.85	0.86	0.86	0.86
MnO_2	0.10	0.05	0.10	0.10
CBD-extractable Al, Fe, and Si				
Tystofte	Ap	Bt	Btg	Ck
Al_2O_3	0.39	0.40	0.37	0.28
Fe_2O_3	2.27	2.82	3.04	2.43
SiO_2	-	-	-	-
Bjeverskov	Ap	Btg1	Btg2	Ckg
Al_2O_3	0.75	0.70	0.55	0.32
Fe_2O_3	3.11	3.42	2.78	3.04
SiO_2	0.26	0.28	0.29	0.43

Table 4. Total elemental analysis of the CBD-treated clay and results of the CBD-extractions on the clay fraction from different horizons of Bjeverskov and Tystofte (%).

also present in all the soils. Smectite, chlorite and/or vermiculite are present in most of the C horizons. In some cases some HICM and randomly interstratifled layer silicate clay minerals are also present in the C horizon. Fe-oxyhydroxides (sometimes Al-containing) are present in the C horizon of all the soils investigated. Gibbsite is present in most of the parent materials of pre-WG origin.

Assuming that the clay in pre-WG and in the WG materials had a similar composition when first deposited by the glaciers the XRD analyses show that the following changes may have occurred in the pre-WG material:

The less stable primary minerals such as hornblende and Ca-rich plagioclase have disappeared, some illite has changed into other 2:1 layer silicate clay minerals such as smectite and vermiculoite and some gibbsite has been formed.

Whether gibbsite can be used as a tracer-mineral for identification of pre-WG parent materials present in Denmark is still an open question, as the number of relevant investigations are limited. But the results obtained so far indicate that gibbsite is present in these materials but absent in materials deposited by WG in the eastern part of Denmark.

The results of the sequential extractions (Al, Fe, and Si extractable by cold Na_2CO_3-solution,

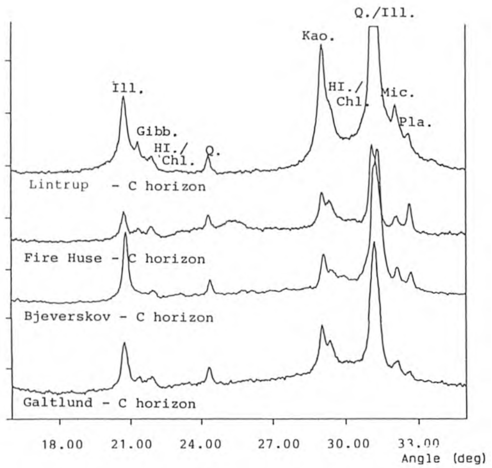

Fig. 1. XRD diagrams of the clay fraction from the C horizons in the Lintrup, Fire Huse, Bjeverskov, and Galtlund soil profiles.

The following abbreviations are used in figs. 1-13.

Chi.	-	Chlorite
Gibb.	-	Gibbsite
Goe.	-	Goethite
HI.	-	Hydroxy interlayered layer silicate clay minerals (HICM)
Horn.	-	Hornblende
Ill.	-	Illite
Int.	-	Interstratified clay minerals
Kao.	-	Kaolinite
Lep.	-	Lepidocrocite
Mic.	-	Microcline
Plag.	-	Plagioclase
Q.	-	Quartz
2:1	-	Smectite and/or Vermiculite and/or Chlorite.

NH$_4$-oxalate-solution, citrate-bicarbonate-dithionite (CBD)-solution, and boiling NaOH-solution), and the TEA of the clay left after the CBD-treatment (table 4) support the XRD-findings. For instance, the amounts of CaO, Na$_2$0, and K$_2$0 found by TEA are smaller and that of Ti0$_2$ larger in the the clay fraction of soils developed on pre-WG materials than in materials brougth in from outside by the Weichselian glaciers.

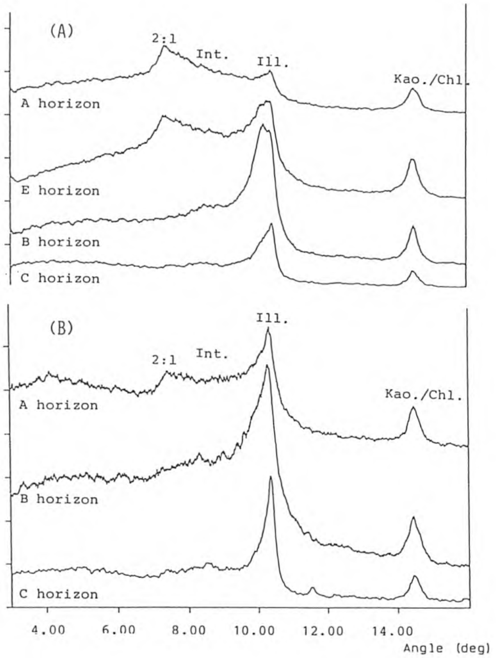

Fig. 2. XRD diagrams (3-16°) of the clay fraction from horizons in the Bjeverskov (A) and Tystofte (B) soil profiles.

Changes in the soil clay fractions of the A and B horizons

A. Soils developed on CaCO$_3$-rich, only lighdy weathered morainic materials, deposited by the Weichselianglaciers. Results of XRD analyses of the clay fraction from Bjeverskov and Tystofte after CBD-extraction are shown in the figures 2 and 3 and those of the TEA and the CBD-extraction are shown in table 4.

The following minerals were identified from the XRD diagrams. In the C horizon: Illite, kaolinite, quartz, K-feldspars, and Ca-Na-feldspars. Hornblende was also detected in the Bjeverskov profile (fig. 2).

In the A and B horizons some illite has changed into other 2:1 layer silicate clay minerals and randomly interstratified 2:1 layer silicate clay minerals (fig. 2), and HICM (fig. 3). In Bjeverskov some chlorite (possibly trioctahedral) is present in the C horizon (fig. 4). In the A and B

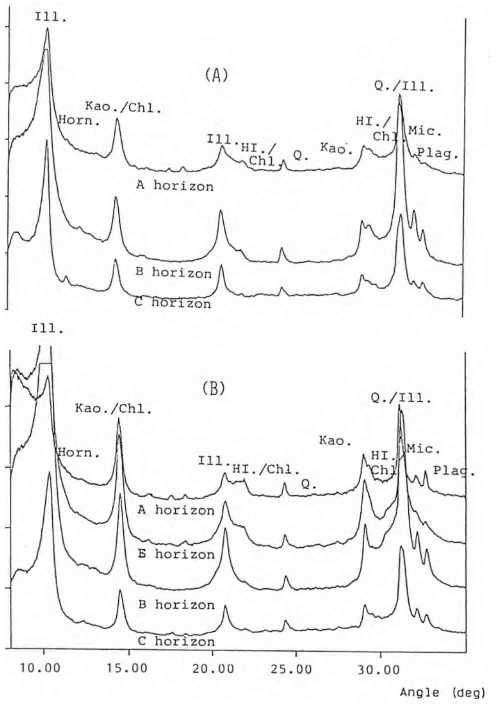

Fig. 3. XRD diagrams (8-35°) of the clay fraction from horizons in the Bjeverskov (A) and Tystofte (B) soil profiles.

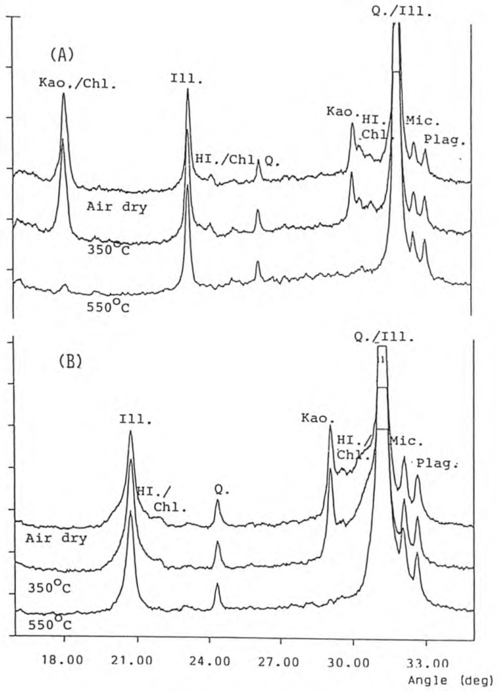

Fig. 4. XRD diagrams of the heat-treated clay fraction from horizon in the Bjeverskov (A) and Tystofte (B) soil profiles.

horizons some of it may have changed into HICM.

The change of illite and chlorite to other 2:1 layer silicate clay minerals has mainly occurred in the eluvial horizons. The results of the TEA support these findings, as the K and Mg contents are much lower in the upper horizons in these two soils than in the C horizon. The decrease in the Si/Al ratio from the A to the C horizon points in the same direction, as that ratio is higher in e.g. smectite than in illite. The TEA also indicate that some Ca-rich plagioclase has been lost by weathering in the upper horizons since the content of Ca in the clay of the A horizon is only half of that of the clay in the C horizon. The released Mg, Ca, and K may have been lost by leaching or removed by the vegetation, the CBD-data indicate that at least some of the released Fe and Al have been retained in the A and B horizons ias poorly crystalline oxyhydroxides.

B. Loamy to clay-rich soils without significant podsolization developed on pre-WG deposits. In these soils, represented here by Lintrup and Troldholm, the oxyhydroxide-free clay contains some smectite, interstratified 2:1 layer silicate clay minerals, illite, kaolinite (fig. 5) and HICM besides quartz, feldspars and gibbsite (fig. 6). Chlorite has also been identified (fig. 7).

A comparison of the A and B horizons with the C horizon indicates that weathering during the post-glacial period has resulted in formation of HICM and secondary chlorite. The formation of HICM is mainly observed in the B horizon.

The development is clearly shown by the results of the TEA in the sample from Troldholm where the clay fraction in the A horizon contains much less Mg and Fe than the clay in the C horizon and the Si/Al ratio is much higher in the A than in the C horizon (table 5). These differences are less clearly expressed in the Lintrup profile than in the Troldholm profile. This may

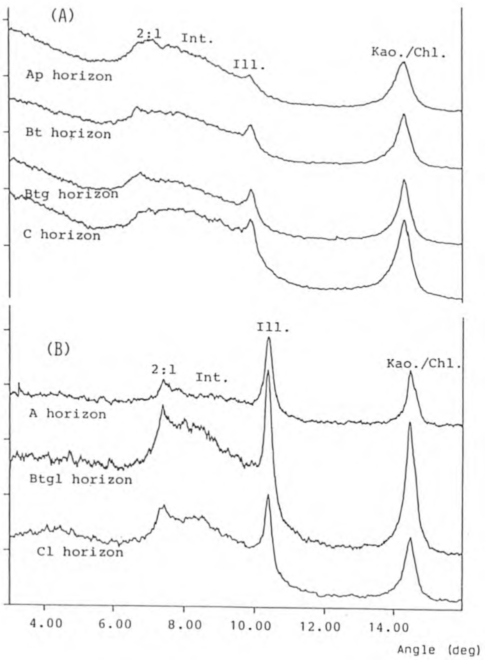

Fig. 5. XRD diagrams (3-16°) of the Mg-saturated clay fraction from horizons in the Lintrup (A) and Troldholm (B) soil profiles.

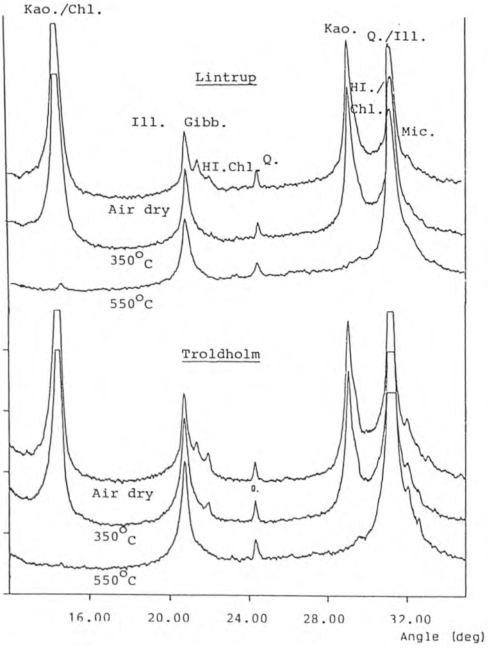

Fig. 7. XRD diagrams (12-35°) of the heat-treated clay fraction from the Lintrup Btg horizon and the Troldholm Btgl horizon.

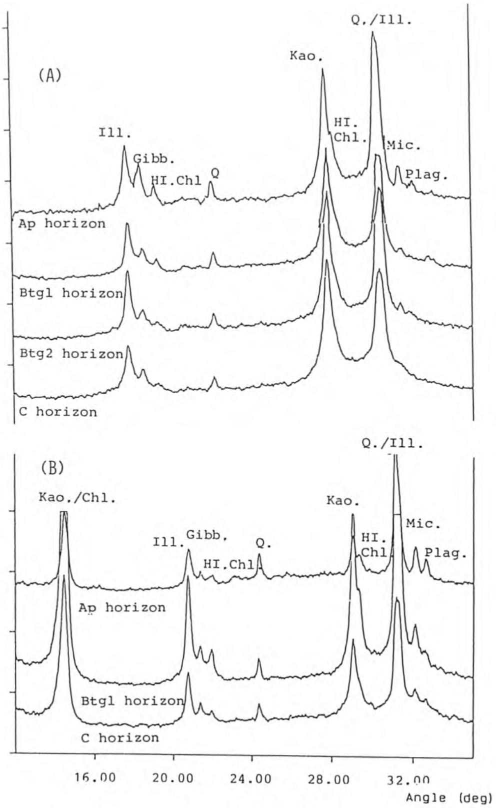

Fig. 6. XRD diagrams (16-35°) of the K-saturated clay fraction from horizons in the Lintrup (A) and Troldholm (B) soil profiles.

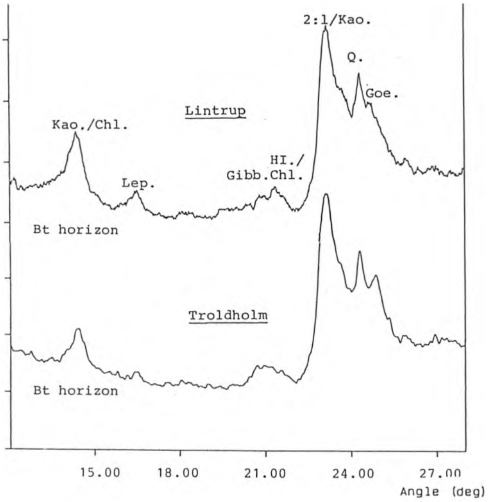

Fig. 8. XRD diagrams (12-28°) of the non-CBD-treated clay fraction from the Lintrup Bt horizon and the Troldholm Btg horizon.

TEA				
Troldholm	Ap	Btg1	Btg2	C
SiO_2	59.6	51.5	55.8	52.3
Al_2O_3	17.7	21.8	21.0	21.3
Fe_2O_3	4.22	7.21	7.72	7.74
MgO	1.10	2.04	2.11	2.23
CaO	0.13	0.06	0.05	0.05
K_2O	2.54	2.62	2.81	2.95
Na_2O	0.46	0.19	0.22	0.24
TiO_2	1.33	0.96	0.95	0.98
MnO_2	0.04	0.03	0.03	0.04
Lintrup	Ap	Bt	Btg	C
SiO_2	50.2	49.5	51.0	51.1
Al_2O_3	25.4	25.6	25.2	25.7
Fe_2O_3	6.36	6.46	6.03	6.25
MgO	1.55	1.74	1.75	1.74
CaO	0.06	0.03	0.03	0.02
K_2O	2.34	2.42	2.45	2.51
Na_2O	0.13	0.05	0.05	0.04
TiO_2	1.23	1.02	1.01	0.92
MnO_2	0.03	0.03	0.02	0.02

Table 5. Results of total elemental analysis of the clay fraction from horizons of Troldholm and Lintrup after sequential extractions except the NaOH-treatment (%).

be due to differences in clay content and to the pre-SG origin of the parent material of the Lintrup profile. On the other hand, the results of the sequential extractions (table 6) indicate that changes have also occurred in the Lintrup profile. In both profiles the amounts of extractable Fe and Al are much higher in the clay in the upper horizons than in the C horizon. In both profiles some of the Fe-oxyhydroxides are so well crystallized that lepidocrocite and goethite can be identified by XRD (fig. 8). In most other soil orders present in Denmark the Fe-oxyhydroxides are less well crystallized.

Troldholm	Ap	Btg1	Btg2	C
Na_2CO_3				
Al_2O_3	0.36	0.19	0.09	0.05
SiO_2	0.05	0.14	0.11	0.13
Oxalate				
Al_2O_3	1.49	0.86	0.89	0.74
Fe_2O_3	5.08	0.43	0.96	1.05
SiO_2	0.56	0.25	0.25	0.22
CBD				
Al_2O_3	0.26	0.92	0.36	0.28
Fe_2O_3	1.83	4.30	2.22	1.93
SiO_2	0.83	0.45	0.61	0.63
NaOH				
Al_2O_3	2.40	3.23	2.70	2.52
SiO_2	13.37	5.33	5.03	4.90
Lintrup	Ap	Bt	Btg	C
Na_2CO_3				
Al_2O_3	0.22	0.08	0.06	0.05
SiO_2	0.05	0.02	0.04	0.06
Oxalate				
Al_2O_3	0.81	0.50	0.45	0.45
Fe_2O_3	1.45	1.09	0.72	0.55
SiO_2	0.19	0.14	0.13	0.17
CBD				
Al_2O_3	0.59	0.41	0.24	0.18
Fe_2O_3	7.32	4.73	2.89	2.29
SiO_2	0.19	0.19	0.24	0.29
NaOH				
Al_2O_3	2.23	2.22	1.96	2.10
SiO_2	3.14	2.86	2.67	2.87

Table 6. Results of the sequential extractions of the clay fraction from horizons of Troldholm and Lintrup (%).

C. *Sandy soils developed on pre-WG or reworked pre-WG glacial deposits.* The post glacial changes in the clay composition are most easily detectable in the sandy soils. The clay in these soils contain smectite, chlorite, vermiculite and some randomly interstratified layer silicate clay minerals (fig. 9). Kaolinite, gibbsite, HICM, quartz, and feldspars are also present in these soils (fig. 10 and 11). The XRD data (fig. 9) show that the layer silicate clay minerals are much less crystalline in the A and E horizons than in the deeper horizons, causing less clear diffration patterns and a higher background in these eluvial horizons. This tendency towards formation of microcrystalline layer silicate clay minerals is most noticeable in case of the Galtlund soil. The data also indicate that it is not only 2:1 layer silicate clay minerals which are disintegrating in the eluvial horizons, where the soil solution is strongly acidic with very low Al- and Fe-activity; neither

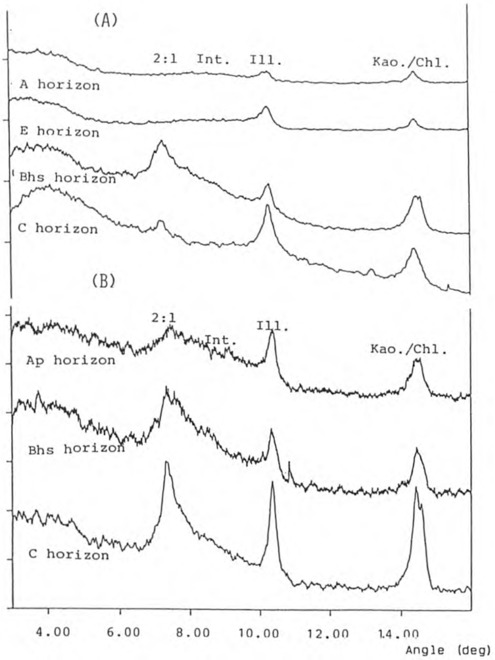

Fig. 9. XRD diagrams (3-16°) of the Mg-saturated clay fraction from horizons in the Galtlund (A) and Dyrvig (B) soil profiles.

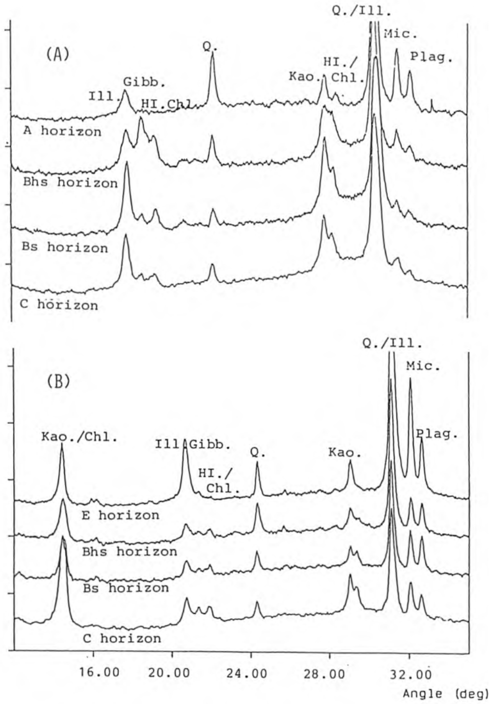

Fig. 10. XRD diagrams (16-35°) of the Mg-saturated clay fraction from horizons in the Galtlund (A) and Dyrvig (B) soil profiles.

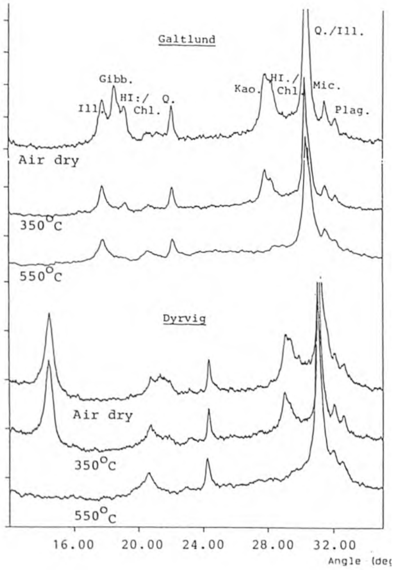

Fig. 11. XRD diagrams (16-35°) of the K-saturated, heat-treated clay fraction from Galtlund Bhs horizon and Dyrvig Bs horizon.

kaolinite nor gibbsite seem to be stable under these conditions (fig. 10).

The results of TEA (table 7) reflect the development which has occurred in these soils. A large, relative accumulation of Si has taken place in the eluvial horizons and the clay has been deprived of Al, Fe, Mg, and Ca. The constancy of K down through the profile possibly indicates that the relative increase in K-feldspars to a certain extent may have kept pace with the transformation of illite into other 2:1 layer silicate clay minerals.

The results of the sequential extractions reflect the same development (table 8). The Fe and Al released by the destruction of the layer silicate clay minerals and gibbsite in the eluvial horizons have to a large extent accumulated in the B subhorizons.

The large amount of Fe in the A and E horizons of the Dyrvig profile is possibly due to oc-

Galtlund	Ap	E	Bhs	Bs1	C
SiO_2	74.9	70.2	51.7	53.4	50.6
Al_2O_3	12.1	15.3	22.1	22.2	23.6
Fe_2O_3	1.11	1.14	6.00	5.74	5.79
MgO	0.48	0.43	2.19	2.06	1.78
CaO	0.14	0.07	0.10	0.08	0.10
K_2O	2.45	3.12	2.62	2.75	2.53
Na_2O	0.66	0.67	0.35	0.24	0.18
TiO_2	1.85	2.17	1.05	0.86	1.01
MnO_2	0.04	0.04	0.05	0.04	0.04

Dyrvig	Ap	E	Bhs	C
SiO_2	62.3	64.5	56.2	56.2
Al_2O_3	15.3	17.4	16.1	18.3
Fe_2O_3	4.32	2.15	4.12	4.79
MgO	1.05	0.56	1.20	1.56
CaO	0.11	0.10	0.15	0.17
K_2O	2.27	3.95	2.61	2.57
Na_2O	0.49	1.09	0.70	0.54
TiO_2	1.13	1.60	1.26	1.13
MnO_2	0.04	0.05	0.07	0.06

Table 7. Results of total elemental analysis of the clay fraction from horizons of Galtlund, and Dyrvig after sequential extractions except the NaOH-treatment (%).

casional flooding occurring before the soil was brought under cultivation.

D. Soils of post-glacial age. Both the XRD data (fig. 12) and the results of the TEA and sequential extractions (table 9) show that very little development has taken place in the clay fraction of the Vang soil, which is included here as a representative of relatively young Danish soils.

The minerals detectable by XRD are illite, kaolinite, HICM, randomly interstratified 2:1 layer silicate clay minerals, small amounts of smectite/vermiculite, and substantial amounts of quartz and feldspars. Except for some release of Fe and Si from the minerals in the A horizon neither the XRD data nor the results of the TEA and the sequential extractions indicate that changes have occurred to any significant extent in that soil.

Galtlund	Ap	E	Bhs	Bs1	C
Na_2CO_3					
Al_2O_3	0.82	0.27	0.31	0.40	0.05
SiO_2	0.02	0.02	0.02	0.02	0.05
Oxalate					
Al_2O_3	0.59	0.24	3.72	1.75	0.77
Fe_2O_3	1.89	0.51	2.13	0.71	1.31
SiO_2	0.09	0.03	1.15	0.35	0.24
CBD					
Al_2O_3	0.04	0.02	0.72	0.43	0.30
Fe_2O_3	0.12	0.13	5.33	2.95	4.37
SiO_2	0.34	0.08	0.16	0.17	0.20
NaOH					
Al_2O_3	0.40	0.44	3.58	3.22	3.85
SiO_2	6.59	1.35	3.00	4.25	4.88

Dyrvig	Ap	E	Bhs	c
Na_2CO_3				
Al_2O_3	0.40	0.19	1.83	0.66
SiO_2	0.05	0.06	0.03	0.10
Oxalate				
Al_2O_3	1.73	1.25	14.9	6.67
Fe_2O_3	15.0	10.1	4.86	1.83
SiO_2	0.71	0.45	4.31	2.89
CBD				
Al_2O_3	0.52	0.20	0.53	0.43
Fe_2O_3	5.69	3.15	2.70	0.74
SiO_2	0.68	0.34	0.22	0.62
NaOH				
$4Al_2O_3$	1.74	1.74	2.78	2.97
SiO_2	20.2	2.91	5.69	5.25

Table 8. Results of the sequential extractions of the clay fraction from horizons of Galtlund and Dyrvig (%).

Processes causing changes of the clay fraction

In order to explain the findings above, the following processes may have taken place: Transformation of mica/illite into other 2:1 layer silicate clay minerals such as randomly interstratified layer silicate clay minerals, vermiculite, smectite, and HICM.

The changes observed from the XRD diagrams from the different horizons of some of the soils (fig. 2 and 9) indicate that randomly interstratified clay minerals have been formed from illite as an intermediate component. This agree with findings of Whittig & Jackson (1955), Ta-

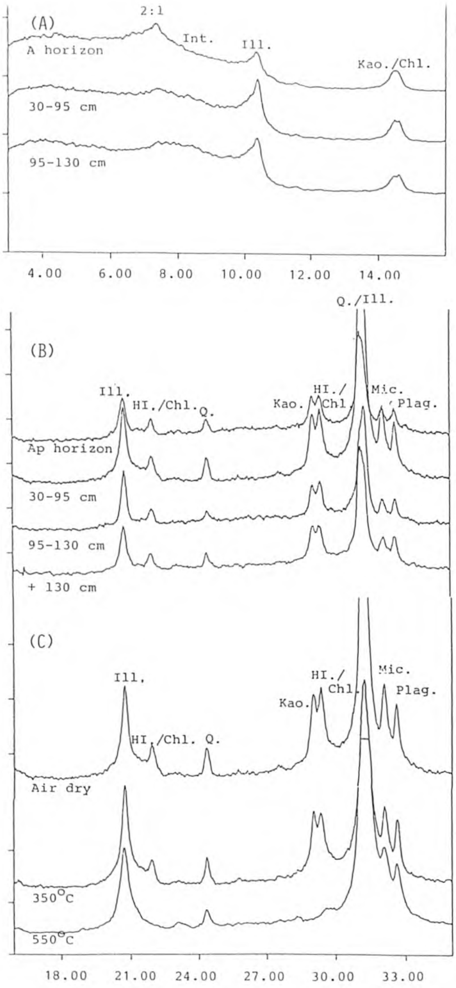

Fig. 12. XRD diagrams of the clay fraction from the different horizons in the Vang soil profile (A) Mg-saturated, 3-16°, (B) Mg-saturated 16-35°, (C) K-saturated, heat-treated, 16-35°.

	Ap	Cg1	Cg2	C
TEA				
SiO_2	53.5	54.8	54.4	54.2
Al_2O_3	19.5	19.8	19.3	19.6
Fe_2O_3	6.57	7.81	7.82	8.30
MgO	2.62	3.13	3.24	3.38
CaO	0.45	0.22	0.25	0.27
K_2O	3.25	4.01	3.94	3.93
Na_2O	0.63	0.51	0.60	0.59
TiO_2	0.92	0.92	0.83	0.97
MnO_2	0.07	0.07	0.06	0.06
Sequential extractions				
Na_2CO_3				
Al_2O_3	<0.01	<0.01	<0.01	<0.01
SiO_2	0.11	0.05	0.04	0.04
Oxalate				
Al_2O_3	0.69	0.33	0.27	0.24
Fe_2O_3	2.93	1.96	1.54	2.28
SiO_2	0.46	0.17	0.14	0.17
CBD				
Al_2O_3	0.13	0.09	0.08	0.08
Fe_2O_3	0.46	0.34	0.28	0.32
SiO_2	0.30	0.26	0.27	0.28
NaOH				
Al_2O_3	1.15	0.91	0.64	0.60
SiO_2	4.0	2.07	1.83	1.78

Table 9. Results of TEA of the clay fraction from horizons of Vang after sequential extractions except the NaOH-treatment and results of the sequential extractions (%).

mura (1956), Mortland (1958), Ross & Rich (1973), and Sawhney (1989). From there the transformation has gone on into vermiculite and smectite. A process also commonly recorded in the literature (Bray, 1937; Borchardt & Jackson, 1966; Robert, 1973; Loveland & Bullock, 1975; Vicente et al., 1977; Borchardt, 1989; Douglas, 1989).

This investigation indicates that illite/mica and chlorite may change into different types of HICM. Barnhisel & Bertsch (1989) have shown how the transformation may take place. Recent studies on clay fractionated by magnetic treatment indicate that the interlayer may not only be composed of a brucite or a gibbsite layer but Fe-hydroxy interlayers may also be present (Ghabru et al., 1990; Weed & Bowen, 1990). Results of similar studies on Danish soils (Nehmdahl & Møberg, unpubl. data) have shown that the following processes may take place under certain conditions.

Biotite/glauconite (illite) ------> Fe-hydroxy interlayered HICM ------> vermiculite/smectite (or secondary chlorite) + Fe-oxyhydroxides

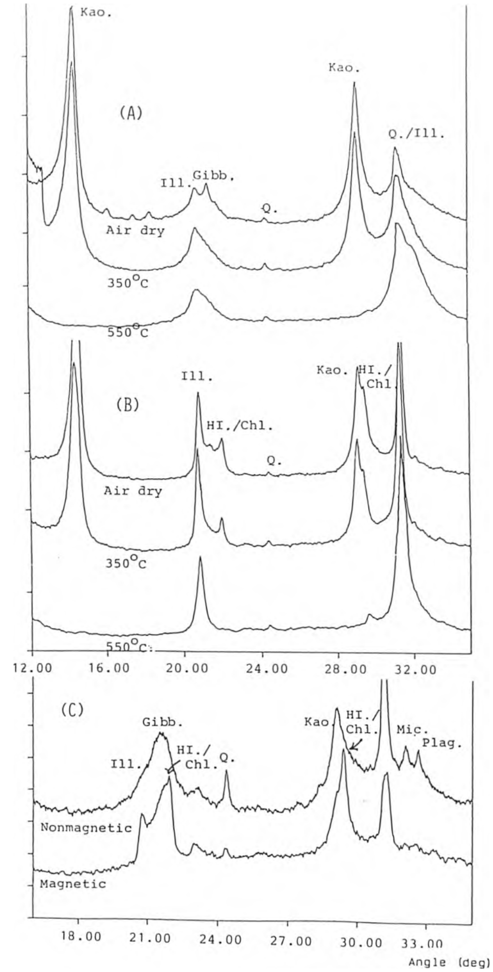

Fig. 13. XRD diagrams of the K-saturated, heat-treated, non-magnetic and magnetic clay fractions. (A) The K-saturated, nonmagnetic clay fraction from and (B) the K-saturated, magnetic clay fraction from Lintrup Bt horizon. (C) The air-dry magnetic and nonmagnetic clay fraction from Jyndevad.

	Magnetic		Nonmagnetic	
	Bt	c	Bt	C
TEA				
SiO_2	44.0	45.4	42.4	45.3
al $_2O_3$	25.3	24.2	26.6	25.4
Fe_2O3	10.3	7.96	6.83	6.15
MgO	4.10	4.11	2.95	2.65
CaO	0.07	0.06	0.06	<0.01
K_2O	2.98	2.99	2.14	2.17
Na_2O	0.18	0.08	0.63	0.26
% distribution of magnetic and nonmagnetic fractions				
	10.0	9.2	90.0	90.8
% ferro ions in the magnetic and nonmagnetic fractions				
	12.7	-	4.4	

Table 10. TEA of magnetic and nonmagnetic clay from the E, Bt and C horizons of the Lintrup soil profile (%).

Results of XRD and TEA on the magnetic and nonmagnetic clay fraction from Lintrup Bt horizon are shown in fig. 13 and in table 10. These data support the processes outlined above, as only the magnetic clay fraction contains HICM, and the magnetic clay fraction contains much more Fe, Mg, and K than the nonmagnetic one.

The processes involved may be as follows: In well drained soils the Fe^{2+} in the octahedral layers of biotite and glauconite is oxidized to Fe^{3+}. The change in charge in the octahedral layer may cause the interlayer K^+ to be expelled. Due to the smaller size of the Fe^{3+} ion it moves easily out of the octahedral layer into the interlayer space. Due to the conditions there the Fe^{3+} ions are hydroxylized forming a ferri-hydroxide interlayer.

In the beginning, the hydroxy interlayer in such a HICM may be composed mainly of Fe-hydroxide. Under more acidic conditions Al may enter the interlayer and form Al-hydroxide pillars in between the 2:1 layer silicate layers, resulting in formation of HIV or HISM. The alumination may finally lead to formation of secondary chlorite in which the hydroxy interlayer is composed entirely of Al-hydroxide.

Under less acidic conditions the Fe-hydroxide layer may slowly be replaced by exchangeable cations resulting in formation of vermiculite and/ or smectite and poorly crystalline Fe-oxyhydroxides.

Under acidic conditions, where podzolization is a dominant process in sandy Danish soils, chlorite, vermiculite, smectite, and even kaolinite and gibbsite seem to disintegrade in the eluvial horizon. The disappearance of the 1.4 nm peak and the high background measured by XRD (fig. 9) point in that direction. The high Si/Al ratio and low content of Mg found by TEA (table 7) and the high Si/Al ratio found in the same horizon by the sequential extraction when compared with that in the deeper horizons points in the same direction. This interpretation is also confirmed by the findings of Dudas & Harward (1971) and Karathanasis & Hajek (1984), which show that layer silicate clay minerals are unstable under highly acidic conditions in an environment very low in Al, Fe, and Mg.

Briefly the processes taking place in the eluvial horizons during podzolization may be considered to be the following: Due to acidification, formation of Al-organo-complexes and strong leaching there will be a tendency for Mg and Al to leave the octahedral layers in the layer silicate clay minerals and the gibbsite structure. As the Si concentration is still high in these horizons (table 7) there will be a tendency for the 2:1 layer silicate clay minerals not to dissolve at once but slowly to disintegrate and become more and more micro crystalline and Si-rich. The high Si concentration will not have this stabilizing effect on kaolinite and gibbsite, these minerals will therefore dissolve slowly. This means, that 2:1 layer silicate clay minerals may become more and more micro crystalline and dissolve slowly in the eluvial horizons of Spodosols but they may still be more stable there under these conditions than kaolinite and gibbsite (Møberg, 1976). In the spodic horizon the podzolization process results in accumulation of Al and Fe and less depletion of e.g. Mg. In the Bh and Bhs horizons Al and Fe will partly be present in form of metal-organo-complexes, as indicated by the substantial amount of sodium pyrophosphate-extractable Al and Fe usually found in these horizons, and partly also as Al-Fe-oxyhydroxides, poorly crystalline Al-hydroxides, and as Al-Si-oxyhydroxides, sometimes called proto-imogolite-allophane (Farmer et al., 1980; Farmer et al., 1983; Farmer, 1984) as indicated by the results of the sequential extractions (table 8).

Whether the high content of extractable Al in the Spodic horizon besides causing formation of poorly crystalline Al-hydroxides and protoimogolite-allophane in some cases also may lead to formation of gibbsite is still an unsettled question. The XRD data in fig. 9 could indicate that also gibbsite may have been formed in post glacial time.

Summary

Formation of the clay fraction in Danish soils started long before the WG came to a close. So a substantial proportion of the constituents present may be considered to stem from the parent material.

The presence of quartz, feldspars and hornblende may be due to the disintegration caused by the action of glacial transport and by frost and thaw on more coarse grained material. All or almost all of the illite, trioctahedral chlorite, and kaolinite, and some of the smectite present in the soils are inherited from the parent material. This may also be the case of the gibbsite present in the soils developed on pre-WG deposits.

However, most of the HICM and randomly interstratified layer silicate clay minerals seem to have been formed in the soil during the post-glacial period. During that period podzolization has caused disintegration of 2:1 layer silicate clay minerals and dissolution of some gibbsite and kaolinite in the eluvial horizons of Spodosols and accumulation of poorly crystalline Fe-oxyhydroxides, Al-hydroxides and Al-Si-oxyhydroxides in the spodic horizon.

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References

Barnhisel, R.L.& Bertsch, P.M. (1989): Chlorites and hydroxy-interlayered vermiculite and smectite, p. 729-788. In: Minerals in Soil Environments. 2. edition. (Eds. J.B. Dixon and S.B. Weed). Soil Science Society of America, Madison, Wisconsin, USA.

Borchardt, G. (1989): Smectites, p. 675-727. In: Minerals in Soil Environments. 2. edition. (Eds. J.B. Dixon and S.B. Weed). Soil Science Society of America, Madison, Wisconsin, USA.

Borchardt, G.A., Jackson, M.L. & Hole, F.D. (1966): Expandable layer silicate genesis in soils deplited in mica pseudomorphs. p. 175-186. In: Proc. Int. Clay Conf. 1966, Vol 1. (Eds. L. Heller and A. Weiss). National Academy of Science, National Research Council, Washington D.C.

Bray, R.H. (1937): Chemical and physical changes in soil colloids with advancing development in Illinois soils. Soil Sci. 43: 1-14.

Douglas, L.A. (1989): Vermiculites. p. 636-674. In: Minerals in Soil Environments. 2. edition. (Eds. J.B. Dixon and S.B. Weed). Soil Science Society of America, Madison, Wisconsin, USA.

Dudas, M.J. & Harward, M.E. (1971): Effect of dissolution treatment on standard and soil clays. Soil Sci. Soc. Amer. Proc. 35: 134-140.

Farmer, V.C. (1984): Distribution of allophane and organic matter in podzol B horizons. Reply to Buurman & Van Reeuwijk. J. Soil Sci. 35: 453-458.

Farmer, V.C., Russell, J.D., & Berrow, M.L. (1980): Imogolite and proto-imogolite allophane in Spodic horizons. Evidence for a mobile aluminum silicate complex in Podzol. J. Soil Sci. 31: 673-684.

Farmer, EC, *Russell, J.D., & Smith, B.F.L.* (1983): Extraction of inorganic forms of translocated Al, Fe, and Si from a Podzol Bs horizon. J. Soil Sci. 34: 571-576.

Ghabru, S.K., Mermut, A.R. & Amaud, R.J.St. (1990): Isolation and characterization of an iron-rich chlorite-like mineral from soil clays. Soil Sci. Soc. Amer. J. 54: 281 — 287.

Karathanasis, A.D. & Hajek, B.F. (1984): Evaluation of aluminum-smectite stability equilibria in naturally acid soils. Soil Sci. Soc. Amer. J. 48: 413-417.

Loveland, P.J. & Bullock, P. (1975): Crystalline and amorphous compounds of the clay fraction in brown podzolic soils. Clay Minerals. 10: 451-469.

Mortland, M.M. (1958): Kinetics of potassium release from biotite. Soil Sci. Soc. Amer. Proc. 22: 503-508.

Møberg, J.P. (1991): Composition and development of the clay fraction in Danish soils - An Overview. Sciences Geologiques.

Møberg, J.P. (1976): A chemical andphysicochemical invest igation of two Danish Podzol profiles. Royal Veterinary and Agricultural University Yearbook 1976: 112-132.

Møberg, J.P., Petersen, L. & Rasmussen K. (1988): Constitu ents of some widely distributed soils in Denmark. Geoderma 42: 295-316.

Møberg, J.P. & Nielsen, J. Dissing (1987): Den mineralogiske sammensætning af jorde fra danske forsøgstationer. Tidskr. Planteavl, Beretning nr. S 1870.

Nehmdahl, H. & Møberg, J.P.: Mineralogical composition of the magnetic separated clay fraction of some Danish soils. Unpublished data.

Robert, M. (1973): The experimental transformation of mica toward smectite: Relative importance of total charge and tetrahedral substitution. Clays & Clay Min. 21: 167-174.

Ross, G.J. & Rich, C.I. (1973): Effect of particle size on potassium sorption by potassium depleted phlogopite. Clays & Clay Min. 16: 239-247.

Sawhney, B.L. (1989): Interstratification in layer silicates, p. 789-828. In: Minerals in Soil Environments. 2nd edition. (Eds. J.B. Dixon and S.B. Weed). Soil Science Society of America, Madison, Wisconsin, USA.

Schachtschabel, P., Blume, H-P., Brünner, G., Hartge, K.-H., und Schwertmann, U. (1989): Lehrbuch der Bodenkunde. 12. edition, p. 33-34. Ferdinand Enke Ferlag, Stuttgart.

Tamura, T. (1956): Weathering of mixed layer clays in soils. Clays & Clay Min. 4: 413-422.

Vicente, M.A., Razzaghe, M. & Robert, M. (1977): Formation of aluminum hydroxy ver-miculite (intergrade) and smectite from mica under acidic conditions. Clay Min. 12: 101-112.

Weed, S.B. & Bowen, L.H. (1990): High-gradient magnetic concentration of chlorite and hydroxy-interlayered minerals in clays. Soil Sci. Soc. Amer. J. 54: 274-281.

Whittig, L.D. & Jackson, M.L. (1955): Interstratified layer silicates in some soils of northern Wisconsin. Clays & Clay Min. 3: 322-336.

Potential acidity in relation to soil characteristics

Henrik Breuning Madsen and Niels H. Jensen

Madsen, Henrik Breuning & Jensen, Niels H.: Potential acidity in relation to soil characteristics.

Potentially acid sulfate soils due to excess of pyrite over soil neutralizing capacity are formed in wetlands where the essential conditions for formation of pyrite are present. On the basis of analytical results from about 14,000 samples collected in wetlands of Jutland, Denmark, the relationship between potential acidity and profile characteristics is considered.

Keywords: *pyrite, potential acidity.*

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In the western part of Denmark, Jutland, may newly drained soils become extremely acid because of oxidation of sulfides, mainly pyrite. This leads to a decrease in the agricultural production, to sedimentation of ochre in the tile drainage system, and to heavy ochre pollution of nearby watercourses. To avoid this a soil survey has been carried out for mapping the potentially acid sulfate soils in Jutland.

In the wetlands 8000 augerholes were described and 13,500 soil samples were collected and analysed for potential acidity.

All field descriptions and analytical data have been stored in a computer system. Based on these data the relationship between potential acidity, landform and the soil characteristics described in the field is considered in this paper.

The formation and location of potential acidity

Potentially acid sulfate soils are formed in wetlands where the essential ingredients for the formation of pyrite are present - sulfate, iron containing minerals, metabolizable organic matter, sulfate-reducing bacteria, and anaeroby alternating with limited aeration. Thus, these soils occur mainly in one of the three following land systems (Pons et al. 1982):

1. Saline and brackish tidal flats and tidal swamps.
2. Bottoms of saline and brackish lagoons, seas and lakes.
3. Inland valleys subject to influx of sulfate-rich water.

Potentially acid sulfate soils have been and are mainly formed in tidal flats (Pons & van Breemen, 1982) corresponding to land system 1. In this land system about 12.5 million ha of fine-textured marine and fluvial sediments are potentially acid sulfate (Kavalec, 1973). They have mainly been described in the tropics and the warmer parts of the mid-latitudes (Pons, 1965, 1973; Breemen, 1976; Allbrook, 1973; Thomas & Varley, 1982; Viellefon, 1973; Verhoeven, 1973). In Denmark it has been described in the delta region of the river Skjernå at the west coast of Jutland (Halaburt et al. 1978; Postma, 1977, 1982), and Madsen & Jensen (1988) showed that approximately half of the marsh area in Denmark contains potentially acid sulfate material.

In sediments of land system 2 potentially acid sulfate soils have only been described for a few places. Wiklander et al. (1950) described pyrite-containing gyttja soils on the littorina plateau related to the Botnic Gulf, and Madsen (1983) found similar soils on sandy deposits of the littorina plateau in Northern Jutland. Madsen & Jensen (1988) showed that approximately 20 % of land system 2 in Jutland is potentially acid.

In the non-marine land system 3, the development of potentially acid sulfate soils is restricted to areas with influx of SO_4^{--} -rich water. The presence of these soils is rare compared with marine areas, but is described by Chenery (1954) and Poelman (1973). The latter describes pyritic soils located in valley bottoms between hills with outcrops of Tertiary marine clay, in the eastern part of the Netherlands. The pyrite was mostly found in bog soils where it was concentrated in and below the transition zone between peat and the underlying sand, called catsand. In Denmark the same type of pyritic soils is found in wetlands in or adjacent to Saale tills containing some pyrite (Jakobsen, 1985; Madsen & Jensen, 1988).

On the basis of a landform map, fig. 1, Jutland has been divided into the three land systems. In fig. 1 land system 1 corresponds to the landform 1, the salt marsh. Land system 2 corresponds to the landforms 2 and 3, raised sea-floors. Land system 3 is found in the landforms 4, 5, 6, and 7, which are the non-marine landforms.

Field work

The field work consisted of soil sampling and profile description. Based upon geological maps, soil maps and maps from previous moorland investigations approximately 8000 augering sites were selected with a view to get an even distribution in wetland areas and soil materials. The description in the field included organic matter, texture, soil colour, presence of calcium carbonate, odeur of H_2S, and other characteristics such as mottlings, (Madsen et al. 1985).

The organic sediments were described as gyttja or as poorly, medium or well decomposed peat named fibric, hemic and sapric peat respectively. The inorganic sediments were classified according to texture. Presence or absence of calcium carbonate was checked with dilute acid. The augering depth was normally 2.5 m and samples were taken from each major layer below or near the groundwater table. Immediately after sampling the pH was measured potentiometrically by placing the electrode (Ingold U456-KN) directly in the sample, and the colour of the samples were described using Munsell soil colour charts. The same day as the sampling took place, the calcium carbonate containing samples were dried at 105 °C, in order to avoid oxidation of any pyrite present.

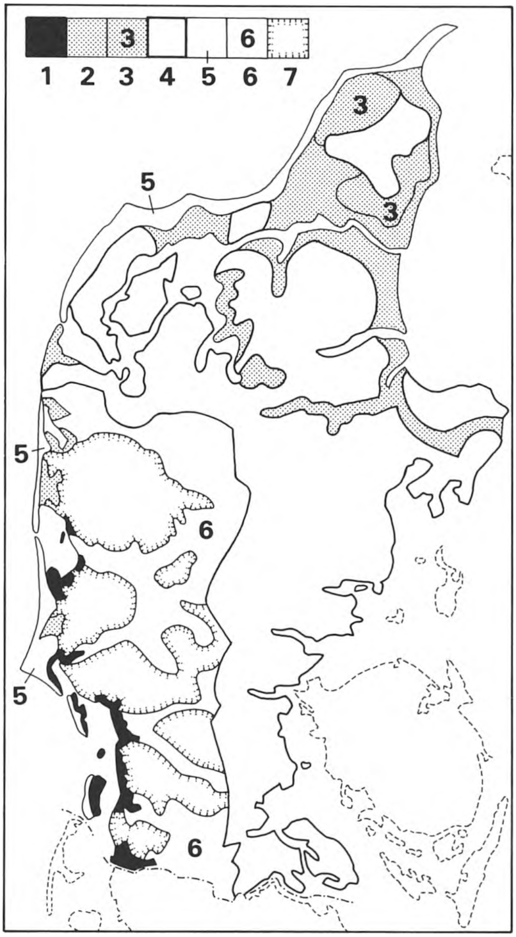

Fig. 1. Landform and land system map of Jutland.

Landforms: 1: Salt marsh. 2: Marine forelands built up since the Atlantic (Littorina) transgression including reclaimed areas. 3: Late glacial raised sea-floors (Yoldia plateau). 4: Young moraine landforms from the Weichsel glaciation. 5: Dune landforms. 6: Outwash plains from the Weichsel glaciation. 7: Old moraine landforms from the Saale glaciation.

Land systems: Black areas: land system 1 (=landform 1). Grey areas: land system 2 (=landform 2-3). White areas: land system 3 (=landform 4-7).

Analyses

In the laboratory the carbonate-free samples were inoculated with soil water from an acid sulfate bog and then incubated at room temperature under oxidative conditions. The samples were frequently remoistened, in order to accelerate pyrite oxidation (Stumm-Zollinger, 1972; Breemen, 1976). The pH-values were measured potentiometrically after 2, 8 and 16 weeks by placing the electrode directly in the samples. Samples were excluded from further incubation after either two or eight weeks, if pH during these periods dropped below 3.0, or if there had been nearly no decrease in pH.

On the calcium carbonate-containing samples, dried at 105 °C, a semiquantitative determination of pyrite and test for the presence of siderite and calcium carbonate was made by X-ray diffraction (Rasmussen, 1961). On samples containing calcium carbonate and pyrite, acid-neutralizing capacity (ANC), defined as meq. Ca + Mg/100 g soil, was determined as follows: 1 g of the sample was weighed into a flask with 100 ml 4N HCl. The flask was frequently shaken without stopper during the next two hours at room temperature. Then the flask was shaken with stopper for 16 hours. After filtration Ca and Mg were determined in the filtrate by atomic absorption spectrophotometry.

The pyrite content determined by X-ray diffraction was compared with the acid-neutralizing capacity of the sample. If this indicated that a sample was potentially acid a quantitative pyrite determination was carried out according to the method described by Petersen (1969).

A portion of all sandy samples were dried at 105 °C immediately after sampling, and a quantitative pyrite determination was later carried out on the samples which became extremely acid during the incubation period. These determinations were carried out to estimate the amount of pyrite needed to make the samples, which had a very low content of exchangeable bases, extremely acid.

material	depth cm	pH at the time of sampling	pH after 2 weeks	PH after 8 weeks	PH after 16 weeks	pot. acid
sand	100-120	5.8	3.6	3.3	2.5	yes
sand	80-120	6.4	5.8	6.0	-	no
gyttja	130-140	5.6	1.8	-	-	yes
gyttja	140-150	6.2	5.1	4.4	4.3	no
peat	130-150	5.9	2.6	-	-	yes
peat	60-80	5.8	1.6	-	-	yes
peat	155-190	6.5	3.4	2.4	-	yes
loamy sand	110-120	6.3	6.1	6.1		no

Table 1. pH measured at the time of sampling and after 2, 8 or 16 weeks of incubation in samples from different soils.

Definition of potentially acid sulfate material

The definition of potentially acid sulfate material is here based on the lowest pH observed during the incubation period or the relationship between the pyrite content and the acid-neutralizing capacity. The definitions are:

(a) if pH in the carbonate-free samples drops below 3.0 during the incubation period, the soil samples are classified as potentially acid sulfate samples. All other samples investigated by incubation are considered as not potentially acid sulfate samples (table 1).

(b) the calcium carbonate containing soil samples are classified as potentially acid sulfate samples if ANC (meq. Ca + Mg) < 34 x % pyrite.

The figure 34 corresponds to the meq. sulfuric acid produced by oxidation of 1 % pyrite. If the condition is not fulfilled, the soil samples are classified as not potentially acid sulfate samples (table 2).

In the definition of potentially acid sulfate samples a pH below 3.0 is used here and not 3.5 as proposed by Soil Survey Staff (1975) for definition of sulfuric horizon. This difference is due to the fact that some Danish peats not containing any pyrite might have a pH around 3.5.

Results and discussion

About 12,300 incubation analyses were carried out on carbonate-free samples, and roughly 1280 X-ray analyses and about 1440 quantitative py-

material	depth cm	Ca meq,/100 g	Mg	FeS_2 %	pot. acid
sand	130-140	30	3	1.1	yes
gyttja	150-170	720	13	11.2	no
gyttja	200-220	42	5	19.8	yes
gyttja	100-13	43	14	2.3	yes
peat	210-240	770	5	13.5	no
loam	190-230	68	4	2.5	yes
loam	150-180	196	6	3.0	no
silt loam	110-130	131	31	2.3	no

Table 2. Analytical results from carbonate-containing samples.

rite determinations were carried out on carbonate-containing, or sandy, samples.

Examples of analytical data and classification of carbonate-free and carbonate-containing samples are shown in tables 1 and 2.

The quantitative determination of pyrite in calcium carbonate containing samples and in sand shows that some samples contain more than 20 % pyrite. Samples with high amounts of pyrite are normally potentially acid, but as shown in table 2 some peat and gyttja soils with high acid neutralizing capacity are not potential acid although they contain more than 10 % pyrite. On the other hand less than 0.5 % might be needed to make sand extremely acid, because of low buffer capacity.

The relationship between soil characteristics described in the field and potential acidity in lime-free samples is shown in the tables 3 to 5. The soil samples were grouped with respect to soil material, colour, mottles, and smell of H_2S. The organic sediments were divided into fibric, hemic and sapric peat, and gyttja. The inorganic sediments were divided into 3 texture classes: less than 5 % clay and less than 30 % silt named sand; 5 % to 45 % clay and less than 40 % silt named sandy clay. The rest, having clayey and/or silty textures, are named clay/silt. The sediments were frequently described as mixtures, e.g. sandy peat.

The colours were grouped into five classes based on the soil colour names on the Munsell soil colour charts. The colour was named black if the value was less than 3 and the chroma less than 2. The other colour groups were based on the hue and were named YR, Y, B or G. YR included 2.5YR, 5YR, 7.5YR, and 10YR, Y included 2.5Y, 5Y, 7.5Y, and 10Y, B included 5B and 5BG, and G included 5G, 10G, 5GY, 10GY and N.

		All land systems	Land syst.1	Land syst.2	Land syst.3
Sand	%	31	38	43	29
	N	4304	175	534	3595
Sandy clay	%	10	9	32	7
	N	373	11	34	328
Clay/silt	%	14	26	26	8
	N	838	111	160	567
Sapric peat	%	28	44	68	17
	N	554	16	112	42
Hemic peat	%	29	-	-	17
	N	28	4	6	18
Fibric peat	%	26	57	26	20
	N	204	30	31	143
Gyttja	%	14	28	19	13
	N	1260	25	183	1052
Mixed gyttja	%	29	52	40	27
and peat	N	1656	71	194	1391
Sandy peat	%	17	50	16	15
	N	2858	108	527	2223
Sandy gyttja	%	21	-	50	15
	N	181	5	20	156
All samples	%	23	40	32	21
	N	12256	556	1801	9899

Table 3. Potential acidity in relation to soil material and land systems. Only lime-free samples. % = % potentially acid soil samples; N = number of samples.

For each group the number of samples and, for groups with 10 or more samples, the percentage of potentially acid samples are shown in the tables 3 to 5. The calculations were based on all samples from Jutland, and for each of the land systems shown in fig. 1.

Table 3 shows the relationship between potential acidity, soil material and land system. Less than a quarter of all samples belonged to potentially acid sulfate soils. Approximately 40 % of the samples from the salt marsh (land system 1) are potentially acid, while in the other marine landforms (land system 2) only 32 % are potential acid. This is probably due to differences in environmental conditions during the sedimentation of the parent material. In the marsh area, except in the outermost parts, clayey materials have

		YR			Y			B			G			black			smell of h_2s			brown and red mottles			black mottles		
Land systems		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Sand	%	24	32	19	45	43	32	-	-	41	33	54	52	_	_	22	_	39	39	-	-	13	53	53	42
	N	58	119	1412	94	357	1901	1	3	12	15	53	213	7	2	57	5	23	116	0	5	65	13	26	151
Sandy clay	%	-	-	-	0	11	8	-	-	0	-	-	11	-	-	-	-	-	-	-	-	0	-	-	17
	N	1	4	62	6	19	202	0	3	10	4	7	47	0	1	7	0	0	2	2	4	45	2	1	12
Clay/silt	*	31	0	4	37	30	12	-	-	8	5	40	3	-	-	6	53	21	15	-	25	2	21	23	9
	N	19	25	194	56	110	273	9	2	12	20	15	56	7	8	32	13	14	13	3	16	39	56	17	53
Sapric peat	%	-	61	9	70	66	26	-	-	-	-	-	6	-	-	7	-	66	27	-	-	-	-	-	28
	N	3	13	134	10	84	205	0	0	1	0	7	16	3	8	70	6	15	44	0	0	6	1	4	14
Hemic peat	%	-	-	9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	N	3	4	11	0	2	5	0	0	0	0	0	0	1	0	2	1	1	2	0	0	0	0	1	0
Fibric peat	%	58	31	20	-	-	13	-	-	-	-	-	-	-	-	22	66	-	20	-	-	-	-	-	-
	N	17	16	92	8	8	15	0	0	0	1	0	0	4	7	36	12	5	40	0	0	0	3	1	3
Gyttja	%	27	15	9	-	36	17	-	-	-	-	-	-	-	22	18	-	28	18	-	-	11	-	-	7
	N	18	126	657	0	22	120	0	0	0	0	0	1	7	35	274	2	21	76	1	1	17	1	5	40
Mixed gyttja	%	54	33	19	56	56	43	_	-	-	-	-	10	44	21	24	60	37	25	-	-	-	-	-	15
and peat	N	37	80	700	16	76	340	0	0	0	0	5	10	18	33	341	25	32	264	1	2	3	3	6	44
Sandy peat	*	42	13	12	-	22	29	_	-	-	-	-	-	66	19	16	50	27	15	-	-	0	70	-	20
	N	71	362	1454	8	53	169	0	0	0	2	0	1	27	112	599	44	79	422	0	2	10	10	7	48
Sandy gyttja	%	-	-	10	-	75	19	-	-	-	-	-	-	-	-	12	-	-	15	-	-	-	-	-	-
	N	1	4	38	4	12	77	0	0	1	0	2	7	0	2	33	1	3	13	0	0	0	2	0	9
Total	%	39	20	15	46	44	29	20	-	17	19	54	35	46	22	18	53	34	22	-	33	6	35	32	26
	N	228	753	4754	202	743	3307	10	8	36	42	89	351	74	208	1451	109	193	992	7	30	185	91	68	374

Table 4. Potential acidity in relation to land systems, soil texture, soil colour, smell of H_2S, and mottling. Only lime-free samples. Soil colours are grouped in YR, Y, B, and G, which are defined in the text. % = % potentially acid soil samp-les; N = number of samples.

been deposited under relatively calm conditions in small bays or lagoons (Jacobsen, 1964; Rasmussen, 1956). Vigorous biological activity in these shallow, brackish, or salt-water bays and lagoons favours formation of pyrite and other iron sulfides, because anaerobic conditions prevail with influx of iron and sulphur.

In land system 2 sandy deposits dominate. The sediments are deposited on more exposed coasts, where the biological activity is lower than in the salt marsh and anaerobic conditions are not so pronounced. This environment does not favour the precipitation of iron sulfides. In non-marine landforms (land system 3) only 21 % is potential acid. The different landforms within land system 3 show great diversity in distribution of potential acidity. The samples from the Weichsel moraine or dune landscapes are less potential acid than those from the outwash plains and the Saale glaciation. This diversity cannot be explained by the genesis of the Quaternary deposits alone, but it may also be due to redeposition of pyrite from sulfur-rich Pre-Quaternary deposits (Madsen & Jensen, 1988).

Together sand, peat and mixed gyttja, and peat have the highest rate of potential acidity, between 26 % and 31 %. Pure gyttja and inorganic materials of finer texture than sand have only 10 to 15 %.

In relation to land system a high frequency of potential acidity - more than 50 % - is found for fibric peat, mixed gyttja/peat and sandy peat in land system 1 and for sapric peat and sandy gyttja in land system 2. Very low values are found in mineral soil samples finer than sand, especially in land system 3. Great variations in potential acidity are found within the textural classes. In sandy peat half of the samples collected in the salt marsh area are potentially acid as compared with about 15 % in the two other land systems. For sapric peat, 2/3 of the samples are potentially acid on the marine forelands; in the salt marsh nearly half of the samples are potentially acid while only 15 % of the samples of sapric peat located in land system 3 are potentially acid.

Potential acidity in relation to land system, soil texture, soil colour, smell of H_2S and mottlings is shown in table 4. The major part of the samples are yellowish red or yellow; only a minor part are blue or grey. Black is an intermediate part. In landform 3 no categories show a frequency of potentially acid samples above 50 %, while five categories within each of the two other land systems have a frequency higher than 50 *%.* Especially yellow and yellowish red samples containing peat seem to have a high frequency of potential acidity. The highest value found is 75 % for yellow sandy gyttja in land system 2. Together, samples with grey and yellow colours have the highest frequency of potential acidity, namely 33 %, while other samples only have about 20 %. There are some differences between the land systems. In land system 1 yellow and black colours indicate a relatively high frequency of potential acidity (46 %), while blue and grey indicate a low frequency. In the other two land systems, yellow and especially grey colours indicate relatively high potential acidity while blue, black and yellowish red show nearly identical low frequencies of about 20 %. Only for samples with grey colours within land system 2 the frequency of potential acidity exceeds 50 %.

In land system 1 the smell of H_2S indicates the possibility of potential acidity, as roughly half of the H_2S-smelling samples are potentially acid. In the other two land systems only 1/3 and 1/4 of the H_2S-smelling samples are potentially acid. The presence of brown or red mottles indicates low frequency of potential acidity while black mottles in sandy material indicate relatively high potential acidity (50 *%).*

Table 5 shows potential acidity in relation to land systems, soil colour, smell of H_2S, and mottles. The combination of smell of H_2S and yellow or black colours coincides with high frequency of potential acidity in land system 1, and very low frequencies are found in samples with red or brown mottles situated in land system 3.

Table 6 shows potential acidity in lime-containing sediments. Only 1300 samples have been analyzed. Potential acidity is rarely found in lime-containing sediments, only 10 *%* were potentially acid.

		smell of H_2S			brown and red mottles			black mottles		
Land systems		1	2	3	1	2	3	1	2	3
colour										
YR	*%*	44	30	15			2	47	22	18
	N	63	115	619	2	8	77	21	22	137
Y	*%*	70	36	38	-	27	10	42	38	32
	N	27	57	206	2	18	89	42	36	144
B	%	-	-	-	-	-	-	-	-	-
	N	1	0	0	0	1	1	6	2	6
G	*%*	-	-	47	-	-	0	5	-	50
	N	3	6	17	1	1	12	17	3	40
black	%	67	33	22	-	-	-	-	-	10
	N	15	15	149	2	2	6	5	5	46

Table 5. Potential acidity in relation to land systems, soil colour, smell of H_2S and mottling. Only lime free samp-les. *%* - *%* potentially acid soil samples; N = number of samples.

Material	Number of samples	% pot. acid samples
Peat	100	11
Gyttja	489	7
Sand	197	4
Sandy clay + clay/silt	514	14
Total	1300	10

Table 6, Percent potentially acid soil samples containing lime.

Conclusions

In Jutland approximately 14,000 soil samples have been collected in wetlands and analyzed for potential acidity. The investigation shows that potential acidity in wetlands in the western part of Denmark is a common feature; approximately a quarter of the samples were potentially acid.

The data were divided in groups according to land system, texture, colour, mottlings and smell of H_2S in order to investigate the relation between field criteria and potential acidity. Hereby it should be elucidated if it is possible from field criteria alone to determine and map potentially acid sulfate soils. The results show that only very few combinations of field criteria coincides with a frequency of potential acidity above 50 %, and the highest frequency found was 75 %. On the other hand, several combinations show very low frequencies less than 10 %; some even zero. Based on these results it must be concluded that field determination of potential acidity based on land system, texture, colours, mottling and smell of H_2S is very unreliable, if possible at all. A mapping of potentially acid sulfate soils should therefore be based on laboratory analyses of soil samples.

References

Allbrook, R.F. (1973): The identification of acid sulphate soils in Northwest Malaya. In: Acid Sulphate Soils. Proceedings of the Int. Symp. on Acid Sulphate Soils. (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Breemen, N. Van (1976): Genesis and solution chemistry of acid sulfate soils in Thailand. Doctoral Thesis, Wageningen Univ., 263 p.

Brinkman, R & Pons, L.J. (1973): Recognition and prediction of acid sulphate soil conditions. In: Acid Sulphate Soils. Proceedings of Int. Symp. on Acid Sulphate Soils. (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Chenery, E.M. (1954): Acid sulphate soils in Central Africa. Trans. 5th Int. Congress Soil Sci., Leopoldville, 4: 195-98.

Halaburt, J., Larsen, V. & Postma, D. (1978): Skjernå deltaets forvitringssituation. Ringkøbing amtsråd.

Jacobsen N. Kingo (1964): Tøndermarskens naturgeografi med særligt henblik på morfogenesen (with English summary). Folia Geographica Danica. VII, 1.

Jakobsen, B. Holm (1985): An interpretation of the occurrence of pyrite at two locations in western Jutland, Denmark. Geografisk Tidsskrift 85: 9-14.

Kawalec, A. (1973): World distribution of acid sulphate soils. References and map. In: Acid Sulfate Soils. Proceedings of Int. Symp. on Acid Sulphate Soils. (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Kolle, W. & Schreeck, D. (1982): Effect of agricultural activity on the quality of groundwater in a reducing underground. pp. 191-202. In: Proceedings of the Int. Symp. on Impact of Agriculture Activity on Ground water. (eds. J. Vrba & J. Svoma). International Association of Hydrogeologist, Memories XVI, 2. Novinar, Prag.

Kristiansen, H. & Hansen, E.Z. (1986): Sårbarhedsprojektet. Reducerende stoffer i undergrunden i et hedesletteområde. Slutrapport for delprojekt 2.4 i sårbarhedsprojektets 2. etape. Ministry of Environment, Copenhagen.

Madsen, H. Breuning (1983): Himmerlands jordbundsforhold (with English summary). Folia Geographica Danica XVI. C.A. Reitzel. Copenhagen.

Madsen, H. Breuning, Jensen, N.H., Jakobsen, B. Holm & Platou, S.W. (1985): A method for identification and mapping potentially acid sulfate soils in Jutland, Denmark. Catena 12: 363-71.

Madsen, H. Breuning & Jensen, N.H. (1988): Potentially Acid Sulfate Soils in Relation to Landforms and Geology. Catena 15: 137-45.

Petersen, L., Rasmussen, K. & Jensen. T. (1967): Soil problems and tree growth after lignite strip mining. Royal Vet. and Agri. Coll. Yearbook 1968. Copenhagen.

Petersen, L. (1969): Chemical determination of pyrite in soils. Acta Agric. Scand.,19: 40-44.

Poelman, J.N.B. (1973): Soil material rich in pyrite in non-coastal areas. In: Acid Sulphate Soils. Proceedings of the Int. Symp. on Acid Sulphate Soils. (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Pons, L.J. (1965): Pyrites as a factor controlling chemical ripening and formation of cat clay, with special reference to the coastal plain of Suriname. Agric. Exp. Stat. Paramaribo, Bull. no. 82: 141-62.

Pons, L.J. (1973): Outline of the genesis, characteristics, classification and improvement of acid sulfate soils. In: Acid Sulphate Soils. Proceedings of the Int. Symp. on Acid Sulphate Soils. (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Pons, L.J. & Breemen, N.Van (1982): Factors influencing the formation of potential acidity in tidal swamps. In: Proceedings of the Bangkok Symposium on Acid Sulfate Soils. (ed. H. Dost & N. van Breemen). International Institute for Land Reclamation and Improvement, Wageningen.

Pons, L.J., Breemen, N. Van & Driessen, P.M. (1982): Physiography of coastal sediments and development of potential soil acidity. pp. 1-18. In: Acid sulfate weathering. (ed. D.M. Kral). SSSA Special Publication Number 10, Soil Sci. Soc. Am., Madison, Wisconsin.

Postma, D. (1977): The occurrence and chemical composition of recent Ferich mixed carbonates in a river bog. Jour. Sed. Petrology 47: 1089-98.

Postma, D. (1982): Pyrite and siderite formation in brackish and freshwater swamp sediments. Am. Jour. Sci. 282: 1151-83.

Rasmussen, K. (1956): Investigations of marsh soils and Wadden Sea sediments in the Tønder region. Geografisk Tidsskrift 56: 147-70.

Rasmussen, K. (1961): Uorganiske svovlforbindelsers omsætning i jordbunden (with English summary). Thesis, DSR, Copenhagen, 176 p.

Soil Survey Staff (1975): Soil Taxonomy. USDA Handb. 436, U.S. Government Printing Office, Washington, D.C.

Stumm-Zollinger, E. (1972): Die bakterielle Oxidation von Pyrit. Arch.Mikrobiol. 83: 110-19.

Thomas, P. & Varley, J.A. (1982): Soil survey of tidal sulphuric soils in the tropics: a case study. In: Proceedings of the Bangkok Symposium on Acid Sulphate Soils, (eds. H. Dost and N. van Breemen). International Institute for Land Reclamation and Improvement, Wageningen.

Verhoeven, B. (1973): Acid sulphate soils in the Wieringermeer Polder, a good 40 years after reclamation. In: Acid Sulphate Soils. Proceedings of the Int. Symp. on Acid Sulphate Soils. (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Vieillefon, J. (1973): Sur quelques transformations sedimentologiques et mineralogiques dans les sols sulfates acides du Senegal. In: Acid Sulphate Soils. Proceedings of Int. Symp. on Acid Sulfate Soils, (ed. H. Dost). International Institute for Land Reclamation and Improvement, Publication 18. Wageningen.

Wildander, L., Hallgren, G., Brink, N. & Jonsson, E. (1950). Studies on gyttja soils. II. Some characteristics of northern Sweden. Ann. Royal Agric. College Sweden, 17: 24-36.

Soil acidity and soil acidification - Fundamental concepts and status for five Danish forest soils

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In order to obtain a meaningful quantitative description of the acid-base properties of soils two concepts are introduced: Soil acidification and Soil acidity. Soil acidification is considered the process where protons are neutralized in the soil leading to a decrease in the amount of bases ("decrease in acid neutralization capacity"). Soil acidity is both an intensity term (proton activity in the soil solution) and a capacity term (strong base titratable acidity). Acid neutralization by mineral weathering (e.g. $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$*) where the products are removed, leads to soil acidification but does not change soil acidity. Soil acidity may be developed, however, when the acid production rate in the soil system exceed the acid neutralization rate. Exchangeable aluminium, sulphate-aluminium compounds and organic acids are the main sources for soil acidity. Important sources of protons in forest ecosystems are: i) dissolution of carbon dioxide in the soil solution; ii) production of organic acids; iii) utilization of biomass; iv) netoxidation of sulphur, nitrogen and iron compounds; v) acid rain.*

Investigations of acid and base properties in five Danish forest soils shows, that in soils with low base contents soil acidification is small but the increase in soil acidity is high, whereas in soils rich in bases soil acidification is high due to leaching of bases but the development of soil acidity is limited.

Keywords: *natural acidification, air pollution, soil fertility, soil development.*

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Acid soils are widely distributed over the World and have for a long time been the object of intensive research, mainly because of their generally low fertility. Low availability of essential plant nutrients, high activity of toxic aluminium and manganese species, and often a relatively slow turnover of organic materials are important causes for the low fertility. To counteract soil acidity, agricultural and horticultural soils are limed regularly. Liming of forest soils, particularly soils under conifers, has generally not resulted in increased growth, but the results are very scattered and indicate both positive and negative effects of lime on the chemical and biological conditions in the soil (Raulund-Rasmussen, 1989). Soil acidity per se is generally not considered to be harmful to the growth of conifers particularly.

The claimed adverse effect of the potentially acid nitrogen and sulphur compounds due to air pollution on the stability of forest ecosystems often has been attributed to impacts on soil properties, although their importance is still a matter of great controversy. Some researchers, e.g. Rosenquist (1977) and Krug & Frink (1983), draw attention to the acid production which takes place during humus accumulation. Others, e.g. Ulrich (1989), emphasize the importance of acid rain as the cause of accelerated leaching of calcium and magnesium, and increased mobilization of toxic aluminium compounds in the soil solution, leading to reduced fertility and destabilization of the forest ecosystem. Quantification of effects such as cultivation and air pollution (acid rain) on soil properties only seems meaningful, if both acid and base properties of soils are considered. Furthermore, it should be recognized that changes in these properties may take place independently of each other, since soil is an open (non-equilibrium) system with fluxes of energy and matter in and out of the system. Further, the main base properties originate from the weathering of silicate minerals which is often extremely slow (Sverdrup, 1990). Assessment of the effects of natural as well as anthropogenic proton sources therefore need unambiguous concepts of soil acid and base properties and changes in these.

The purpose of this paper is to present precise and useful definitions of the terms *soil acidity* and *soil acidification*, and to discuss processes which illustrate the important differences between the two terms. Emphasis is put on forest soils in humid temperate climates and the processes are exemplified by data from five Danish forest soils.

Fundamental concepts

Since soils react with acids and bases, i.e. accept and donate protons, they have acid and base (Brønsted) properties (Bjerrum and Gjaldbæk, 1919a).

The base properties or the acid buffering capability of the soil are caused by the presence of proton accepting groups, mainly on carbonates, oxides (including also hydroxides and oxyhydroxides) and silicates. The reactions involved may be fast (cation exchange) or slow to very slow (mineral weathering). The base properties may be characterized by (i) proton *affinity* (pKa's of the conjugate acid/base pairs), (ii) base *concentration,* (iii) base *reactivity* (reaction rate).

Soil *acid properties* are caused by acid producing processes and incomplete neutralization of the acids. They are mainly associated with organic matter and with exchangeable aluminium.

Since pH is an intensity parameter giving no quantitative information about the various acid/ base systems in soils van Breemen et al. (1983) introduced the concept of *Acid Neutralization Capacity (ANC)* as the amount of strong acid required to decrease pH of a soil system to a reference pH. They designated a decrease in ANC as *soil acidification* and an increase in ANC as *soil alkalinization,* corresponding to decrease and increase in base properties. However, ANC and soil acidification/alkalinization only consider base properties, the status quo (ANC), and changes (soil acidification/alkalinization). Therefore to account for the acid properties the *base neutralization capacity (BNC)* may be introduced as the amount of strong base required to increase soil pH to a reference pH. Changes in BNC may be designated as increase or decrease in *soil acidity.* So defined ANC and BNC correspond to total alkalinity (TAl) and total acidity (TAc) used in aquatic systems (Stumm and Morgan, 1981). The conceptual difference between soils and aquatic systems is only one of reactivity.

As reference pH's 5 for ANC and 8.3 for BNC are appropriate, since at pH 5 dissolution of aluminium oxides will not contribute to ANC and pH 8.3 corresponds to equilibrium between calcium carbonate and carbon dioxide at its ambient partial pressure in the atmosphere (Bjerrum & Galdbæk, 1919b).

Determination of ANC by titration is impossible due to the very slow acid neutralization of silicate minerals. Alternatively van Bremen et al. (1983) suggested that ANC be estimated from the component composition of the soil system including soil solution, solid particles and adsorbed ions. In addition, organic matter must be included as suggested by de Vries and Breeuwsma (1987). In well aerated soils calcium, magnesium, sodium and potassium, adsorbed onto the adsorption complex and part of the mineral structures are the main base cations. Although not proton acceptors themselves these cations account for the proton acceptor sites, unless associated with anions of strong acids e.g. sulphate. However, in most freely drained humid soils that might only be minor parts. Oxidizable cations such as iron(II) and manganese(II) will not directly contribute to ANC ($FeO + 1/4O_2 + 3/2H_2O \rightarrow Fe(OH)_3$). Of course, aluminium oxides as well as iron oxides are important proton acceptors in acid soils.

Determination of BNC by titration is possible due to the relatively fast reaction rate of the contributing acids. These will be acid cationic Al- and Fe-species and protons from the adsorption complex, and protons of organic acids dissociating below the upper reference point

(8.3).

In short, soil acidification takes place when produced acids are neutralized by exchange of adsorbed base cations and by weathering of minerals, provided the released base cations are removed from the soil. Increase in soil acidity takes place when acids are retained in the soil. The processes are discussed in detail later.

Acid production in the ecosystem

Soil base properties (ANC) are depleted and soil acid properties (BNC) are developed because of acid producing processes in the soil system. These processes are caused by fluxes of energy and matter to the ecosystem defined as an integrated unit consisting of autotrophic primary producers, heterotrophic secondary producers, and the inorganic surroundings including the soil. The primary producers (green vegetation) produce organic matter and free oxygen from carbon dioxide, water, nutrients and energy (E). The secondary producers utilize the energy in the organic matter during mineralization. In principle the processes are opposite:

$$CO_2 + H_2O + xMe^+ + yA^- + (y - x)H^+ + E \leftrightarrow CH_2OMe_xA_y + O_2 \quad (1)$$

x and y are stoichiometric coefficients to uptake and release of cations (Me^+: ½Ca^{2+}, ½Mg^{2+}, K^+, Na^+, NH_4^+) and anions (A^-: NO_3^-, ½SO_4^{2-} Cl^-). Electroneutrality is maintained by uptake or release of protons. Despite this mass balance seems to be acid-base neutral at steady state (uptake balanced by release), several processes listed below may result in acid production.

Carbonic acid

Depending on aeration and pH in the soil solution, carbon dioxide will dissolve in the soil solution and form carbonic acid:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (2)$$

The carbonic acid causes soil acidification, when $Me^+HCO_3^-$ is leached, and may cause increase in soil acidity depending on the base reactions with the soil (discussed later). The acidification rate depends on pH and the carbon dioxide pressure as well as the leaching rate. Assuming overall equilibrium the acidification rate can be calculated by use of Henry's law constant, the acid constants, the partial pressure of carbon dioxide in the soil atmosphere and the yearly precipitation excess (Hovmand & Petersen, 1984; Raulund-Rasmussen & Larsen, 1990). At 1% CO_2 ($P_{CO2}{}^{=}{}_{0.01}$ atm) and a precipitation excess of 400 mm per year the maximum acidification rate will be 17.8 Keq/ha at pH 7.5 (calcareous soil), but only 0.56 keq/ha at pH 6.0 and 0.02 keq/ha at pH 5.0.

Organic acids

Relatively strong organic acids are produced when mineralization of organic matter is restricted. Organic acids are intermediate products in the mineralization of dead organic matter to carbon dioxide and water:

$$(CH_2O)_n + ½O_2 \rightarrow R\text{-}COOH + E$$

$$R\text{-}COOH + O_2 \rightarrow H_2O + CO_2 + E \quad (3)$$

The conditions for mineralization depends on vegetation (Ovington, 1953,1954), on availability of nutrients for the microbial decomposers (Kriebietzsch, 1978), and on physical conditions, mainly temperature and humidity. Growth of dense conifer stands (Picea ssp. and Pinus ssp.) on poor soils causes severe accumulation of organic acids, whereas invasion of deciduous trees (Quercus robur and Betula ssp.) on former acid heather soils has been shown to reduce the content of organic acids (Miles & Young, 1980; Nielsen et al., 1987).

Acid production as a result of processes involving nitrogen

Soil nitrogen is mainly organic and originates from biological fixation of free nitrogen (N_2), and assimilation of nitrogen oxides and ammonia. Biological uptake of gaseous nitrogen does not include any net acid-base reactions:

$$R\text{-}OH + ½N_2 + ½H_2O \rightarrow R\text{-}NH_2 + 3/4O_2 \quad (4)$$

$$R\text{-}OH + NO_2 + 7/4CH_2O \rightarrow R\text{-}NH_2 + 7/4CO_2 + 5/4H_2O \quad (5)$$

$$R\text{-}OH + NH_3 \rightarrow R\text{-}NH_2 + H_2O \quad (6)$$

Mineralization of organic nitrogen to ammonium or nitrate neither produce acid nor base *if* the produced ammonium and nitrate are immobilized again by organisms:

$$R\text{-}NH_2 + H_2O + H^+ \leftrightarrow R\text{-}OH + NH_4^+ \qquad (7)$$

$$R\text{-}NH_2 + 2O_2 \leftrightarrow R\text{-}OH + H^+ + NO_3^- \qquad (8)$$

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3 + H_2O \qquad (9)$$

If, however, no uptake by organisms (vegetation or decomposers) occurs mineralization of organic nitrogen to ammonium and nitrate will result in production of base and acid, respectively. Furthermore, net acid or base production takes place, when ammonium and nitrate are added to the soil (e.g. due to fertilization or air pollution).

Except at very high deposition rates, leaching of ammonium is inhibited because of adsorption and nitrification (van Breemen & van Dijk, 1988). Nitrification is retarded at C/N-ratio above 30 and by poor nutrient conditions (Zoettl, 1960; Kriebietzsch, 1978). The effects of nitrate and ammonium deposition will be counteracted, if nitrate is deposited together with protons (oxidation of NO_x) and if ammonium is deposited together with hydroxide (HN_3). However, this state, characterized by no apparent effect of added nitrogen on soil acid-base status, only applies for complete retention of nitrogen. Loss of nitrogen by leaching of nitrate will thus be accompanied by acid production (nitric acid) which may cause soil acidification and increase in soil acidity. Soil organic nitrogen therefore represents a potential acid. Many forest ecosystems can adsorb the actual deposition of nitrogen, but examples of forest ecosystems characterized by leaching of nitrate are found in polluted areas in western and central Europe (van Breemen & van Dijk, 1988).

Acid production as a result of processes involving sulphur

Soil sulphur occurs as organic (R-SH) and inorganic compounds, where the latter can be as sulphate or in a lower oxidation state (often as pyrite, FeS_2).

Sulphur interacts with biota as does nitrogen: Neither acid nor base is produced when sulphur dioxide is immobilized by biota and as long as the sulphur cycle is closed. Sulfuric acid is, however, produced when net oxidation takes place. In contrast to nitrogen most forest ecosystems are saturated with sulphur, but sulphate can - to some degree - be retained by aluminium and iron oxides (discussed later).

Substantial amounts of sulfuric acid is produced when pyrite is oxidized (Rasmussen, 1961). The net reaction is:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad (10)$$

Acid production as a result of biomass harvest

The acid-base neutrality of reaction 1 can be interrupted by biomass harvesting. Thus removal of cations (Ca^{2+}, Mg^{2+}, K^+ etc) results in permanent soil acidification and the delivered protons may increase soil acidity. Removal of anions (SO_4^{2-} and $H_2PO_4^-$) from the soil minerals will decrease soil acidity permanently, whereas removal of nitrogen and sulphur from biological fixation of gaseous nitrogen compounds and sulphur dioxide have no effects despite uptake has taken place as ammonium or nitrate, and sulphate.

Deposition of potential acid compounds due to air pollution

Special interest is given to nitrogen and sulphur compounds emitted during combustion of fossil fuels and by evaporation of nitrogen from manure and soils. Emission takes place as gaseous components (NO_x, NH_3 and SO_2). Deposition takes place either as dry deposition of gasses and particles on vegetation surfaces, or as wet deposition as ammonium, nitric acid and sulfuric acid dissolved in precipitation. The effects on soil of such deposition have been outlined above.

Soil acidification and increased soil acidity

The coexistence of acidity and thermodynamical unstable minerals in soils indicates non-equilibrium. In fact the concept of equilibrium cannot strictly be applied to open systems like soils. The interaction between the soil and the external fluxes may either result in soil development or in a steady-state, where constructual processes balance degradational processes (Smeck et al., 1983). Regarding the acid-base properties of soil, the external effects cause acid production in the soil system, which will be counteracted by the inherited base properties. The reactions between acids and bases will depend on energy relations (pKa's of acid/base pairs) and on the reactivity of the systems. Several types of reactions are possible, the most important are:

- ion exchange reactions
- weathering of easily weatherable minerals (carbonates)
- weathering of silicates
- weathering of iron and aluminium oxides and anion retention
- accumulation of organic acids.

Carbonates such as calcite, aragonite, and dolomite are very important contributors to ANC due to their high reactivity compared to the other soil minerals. The carbonate minerals dissolve completely during the weathering processes:

$$MeCO_3 + HA \rightarrow Me^{2+} + HCO_3^- + A^- \qquad (11)$$

$$MeCO_3 + 2HA \rightarrow Me^{2+} + 2A^- + CO_2 + H_2O \qquad (12)$$

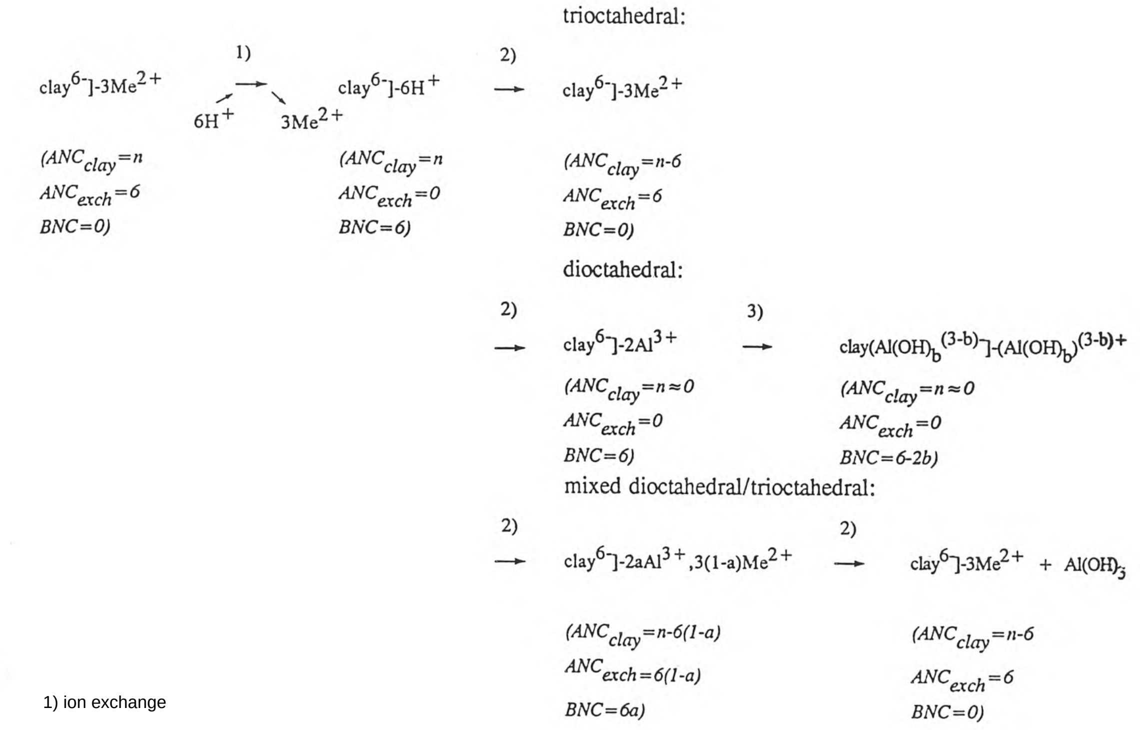
Above pH 5 one proton is neutralized (reaction 11), and below pH 5 (e.g. when liming acid soils) two protons are neutralized (reaction 12). The products may be leached. During dissolution and subsequent leaching no increase in BNC takes place, but ANC decreases equivalent to the amount of leached Me^{2+}. Soil acidification rate will be very high in calcareous soils due to production and dissociation of carbonic acid in the soil solution.

Quantitatively ANC is often dominated by silicates. Although thermodynamically unstable at acid pH most silicate minerals react very slowly (van Breemen & Wielemaker, 1974a,b; Sverdrup, 1990). Contrary to carbonates, primary silicates seldom dissolve after protonization; instead they transform to secondary minerals such as layer-silicate clay minerals and aluminium and iron oxides, as shown in fig. 1. Protons are strongly adsorbed on exchange sites, but proton-saturated clays are not stable. Proton saturated clays transform spontaneously into mainly aluminium or magnesium saturated clays depending on the approximate proportions of the two elements in the clay structure (Coleman & Craig, 1961; Tiller, 1968). During this weathering trioctahedral 2:1 clay minerals release mainly magnesium or iron, while dioctahedral clays mainly release aluminium. Trioctahedral minerals are the most easily weatherable and will start weathering at less proton activity (higher pH) than dioctahedral species. The composition of the exchange complex consequently indicates cation release due to structural weathering. Therefore 2:1 clay minerals are mainly dioctahedral in old naturally acid soils (Thomas, 1988). Aluminium saturated clays exhibit acid properties (BNC). Released silica may polymerize or be leached (Tiller, 1968). The changes in ANC and BNC following these transformations are also shown in fig.1.

During the weathering oxides of iron and aluminium are precipitated, since they are heavily soluble (pKs($Al(OH)_3$)=32-35 and pKs-($Fe(OH)_3$)=38-44, Lindsay, 1979; Borggaard, 1990). Dissolution of aluminium and iron oxides is negligible above pH 4.5 and pH 3.0 respectively. Below these pH values aluminium and iron oxides are strong proton acceptors. Since, however, aluminium and iron ions are rather strong acids, they are not included in the base properties. The reaction represents acid exchange, where a stronger acid (H^+) replace a weaker acid (Al^{3+} or Fe^{3+}).

The oxides can adsorb anions either by coordinative bond directly to the metal ion followed by release of OH^- or by electrostatic adsorption on protonized surfaces below ZPC (Hingston et al. 1967; Borggaard, 1990). According to several authors (e.g. van Breemen, 1973; Nordstrom, 1982; Prenzel, 1983; von Freiesleben, 1988) the reaction of sulphate with aluminium oxides have been postulated to be due to formation of jurbanite ($AlOHSO_4$). Presently no definite proof exists for the presence of jurbanite in soils. Irrespective of the precise mechanism the overall reaction may be written:

$$Al(OH)_3 + H_2SO_4 \rightarrow AlOHSO_4 + 2H_2O \qquad (13)$$



1) ion exchange

2) structure weathering

3) structure weathering followed by Al-hydroxy-interlayering and decrease in CEC

a) degree of Al release due to structure weathering.

b) factor indicating formation of Al-hydroxy species due to weathering.

Fig. 1. Schematic changes in the base properties (ANC) and the acid properties (BNC) of clay minerals following proton saturation on exchange sites. Base properties are separated between those represented by exchangeable base cations (Me^{2+}, ANC_{exch}), and those represented by structure cations (ANC_{clay}) characterizing weathering.

This neutralization process causes no decrease in ANC, but an increase in soil BNC due to acid properties of $AlOHSO_4$:

$$AlOHSO_4 + 2OH^- \rightarrow Al(OH)_3 + SO_4^{2-} \tag{14}$$

The dissolution process may be written:

$$AlOHSO_4 + H^+ \rightarrow Al^{3+} + SO_4^{2-} + H_2O \tag{15}$$

This process consumes 1 mole acidity from the solution plus 2 mole acidity from the soil and produces 3 mole acidity to the soil solution. The processes involving adsorption and mobilization of aluminium are mainly reported from soils receiving large amounts of acid rain.

Organic acids in the soil can be considered as a metastable phase in the carbon cycle (reaction 3) and their content changes according to net production and mineralization. The organic acids contribute to BNC but can take up metal cations. The metal cations may originate from weathering of soil minerals (Me_2O):

$$R\text{-}(COOH)_2 + Me_2O \rightarrow R\text{-}(COOMe)_2 + H_2O \tag{16}$$

Since, the base properties (ANC) of the base cation saturated organic matter originate from the soil no change in ANC takes place, and since the organic acid is neutralized by weathering there will neither be change in soil acidity. Organic acids accelerate the weathering (Baker, 1973; Lundström & Öhmann, 1990) due to increased acidity and due to complexation of mainly aluminium and iron ions (Petersen, 1976; Stevenson, 1977; Sposito, 1986).

Soil acidification does take place when the organic acids are soluble and cause leaching of base cations. The solubility of the organic acids depends on pH and on complex formation between organic anions and metal ions. Aluminium and iron are particular effective in precipitating organic anions (Petersen, 1976).

A hypothetical case story

The changes in base properties and development of acid properties during soil development may be illustrated by the following hypothetical case story (fig. 2): Consider a freely drained, well aerated soil with an excess of precipitation and containing limestone and various silicate minerals. Free drainage ensures that the partial pressure of carbon dioxide and the concentrations of anions of strong acids remain constant. pH in the soil solution will be about 8.3 as long as free limestone exists in the soil. The most important acid process will be production of carbonic acid. Protons will be neutralized by dissolution of limestone, and the soil will not develop acidity (c in fig. 2). When limestone has been exhausted, protons will associate with the next available proton energy level. That might be easily weatherable silicate minerals (e.g. hornblende, epidote, trioctahedral mica, primary chlorites and calcium containing feldspars), which weather under formation of secondary silicates and oxides and release of base cations. When all limestone is just consumed all exchangeable sites will be saturated by base cations mainly Ca^{2+}. Neutralization processes will simultaneously be ion exchange and regeneration by weathering. If acid production rate exceeds acid neutralization rate the soil starts to develop acid properties and pH decreases (d in fig. 2). This would be the case when easily weatherable minerals are exhausted. As pH decreases the effect of carbonic acid also decreases due to decreasing dissociation. Below pH 4.8 the effect of carbon dioxide is negligible. The relative importance of strong acid and base cation depletion due to biomass harvest is normally small in neutral soils but they can be important in acid soils. Strong acids and biomass utilization are able to exhaust the base properties further, but the decreased weatherability - despite the fact that the weathering rate increases as pH decreases - will increase soil acidity in the form of exchangeable aluminium (e in fig. 2). Adsorption of anions on oxides also increases soil acidity. At severe soil acidity (pH≈4) further production of strong acid will mainly be buffered by exchange reactions with adsorbed aluminium and by dissolution of oxides; and leaching of Al takes place (e in fig. 2). At that point the increase in soil acidity is low since acidity is leached (Wiklander, 1975). Soil acidification will also be low but not insignificant because relatively resistent silicates (eg. primary minerals in the sand fraction, potassium feldspars and dioctahedral mica) weathers (e in fig. 2).

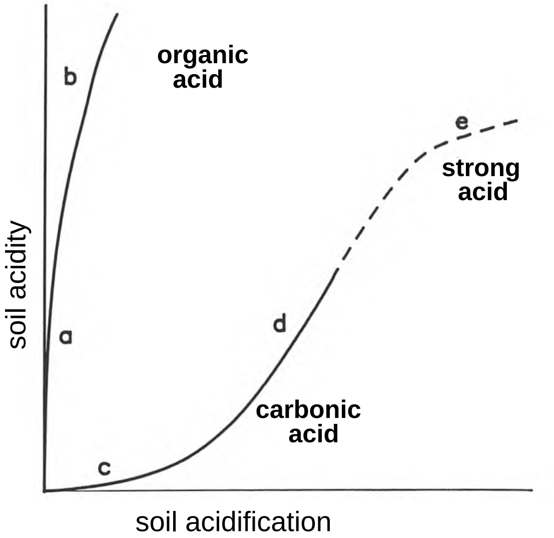


Fig. 2. Effects of organic acids carbonic, and strong acids on soil acidification (decrease in soil base properties) and increase in soil acidity (acid properties), a-e refer to discussion in text.

Together with these processes leading to decrease in the base properties and increase in soil acidity, organic acids will accumulate in the soil (a in fig. 2). On the other hand, organic acids are relatively insoluble and will only cause weak base depletion (b in fig. 2).

In fig. 2 the effect of organic acids and carbonic acid/strong acids are separated which of cause will not be the case in real soils because the two processes proceed simultaneously. On the other hand, which of the processes, base exhausting or organic acid accumulation, will be the most important depend on i) parent material (weatherability of the minerals), ii) organisms (kind of vegetation and decomposers), iii) topography (drainage and erosion), iv) climate (temperature and excess of water), and v) time, i.e. soil forming factors (Jenny, 1941).

The crucial factor for soil acidification and development of soil acidity are the acid production rate in the ecosystem (includes the acid deposition rate), the acid neutralization rate and, in particular, the acid neutralization rate relative to the acid production rate. As long as acid neutralization balances the acid production no development of soil acidity occurs, despite soil acidification might be serious. Excess acid production will cause increase in soil acidity and leaching of acidity as aluminium; and of protons in very acid soils (Wiklander, 1980; Mulder et al., 1989). The most vulnerable soils are soils with low content of weatherable minerals such as many sandy soils.

Acid-base status for five Danish forest soils

To further illustrate the concepts of soil acidity and soil acidification five Danish forest soils will be considered. The evaluation will be based on data by Raulund-Rasmussen (1991). pH and base and acid properties of these soils are shown in fig. 3. The following definitions are used:

ANC_{tot}: the sum of Ca^{2+}, Mg^{2+}, K^+ and Na^+ from total element analysis

ANC_{exch}: the sum of exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ (by use of NH_4NO_3 as exchange agent)

BNC_{tot}: release of protons to pH 8.1 (nitrophenol-nitrophenolate buffer)

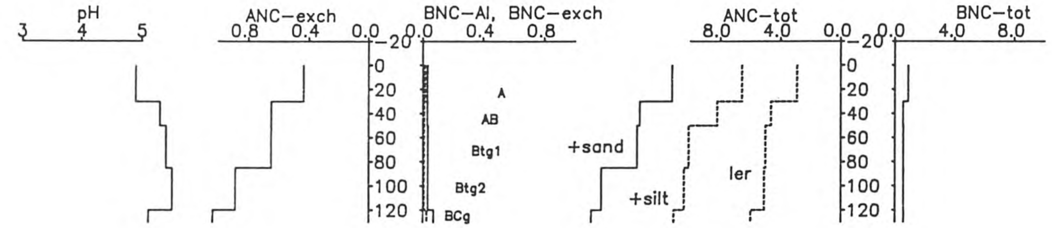
BNC_{exch}: exchangeable acidity at soil pH (titratable acidity released to NH_4NO_3-solution)

BNC_{A1}: exchangeable aluminium at soil pH (by use of NH_4NO_3 as exchange agent)

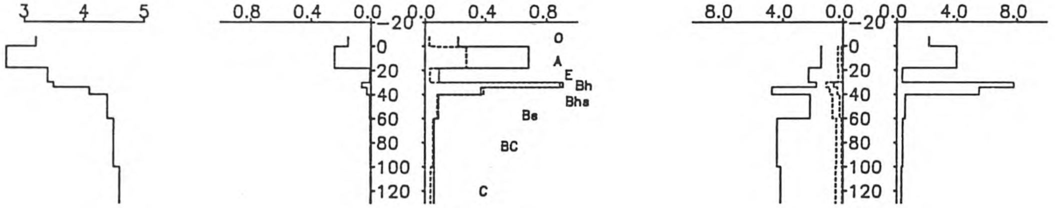
Soil acidification can be estimated either as present rate by flux studies (de Vries & Breuwsma, 1987), or as historical by change in the element composition over time. The soil acidification in the past cannot be estimated exactly in the investigated soils, because the exact composition of the parent material is unknown. However, a relative estimate can be made, if it is assumed that the composition of the C horizon in each profiles represents the parent material, and that no acidification has taken place in the C horizon. Obviously acidification of the C horizons has taken place, but it must be small compared to acidification of the upper horizons.

Under these premises, the increase in ANC_{tot} by increasing depth reflects acidification in the upper horizons. Consequently soil acidification has been strongest at Stenholts Vang followed by Trinderup, whereas it has been low at Ulborg, Lindet and Klosterheden. The decrease in ANC_{tot} the upper horizons clearly reflect ANC_{tot} in the C horizons. However, this relation will only have limited validity because the crucial point is not the total amount of bases, but merely the rate of base release, which depends on the weatherability of the present assemblage of minerals and the exposed surface (Sverdrup, 1990), in relation to the total acid load. Regarding the total acid load during pedogenesis differences between the investigated soils can mainly be attributed to the greater effect of carbon dioxide in Stenholts Vang and to a certain degree in Trinderup, because the greater acid neutralization capability in these soils delay decrease of pH. The substantial content of clay sized minerals in Stenholts Vang (15-20%) might be one of the main causes for the high acid neutralization capability, whereas the low clay contents in Ulborg Lindet and Klosterhede (1-3%) might be one main cause of the low acid neutralization capability in these soils. However, the difference must also be due to difference in ANC_{tot} and

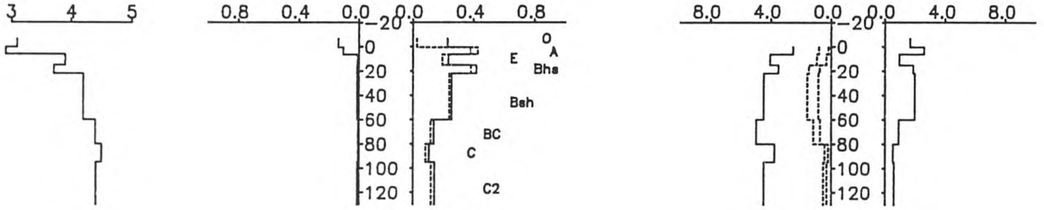
STENHOLTS VANG (*Typic Hapludalf*)



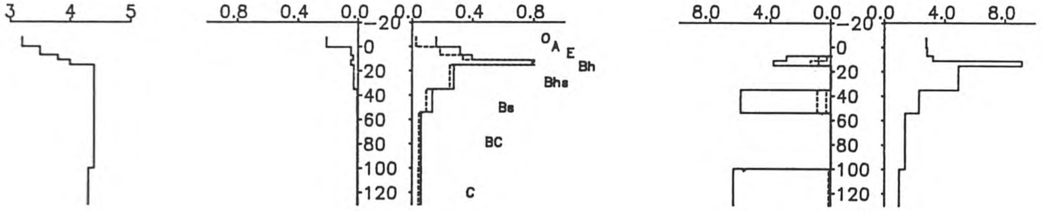
ULBORG (*Typic Haplohumod*)



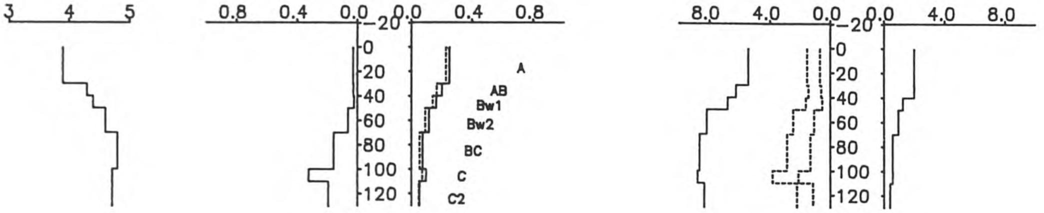
LINDET (*Typic Udipsamment)*



KLOSTERHEDE (*Typic Haplorthod)*



TRINDERUP (*Psammentic Haplumbrept)*



mineralogical composition. The Stenholts Vang and Trinderup soils are probably the youngest, but differences in time of pedogenesis of the five soils does not contribute to the explanation of these results.

Determination of accumulated acidity in the soils is possible, because it can be assumed that BNC of the basic materials is zero. Thus soil acidity shows an opposite pattern than soil acidification: BNC_{tot} is lowest in Stenholts Vang and highest in Ulborg and Klosterhede. Obviously accumulation of soil acidity takes place when acid neutralization is reduced due to low weatherability. Although soil acidity decreases with increasing depth, the two spodosols (Ulborg and Klosterhede) have also accumulated severe acidity in the spodic horizons.

Regarding the exchangeable base properties, Stenholts Vang and Trinderup show increasing ANC_{exch} with depth, whereas the opposite is seen in Lindet, Ulborg and Klosterhede. At least three factors might be responsible for this difference: i) the exchangeable base cations are related to the exchange properties of clays and organic matter; ii) biocycling of the elements results in uptake from the root zone and return of these elements to the soil surface; iii) the acid production takes place in the upper horizons and neutralization will, if occurring, therefore mainly be there. In the three sandy soils (Lindet, Klosterhede and Ulborg) most exchangeable base cations are concentrated in the upper most layers indicating the importance of biocycling, and the fact that the CEC is totally dominated by organic matter. In contrast, in Stenholts Vang and Trinderup the base properties seem sufficient to bring about mineralization, and ANC_{exch} therefore reflects the clay content and the acid neutralization capability.

In most horizons exchangeable aluminium (BNC_{A1}) accounts for nearly all exchangeable acidity (BNC_{exch}) in agreement with the fact that proton saturated minerals are unstable and transform to be aluminium saturated, if complete neutralization does not take place (fig. 1). The O, A and E horizons in Lindet, Ulborg and Klosterheden are important exceptions. The soil acidity in these horizons is mainly due to accumulation of organic acids because of low weatherability of the minerals and high production rate of organic acids.

Fig. 3. pH (in 0.01 M $CaCl_2$ and base- and acid properties (se definitions in text) of five Danish forest soils. Units for ANC's and BNC's are cmol m^{-2} cm $depth^{-1}$

pH in the three sandy soils (Lindet, Ulborg and Klosterhede) exhibits a similar patterns: In the upper horizons containing relative large amounts of relatively strong organic acids pH is about 3.0, increasing with increasing depth to about 4.4 - 4.6 indicating aluminium buffering in the B and C horizons. In Stenholts Vang pH is about 5.0-5.5 in agreement with the larger acid neutralization capability and consequently higher degree of acid neutralization. Trinderup is intermediate between the sandy soils and Stenholts Vang.

Usually pH is correlated to the degree of base saturation depending on the type of clay minerals and the organic matter (Jensen, 1936; Peech, 1941; Mehlich, 1941). If only soil horizons with pH above 4.5 are considered there appears to be an approximately linear relationship between pH and base saturation (fig. 4). At pH values below 4.5 there is no correlation, for instance O and A horizons with organic matter of the moor type with pH about 3.0 have base saturations between 5 and 10 %. This is possible only if the acids are quite strong. In accordance Raulund-Rasmussen (1989) found that pH in the O horizon of a Danish spodosol was unaffected about 2.8 after a 62 % reduction of the base cation content due to artificial acid rain.

Summarizing, the five investigated soils exhibit clear differences in acid and base properties (fig. 5). The Stenholts Vang soil both has the largest content of bases and a significant weathering rate as indicated by loss of ANC_{tot} in the upper horizons. The increase in soil acidity is consequently rather low. In contrast the three sandy soils exhibit low soil acidification and high increase in soil acidity. The Trinderup soil is intermediate.

A main cause of the higher content of acidity

(BNC_{Al}, BNC_{exch}, BNC_{tot} and low pH) in the three sandy soils is undoubtedly caused by the low weathering rate, but also the dense conifer stands covering these soils (Norway spruce, Scots pine). Conifers are characterized by a high production rate of very resistant organic matter. The Stenholts Vang soil is under Beech and Trinderup is under a very open Norway spruce stand with herbaceous ground flora. However, it is hardly possible to estimate the relative importance of vegetation and of weathering rate, because they mutually affects each other. A better understanding of these effects and the acid base processes involved is mandatory for evaluating the effect of natural processes and of acid rain, as well as the effects of management of the forest, on soil acidification and development of soil acidity; and consequently soil fertility.

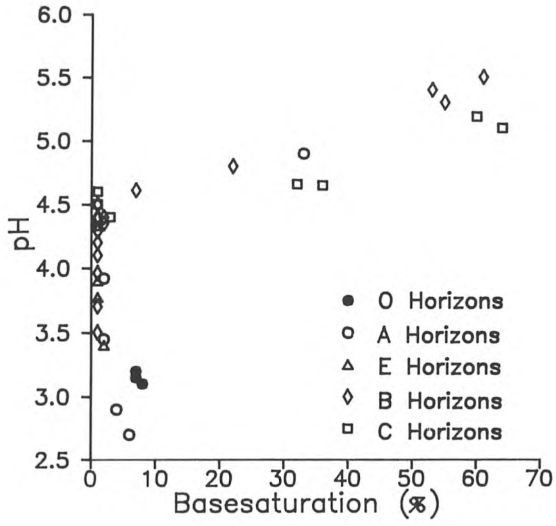


Fig. 4. Soil pH (in 0.01 M $CaCl_2$) as function of percent base saturation

$$\left(\frac{ANC_{exch} \cdot 100}{ANC_{exch} + BNC_{tot}} \right)$$

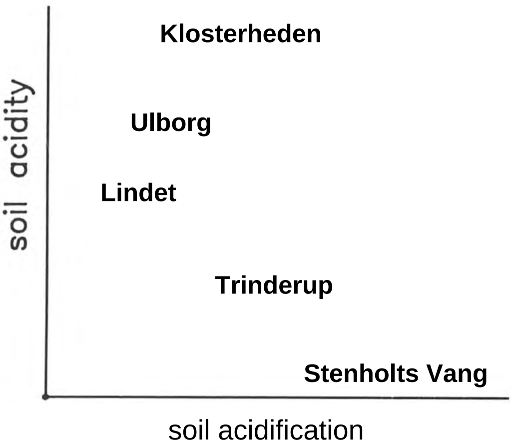


Fig. 5. Relative placement of five Danish forest soils according to soil acidification (decrease in ANC) and increase in soil acidity (BNC). The placement is based on fig. 3 and discussion in text.

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References

Baker, W.E. (1973): The role of humic acids from Tasmanian podzolic soils in mineral degradation and metal mobilization. Geochemica et Cosmochemica Acta, 37: 269-81.

Bjerrum, N. & Gjaldbæk, J.K. (1919a): Undersøgelser over de faktorer, som bestemmer jordbundens reaktion. I. Om bestemmelse af en jords sure eller basiske egenskaber. Den Kongelige Veterinær- og Landbohøjskole Aarsskrift: 48-64.

Bjerrum, N. & Gjaldbæk, J.K. (1919b): Undersøgelser over de faktorer, som bestemmer jordbundens reaktion. II. Om reaktionen af vædsker, som er mættet med kalciumkarbonat. Den Kongelige Veterinær- og Landbohøjskole Aarsskrift: 64-91.

Borggaard, O.K. (1990): Dissolution and adsorption properties of soil iron oxides. Thesis. DSR, Copenhagen, 122pp.

Coleman, N.T. & Craig, D. (1961): The spontaneous alteration of hydrogen clay. Soil Science, 91: 14-18.

de Vries, W. & Breeuwsma, A. (1987): The relation between soil acidification and element cycling. Water, Air, and Soil Pollution, 35: 293-310.

Hingston, F.J.; Atkinson, J.; Posner,A.M. & Quirk, J.P. (1967): Specific adsorption of anions. Nature, 215: 1459-61.

Hovmand, M. & Petersen, L. (1984): Forsuringsprojektet: Jordbundsforsuring. Miljøstyrelsen, Miljøministeriet, Copenhagen, 89pp.

Jenny, H. (1941): Factors in soil formation. A system of quantitative pedology. McGraw-Hill Book Company, Inc., New York and London, 281pp.

Jensen, S.T. (1936): Kalkens omsætninger i jordbunden, teoretisk og eksperimentelt belyst. Tidsskrift for Planteavl, 41: 571-649.

Kriebietzsch, W.-U. (1978): Stickstoffnachlieferung in sauren Waldböden Nordwestdeutschlands. Scripta Geobotanica, XIV: 66pp.

Krug, E.C. & Frink, C.R. (1983): Acid rain on acid soil: A new perspective. Science, 221: 520-24.

Lindsay, W.L. (1979): Chemical Equilibria in soils. John Wiley & Sons, New York, 499pp.

Lundström, U. & Öhman, L.-O. (1990): Dissolution of feldspars in the presence of natural organic solutes. Journal of Soil Science, 41: 359-69.

Mehlich, A. (1941): Base unsaturation and pH in relation to soil type. Soil Science Society of America, Proceedings, 6: 150-56.

Miles, J. & Young, W.F. (1980): The effects on heathland and moorland soils in Scotland and Northern England following colonization by birch (Betula ssp). Bulletin d'Ecologie, 11: 233-42.

Mulder, J.; van Bremen, N. & Eijck, H.C. (1989): Depletion of soil and implications for acid neutralization. Nature, 337: 247-49.

Nielsen, K.E.; Dalsgaard, K. and Nørnberg, P. (1987): Effects on soils of an oak invasion of a calluna heath, Denmark. II. Changes in organic matter and cellulose decomposition. Geoderma, 41: 97-106.

Nordstrom, D.K. (1982): The effect of sulfate on aluminium concentrations in natural waters: som stability relations in the Al_2O_3-SO_3-H_2O at 298 K. Geochemica et Cosmochemica Acta, 46: 681-92.

Ovington, J.D. (1953): Studies of the development of woodland conditions under different trees. I. Soils pH. Journal of Ecology, 41: 13-34.

Ovington, J.D. (1954): Studies of the development of wood land conditions under different trees. II. The forest floor. Journal of Ecology., 42: 71-80.

Peech, M. (1941): Avalability of ions in light sandy soils as affected by soil reaction. Soil Science, 51: 473-86.

Petersen, L. (1976): Podzols and podzolization. Thesis. DSR, Copenhagen, 293pp.

Prenzel, J. (1983): A mechanism for storage and retrieval of acid in acid soils. In. Ulrich, B. & Pankrath, J. (Eds.). Effects of accumulation of air pollutants in forest ecosystems. Reidel Publishing Company, Dordrecht, Holland, 157-70.

Rasmussen, X (1961): Uorganiske svovlforbindelsers omsætninger i jordbunden. Thesis, DSR., Copenhagen, 176 pp.

Raulund-Rasmussen, K. (1989): Effect of artificial acid rain and liming on the base status in an acid forest (Picea Abies (L.), Karst.) soil (Typic Haplohumod). Scandinavian Journal of Forest Research, 4: 417-25.

Raulund-Rasmussen, K. (1991): Pedological and mineralogical investigations of five Danish forest soils. In preparation.

Raulund-Rasmussen, K. & Larsen, J.B. (1990): Jordbundsforsuringens årsager og virkninger i skove - med særlig henblik på effekten af luftforureningen og skovdyrkningspraksis. Dansk Skovbrugs Tidsskrift,75:1-41.

Rosenquist, I.T. (1977): Sur jord surt vann. Ingeniørforlaget, Oslo, Norway, 123pp.

Smeck, N.E.; Runge, E.C.A. & Mackintosh, E.E. (1983): Dynamics and genetic modelling of soil systems. In: Wilding, L.P.; Smeck, N.E. & Hall, G.F. (eds). Pedologenesis and soil taxonony. I. Concepts and interactions. Developments in soil science 11A, Elsevier, Amsterdam-Oxford-New York, 51-81.

Sposito, G. (1986): Sorption of trace metals by humic materials in soils and natural waters. Critical Reviews in Environmental Control, 16: 193-229.

Stevenson, F.J. (1977): Binding of metal ions by humic acids. Environmental Biogeochemistry, 2: 519-40.

Stumm, W. & Morgan, J.J. (1981): Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters, 2nd edition. John Wiley & Sons, New York, 780pp.

Sverdrup, H. (1990): The kinetics of base cation release due to chemical weathering. Lund University Press, Lund Sweden, 246pp.

Thomas, G.W. (1988): Beyond exchangeable aluminium: Another ride on the Merry-Go-Round. Communications in Soil Science and Plant Analysis, 19: 833-57.

Tiller, K.G. (1968): Stability of hectorite in weakly acidic solutions. I. A chemical study of the dissolution of hectorite with special reference to the release of silica. Clay Minerals, 7: 245-59.

Ulrich, B. (1989): Effects of acidic precipitation on forest ecosystems in Europe. In. Adriano, D.C. & Johnson, A.H. (eds): Acidic precipitation, Vol 2. Biological effects. Springer Verlag, New York, 188-272.

van Breemen, N. (1973): Dissolved aluminium in acid sulfate soils and in acid mine waters. Soil Science Society of America, Proceedings, 37: 694-97.

van Breemen, N. & van Dijk, H.F.G. (1988): Ecosystem effects of atmospheric deposition of nitrogen in the Netherlands. Environmental Pollution, 54: 249-72.

van Breemen, N. & Wielemaker, W.G. (1974a): Buffer intensities and equilibrium pH of minerals and soils: I. The contribution of minerals and aqueous carbonate to pH buffering. Soil Science Society of America, Journal, 38: 55-60.

van Breemen, N. & Wielemaker, W.G. (1974b): Buffer intensities and equilibrium pH of minerals and soils: II. Theoretical and actual pH of minerals and soils. Soil Science Society of America, Journal, 38: 61-66.

van Breemen, N.; Mulder J. and C.T. Driscoll (1983): Acidification and alkalinization of soils. Plant and Soil, 75: 283-308.

von Freiesleben, N.E. (1988): Sulfate mobility in an acid Danish forest soil. Journal of Environmental Quality, 17: 278-84.

Wiklander, L. (1975): The role of neutral salts in the ion exchange between acid precipitation and soil. Geoderma, 14: 93-105.

Wiklander, L. (1980): The sensitivity of soils to acid precipitation. In. Hutchinson, T.C. & Havas, M. (Eds). Effects of acid precipitation on terrestical ecosystems. Nato conference series. Serie I: Ecology vol 4. Plenum Press, New York and London: 553-69.

Zoettl, H. (1960): Dynamik der Stickstoffmineralisation im Organischen Waldbodenmaterial, III. pH-wert und Mineralstickstoffnachliefeung. Plant and Soil, 13: 207-23.

Iron Oxides and Organic Matter in Danish Spodosols in relation to Phosphate Adsorption

Ole K. Borggaard and Birgitte Raben-Lange

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This cursory review describes occurrences and nature of iron oxides and organic matter as well as the influence of organic matter on phosphate adsorption by iron oxides in Danish Spodosols. Ferrihydrite in association with organic matter and goethite are the commonly occurring iron oxides. Organic matter stabilizes ferrihydrite with high specific surface area leading to high phosphate adsorption capacity. Organic matter may compete with phosphate for adsorption sites, but the measured effects are very small.

Keywords: *fulvic acid, humic acid, ferrihydrite, goethite, phosphate adsorption capacity.*

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Iron oxides (including all iron compounds of the Fe_2O_3-H_2O system) and organic matter (including humin, fulvic acid, and humic acid) are common products of soil formation and occur in almost all soils. They are easily recognized in soils because they determine, by the Munsell Color Chart notation, the yellow to red hues (iron oxides) and the brown to black values (organic matter) of soils. Due to their high specific surface areas and functional surface groups iron oxides and organic matter are highly reactive, often affecting chemical and physical soil properties decisively (Stevenson, 1982; Aiken et al. 1985; Schwertmann, 1988; Borggaard, 1990).

Various interactions between iron oxides and organic matter such as the inhibitory effects of organic matter on iron oxide formation or crystal growth and the effect of iron oxides on organic matter mobility and decomposition have been reported (Schwertmann et al., 1986). Spodosols, particularly their A and Bh/Bhs horizons, offer favourable conditions for studying these effects. The interactions may be expected to be strong in Bh/Bhs but limited in the A horizons, according to the prevailing concept of Spodosol formation. To identify and quantify these interactions several chemical and instrumental techniques can be used including selective dissolution, Mössbauer spectroscopy, X-ray diffraction, and NMR spectroscopy (Wilson, 1987; Borggaard, 1988; Schwertmann, 1988; Schwertmann & Murad, 1988; Steelink et al., 1989). A combination of such techniques with phosphate adsorption studies appears particularly suited (Sibanda & Young, 1986; Borggaard et al., 1990; Jørgensen & Borggaard, 1991). On the other hand, information about interactions is needed for estimating socalled critical phosphate loads in order to establish guidelines for optimal phosphate fertilization without causing environmental adverse effects (pollution) due to phosphate leaching (Jørgensen & Borggaard, 1991).

In Denmark Spodosols mainly occur in the southwestern and western parts of Jutland and comprise Humods and Orthods formed on sandy deposits from the Saale and Weichsel Glaciations or aeolian sand (Petersen, 1976; Møberg et al., 1988; Borggaard et al., 1990). In such soils the main phosphate adsorbents are aluminium and iron oxides, which are concentrated in the Bh, Bhs, and Bs horizons (Parfitt, 1978; Borggaard, 1986; Borggaard et al., 1990; Jørgensen & Borggaard, 1991).

This cursory review describes iron oxides and organic matter in selected Danish Spodosols (Humods and Orthods) and demonstrates the influence of organic matter on phosphate adsorption by iron oxides. It is also attempted to elucidate interactions between iron oxides and organic matter and to estimate the importance of such interactions on phosphate behaviour in Spodosols. The review is primarily based on results obtained during recent investigations in this laboratory.

Spodosol formation

In the following, formation of Spodosols will be outlined briefly because this mode of formation is reflected in soil compounds such as iron oxides and organic matter. The organic complex concept seems to offer the most plausible explanation for Spodosol formation (Petersen, 1976; Buurman & Van Reeuwijk, 1984; McKeague et al., 1986). According to this concept, negatively charged, water-soluble organic compounds formed in sandy, base-cation-depleted (acid) topsoils under cold humid climatic conditions take up aluminium and iron from inorganic soil components such as the oxides when moving downwards with percolating water. Increasing uptake of aluminium and iron results in a gradual reduction of the negative charge of the organic compounds until they are saturated with aluminium and/or iron. At this stage mutual precipitation of aluminium/iron and organic matter occurs. Continued leaching and production of organic compounds with varying composition with regard to molecular weight and functionalities result in the formation of various spodic subhorizons (Bh, Bhs, Bs) and the gradually descending of the spodic horizon.

The crucial feature of this concept is the translocation of aluminium and iron in the form of organic complexes. Accordingly, Petersen (1976) and McKeague et al. (1986) pointed out the capacity of organic matter to form complexes with aluminium and iron. A recent investigation employing sensitive spectroscopic methods was, however, unable to show complex formation between iron and organic matter (Goodman, 1988).

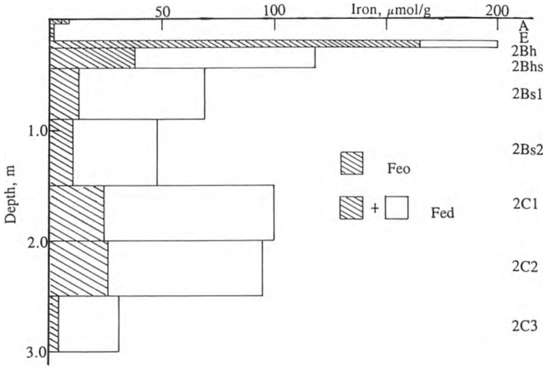

Fig. 1. The distribution of oxalate(Feo)- and dithionite-citrate-bicarbonate(Fed)-extractable iron in the Galtlund (Haplorthod) soil.

Rather than complexes sensu stricto iron and organic matter seem to form associations. Thus ferrihydrite and goethite have been identified in extracts from Spodosols (McBride et al., 1983; Kassim et al., 1984) indicating the occurrence of clusters of iron oxides embodied in organic matter.

Iron oxides

According to the Spodosol formation concept increased amounts of iron should occur in the spodic horizon. This is reflected in fig. 1, particularly by oxalate-extractable iron (Feo). Although the iron content in this soil (Galtlund) is higher than in most Danish Spodosols, the distribution pattern is similar to that observed in many other profiles (Petersen, 1976; Jørgensen & Borggaard, 1991; Møberg et al., unpublished results). Dithionite-citrate-bicarbonate (DCB)-extractable iron (Fed) also exhibited a maximum in the spodic horizon but substantial amounts of iron were extracted by this method from the C horizons.

Fed is considered to be a fair estimate of the total amount of pedogenic iron oxides, whereas Feo includes only poorly crystalline and organic matter-associated iron oxides (Borggaard, 1988). The difference between Fed and Feo is considered to represent crystalline iron oxides.

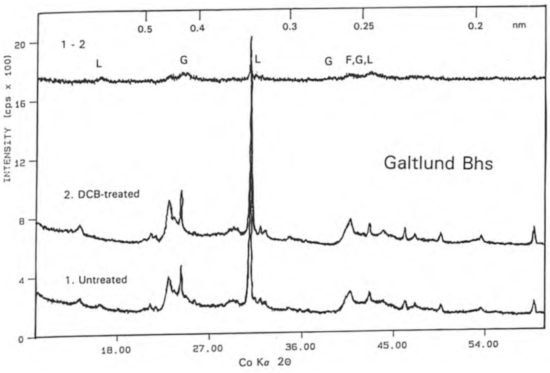

Fig. 2. X-ray diffraction patterns for untreated (1) and DCB-treated (2) clay from the Bhs horizon from the Galtlund soil (Haplorthod) and the difference X-ray diffraction pattern (1-2). F: ferrihydrite; G: goethite; L: lepidocrocite.

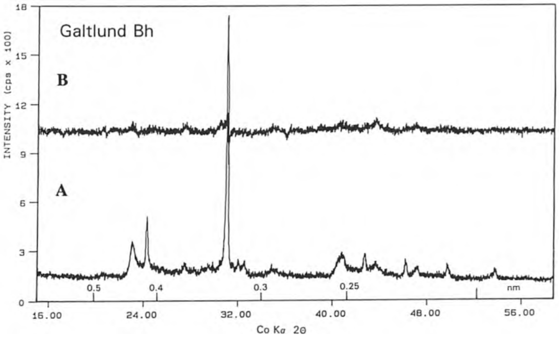

Fig. 3. X-ray diffraction pattern for untreated clay (A) from the Bh horizon from the Galtlund soil (Haplorthod) and the difference X-ray diffraction pattern (B) between untreated and DCB-treated clay.

Organic matter-associated iron oxides are often estimated by the pyrophosphate method but due to reproducibility problems and uncertainties about the dissolution mechanism, it may be preferable to use Feo alone (Borggaard, 1988; Parfitt & Childs, 1988). In fact, similar amounts of iron have often been extracted by oxalate and pyrophosphate from Danish Spodosols, particularly from their spodic horizons (Jørgensen & Borggaard, 1991; Møberg et al., unpublished results). Various selective dissolution techniques including the above-mentioned have been reviewed by Borggaard (1988) and Parfitt and Childs (1988).

The mineralogy of the iron oxides can be assessed by X-ray diffraction analysis (XRD), particularly by differential XRD showing the difference between XRD patterns before and after selective dissolution of iron oxides (Schwertmann et al., 1982). However, iron oxide concentrations in whole soil samples are often too low for XRD determination, but due to their small particle size they are concentrated in the clay fraction. Figs. 2 and 3 show the XRD patterns for the untreated and DCB-treated clay fractions from the Galtlund Bhs and Bh horizons together with the differential XRD patterns (difference between untreated and DCB-treated clay). The clay was isolated by means of a particle size centrifuge after hydrogen peroxide treatment to remove organic matter and ultrasonic dispersion, as described by Jørgensen & Borggaard (1991). XRD was also carried out on the clay fractions from the Bs1 and C1 horizons.

The clay fractions are seen to be dominated by quartz, feldspars, and 2:1 layer silicates, but in addition the Bhs clay fraction also contained the crystalline iron oxides, goethite and lepidocrocite. This is most clearly shown in the differential XRD (fig. 2) by small but distinct peaks indicative of these minerals. In contrast, no crystalline iron oxides could be identified in the Bh sample (fig. 3). The differential XRD only exhibited a very broad hump around 0.25 nm, even though DCB removed 14.5% of iron. According to Schwertmann et al. (1982) even ferrihydrite should be identifiable by differential XRD in samples, when ≈ 10% of iron can be removed by selective dissolution. This indicates that the iron oxides in the Bh horizon are very poorly ordered. Probably, they resemble socalled 2-line ferrihydrite, which may be formed in a peaty environment (Schwertmann & Murad, 1988). Similarly, poorly ordered iron oxides were found in both the Bh and Bhs horizons of another Danish Orthod (Jørgensen & Borggaard, 1991). In those horizons Feo≈Fed, whereas in the Galtlund Bhs horizon, where crystalline iron oxides were identified, Fed > Feo (fig. 1). Goethite was the only iron oxide that could be identified by XRD in the Galtlund Bs1 and C1 horizons, also exhibiting substantial Fed-Feo differences (fig. 1). This suggests that Feo and Fed-Feo may be considered estimates of poorly ordered and crystalline iron oxides, respectively in these Spodosols in agreement with their interpretation in other soils and soil materials (Schwertmann et al., 1982; Borggaard, 1988, 1990; Parfitt & Childs, 1988). This is a fortuitous situation, since selective dissolution techniques are inexpensive and simple, and they can determine iron oxide concentrations much lower than can be detected by instrumental techniques such as XRD (Borggaard, 1988).

Therefore, considering Feo and Fed (fig. 1) it may be seen that only poorly crystalline iron oxides are present in the A and E horizons and dominate in the Bh horizon. In the Bhs, Bs, and C horizons most iron oxides are crystalline. The very small iron oxide contents in the A and E horizons compared to the other horizons can be ascribed to different parent materials; the A and E horizon being formed in aeolean sand but the other horizons in Saale till. In another Orthod, where the iron contents (Fed) in the A, Bh, and Bhs horizons were of similar magnitude, the A horizon contained appreciable amounts of crystalline iron oxides and the Bh, Bhs, and even Bs1 horizons were strongly dominated by poorly crystalline iron oxides (Jørgensen & Borggaard, 1991). Similar patterns have been found in other Danish Spodosols (Møberg et al., unpublished results), showing crystalline iron oxide occurrence in A and E horizons except where the iron oxide contents were very low. This indicates limited suppression of iron oxide development in the A and E horizons in contrast to spodic horizons, particularly Bh horizons.

Organic matter

The organic matter exhibited a maximum in the Bh horizon (table 1) and closely matched Feo distribution in the Galtlund soil (fig. 1) in agreement with the Spodosol formation concept. Similar distributions have been found in other Danish Spodosols (Petersen, 1976; Jørgensen & Borggaard, 1991). Table 1 also shows the contents of fulvic acid (FA) and humic acid (HA) in the A and Bh horizons. These acids were extracted by sodium hydroxide and HA was precipitated by acidification of the extract with hydrochloric acid. Total organic carbon (TOC) determination before and after hydrochloric acid addition gave the sum (FA+HA) and FA, respectively. HA was purified by combined treatments with hydrofluoric acid and hydrochloric acid and used for further analyses. HA isolation and purification procedures were according to the recommendation of the International Humic Substance Society.

Soil/horizon/ depth (cm)	% C	% HA	% FA
Galtlund			
A(0-5)	3.09	36	13
E (5-20)	0.57		
2Bh (20-25)	3.36	45	25
2Bhs (25-45)	0.88		
2Bs1 (45-90)	0.27		
2Bs2 (90-150)	0.14		
Lundgård			
Ap (0-35)	2.95	47	14
Bh (35-50)	1.76	67	29
Bs (50-90)	0.33		
C1 (90-105)	0.24		
C2 (105-120)	0.20		
2Cx (120-125)	0.25		

Table 1. The distribution of organic matter in soils from Galtlund (Haplorthod) and Lundgård (Fragihumod) and the relative contents of humic acid (HA) and fulvic acid (FA) in total organic matter.

More organic matter could be extracted (FA+HA) from the Bh horizons than from the A horizons (table 1). Furthermore, the FA/HA ratio was considerably higher in Bh than in A horizons. Relatively high extractabilities and FA/HA ratios of organic matter in Bh horizons in agreement with the Spodosol formation concept have been found in other Danish Spodosols (Borggaard, 1974; Nielsen et al., 1987).

Some properties of HA from A and Bh horizons in the two Spodosols are shown in table 2. All four samples had the same carbon contents,

	Galtlund		Lundgård	
	A	Bh	Ap	Bh
% C	53.5	53.1	53.6	52.2
% N	2.58	2.08	2.96	1.52
% ash	0.41	0.75	0.91	1.06
CEC, pH 7.8 meq/gC	7.7	9.4	6.7	9.5
E_4/E_6	4.87	6.23	5.29	6.75

Table 2. Some characteristics of humic acid isolated from A and Bh horizons from the Galtlund (Haplorthod) and Lundgård (Fragihumod) soils.

whereas the nitrogen contents in the Bh horizons, particularly from the Humod (Lundgård), were lower than in the A horizons, in agreement with previous observations (Borggaard, 1974; Nielsen et al., 1987). The cation exchange capacities (CEC) determined by titration to pH 7.8 (the most pronounced inflection point on the titration curve) of HA from the two Bh horizons were equal but substantially higher than CEC of HA from the A horizons. Slightly higher values were obtained for HA extracted by EDTA from another Danish Spodosol (Borggaard, 1974). The discrepancy is presumeably due to different extractants. HA from the Bh horizons exhibited higher E_4/E_6 ratios than HA from the A horizons (table 2). FA and HA are often characterized by this ratio, which is the ratio between absorbances at 465 nm and 665 nm of HA dissolved in 0.05 M sodium bicarbonate and it reflects particle size (molecular weight) and contents of oxygen and carboxyl groups (Chen et al., 1977). The higher E_4/E_6 ratios found for HA from the Bh horizons are therefore in good agreement with their higher CEC, suggesting HA from Bh horizons to be more oxidized (lower particle size, higher carboxyl content) than HA from the corresponding A horizons.

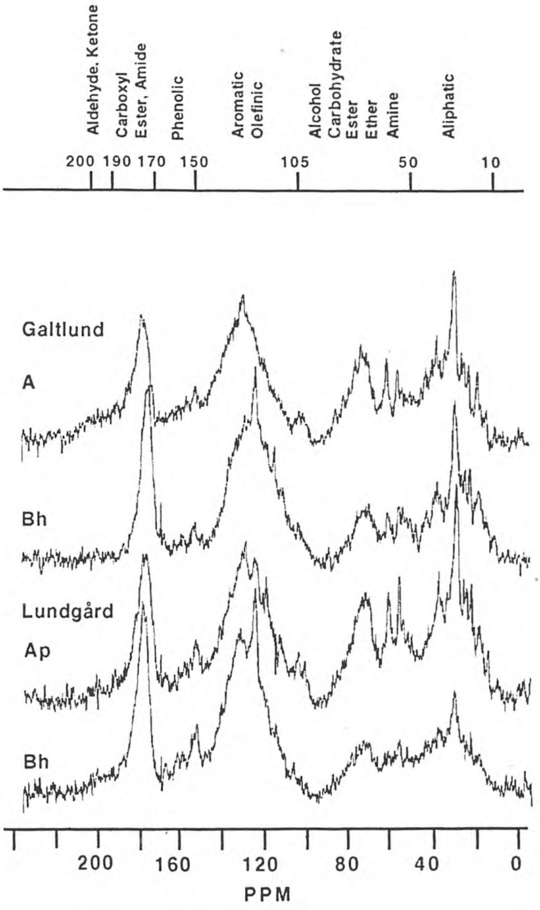

Fig. 4. Proton-decoupled ^{13}C-NMR spectra of humic acid from Galtlund (Haplorthod) and Lundgård (Fragihumod) A and Bh horizons recorded at 62.9 MHz. 150 mg humic acid per ml of 1M NaOD, 5 mm probe head, 50000 accumulated scans, line broadening 20 Hz, polynomial baseline correction.

The ^{13}C-NMR spectra of the four HA samples are shown in Fig. 4. Typical resonance regions are also shown for carbon in various environments, e.g. aliphatic carbon (10-50 ppm), aromatic carbon (105-170 ppm), and carboxyl carbon (170-190 ppm) (Wilson, 1987; Steelink et al., 1989). Due to the non-quantitative performance of the analysis, peak areas are not strictly proportional to the number of carbon atoms in the different environments (Steelink et al., 1989). Qualitatively, however, these spectra can give very useful information. Thus, HA from the A horizons contained more aliphatic and carbohydrate carbon than HA from the Bh horizons, particularly from the Lundgård soil. The difference in aliphatic carbon in the two samples from the Bh horizons may be due to different biological origin of the organic material in the two soils, since the Lundgård soil is a cultivated soil (neutral pH) and Galtlund is an acid soil with a pine forest vegetation.

The ratio between aromatic and aliphatic carbon increased from A to Bh horizons but also the band shape changed, as shown by the peaks at 130 and 126 ppm, respectively (fig. 4). This band shift to lower ppm indicates more protonation of aromatic carbon in Bh than in A samples. Furthermore, compared to the A horizon samples HA from the Bh horizons contained more carboxyl carbon, as shown by the stronger signals at 180 ppm. This is in good agreement with the higher CEC of the Bh samples (table 2).

Adsorption

Synthetic samples of 2-line ferrihydrite and goethite, the commonly occurring iron oxides in Danish Spodosols, were used as adsorbents in an investigation of adsorption of organic matter (FA, HA) and phosphate, alone and in combination (Raben-Lange et al., unpublished results). Suspensions of 1 mg ferrihydrite or 2 mg goethite per ml of 0.2 M sodium chloride containing 0-115 (130) mg C/l as FA (HA) and 0-1.6 mM K_2HPO_4, were shaken (equilibrated) for 6 days at pH 5.0. HA was used as described in the previous section, whereas FA was purified by means of the resin XAD 7 as described by Gregor and Powell (1986). After centrifugation and membrane filtration (0.45 μm) organic matter and phosphate concentrations were determined by TOC and the molybdenum blue method, respectively. Adsorbed organic matter and phosphate were taken as the difference between organic matter and phosphate concentrations before and after shaking with the iron oxides. Isotherms, showing adsorbed organic matter or phosphate versus solution concentrations, were recorded.

Using phosphate alone as adsorbate, plateaux were reached on the isotherms (socalled high-affinity isotherms; Parfitt, 1978), whereas with FA or HA as adsorbates isotherms were still slightly increasing at the highest solution concentrations. To allow for comparison, results in table 3 for organic matter correspond to adsorption at a solution concentration of 30 mg C/l. Similar or higher (up to ≈130 mg C/l) organic matter concentrations were found in soil solutions from another Danish Humod (Raulund-Rasmussen, 1989).

Comparable amounts of phosphate were adsorbed by the two iron oxides (table 3) and the figures are in good agreement with previously reported results (Borggaard, 1983, 1986). The investigations showed phosphate adsorption to be a linear function of the surface area of the iron oxides independent of iron oxide mineralogy (Borggaard, 1983, 1986). In contrast, goethite is seen to adsorb much more organic matter, particularly HA, than ferrihydrite. The specific surface areas of ferrihydrite and goethite were 264 m^2/g and 76 m^2/g, respectively, indicating that the amount rather than the surface area determines organic matter adsorption by iron oxides, as suggested by Jardine et al. (1989). Furthermore, while ferrihydrite adsorbed more FA than HA, goethite did the reverse. Similarly, iron oxide minerals were found to adsorb different amounts (mg/m^2 or mg/g) of organic matter isolated from natural waters (Tipping, 1981 a,b). Thus, phosphate adsorption seems independent of the iron oxide mineralogy, whereas organic matter adsorption seems to depend on the mineral form of the iron oxides.

According to Parfitt (1978) and Tipping (1981a) FA, HA, and phosphate are adsorbed by the same mechanism, i.e. by ligand exchange, suggesting competition for adsorption sites between organic matter and phosphate when present together. Phosphate adsorption by goethite was markedly reduced in the presence of high concentrations of organic matter, especially FA at low pH (Sibanda & Young, 1986). But organic matter in concentrations comparable to those found in soil solutions only reduced phosphate adsorption by 10-14% for goethite and <5% for ferrihydrite (Raben-Lange et al., unpublished results). Obviously, the reduction depends on organic matter concentration, whether FA or HA, pH, and iron oxide mineralogy.

The competitive effect of phosphate on organic matter adsorption was more pronounced, particularly by goethite. For example, 0.1-0.01 mM phosphate reduced organic matter adsorp-

	Ferrihydrite	Goethite
Galtlund		
FA, Bh	0.21	0.38
HA, A		0.61
HA, Bh	0.16	0.70
Lundgård		
FA, Bh	0.22	0.38
HA, Ap	0.16	0.57
HA, Bh	0.12	0.49
Phosphate	4.28	2.99

Table 3. Amounts of organic matter and phosphate adsorbed by synthetic ferrihydrite and goethite, expressed as mg C/m^2 and μmol P/m^2. Adsorbed phosphate was read at the isotherm plateau and adsorbed organic matter at a 30 mg C/l solution concentration. The fulvic and humic acids were from the indicated Galtlund (Haplorthod) and Lundgård (Fragihumod) soil horizons.

tion to 20-50% of that without phosphate (Tipping, 1981a; Raben-Lange et al., unpublished results). However, adsorption of organic matter and of phosphate were not additive; it did not occur according to number of adsorption sites only. More were adsorbed, when the two adsorbates were mixed than when used separately (Raben-Lange et al., unpublished results). For example, from mixtures of FA and phosphate goethite adsorbed 0.15 mg C/m^2 + 2.8 μmol P/m^2 and ferrihydrite adsorbed 0.12 mg C/m^2 + 4.0 μmol P/m^2. These results may be compared with those shown in table 3.

Although these results show that organic matter due to its carboxyl groups may compete with phosphate for adsorption sites on iron oxides (and vice versa), mechanisms other than ligand exchange (Parfitt, 1978; Tipping, 1981a) should also be considered. An additional mechanism for organic matter adsorption could be physical adsorption due to hydrophobic interactions or adsorption on different sites (Earl et al., 1979; Jardine et al., 1989). However, the results may also be explained if only a fraction of the carboxyl groups is adsorbed by the iron oxides as suggested by Tipping (1981b). Presumably, only organic matter having two or more carboxyl groups at neighbouring carbon atoms can compete with phosphate, since citrate and tartrate but not acetate were found to reduce phosphate adsorption (Earl et al., 1979).

Indirectly, organic matter strongly affects phosphate adsorption by Spodosols because it stabilizes ferrihydrite having a high specific surface area and thus high phosphate adsorption capacity (Borggaard, 1983, 1986; Borggaard et al., 1990; Jørgensen & Borggaard, 1991).

Interactions

The effect of organic matter on iron oxide crystallinity is demonstrated by comparing results in fig. 1 and table 1. Feo (or Feo/Fed) follows the organic matter content. Other Spodosols exhibited the same trend in agreement with the general observation that Feo/Fed ratios are high in organic matter-rich environments (Schwertmann et al., 1986; Schwertmann & Murad, 1988; Borggaard et al., 1990).

Feo corresponds to poorly crystalline iron oxides, mainly ferrihydrite (Schwertmann et al., 1982; Borggaard, 1988,1990) suggesting that organic matter favours formation of and/or stabilizes this mineral. In Danish Spodosols ferrihydrite seems to occur in its least ordered form, i.e. as 2-line ferrihydrite (Jørgensen & Borggaard, 1991; fig. 3). Where the organic matter content is relatively low crystalline iron oxides (mainly goethite) occur, as indicated by XRD (fig. 2) and substantial Fed-Feo differences (Borggaard et al., 1990; fig. 1). In contrast to ferrihydrite, crystalline iron oxide distribution seems little affected by organic matter (fig. 1), although high organic matter contents in Bh horizons may cause reducing conditions leading to lepidocrocite occurrence in Bhs horizons (Buurman & Van Reeuwijk, 1984; fig. 2).

Ferrihydrite should transform to more stable iron oxides such as goethite and hematite, but organic matter may inhibit this transformation (Schwertmann, 1988; Borggaard, 1990). Thus, 2-line ferrihydrite found in a peaty environment was considered to consist of extremely small ferrihydrite particles separated by associated organic matter (Schwertmann & Murad, 1988). Also the capacity of iron oxides to adsorb organic matter has clearly been demonstrated (Tipping, 1981a,b; Jardine et al., 1989; table 3). Furthermore, addition of FA and HA in solution reduced phosphate adsorption by iron oxides (Sibanda & Young, 1986), although, as mentioned above, the reduction was low at organic matter concentrations comparable to those in soil solutions (Raben-Lange et al., unpublished results). Jørgensen and Borggaard (1991) postulated an "in situ" effect of organic matter on iron oxide adsorption of phosphate in Bh/Bhs horizons. This interaction seems, however, to be weak. Phosphate adsorption by soil samples, which have been air-dried before use, was found to be unaffected by the organic matter content (Borggaard et al., 1990). This suggests that air-drying can eliminate the competitive effect of organic matter on phosphate adsorption (Jørgensen & Borggaard, 1991). By interaction organic matter may therefore stabilize ferrihydrite and inhibit its transformation into crystalline iron oxides. On the other hand, this interaction seems to be strongly reduced or eliminated by air-drying.

Energy considerations may tentatively explain these observations. The difference between free energies of ferrihydrite and goethite/hematite is only 20-40 kJ/mol, as calculated from the solubility products (Borggaard, 1990). This difference is comparable to the binding energy of van der Waals interactions and hydrogen bonding and to the free energy of adsorption by goethite of humic substances from lakes (Tipping, 1981b). It may therefore be postulated that organic matter by association with ferrihydrite accounts for this energy difference. On drying organic matter rearranges under formation of van der Waals forces/hydrogen bonding between various groups/parts of the organic matter itself, leading to clustering/aggregation of the organic matter. Possibly, during this rearrangement hydrophobic groups may concentrate on outer surfaces, whereas hydrophilic groups, participating in hydrogen bonding, may occur mainly in the central part of such clusters. In this process iron oxide-organic matter interactions competing with phosphate for adsorption sites are eliminated.

According to Schwertmann et al. (1986) interactions of organic matter and iron oxides are of a mutual nature, but although the effect of organic matter on iron oxides seems dear, the iron oxide influence on the organic matter in Spodosols is more obscure. Despite an apparently mutual precipitation of iron oxides and organic matter in the spodic horizon (fig. 1; table 1), the participation of aluminium in Spodosol formation including organic matter precipitation should certainly also be recognized (Petersen, 1976). Furthermore, the obviously higher extractability of organic matter in Bh than in A horizons (table 1) as well as the differences between HA samples from these horizons (tables 2 & 3; fig. 4) may be attributed, at least partly, to interactions with iron oxides (and aluminium) but differences in biological origin should not be overlooked.

Conclusion

In Danish Spodosols the crystalline iron oxides corresponding to Fed-Feo seem to consist mainly of goethite with the occasional occurrence of lepidocrocite in Bhs horizons. The poorly crystalline iron oxides, corresponding to Feo, presumably consist of 2-line ferrihydrite. The latter strongly dominates in Bh (and also often in Bhs) horizons, whereas different proportions of crystalline to poorly crystalline iron oxides occur in the other horizons. The close relationship between ferrihydrite and organic matter contents could be attributed to stabilization of ferrihydrite because of interaction with organic matter. This interaction seems weak, inasmuch as organic matter exhibited a very limited effect on phosphate adsorption by iron oxides, determined in the laboratory. However, a more pronounced effect is postulated to occur under field conditions. By stabilizing ferrihydrite with high specific surface area, organic matter indirectly affects phosphate adsorption strongly.

More organic matter could be extracted from Bh than from A horizons and the ratio between fulvic acid and humic acid was considerably higher for Bh than for A horizons. Humic acid from

Bh horizons contained more aromatic carbon and carboxyl groups but less nitrogen than humic acid from A horizons. These differences may be due to interaction of organic matter with the iron oxides in the soils, but could also be attributed to other factors such as the presence of aluminium and differences in biological origin.

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References

Aiken, G.R., McKnight, DM., Wershaw, R.L. & MacCarthy, P. (Eds.) (1985): Humic Substances in Soil, Sediment, and Water. Wiley-Interscience, New York.

Borggaard, O.K. (1974): Experimental conditions concerning potentiometric titration of humic acid. J. Soil Sci. 25: 189-95.

Borggaard, O.K. (1983): Effect of surface area and mineralogy of iron oxides on their surface charge and anion-adsorption properties. Clays Clay Miner. 31: 230-32.

Borggaard, O.K. (1986): Iron oxides in relation to phosphate adsorption by soils. Acta Agric. Scand. 36: 107-18.

Borggaard, O.K. (1988): Phase identification by selective dissolution techniques. In: Iron in Soils and Clay Minerals (Stucki, J.W., Goodman, B.A. & Schwertmann, U., Eds.). NATO ASI, Bad Windsheim 1985, Reidel, Doordrecht, 83-98.

Borggaard, O.K. (1990): Dissolution and Adsorption Properties of Soil Iron Oxides. Thesis, DSR Forlag, Copenhagen.

Borggaard, O.K., Jørgensen, S.S., Møberg, J.P. & Raben-Lange, B. (1990): Influence of organic matter on phosphate adsorption by aluminium and iron oxides in sandy soils. J. Soil Sci. 41: 443-49.

Buurman, P. & Van Reeuwijk, L.P. (1984): Proto-imogolite and the process of podzol formation: a critical note. J. Soil Sci. 35: 447-52.

Chen, Y., Senesi, N. & Schnitzer, M. (1977): Information provided on humic substances by E4/E6 ratios. Soil Sci. Soc. Am. J. 41: 352-58.

Earl, K.D., Syers, J.K. & McLaughlin, J.R. (1979): Origin of effects of citrate, tartrate, and acetate on phosphate adsorption by soils and synthetic gels. Soil Sci. Soc. Am. J. 43: 674-78.

Goodman, B.A. (1988): The characterization of iron complexes with soil organic matter. In: Iron in Soils and Clay Minerals (Stucki,J.W., Goodman, B.A. & Schwertmann, U., Eds.). NATO ASI, Bad Windsheim 1985, Reidel, Doordrecht, 677-87.

Gregor, J.E. & Powell, H.J. (1986): Acid pyrophosphate extraction of soil fulvic acids. J. Soil Sci. 37: 577-85.

Jardine, P.M., Weber, N.L. & McCarthy, J.F. (1989): Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci. Soc. Am. J. 53: 1378-85.

Jørgensen, K.L. & Borggaard, O.K. (1991): Sorption and mobility of phosphate in a Danish Spodosol. Acta Agric. Scand., submitted.

Kassim, J.K., Gafoor, S.N. & Adams, W.A. (1984): Ferrihydrite in pyrophosphate extracts of podzol B horizons. Clay Miner. 19: 99-106.

Møberg, J.P., Petersen, L. & Rasmussen, K. (1988): Constituents of some widely distributed soils in Denmark. Geoderma 42: 295-316.

McBride, M.B., Goodman, BA., Russell, J.D., Fraser, A.R., Farmer, V.C. & Dickson, D.P.E. (1983): Characterization of iron in alkaline EDTA and NH_4OH extracts of podzols. J. Soil Sci. 34: 825-40.

McKeague, J.A., Cheshire, M.V., Andreux, F. & Berthelin, J. (1986): Organo-mineral complexes in relation to pedogenesis. In: Interactions of Soil Minerals with Natural Organics and Microbes (Huang, P.M. & Schnitzer, M., Eds.). Soil Science Society of America, Madison WI, 549-92.

Nielsen, K.E., Dalsgaard, K. & Nørnberg, P. (1987): Effects on soil of an oak invasion of a Calluna heath, Denmark, II. Changes in organic matter and cellulose decomposition. Geoderma 41: 97-106.

Parfitt, R.L. (1978): Anion adsorption by soils and soil materials. Adv. Agron. 30: 1-50.

Parfitt, R.L. & Childs, C.W. (1988): Estimation of forms of Fe and Al: A review, and analysis of contrasting soils by dissolution and Moessbauer methods. Aust. J. Soil Res. 26: 121-44.

Petersen, L. (1976): Podzols and Podzolization. Thesis, DSR Forlag, Copenhagen.

Raulund-Rasmussen, K. (1989): Aluminium contamination and other changes of acid soil solution isolated by means of porcelain suction-cups. J. Soil sci. 40: 95-101.

Schwertmann, U. (1988): Some properties of soil and synthetic iron oxides. In: Iron in Soils and Clay Minerals (Stucki, J.W., Goodman, B.A. & Schwertmann, U., Eds.). NATO ASI, Bad Windsheim 1985, Reidel, Doordrecht, 203-50.

Schwertmann, U. & Murad, E. (1988): The nature of an iron oxide-organic iron association in a peaty environment. Clay Miner. 23: 291-99.

Schwertmann, U., Schulze, D.G. & Murad, E. (1982): Identification of ferrihydrite in soils by dissolution kinetics, differential X-ray diffraction and Mössbauer spectroscopy. Soil Sci. Soc. Am. J. 46: 869-75.

Schwertmann, U., Kodama, H. & Fischer, W.R. (1986): Mutual interactions between organics and iron oxides. In: Interactions of Soil Minerals with Natural Organics and Microbes (Huang, P.M. & Schnitzer, M., Eds.). Soil Science Society of America, Madison WI, 223-50.

Sibanda, H.M. & Young, S.D. (1986): Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. J. Soil Sci. 37: 197-204.

Steelink, C., Wershaw, R.L., Thorn, K.A. & Wilson, M.A. (1989): Application of liquid-state NMR spectroscopy to humic substances. In: Humic Substances II. In Search of Structure (Hayes, M.B.H., MacCarthy, P., Malcolm, R.L. & Swift, R.S., Eds.). Wiley-Interscience, Chichester, 281-308.

Stevenson, F.J. (1982): Humus Chemistry: Genesis, Composition, Reactions. Wiley-Interscience, New York.

Tipping, E. (1981a): The adsorption of aquatic humic substances by iron oxides. Geochim. Cosmochim. Acta 45: 191-99.

Tipping, E. (1981b): Adsorption by goethite (α-FeOOH) of humic substances from three different lakes. Chem. Geol. 33: 81-89.

Wilson, M.A. (1987): NMR Techniques and Applications in Geochemistry and Soil Chemistry. Pergamon Press, Oxford.

Genesis of placic horizons in spodosols

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Two spodosols with a placic horizon (a Placorthod and a Placohumod) have been investigated in the field and in the laboratory by chemical, mineralogical, and textural analysis. The chemical composition of the placic horizons differs from normal spodic horizons in their high iron content. The iron oxide mineralogy of the placic horizons is dominated by ferrihydrite with small amounts of lepidocrocite. The formation of the placic horizon is due to two processes: oxidation of ferrous iron at the lower boundary of a water-saturated surface layer and translocation of metal-organic matter complexes mainly involving aluminium.

Key words: *placic, spodosol, soil formation.*

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The soil forming processes causing formation of placic horizons in spodosols are not known in detail. In particular, it is of interest to evaluate whether the formation of the placic horizon is independent of the formation of the spodic characters, and if not, how the formation of the placic and spodic horizons interact.

A placic horizon is in Soil Taxonomy described as "a thin, black to dark reddish pan cemented by iron and manganese, or by an iron-organic matter complex. Its thickness ranges generally from 2-10 mm. Rarely, it is as thin as 1 mm or as thick as 20 to 40 mm in spots. It may be, but not necessarily associated with stratification in the parent materials. It is in the solum, roughly parallel to the soil surface, and it is commonly within the upper 50 cm of the mineral soil. It has a pronounced wavy or even convolute form. It is a barrier to water and roots.

An iron-cemented pan is strong brown to dark reddish brown. A pan cemented by iron and manganese or by iron-organic matter complexes is black or reddish black. A single pan may contain two or more layers cemented by different agents. Iron-organic matter cements commonly are present in the upper part of the pan.

Identification is seldom difficult. The hard brittle pan differs so much from the material in which it occurs and is so close to the surface of the mineral soil material that it is obvious unless its thickness is minimal. A few analyses of placic horizons show that organic carbon is present in amounts ranging from 1 percent to 10 percent or more. The presence of organic carbon as well as the shape and the position of the pan distinguish the placic horizon from the ironstone sheet that may form where water hangs or moves laterally at a lithologic discontinuity" (Soil Survey Staff, 1975). This description indicates that the chemical composition and morphology of placic horizons are very variable and that morphological criteria in addition to the chemical may be necessary to distinguish placic horizons from other features.

A number of processes have been suggested to cause the formation of the placic horizon. Early studies were much concerned with the high iron content and suggested that the iron was oxidized and precipitated at a boundary between an oxidizing and a reducing layer. Müller (1924) suggested an upper oxidized layer with a temporarily high ground water table, whereas Damman (1965) suggested an upper reduced layer hanging from a peaty surface. McKeague et al. (1967, 1968) distinguished between iron-manganese pans formed by a reduction/oxidation process and iron-organic matter pans formed by translocation

Skonager 1

Horizon	Depth, cm	Description
Oi	—9 — 8	Only slightly decomposed plant residues; few, bleached sand grains; no roots; abrupt, smooth boundary.
Oe	—8—0	Intermediately decomposed organic matter; few, bleached sand grains; many roots; abrupt, smooth boundary.
Al	0—30	Very dark grey (10 YR 3/1, m); humus—containing sand; common bleached sand grains; weak, fine subangular blocky; nonsticky, nonplastic when wet, loose when moist and dry; few, medium, many fine roots; ants present and very active; clear, smooth boundary.
2A2	30—37	Black (7.5 YR 2/0, m); slightly gravelly, humus-containing sand; weak, fine subangular blocky; consistence as above; many fine roots; clear, smooth boundary.
2E	37—47	Dark grey (10 YR 4/1, m); gravelly, humus-containing sand; weak, medium subangular blocky; consistence as above; many fine roots; abrupt, smooth boundary.
2Bh	47—53	Very dusky red (2.5 YR 2.5/2, m); gravelly, humus-containing sand; weak, medium, angular blocky; very friable when moist, loose when dry; many fine roots; a rootmat is present at the lower boundary; abrupt, wavy boundary.
2Bsh	53—53.5	A continuous 3—6 mm thick, platy pan weakly cemented (placic) by iron and organic material. It consists of an upper dark reddish brown (5 YR 3/2, m) part (2—4 mm thick) and a lower dark reddish (5 YR 3/4, m) part. The layer imbed particles of gravel size. The upper surface of the pan has abundant cracks, some of them transect the upper layer of the pan. The pan breaks into small fragments of different sizes when dug. Few, fine vertical roots in the cracks. In the upper part of the horizon occasionally tubular pores containing iron precipitates are found.
2Bs1	53.5—72	Dark brown (7.5 YR 3/4, m) with approx. 10% very dusky red Bh material as stria and chimneys and approx. 5% dark yellowish brown Bs2 material; slightly gravelly sand; weak, medium subangular blocky; nonsticky, nonplastic when wet, loose when moist and dry; few, fine and medium roots; gradual, smooth boundary.
2Bs2	72—88	Dark yellowish brown (10 YR 4/6, m); slightly gravelly sand; weak, medium subangular blocky; consistence as above; gradual, smooth boundary.
2Cgl	88—115	Light yellowish brow (10 YR 6/4, m) with approx. 5% strong brown (7.5 YR 5/4, m) as stria; slightly gravelly sand; weak, medium subangular blocky; consistence as above; clear, smooth boundary.
2Cg2	115—140	Light yellowish brow (10 YR 6/4, m); slightly gravelly sand; structure and consistence as above.

Investigated until 140 cm.

of iron-organic matter complexes. Stahr (1973) suggested that the placic horizon formed at the lower boundary of a soil layer having low water conductivity causing temporarily reducing conditions in this layer. Righi et al. (1982) suggested that formation of a Bh horizon with low water conductivity was an important step in the formation of the placic horizon. Similarly, Mückenhausen (1982) considered intense podzolisation as a prerequisite for the formation of the placic horizon. Anderson et al. (1982) suggested that the placic horizon forms due to impeded water percolation in the Bs horizon caused by deposition of allophanic material and iron oxides during the initial phases of soil formation. Once the placic horizon has formed the perched watertable induces seasonally reduction of ferric-humate complexes in the Bh horizon. Following mobilization the divalent iron ions diffuse through the iron pan where they oxidize and precipitate, predominantly as iron oxides.

In the present work the results of studies on

Skonager 2

Horizon	Depth, cm	Description
Oi	—13—8	Only slightly decomposed plant residues; abrupt, smooth boundary.
Oe	—8—3	Intermediately decomposed organic matter; abundant small roots; abrupt, smooth boundary.
Oa	—3—0	Strongly decomposed organic matter; few, medium and fine roots; abrupt, smooth boundary.
Alp	0—26	Dark brown (7.5 YR 3/2, ml with approx. 20% light brownish grey (10 YR 6/2, m); humus-containing sand; weak, fine subangular blocky; nonsticky, nonplastic when wet, loose when moist and dry; few fine roots; abrupt, smooth boundary.
A2	26—29	Dark grey (10 YR 4/1, m); humus-containing sand; weak, fine subangular blocky; consistence as above; few fine roots; abrupt, smooth boundary.
A3	29—31	Very dark grey (10 YR 3/1, m); humus—containing sand; weak, fine subangular blocky; consistence as above; few fine roots; abrupt, smooth boundary.
2E	31—42	Grey (10 YR 5/1, nr); gravelly, humus—containing sand; weak fine subangular blocky; consistence as above; few fine roots; abrupt, smooth boundary.
2Bh	42—45	Dark reddish brown (5 YR 3/2, m); slightly gravelly, humus—containing sand; weak, medium, angular blocky; very friable when moist, loose when dry; a rootmat is present at the lower boundary; abrupt, wavy boundary.
2Bsh (placic)	45—45.6	A continuous 3—10 mm thick, platy pan weakly cemented by iron and organic material. It consists of an upper dark reddish brown (5 YR 3/2, m) coloured part (1—4 mm) and a lower dark reddish brown (5 YR 3/4, m) coloured part. The layer imbed particles of gravel size. The upper surface of the pan exhibits abundant cracks, some of them transect the upper part of the pan and a few the whole pan. Few, fine roots in the cracks. The pan breaks into small fragments with a mixture of sizes when dug.
2Bs1	45.6—59	Dark brown (7.5 YR 3/4, m); slightly gravelly sand; weak, medium subangular blocky; nonsticky, nonplastic when wet, loose when moist and dry; gradual, smooth boundary.
2Bs2	59—80	Dark yellowish brown (10 YR 4/6, m); slightly gravelly sand; consistence as above; gradual, smooth boundary.
2C	80—110	Light yellowish brown (10 YR 6/4, m); slightly stony, slightly gravelly sand; weak, medium subangular blocky; consistence as above.

Investigated until 110 cm.

two spodosols with placic horizons are presented and their genesis is discussed.

Materials and Methods

Profile descriptions

The studied profiles are located in Nørbæk Plantation, Skonager (8°33'33"E, 55°38'50"N). Profile 1 is located at the erosion bank of Varde River and profile 2 is located 20 m SE of profile 1 within the plantation. The altitude is approx. 10 m a.s.l. and 7 m above the water level of the river. The location has a yearly mean air temperature of 7.6 °C and an annual precipitation of 769 mm. The profiles have developed in Weischselian glacial outwash/sandy Saalean moraine covered by windblown sand (inland dunes). No evidence of cryoturbation was observed in the profiles described below. However, frost stirring is clearly evident in a trench dug approx. 50 m to the NE (Kolstrup, 1987). The profiles in the trench also exhibit placic horizons. As the placic horizon probably not can withstand the forces acting during the cryoturbation it may be expected that the placic horizon developed after the period where climatic conditions favoured cryoturbation. The soil of profile 1 is presently covered by erica and grasses and profile 2 is covered by coniferous trees (plantation). The profiles are classified as a

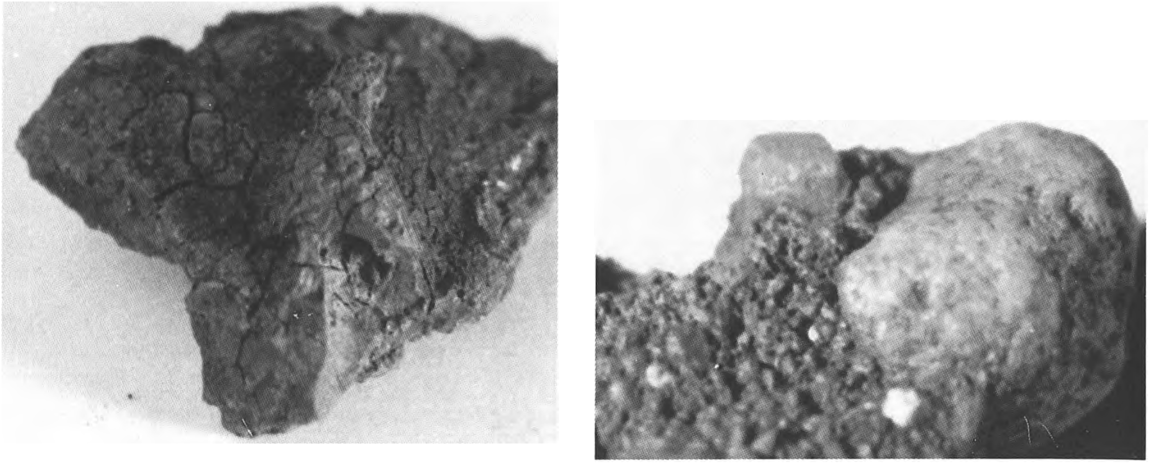

Fig. 1. Fragments of the placic horizon from Skonager 1 showing cracks and horizontal iron-filled pore in the upper part of the horizon (left) and imbedded gravel. Magnification is 5x.

Placorthod (profile 1) and a Placohumod (profile 2) (Soil Survey Staff, 1975).

In addition to horizontal colour differences the placic horizon show other features of inhomogeneity. In fig. 1. is shown a photograph of a fragment of a placic horizon dissected by vertical cracks and having an iron oxide filled pore in the upper part. Another fragment shows imbedding of a piece of gravel. Thin sections (not shown) reveal an inhomogeneous distribution of iron oxide matrix as areas of several mm^2 where skeleton grains are absent and replaced by iron oxides.

Analyses

Samples from the genetic horizons were subjected to chemical analysis of the air-dry < 2 mm fractions. Additional information on the placic horizons were obtained from analyses of < 20 μm fractions by chemical analysis, X-ray diffraction, infrared spectroscopy, Mössbauer spectroscopy, and analytical electron microscopy.

Chemical analyses. Soil pH was measured in water and in $CaCl_2$. Total carbon content was determined as carbon dioxide following dry combustion. The content of carbon in the pyrophosphate extract was determined by oxidation with dichromate in conc. sulphuric acid and assuming an oxidation number of zero. Total nitrogen content was determined by a Kjeldahl digestion procedure. Iron and aluminium were determined by extraction with warm 20% HCl (8 hrs of extraction), dithionite-citrate-bicarbonate (extracted over night at room temperature), alkaline pyrophosphate (pH 10, extracted 16 hrs.) and acidified oxalate (pH3, extracted for 2 hrs.). The details of the analytical procedures are given by Koch (1987).

Mineralogy. X-ray diffractograms were obtained using a Philips 1050 diffractometer, CoK_α radiation and a diffracted beam graphite monochromator. Infrared spectra were obtained using the KBr pressed pellet technique and recorded on a Perkin-Elmer 580 spectrometer as prepared (unheated) and following heating at 150 °C for 16 hrs. Mössbauer spectra were obtained at absorber temperatures of 13, 20, 80, and 298 K using a conventional constant acceleration spectrometer. Isomer shifts are given relative to the centroid of an absorber of natural iron at 298 K.

Hor.	$P^{H}CaCl_2$	$P^{H}H_2O$	N, wt%	C_t, wt%	C_P,wt%	C_t/N	C_p/C_t
Oi	n.d.	4.54#	0.986	34.63	2.33	35	0.067
Oe	n.d.	4.10#	0.709	21.06	2.06	30	0.098
Al	3.79	4.59	0.036	2.16	0.41	60	0.190
2A2	3.92	4.70	0.061	2.16	0.88	35	0.407
2E	4.05	4.70	0.027	1.24	0.43	46	0.347
2Bh	4.04	4.59	0.189	5.15	2.60	27	0.505
2Bsh	n.d.	n.d.	n.d.	5.11	2.74	–	0.536
2Bs1	4.42	4.81	0.017	0.58	0.31	34	0.534
2Bs2	4.58	4.91	0.006	0.24	0.150	40	0.625
2Cg1	4.67	4.98	0.004	0.15	0.099	38	0.660
2Cg2	4.71	5.03	0.004	0.13	0.064	33	0.492

n.d. = not determined
# solid: solution ratio 1:10

Table 1. Soil pH (pH_{CaCl2}, $^{pH}H_2O$), total nitrogen content (N), total carbon content (C_t), carbon extracted by pyrophosphate (C_p), C_t/N ratio, and C_p/C_t ratio of Skonager 1.

Hor.	pH_{CaCl2}	$^{pH}H_2O$	N, wt%	C_t, wt%	C_p, wt%	C_t/N	C_p/C_t
Oi	n.d.	4.37#	1.171	47.76	1.02	41	0.021
Oe	n.d.	3.51#	1.314	42.16	2.11	32	0.050
Oa	n.d.	3.50#	0.581	24.22	2.05	42	0.085
Ap1	3.52	4.14	0.050	1.06	0.46	21	0.433
A2	3.82	4.35	0.056	1.45	0.43	26	0.297
A3	3.83	4.36	0.071	2.15	0.63	30	0.293
2E	3.98	4.51	0.029	1.01	0.20	35	0.198
2Bh	3.81	4.19	0.298	8.54	4.55	29	0.532
2Bsh	n.d.	n.d.	n.d.	8.34	4.93	–	0.591
2Bsl	4.24	4.47	0.026	0.86	0.57	33	0.663
2Bs2	4.37	4.59	0.016	0.39	0.22	24	0.564
2C	4.51	4.75	0.006	0.19	0.078	32	0.410

n.d. = not determined
# solid solution ratio 1:10

Table 2. Soil pH ($P^{H}CaCl_2$, $P^{H}h_{2}o$), total nitrogen content (N), total carbon content (C_t carbon extracted by pyrophosphate (C_p), C_t/N ratio, and C_p/C_t ratio of Skonager 2.

Transmission electron micrographs and selected area electron diffraction patterns were obtained using a Philips EM 430 operated at an acceleration voltage of 300 kV. The chemical composition of particles were analyzed using an EDAX energy-dispersive X-ray system attached to the EM 430. Samples for electron microscopy were dispersed in water and pipetted onto holey carbon-coated copper grids.

Textural analyses. The texture of the inorganic horizons, except the placic horizons, was determined by dry sieving using sieves with nominal apertures of 800, 400, 250, 125, and 50 *µm.* The results for the fractions larger than 2 mm are given as weight percentage of the whole soil and the results for the fractions smaller than 2 mm are given as weight percentages of the fraction smaller than 2 mm.

Results

Chemical analysis. The soil pH (tables 1 and 2) show that the soils are rather acid and there is a general trend of increasing pH with increasing

Hor.	Fe_{HCl}	Fe_{DCB}	Fe_p	Fe_{Qx}	Al_{HCl}	$A1_{DCB}$	Al_p	Al_{Qx}
Oi	2890	1380	630	1030	2200	680	730	720
Oe	3670	2180	1770	1610	3560	1120	1100	1300
A1	360	230	125	190	1040	860	570	920
2A2	430	37	49	44	2110	1090	1490	1430
2E	320	80	38	40	840	510	550	600
2Bh	2410	650	590	680	8080	4520	7640	5960
2Bsh	104570	92900	51030	95800	14370	8050	8740	10740
2Bs1	2620	1300	570	680	2760	1260	1480	1660
2Bs2	2300	560	120	145	1460	570	600	710
2Cg1	1710	390	78	120	1020	290	360	400
2Cg2	450	70	32	41	1120	130	190	220

Table 3. Iron and aluminium extracted by HCl, DCB, pyrophosphate (p) and oxalate (ox) for Skonager 1. ($mgkg^{-1}$).

Hor.	Fe_{HCl}	Fe_{DCB}	Fe_p	Fe_{Qx}	Al_{HCl}	Al_{DCB}	Al_p	Al_{qx}
Oi	580	220	89	115	900	340	370	250
Oe	1810	1480	500	950	1730	840	800	870
Oa	1980	1220	760	1100	2000	530	1020	860
Ap1	580	370	290	300	860	580	530	580
A2	430	280	270	250	840	530	630	600
A3	1200	480	460	470	1240	820	900	930
2E	560	160	110	125	420	260	240	250
2Bh	1550	630	600	480	9950	7910	9330	7330
2Bsh	88860	83800	63850	87000	12220	8160	9815	10100
2Bs1	4150	1600	760	730	3040	1670	1810	1680
2Bs2	1780	590	140	170	1350	740	770	850
2C	1380	480	76	110	860	340	420	470

Table 4. Iron and aluminium extracted by HCl, DCB, pyrophosphate (p) and oxalate (ox) for Skonager 2. ($mgkg^{-1}$).

depth in the mineral part of the profile. The total carbon content (tables 1 and 2) in the horizons vary considerably being very high in the O horizons and decreases with depth with the exception of a secondary maximum in the Bh and Bsh horizons. The contents of carbon in the placic horizons of the two profiles are very different, but a similar difference is noted between the Bh horizons. The carbon/nitrogen ratios (tables 1 and 2) vary between 21 and 60 indicating low degree of humification. The ratio of pyrophosphate extractable carbon to total carbon (tables 1 and 2) is low to very low in the O and E horizon and medium to high in the A and B horizons. The four extraction methods used in the present investigation (tables 3 and 4) all reveal a maximum content of both iron and aluminium in the placic horizon. On a weight basis the content of iron in the placic horizon is approximately an order of magnitude higher than the aluminium content. Furthermore, a comparison of the placic horizon with the over- and underlying horizons show comparable aluminium content, whereas the iron contents are several orders of magnitude higher.

Analyses of the < 20 *μm* fractions from the placic horizons for DCB extractable iron and total carbon yielded 21.48 wt% iron and 16.24 wt% carbon in Skonager 1, and 13.44 wt% iron and 19.47 wt% carbon in Skonager 2.

Mineralogy. In fig. 2 is shown the X-ray diffractograms of the < 20 fractions of the placic horizons from Skonager 1 and 2. The presence of lepidocrocite in both samples is indicated by the diffraction peak at approximately 0.63 *μm.* The broad diffraction peaks at approximately 0.150, 0.172, 0.194, 0.224, and 0.25 indicate the pre-sence of ferrihydrite in both samples. No other iron oxides can be identified from the diffractograms, but a number of sharp diffraction peaks in the diffractograms may be assigned to quartz, feldspars, and phyllosilicates. The infrared spectra (1400-400 cm $^{-1}$) of the < 20 *μm* frac-

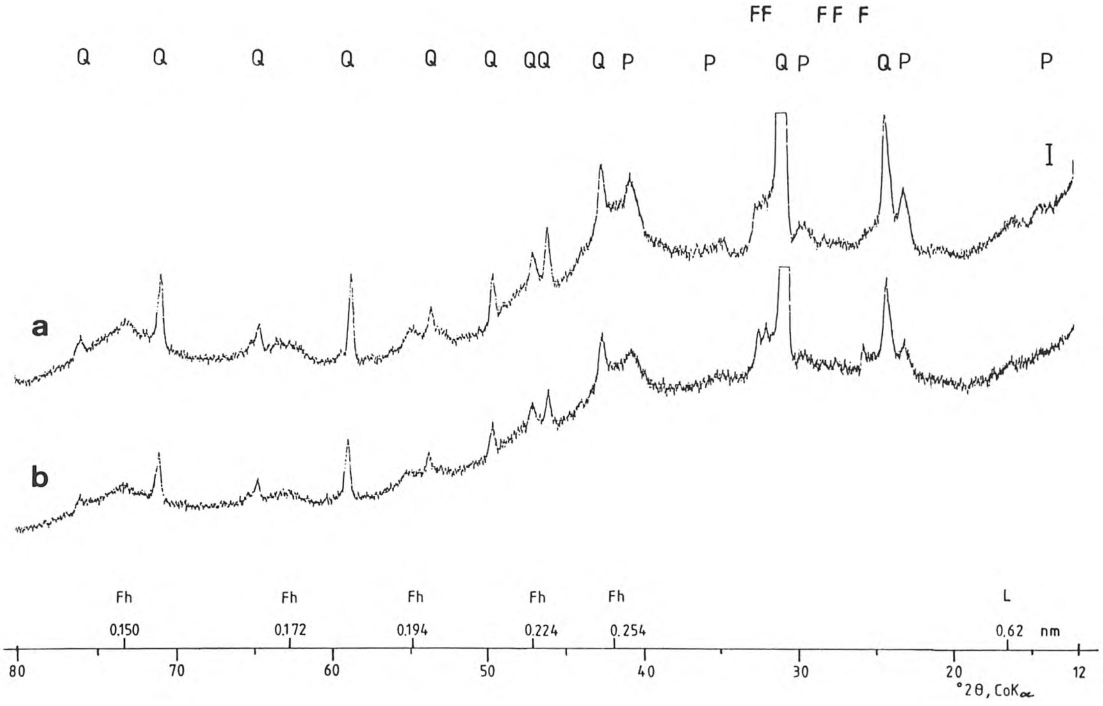

Fig. 2. X-ray diffractograms of the <20 *μ*m fraction from the placic horizons of Skonager 1 (a) and Skonager 2 (b). Intensity scale is 100 cps.

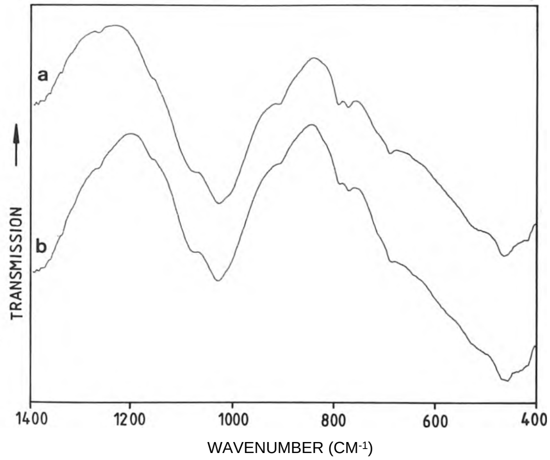

Fig. 3. Infrared spectra (1400-400 cm^{-1}) of the < 20 *μm* fraction from the placic horizons of Skonager 1 (a) and Skonager 2 (b).

tions of the placic horizons from Skonager 1 and 2 are shown in fig. 3. In the the range 4000-1400 cm^{-1} (not shown) the spectra are dominated by absorption bands due to organic matter (aliphatic groups and carboxyl groups). The well-defined absorption bands in the range 1400-400 cm^{-1} may be assigned to quartz (1150, 1080, 800, 780, and 700 cm^{-1}) and phyllosilicates (mica-smectite, kaolinite) (1030, 1010, and 915 cm^{-1}) (Russell, 1987). Thus no absorption bands can unambiguously be assigned to iron oxides. However, the absorption bands in the range 400-600 cm^{-1} show a poorer resolution as compared with those of pure samples of quartz and phyllosilicates, indicating the presence of ferrihydrite in these samples (Russell, 1987).

The Mössbauer spectra of the < 20 *μ*m fractions from the placic horizons are shown in fig. 4. At 298 K the spectra consist of a doublet with an isomer shift of 0.38 mms^{-1} and a quadrupole splitting of 0.70 mms^{-1} typical of high-spin, octahedrally coordinated, ferric ions. Also at 80 K the spectra are dominated by a doublet, but small amounts of a magnetically split sextet can just be detected. At 20 and 13 K a doublet and a magnetically split sextet with broad lines coexist.

	Fe	Si	Al	S	P	K
Skonager 1	65.7	14.1	17.6	0.7	1.1	0.8
	84.9	2.5	11.1	0.6	1.0	0
Skonager 2	47.3	30.9	18.6	2.7	0.6	0
	55.5	23.3	19.4	1.6	0	0.1

Table 5. Chemical compositions (atm.%) of iron-rich particles from placic horizons. Based on the electron diffraction patterns these particles are dominated by ferrihydrite. Only elements with $Z > 11$ (Na) are detected.

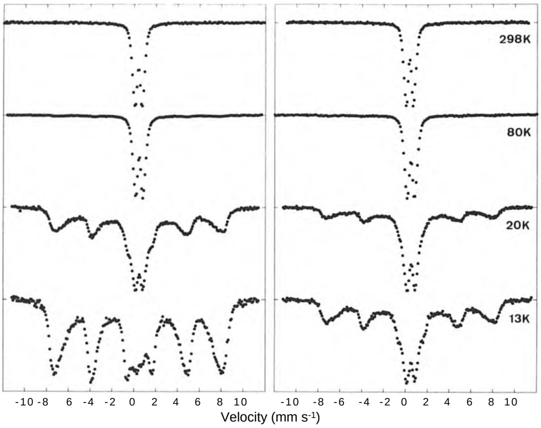

Fig. 4. Mössbauer spectra of the < 20 μm fraction from the placic horizons of Skonager 1 (left) and Skonager 2 obtained at the indicated temperatures.

It is noted that the relative area of the two components vary with temperature and also that it differs among the samples. The blocking temperature (defined by 50% of the spectral area in the sextet) for the two samples can be estimated to approximately 25 and 15 K for the samples from Skonager 1 and 2, respectively. The magnetical split sextets have a hyperfine field of approximately 47 T.

The chemical composition of the ferrihydrite are given in table 5 which present analyses of particles of high and low iron contents, respectively. Analyses of electron diffraction patterns of the particles reveal the presence of small amounts of crystalline material (phyllosilicates). The composition of the particles vary considerably. The sulphur and phosphor presumably originate from organic matter associated with the particles. All of the potassium and a part of the silicon and aluminium originate from phyllosilicates. It is not possible to quantify the amount of silicon and aluminium present in phyllosilicates, but it is probably negligible.

Texture. The results of the textural analysis are given in tables 6 and 7. Both profiles exhibit an abrupt increase in the gravel content at depth (approximately 30-50 cm). This increase is probably caused by wind removal of sand from the area, however, no clear stoneline could be seen. The upper horizons probably developed in a locally derived windblown sand deposit as suggested by the landscape morphology and the similarity of the fine-earth fractions. A change of the texture is noted at the position of the placic horizons, the sediment above the placic horizons being slightly coarser and less well-sorted. However, textural changes are also found in other parts of the profiles.

Discussion

An evaluation of the relative importance of intra- and interprofile processes from elemental mass balances is much simplified, if it may be assumed that the soil profiles developed from a homogeneous parent material. If one make this assumption for the present studied profiles and base the calculations of the mass balances on the extraction data for iron and aluminium in tables 3 and 4, it appears that both of these elements

Hor.	<50μm	50—125μm	125—25μm	250—400μm	400—800μm	800—2000μm	> 2000μm
Al	0.57	2.23	8.20	34.35	46.51	8.14	0
2A2	1.08	4.25	10.69	32.74	42.66	8.58	1.3
2E	2.46	11.96	20.55	30.22	25.46	9.35	51.4
2Bh	1.82	6.62	12.12	24.32	36.97	18.15	39.5
2Bsh							
2Bs1	0.76	1.45	11.85	37.85	36.14	11.95	7.8
2Bs2	0.24	0.78	12.81	46.67	29.70	9.80	1.5
2Cg1	0.04	0.47	18.20	52.93	24.06	4.30	2.1
2Cg2	0.06	0.67	1.66	27.71	49.55	20.35	4.4

Table 6. Texture of Skonager 1 (wt%).

Hor.	<50μm	50—125μm	125—250μm	250-400μm	400—800μm	800—2000μm	>2000μm
Ap1	0.85	4.16	16.61	40.61	33.91	3.86	0
A2	1.16	6.25	19.68	34.15	31.28	7.48	1.6
A3	1.78	8.91	22.99	29.37	28.89	8.06	2.1
2E	2.04	8.95	28.62	29.06	24.31	7.02	28.8
2Bh	1.10	5.67	14.71	22.49	32.27	23.76	15.7
2Bsh							
2Bs1	0.93	2.10	26.09	28.82	31.65	10.41	9.8
2Bs2	0.18	1.34	17.99	45.09	31.47	3.93	2.9
2C	0.09	1.14	15.26	55.66	24.99	2.86	1.7

Table 7. Texture of Skonager 2 (wt%).

have accumulated in the A and B horizons as compared to the C horizons. It is likely that the deposition of windblown material have contributed to the accumulation (i.e. the above assumption is not strictly valid). However, based on evidence presented below, it is suggested that the elements mainly have been transported into the profiles from the adjacent areas.

The X-ray diffraction analyses of the placic horizons show the presence of lepidocrocite and ferrihydrite. The presence of lepidocrocite is important, because it indicates that at least a part of the iron in the placic horizon has formed by oxidation of ferrous iron (Schwertmann, 1985). Furthermore, the common finding of lepidocrocite in placic horizons indicate that oxidation is a general process in the formation of placic horizons, (Campbell & Schwertmann, 1984). It is difficult to quantify the relative contents of lepidocrocite and ferrihydrite, but the absence of a separate component in the Mössbauer spectra due to lepidocrocite, indicate that it is only a minor part of the iron. Also, no indication for lepidocrocite was obtained from the electron diffraction study which, however, only investigated a small number of particles. The width at half height of the (002) diffraction of the lepidocrocite is relatively broad and this indicates that it formed by a relative fast oxidation of the iron. The factors that favour ferrihydrite formation over lepidocrocite is a.o. a very fast oxidation rate and the presence of organic and inorganic elements (particular Si) (Schwertmann, 1985). The elemental analyses show that both Si and organic compounds (as indirectly indicated by the P and S contents) are present in close association with the ferrihydrite. Thus it is likely, that all three factors which inhibit lepidocrocite formation operate in this environment. The fairly large difference in blocking temperature of the two samples indicate an important local influence on the crystallization. It is likely that the higher content of organic matter in Skonager 2, which exhibits the lowest blocking temperature, causes this difference. In summary, the investigation of the iron oxide mineralogy indicates that the placic horizon formed mainly by oxidation of ferrous iron in an environment where fast oxidation of ferrous iron is possible, but the environment also contains compounds interfering with the crystallization process.

The main elements involved in spodosol development are carbon, aluminium, and iron and the content of these elements in the various horizons may be quantified by a number of different extraction methods. As none of these extraction methods are capable to distinguish between different mechanisms of translocation, the contents determined may be considered as fingerprints of the profile, which may be compared to various idealized mechanisms and other spodosols. In addition to the very high absolute iron content in the placic horizons the present studied profiles are characterized by rather low iron contents in the horizons above the placic horizon and by a variation in the C/Al ratio with depth as commonly observed in spodosol (compare data from Mokma & Buurman, 1982). The low iron content is taken as an indication of the relative position of the reduced and oxidized layers. The reducing conditions above the placic horizon have depleted this layer in iron. As the profile mass balances of iron indicated enrichment of A and B horizons in iron and aluminium it is likely that these elements also have translocated by the horizontal flow of water in the upper layer. The variation of the C/Al ratio is taken as evidence of downward translocation of carbon-aluminium complexes. As the placic horizon also contain high amounts of aluminium, it appears that the downward translocating soil solution may pass the placic horizon and that the carbon-aluminium complexes (undersaturated in metal cations) are saturated with metals and deposited in passing the placic horizon (i.e. the placic horizon filters the soil solution).

An extensively developed rootmat is often encountered just above the placic horizon. This rootmat probably developed due to an inhibiting effect of the downward growth of roots due to the low porosity of the placic horizons. However, field observations does not confirm that the placic horizons act as a barrier to roots (Soil Survey Staff, 1975). Assuming that the soil was vegetated when the development of the placic horizon was initiated, the inhibition of roots presumably developed gradually as more and more iron was deposited.

The presence of vegetation during the the development of the placic horizon is indicated by the presence of iron oxide fossilized roots in the upper part of the placic horizon.

The presence of roots may also influence specific features of the placic horizons: Roots may provide volumes free of skeleton grains which after decay of the roots was filled mainly with an iron oxide plasma. At the present development stage of the soils, the rootmat mainly acts as a very localised source of organic matter contributing to the dark colour of the upper part of the placic horizon.

From the discussion above it is concluded that at least two processes are involved in the formation of spodosols with placic horizons. Firstly, oxidation of ferrous iron at the boundary between an upper reduced and a lower oxidized layer is important for the initial development of the placic horizon itself. Secondly, a vertical translocation of carbon-aluminium complexes causes the development of the Bh-horizon. However, important questions of the development of placic horizons remain enigmatic: e.g. which properties determines the position of the transition zone? and is the position stable?

References

Anderson, H.A., Berrow, M.L., Farmer, V.C., Hepburn, A., Russell, J.D., & Walker, A.D. (1982): A reassessment of podzol formation processes. J. Soil Sci., 33:125-36.

Campbell, A.S., & Schwertmann, U. (1984): Iron oxide mineralogy of placic horizons. J. Soil Sci., 35:569-82.

Damman, A.W.H. (1965): Thin iron pans, their occurrence and the conditions leading to their development. Information Rep. N-X-2, Can. Dep. Forestry, St. John's Newfoundland.

Koch, C.J.W. (1987): A study of placic horizons in spodosols. Unpublished Ph.D. Thesis, Royal Veterinary and Agricultural University, Copenhagen.

Kolstrup, E. (1987): Frost wedge casts in Western Jutland and their possible implications for European periglacial research. Z. Geomorph. N.F., 31:449-61.

McKeague, J.M., Schnitzer, M. & Heringa, P.K. (1967): Properties of an Ironpan Humic Podzol from Newfoundland. Can. J. Soil Sci., 47:23-32.

McKeague, J.M., Damman, A.W.H. & Heringa, P.K. (1968): Iron-manganese and other pans in some soils of Newfoundland. Can. J. Soil Sci., 48:243-53.

Mokma, D.L. & Buurman, P. (1982): Podzols and podzolization in temperate regions, ISM monograph 1, Int. Soil. Museum, Wageningen.

Mückenhausen, E. (1982): Die Bodenkunde und ihre geologischen, geomorphologischen, mineralogischen und petrologischen Grundlagen. DLG Verlag, Frankfurt am Rhein.

Müller, P.E. (1924): Contribution to the natural history of the heathlands in Jutland (in Danish). Det Kgl. Danske Videnskabernes Selskab, Biologiske Meddelelser IV, 2, 244 pp.

Righi, D., Van Ranst, E., de Coninck, F. & Guillet, B. (1982): Microprobe study of a placohumod in the Antwerp Campine (North Belgium), Pedologie, 32:117-34.

Russell, J.D. (1987): Infrared methods. In: A Handbook of determinative methods in clay mineralogy, (M.J. Wilson, ed.), Blackie, London, p. 133-73.

Schwertmann, U. (1985): The effect of pedogenic environments on iron oxide minerals. Advances in Soil Science, 1:171-99.

Soil Survey Staff (1975): Soil Taxonomy. Agricultural Handbook. No. 436. U.S. Govnmt. Printing Office, Washington, D.C.

Stahr, K. (1973): Die Stellung der Boden mit Fe-Bandchen-Horizont (thin iron pan) in der Boden-gesellschaft der nordlichen Schwarzenwaldberge. Arb. Inst. Geol. Palaont. Univ. Stuttgart N.F. 69:85-183.

Mobility of Metals in Soils

Søren Storgaard Jørgensen

Jørgensen, Søren Storgaard: Mobility of Metals in Soils. Folia Geographica Danica, Tom. XIX, Copenhagen 1991.

A group classification scheme is proposed for the mobility of metals in soils. The scheme is based on the periodic table of the elements, relative binding strenghts, and abundance in the soil environment. One group of trace metals was studied experimentally using a chromatographic technique on a sandy and a loamy soil. In both soils cadmium, nickel, and zinc were highly mobile at pH 5, whereas copper and lead were immobilized, probably by organic matter. At pH 8 all the metals were retained in the absence of complex-forming agents. It is indicated that the mobility at a specific pH is determined by the binding strenghts of metals to humus and clay minerals and by the formation of solid compounds. By the chromatographic technique distribution ratios are determined more similar to natural conditions than by batch experiments.

Keywords: *Mobility of metals in soils. Heavy metals. Cadmium, zinc, nickel, copper, lead in soils. Distribution ratios. Mobility of metals by chromatographic technique.*

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Of the 92 terrestrial elements in the periodic table of the elements about 70 are classified as metals, i.e. they are good conductors of heat and electricity in the elemental state and they have a 'metallic' lustre. In chemical compounds and in aqueous solution they have a more or less pronounced tendency to form positively charged elemental ions. However, quantitatively the Earth's crust, including soil, consists mainly of two non-metals, oxygen and silicon. The overwhelming role of silicon becomes particularly impressive when calculated on a volume basis, as first pointed out by V. M. Goldschmidt, one of the founding fathers of geochemistry. In table 1 is shown that 97-98 percent of the crust and soil are made up of oxygen and silicon and the following six metallic elements: aluminium, iron, calcium, magnesium, sodium and potassium.

Element	Crust	Soil
	weight %	
O	47.4	49
Si	27.7	33 (25-41)
Al	8.20	7.10 (1.0-30)
Fe	4.10	4.0 (0.2-5.5)
Mg	2.30	0.5 (0.04-0.9)
Ca	4.10	1.5 (0.07-50)
Na	2.30	0.5 (0.015-2.5)
K	2.10	1.4 (0.008-3.7)
Sum	98.2	(97)
	mg/kg	
N	25	2000 (200-5000)
P	1000	800 (35-5300)
S	260	700 (30-1600)
C	480	20000 (7000-500000)
	mg/kg	
Mn	950	1000 (20-10000)
Cu	50	30 (2-250)
Zn	75	90 (1-900)
Ni	80	50 (2-750)
Cr	100	70 (5-1500)
Co	20	8 (0.05-65)
Pb	14	35*) (2-300)
Hg	0.05	0.06 (0.01-0.5)
Cd	0.11	0.35 (0.01-2)

*) 12 prior to global contamination from leaded gasoline.

Table 1. Elemental composition (selected elements) of the continental crust of the earth, and of soils (median values and range). After Bowen (1979).

In table 1 the soil figures of Bowen (1979) are median and range values derived from an extensive literature survey. The large ranges and the difference between soil and crust values reflects differences in the degree of soil development, where leaching is the most important parameter in this respect. The figures probably also illustrate in the case of Ca, Mg, Na, and K, that some values are only 'pseudo total' (Ure, 1990), or acid soluble amounts.

It is mentioned in passing that the enrichment of the non-metals carbon, nitrogen and sulphur reflects the biological activity in the soil ecosystem, as compared to the total crust. It is remarkable that apparently there is on an average no phosphate enrichment.

All terrestrial metallic elements can be found in an immobile state within the crystal lattice of primary or secondary silicate minerals in soils. Aluminium, and to a lesser extent iron and magnesium, are structure determining elements in primary minerals, such as felspars and micas, and in secondary minerals, such as the aluminosilicate clay minerals. Calcium and sodium are lattice filling elements in plagioclase felspars, potassium is acting similarly in orthoclase felspar and in mica. A range of metals may occupy ion exchange sites of weathered micas and clay minerals.

Trace elements may be found in immobile form in silicate minerals as isomorphous substitutions for structural element atoms of similar size. Well known examples are zinc and manganese(II) substituting for magnesium and chromium(III) for aluminium.

Metallic elements tied up in silicate minerals can be mobilized by acid chemical weathering and in the case of clay minerals by cation exchange. Mobile metallic elements can also appear in soils after being added as fertilizers or liming materials or as an effect of pollution.

The mobility in the soil environment of non-silicate bound metallic elements in the dissolved state varies considerably from one element to another depending on the solution chemistry of the element and the soil chemical conditions.

Classification of metallic elements in soils according to mobility characteristics

The following classification scheme is a proposal for grouping of metallic elements according to their mobility characteristics. It is based on the periodic table of the elements, the relative binding strength with regard to other soil components, and the relative abundance of metallic ions in normal soil environments.

1. Group IA, major elements

Sodium and potassium, present only as Na^+ and K^+ and highly mobile at all pH-values in soils. Mobility is impeded only by ion exchange reactions but sodium and potassium are more loosely bound by exchange reactions than ions with higher charge. Potassium may become "fixed" by mica type clay minerals due to steric preference.

2. Group IIA, major elements

Magnesium and calcium are present in soils as exchangeable Mg^{2+} and Ca^{2+} at pH-values lower than about 8 and mainly as insoluble carbonates at higher pH-values. Especially $CaCO_3$ functions as a pH-buffer by dissolution at pH 8-7. After depletion of carbonates the "first acid front" appears at pH 7-6, where the ion exchange complex starts to lose Ca and Mg and bicarbonates of the two metals are leached.

3. Group IIIA and VIII, oxide forming major elements

Aluminium and iron are present in soils as aluminium(III) and iron(III)-oxides at pH values higher than about 4. They function as pH-buffers and give rise to the "second acid front" around this pH-value followed by partial dissolution as free ions and hydroxo- and organic complexes. At higher pH-values (4-7) iron(III) may be reduced to soluble and thus mobile iron(II) under anaerobic soil conditions.

Under long time anaerobic conditions, such as in shallow brackish areas, iron sulfides and iron pyrite, FeS_2 may be formed. After land reclamation and drainage these components are oxidized to mobile Fe(III) and sulphate, and eventually sulphuric acid and iron(III) hydrous oxides are produced (Rasmussen, 1961).

Socalled "free aluminium and iron oxides" occur in soils with varying, mostly poor, crystallinity. In terms of analytical methods the iron oxides may be described as consisting of only two fractions, one containing distinctly more crystalline compounds than the other (Borggaard, 1985, 1990).

The trace element chromium is found in most soils as Cr(III) which behaves similarly to Al(III) and Fe(III) (McGrath and Smith, 1990).

4. Transition elements and group IIB, trace elements occuring as elemental cations

Copper, zinc, cadmium, mercury, lead, cobalt, and nickel. These elements are immobile at pH-values above 6-7 due to formation of insoluble hydroxides, oxides or carbonates. Mobility at lower pH-values is determined by cation exchange reactions and by complex formation with organic compounds, hydroxyls, sulphate ions, and clay mineral and oxide surfaces (Sposito, 1983; Alloway 1990). The mobility is improved if the complexes are charged and soluble and the mobility is hindered if the complexes are uncharged and insoluble. Cadmium, zinc, and nickel are the more mobile in soils of temperate humid regions. Manganese may also be categorized in this group, when present as Mn^{2+}, but the largest fraction of this element is found in most soils as Mn(IV) in insoluble (but often reducible) forms such as MnO_2. Manganese in MnO_2 might be better classified with the oxides of aluminium and iron.

5. Groups VB and VIB, trace elements occuring as anions

Molybdenum and vanadium. These elements are present in soils primarily as molybdate, MoO_4^{2-} and oxyanions of V^{5+}, such as VO^-_3 and oxygen bridged polymers. Molybdate is adsorbed to aluminium and iron oxides in the soil. The same probably holds for vanadium. The mobility of molybdate increases with increasing pH. Under anaerobic conditions V^{5+} may be reduced to vanadyl(IV) cations, such as VO^{2+} which may be precipitated by organic anions (Jones et al., 1990).

Other categories may be added to this classification scheme, such as the lanthanide elements (elements no. 57-71 in the periodic table) and the platinum group elements (ruthenium, rhodium, palladium, osmium, iridium, and platinum). These elements have not been studied much as to their occurrence and properties in the soil environment. For the platinum group elements there might be reason to do so after the introduction of platinum/palladium catalysts in car exhaust pipes in order to reduce the risks connected with lead, nitrogen oxides and aromatic hydrocarbons in exhaust from cars. It has been estimated that around 1μg of Pt may be released into the atmosphere per vehicle per driven kilometer (Tölg, 1989). This eventually ends up in the soil.

Relative mobilities in soil of selected metallic elements (cadmium, zinc, nickel, lead, and copper). A laboratory investigation

The classification scheme proposed above represents an attempt to arrange a number of major and trace elements in soils according to their relative mobility in broad terms. Within each category differences in mobility also exist. As an example, which may be of some relevance in an environmental context, a laboratory investigation has been performed in order to determine and compare the mobilities of cadmium, zinc, nickel, copper, and lead in a humic sandy soil and in a loamy soil from which it had been attempted to remove organic matter.

Leaching experiments with trace elements using concentrations and leaching rates equal to those under natural conditions are difficult to perform because of the high analytical sensitivity and the long time required before equlibrium is reached. In the present experiments the processes were strongly accelerated by using high metal concentrations and high leaching rates. The experiments were conducted in a "chromatographic" mode, i.e., by adding a concentrated "plug" of all the metals and subsequently leach the soil with a preselected solution at a high leaching rate (compared to natural conditions).

The observed mobilities are compared for the respective elements, and compared to results obtained from batch experiments found in the literature. It is hoped that the results obtained bear some resemblance to the behaviour of these metals under natural conditions.

Materials and methods

The following *two soils* were chosen for the leaching experiments:

Soil A. A humic podzolic soil (Haplortod) developed on inland dune sand in Jylland, Denmark. Due to cultivation for about one hundred years the original A and B horizons have been mixed. The sample was taken from this mixed plough layer.

Soil B. Subsurface layer (25-40 cm) from a loamy soil (Agrudalf) on Sjælland, Denmark. Prior to the leaching experiments this soil was treated with hypobromite (Mitchell and Smith, 1974) in order to destroy organic matter.

The less than 0.2 mm fraction of each soil was used. Some characteristics of the soils are given in table 2.

Soil	A	B
Texture: < 2μm, %	6.9	27.7
< 2μm, %	4.2	12.0
Ignition loss, %	6.87	n.d.
Total carbon, %	2.92	0.32*)
pH (0.01 M $CaCl_2$)	5.48	3.97
CEC, meq/100 g (sodium acetate, pH 8.2)	14.0	5.1*)
Free Fe_2O_3, % (dithionite-citrate-bicarbonate)	0.45	0.33*)
Density, g/cm^3 (pycnometry in water)	2.43	2.51*)

*) Determined on hypobromite treated soil.

Table 2. Soil characteristics.

Leaching experiments

Soil columns with a diameter of 1.55 cm and 30-40 cm high containing 70-80 g of soil A or 115—125 g of soil B (or the same soils thoroughly mixed with 10% calcium carbonate powder) were prepared in glass tubes and conditioned by leaching with one of the solutions specified below. Leaching was continued until the pH of the leachate was constant and equal to the pH of the leaching solution. Then 25.00 ml of a solution containing 0.100 mmol of each of the following ions as acetates: Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, and Cu^{2+} were added to the top of the column followed by leaching with the solution previously used for conditioning the column. The total amount of metal ions added corresponded to about 10% (soil A) and 15 % (soil B) of the CEC of the column. The original contents of these metals in the soils were not determined but were considered insignificant compared to the amounts added.

The following leaching solutions were tested:

Soil A

1. 0.030 M calcium chloride, unbuffered, pH 5.3.
2. 0.0030 M calcium chloride, unbuffered, pH 4.5. Used for soil mixed with 10% calcium carbonate only.
3. Calcium acetate buffer, $[Ca^{2+}]$ = 0.10 M, pH 5.07.
4. Calcium tris-(hydroxymethyl) aminomethane (THAM) buffer, $[Ca^{2+}]$ = 0.01 M, [THAM] = 0.20 M,$[Cl^-]$ = 0.10 M, pH 8.10.
5. Calcium acetate/EDTA buffer, $[Ca^{2+}]$ = 0.10 M, [EDTA] = 0.050 M, pH 5.05.
6. Calcium THAM/EDTA buffer, $[Ca^{2+}]$ = 0.010 M, [THAM] = 0.20 M, $[Cl^-]$ = 0.10 M, [EDTA] = 0.010 M, pH 8.10.
7. Phosphate buffer, $[KH_2PO_4]$ = 0.025 M, $[Na_2HPO_4]$ = 0.025 M, pH 6.82.

Soil B

8. 0.0030 M calcium chloride, unbuffered, pH 4.5.

Solution 8 was also used for leaching soil B mixed with 10% calcium carbonate.

Each column was treated with one leaching solution only. Leaching was carried out at a constant flow rate within the range 30-50 ml

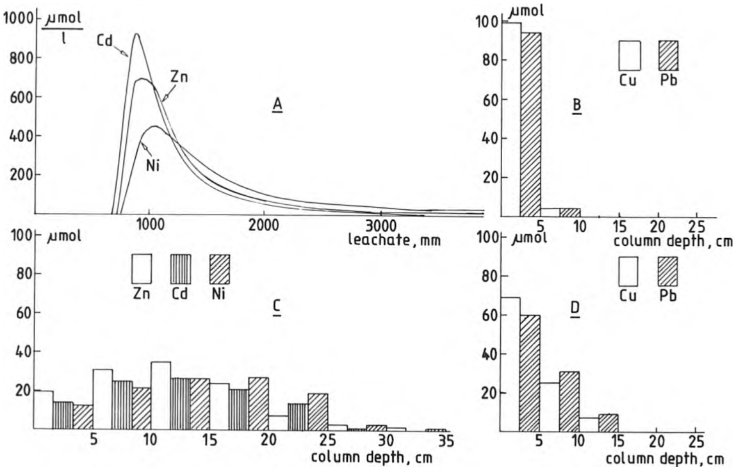

Fig. 1. Movement of metal ions in the humic sandy soil leached with unbuffered $CaCl_2$-solutions.

A. Concentrations of Cd, Zn and Ni i 0.03 M $CaCl_2$-leachate.

B. Distribution of Pb and Cu in soil column (5 cm layers) after leaching with $11.9 \cdot 10^3$ mm of 0.03 M $CaCl_2$ solution.

C. Distribution of Cd, Zn and Ni in soil column mixed with 10% $CaCO_3$ (5 cm layers) after leaching with $31.8 \cdot 10^3$ mm of 0.003 M $CaCl_2$.

D. Distribution of Pb and Cu in soil column mixed with 10% $CaCl_2$ (5 cm layers) after leaching with $31.8 \cdot 10^3$ mm of 0.003 M $CaCl_2$.

cm^{-2} h^{-1} (= 300-500 mm h^{-1}). The flow was maintained by gravity at constant hydraulic head or by means of a peristaltic pump. The leachate was collected in 16 ml fractions using a fraction collector. In each fraction Cd, Zn, Ni, Pb, and Cu were determined by flame atomic absorption spectrophotometry. From 2.0 to 6.0 1 (= 10600-31700 mm) were collected from each column.

If less than the amounts of metals added had been recovered in the leachates, the soil column was removed from its glass tube in 5 cm thick layers. Each layer was then treated with 6 M hydrochloric acid at 100°C for one hour, filtered and the metal content determined in the solution.

Results

Leaching with unbuffered calcium chloride solution

As shown in fig. 1 cadmium, zinc, and nickel were leached from the humic sandy soil (A) with the maximum leachate, concentration appearing at about 1000 mm of leachate whereas the major part of the copper and lead were still found in the upper 5 cm of the column even after the passage of $11.9 \cdot 10^3$ mm of solution. The pH of the leachate was 5.3-5.5 during the whole experiment.

None of the metals added were leached from the humic sandy soil mixed with 10% calcium carbonate after the passage of $31.8 \cdot 10^3$ mm of solution. The pH of this leachate varied within the range 7.4-8.0. During the leaching period cadmium, zinc, and nickel moved about 15 cm down the column, whereas copper and lead were still retained in the upper 5 cm layer.

Fig. 2 demonstrates that cadmium, zinc, and nickel were leached from the loamy soil after the passage of only half the volume (maximum concentration appearing at about 5oo mm) required for leaching these metals from the humic sandy soil. From the loamy soil copper was leached with the maximum concentration appearing at about 1900 mm of leachate, whereas lead was retained in the upper 5-10 cm of the column after the passage of $22.6 \cdot 10^3$ mm of solution. The leachate pH was 4.4-4.6 during the whole leaching period.

The column containing the loamy soil mixed with calcium carbonate showed a more differentiated picture, with nickel being leached out in a very broad band with maximum concentration around $4.2 \cdot 10^3$ mm of leachate. However, only about 60% of the nickel added were recovered in the leachate. The soil column was not analyzed for nickel after the leaching experiment. After the passage of $18.6 \cdot 10^3$ mm of solution, 15% of the cadmium added had been leached out. The remaining cadmium was found distributed in the

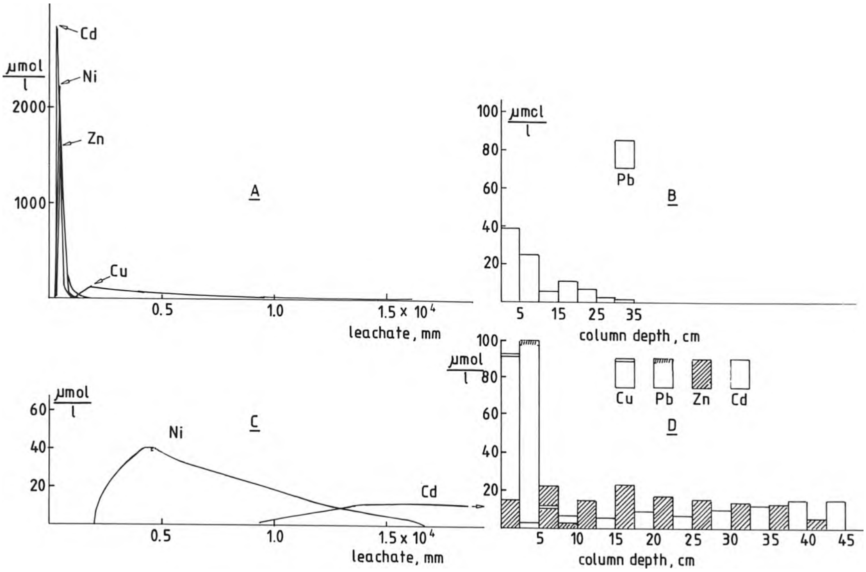

Fig. 2. Movement of metal ions in the loamy soil leached with unbuffered $CaCl_2$-solulion.

A. Concentrations of Cd, Zn, Ni and Cu in 0.003 M $CaCl_2$-leachates. Arrows indicate peak maxima.

B. Distribution of Pb in soil column (5 cm layers) after leaching with $22.6 \cdot 10^3$ mm of 0.003 M $CaCl_2$ solution.

C. Concentrations of Cd and Ni in 0.003 M $CaCl_2$ leachates of soil mixed with 10% $CaCO_3$. The Cd concentration stays constant at 11 µmol/l from $1.36 \cdot 10^3$ to $1.86 \cdot 10^3$ mm of leachate.

D. Distribution of Zn, Cd, Cu and Pb in soil column mixed with 10% $CaCO_3$ (5 cm layers) after leaching with $1.86 \cdot 10^3$ mm of 0.003 M of $CaCl_2$ solution.

soil with maximum concentration in the 35-45 cm layer. Zinc could not be detected in the leachate ($18.3 \cdot 10^3$ mm) but was found in all layers in the column after the passage of this amount, whereas copper and lead were found only in the upper 10 cm layer. The pH of the leachate was initially about 8.0 and then decreased gradually to about 6.5.

Leaching with buffered solutions (pH 5 or pH 8) without or with added EDTA

Cadmium, zinc, and nickel were leached from the humic sandy soil with the maximum leachate concentration appearing around 10^3 mm of a calcium acetate buffer at pH 5.1. The maximum concentration of lead was found at about $2.5 \cdot 10^3$ mm and copper appeared in a broad band with maximum around $7.6 \cdot 10^3$ mm (fig 3). However, only about 25% of the copper had been leached out after the passage of $10.2 \cdot 10^3$ mm. The soil was not analysed at the end of the leaching experiment.

Fig. 3 also indicates that with a calcium acetate buffer containing EDTA, copper and zinc were leached with maximum concentrations around 460 mm and cadmium, nickel and lead with maximum concentrations around 510 mm.

Fig. 4 shows that when the humic sandy soil was leached with a calcium-THAM buffer at pH 8.0 copper came out with a maximum leachate concentration at $1.4 \cdot 10^3$ mm of solution. Cadmium and nickel were found as broad bands with maxima around $8.5 \cdot 10^3$ mm and $11.5 \cdot 10^3$ mm, respectively. However, only 63% of the cadmium and 18% of the nickel had been leached out after the passage of $20.4 \cdot 10^3$ mm of solution. At the same time lead was found in the upper 5 cm of the column and zinc had maximum concentration in the 5-10 cm layer.

Cadmium, lead and zinc were leached out with a calcium-THAM buffer containing EDTA in a narrow band with maximum concentrations appearing at 420 mm. Nickel and, to a lesser extent, copper were leached out in broad bands

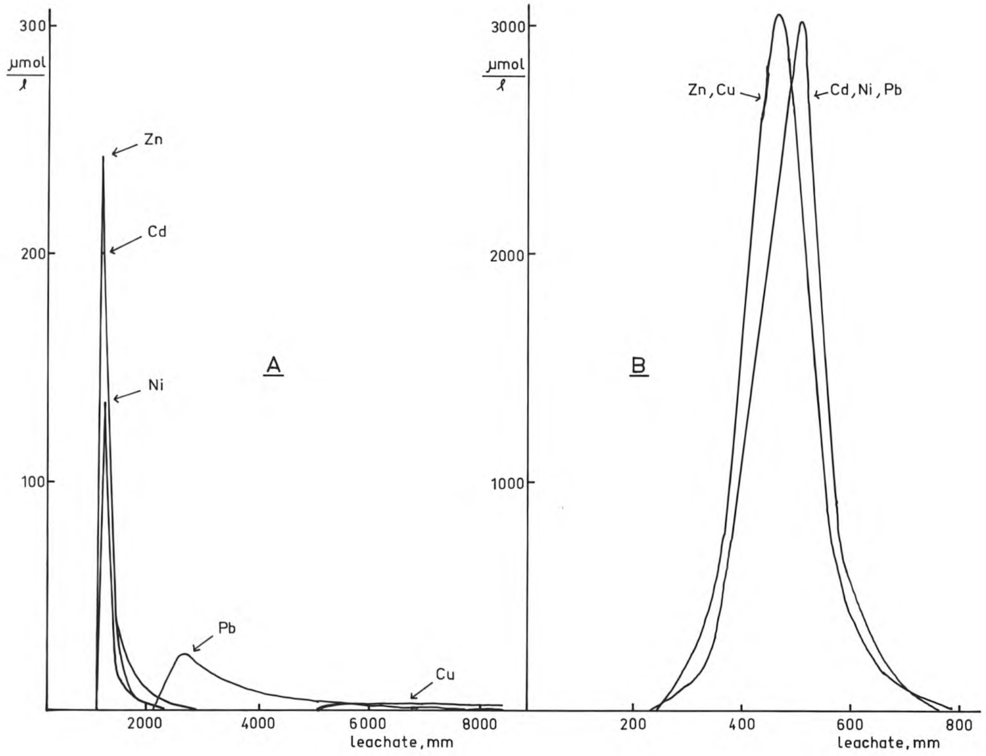

Fig. 3. Movement of metal ions in the humic sandy soil leached with calcium acetate buffer at pH 5.0.

A. Metal concentrations in leachates without EDTA. Arrows indicate peak maxima.

B. Metal concentrations in leachates which were 0.050 M in EDTA. Leaching curves for Zn and Cu are identical within experimental error. So are the curves for Cd, Ni and Pb.

with maxima around 340 and 600 mm, respectively.

When adding the solution of the five metal acetates to the humic sandy soil which had been conditioned with a phosphate buffer at pH 6.82 a white-bluish precipitate was formed at the top of the column. After leaching with 21.2 · 10 mm of the phosphate buffer copper was found exclusively in the upper 5 cm of the column which also contained about 70% of the zinc, cadmium, and lead with the remaining parts being present in the 5-10 cm layer. About 40% of the nickel was found in the upper 5 cm and 60% in the 5-10 cm layer.

The leaching curves obtained with calcium acetate-EDTA solution were symmetrical and approximately Gaussian. All other leaching curves observed showed pronounced "tailing".

Distribution ratios

The retention of metal ions in a soil column is determined by solid-solution equilibria and by the rate of the sorption - desorption processes taking place. Under natural conditions where the rate of water infiltration into the soil normally is slow, equilibrium between solid and solution may be assumed. Also in the present experiments equilibrium conditions may be considered to be prevailing.

The distribution at equilibrium of a specific ion species between the solid and the solution phase may be described by the distribution ratio:

$$D = \frac{C_S}{C_M} \tag{1}$$

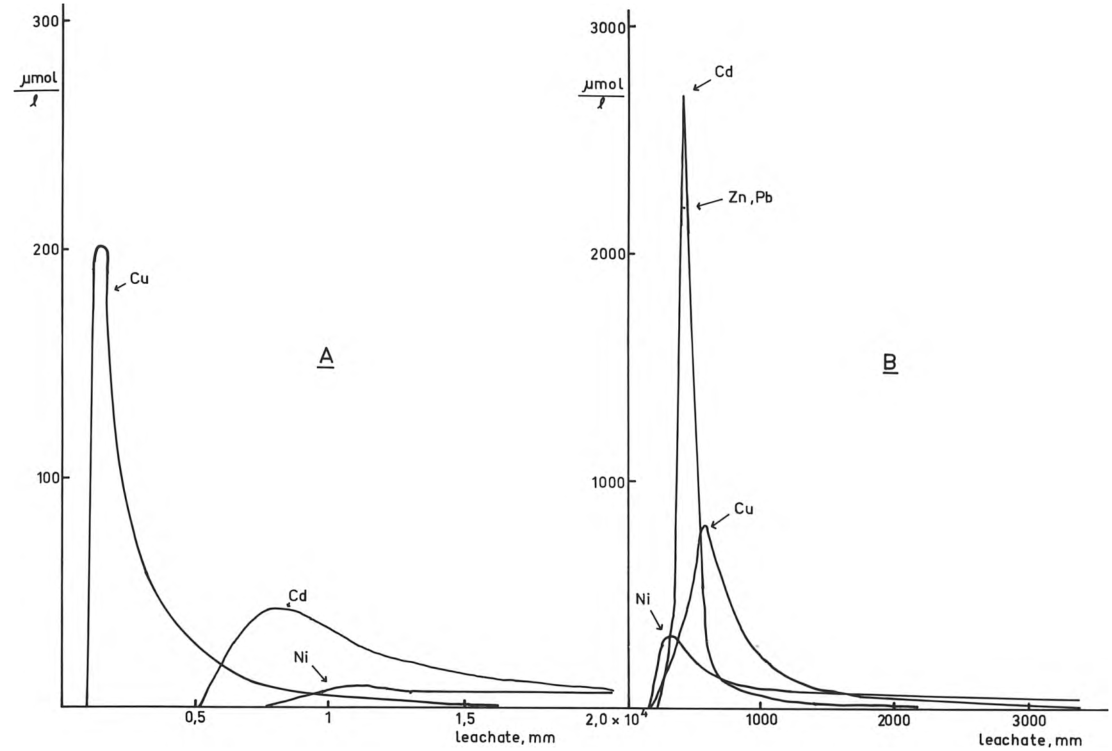

Fig. 4. Movement of metal ions in the humic sandy soil leached with calcium-TFlAM buffer at pH 8.1.

A. Metal concentrations in leachates without EDTA. For Zn and Pb see text.

B. Metal concentrations in leachates which were 0.010 M in EDTA. Leaching curves for Cd, Zn and Pb were identical within experimental error, except that the maximum concentration of Cd was 2700 µmol/l and of Zn and Pb 2200 µmol/l.

where C_S and C_M are the stoichiometric metal concentrations in the stationary (solid) and mobile (solution) phases, respectively, both expressed in weight/volume units in this paper.

The capacity factor k' of a given column is defined as

$$k' = D \frac{V_S}{V_M} \tag{2}$$

where V_S and V_M are the volumes of stationary and mobile phases in a given column.

From chromatographic theory (see e.g. Karger et al., 1973) it follows that an elution peak having the shape of a normal (Gaussian) distribution curve is obtained if the distribution ratio is independent of concentration (linear elution). In this case the value of k' may be calculated from

$$k' = \frac{V_R}{V_M} - 1 \tag{3}$$

where V_R is the retention volume, i.e. the volume of solution which has to pass the column in order to elute the ion in question (peak maximum).

However, most of the elution curves obtained in the present experiments were not Gaussian but showed pronounced "tailing". This may be caused by non-equilibrium within the column or by a non-linear (convex) distribution function (such as the one described by the Langmuir iso-

			Distribution ratio, D				
Soil	solution	pH	Cd	Zn	Ni	Pb	Cu
A	$CaCl_2$	5.3	3.54	3.80	4.60	$\approx 10^3$	$\approx 10^3$
A+$CaCO_3$	$CaCl_2$	7.4-8.0	$3.7\text{-}10^2$	$3.7 \cdot 10^2$	$3.2 \cdot 10^2$	$> 1.3 \cdot 10^3$	$>1.3 \cdot 10^3$
A	CaAc	5.07	4.22	4.22	4.22	13.6	45
A	CaAc + EDTA	5.05	1.03	0.78	1.03	1.03	0.78
A	Ca-THAM	8.0	55	$8.5 \cdot 10^2$	74	$>10^3$	7.6
A	Ca-THAM + EDTA	8.0	0.74	0.74	0.27	0.74	1.68
4B	$CaCl_2$	4.50	0.71	0.71	0.71	$8.5.10^2$	5.6
B+$CaCO_3$	$CaCl_2$	6.5-8.0	69	$2.1 \cdot 10^2$	15	$>7 \cdot 10^2$	$>7 \cdot 10^2$

Table 3. Distribution ratios calculated from peak maxima using equations (2) and (3).

therm). In both cases D-values calculated from peak maxima using equations (3) and (2) will be minimum values.

Mathematical procedures for the calculation of adsorption isotherms from asymmetric chromatographic peaks have been developed and the necessary iterative computer programs are available (Jönsson and Lövkvist, 1989). Attempts to utilize such procedures on the present data are in progress.

Calculated minimum D-values are given in table 3. It is seen that D-values vary from more than 10^3 in cases where no movement of the metal ion could be detected to about 1 in solutions containing EDTA.

The leaching rate of a specific metallic element for a given leachant composition and with continuous leaching can be read directly from figs. 1-4. Extremes are the EDTA-solution, where about 500 mm of leachant transports all the metals about 400 mm down the soil column, and lead and copper under various leachant and soil conditions, where virtually no movement is observed after passage of $1 \cdot 10^3$ - $3 \cdot 10^3$ mm of leachant. Cadmium, zinc, and nickel are transported about 400 mm down the soil column with about 1000 mm of a slightly acid calcium chloride solution, which is probably the leachant most resembling natural conditions. Under natural conditions, however, leaching rates as a function of water infiltration are expected to be considerably slower and discontinuous, allowing a number of chemical processes to take place.

Discussion

The mobility of these metals (Cd, Zn, Ni, Pb, Cu) in soils depends on the balance between their retention by solid soil components and the formation of soluble metal compounds.

The most important metal-retaining components are found in the clay fraction because of its high specific surface area. The fraction is considered to contain phyllosilicate minerals (clay minerals), solid organic matter (humus per se), iron and aluminium oxides, and combinations of these. The humic sandy soil investigated contains very little clay minerals but considerable humus. The loamy soil, treated with hypobromite, contains little humus but a reasonable amount of clay silicates. Binding mechanisms include cation exchange, causing the simultaneous release of other cations, specific adsorption, and formation of insoluble chelates. Formation of insoluble compounds may take place in soils containing an excess of carbonate (or phosphate).

Soluble metal compounds include free hydrated cations, which for most of these metals dominate at acid to neutral pH, cationic hydroxo complexes, cationic and uncharged complexes with other inorganic ligands, such as sulphate and bicarbonate, and soluble complexes with organic ligands (Lindsay, 1979).

In both soils there is a pronounced difference between the mobility of cadmium, zinc, and nickel on one hand and of copper and lead on the other, when the soil is leached with an unbuffered solution with an ionic strength similar to natural soil solution. Distribution ratios for cadmium, zinc, and nickel are small but 5-6 times as large for the sandy as for the loamy soil, probably indicating that ion exchange processes are mobility determining factor in both soils. The difference between the two soils may be due to the dominance of clay in the loamy soil and humus in the sandy soil and/or a function of pH (Anderson and Christensen, 1988; Christensen, 1989).

No movement of copper and lead could be observed in the sandy soil, whereas copper was leached out of the loamy soil and a slight movement of lead was indicated. Strong binding of copper by humus is to be expected (Baker, 1990; McLaren and Crawford, 1974). Binding of lead to soil organic matter is also well documented (Davies, 1990; Hildebrand and Blum, 1975) although leaching of lead in an acid podzol soil has been observed under natural conditions (Jørgensen and Willems, 1987). The retention of lead relative to copper in the loamy soil may be caused by preferential binding of lead by clay minerals (Alloway, 1990) or caused by the leachant being a chloride solution allowing the formation of less charged chloro-complexes of lead but not of copper (Lindsay, 1979).

In the soils mixed with calcium carbonate leaching is strongly impeded, presumably by the formation of insoluble metal carbonates. At a fixed pH above neutrality the solubility of carbonates decrease in the following order: Ni>Zn>Cd>Pb>Cu. (Data from Lindsay (1979) and Smith and Martell (1976) Ni). This order is qualitatively reflected in both the sandy and the loamy soil. Leaching is most strongly impeded in the sandy soil which probably indicates that organic matter is generally more effective for metal binding at high pH than are clay minerals.

The strongly chelating agent, EDTA which forms soluble metal chelates, leaches all five metals from the sandy soil both at pH 5 and pH 8 with distribution ratios near unity. The weakly complexing acetate ion combined with a higher concentration of calcium, which may compete with other metals for binding sites, is able to remove both copper and lead from the sandy soil at pH 5 together with the other three metals.

Maintaining pH 8 with a THAM chloride buffer instead of solid calcium carbonate does not affect the binding of lead and zinc but causes preferential leaching of copper and to a lesser extent cadmium and nickel. Copper forms medium-strength complexes with THAM (formation constants similar to that of the corresponding copper ammine complexes) (Bai and Martell, 1969). Nickel-THAM complexes are considerably weaker and forms more slowly (Bai and Martell, 1969). THAM complexes of the other metals do not seem to have been described in the literature. Chloro complexes of cadmium are stronger than such complexes of the other metals and with formation constants in between those of the THAM copper and THAM nickel complexes.

The immobility of all five metals when a phosphate buffer is used as leachant is due to precipitation of slightly soluble phosphates. The indication of copper being less mobile than the other metals is in accordance with the solubility product values for the five phosphates (Lindsay, 1979).

Conclusion

It is clearly demonstrated that the mobility of a number of metal ions in the two soils used in this experiment is determined by a balance between the binding strength of solid soil components such as clay minerals and organic matter, and the formation of soluble metal species. The soil pH is an important parameter for prediction of metal mobility implying that the mobility is high at low pH, particularly if soluble complexes are formed. At high pH the mobility is strongly impeded by binding to soil components and by formation of insoluble metal carbonates, hydroxy carbonates, or phosphates.

Chromatographic experiments using a soil column as a chromatographic column and cmploying simple chromatographic theory can be used to determine the mobility of several species relative to each other under specified conditions of soils and solutions. Absolute leaching rates can be estimated from such experiments but should be used for predictive purposes only when the conditions under which they are obtained are specified in detail.

Approximate distribution ratios can be determined directly from the "chromatograms" obtained through experiments. It might be argued that such values come closer to a description of the conditions in the field than distribution ratios obtained from batch experiments involving soil/solution ratios much lower than found under natural conditions. At least, it might be of some interest to compare distribution ratios (and sorption isotherms from tailed chromatographic peaks) for the same soil/solution system obtained by chromatographic and batch experiments respectively.

Literature

Alloway, B.J. (1990): Soil processes and the behaviour of metals. In: Alloway, B.J. (ed.) Heavy Metals in Soils. Blackie, London, p. 7-28.

Anderson, P.R. & Christensen, T.H. (1988): Distribution coefficients of Cd, Co, Ni, and Zn in soils. J. Soil Sci. 39: 15-22.

Bai, K.S. & Martell, A.E. (1969): The interaction of 2-amino-2-(hydroxymethyl)-1,3 propanediol with copper(II) and nickel(II) ions. Journ. Inorg. Nucl. Chem. 31: 1697—1707.

Baker, D.E. (1990): Copper. In: Alloway, B.J. (ed.). Heavy Metals in Soils. Blackie, London, p. 151-76.

Borggaard, O.B. (1985): Evidence in favour of considering soil iron oxides as composed of only two fractions. 5th Meeting of the European Clay Groups, Prague 1983, p. 477-83.

Borggaard, O.B. (1990): Dissolution and Adsorption Properties of Soil Iron Oxides. Dissertation, Vetr. and Agric. University, Copenhagen. 122 p.

Bowen, H.J.M. (1979): Environmental Chemistry of the Elements. Academic Press, London. 333 p.

Christensen, T.H. (1989): Cadmium Soil Sorption al Low Concentrations. Dissertation. Polyteknisk Forlag, Lyngby. 40 p.

Davies, B.E. (1990): Lead. In: Alloway, B.J. (ed.) Heavy Metals in Soils. Blackie, London, p. 177-96.

Hildebrand, E.E. & Blum, W.E. (1975): Fixation of emitted lead by soils. Z. Pflanzenern. Bodenk. 138: 279-94.

Jones, K.C., Lepp, N.W. & Obbard, J.P. (1990): Other metals and metalloids. In: Alloway, B.J. (ed.). Heavy Metals in Soils. Blackie, London, p. 280-321.

Jönsson, JÅ. & Lövkvist, P. (1989): Calculation of adsorption isotherms from chromatographic peak shapes. Chemometrics and Intelligent Lab. Systems 5: 303-10.

Jørgensen, S.S. & Willems, M. (1987): The fate of lead in soils: Lead originating from roofs of ancient churches. Ambio 16: 16-19.

Karger, B.L., Snyder, L.R. & Horwath, C. (1973): An Introduction to Separation Science. J. Wiley & Sons, New York, 586 p.

Lindsay, W.L. (1979): Chemical Equilibria in Soils. J. Wiley & Sons, New York, 449 p.

McGrath, S.P. & Smith, S. (1990): Chromium and nickel. In: Alloway, B.J. (ed.). Heavy Metals in Soils. Blackie, London, p. 125-50.

McLaren, R.G. & Crawford, D.V. (1974): Studies on soil copper. III. Isotopically exchangeable copper in soils. J. Soil Sci. 25: 111-19.

Mitchell, B.D. & Smith, B.F.L (1974): The removal of organic matter from soil extracts by bromine oxidation. J. Soil Sci. 25: 239-41.

Rasmussen, K. (1961): Uorganiske svovlforbindelsers ansætninger i jordbunden (Transformations of inorganic sulphur compounds in soil). Dissertation. Vetr. and Agric. University, Copenhagen. 176 p.

Smith, R.M. & Martell, A.E. (1976): Critical Stability Constants, Vol. IV. Inorganic Complexes. Plenum Press, New York. 257 p.

Sposito, G. (1983): The chemical forms of trace metals in soils. In: Thornton, I. (ed.). Applied Environmental Geochemistry. Academic Press, London, p. 123-70.

Tölg, G. (1989): Analytical chemistry and the quality of life. Kontakte, Merck (Darmstadt), 1989 (2): 20-29.

Ure, A.M. (1990): Methods of analysis for heavy metals in soils. In: Alloway, B.J. (ed.). Heavy Metals in Soils. Blackie, London, p. 40-80.

Cation ordering in stichtite, a chromium (III) bearing hydroxy-carbonate of the pyroaurite group

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Stichtite is a lilac coloured chromium(III) bearing anionic clay mineral belonging to the pyroaurite-sjögrenite group. At its type locality at Dundas, Tasmania, stichtite is found to be associated with minor amounts of chromite, chlorite and pyroaurite-like minerals, probably iowaite and mountkeithite. The Dundas stichtite has the approximate composition $Mg_{6.61}Ni^{II}_{0.02}$-$Al_{0.68}Fe^{III}$ *0.16*^{CrIII} *0.94*$^{(OH)}$*16*$^{(Co3)}$*1.29. Its trioctahedral layer is characterised by being iron poor and aluminium rich, and by having a high divalent:trivalent cation ratio. One per nine metal atoms is chromium(III). Determinations of the relative amounts of chromium (III) moromers and hydroxy-bridged chromium (III) polymers present in perchloric acid digests of the stichtite indicate that chromium (III) is not randomly distributed within the octahedral layer. Consequently, its octahedral layer may be regarded as cation ordered From the visible absorption spectrum, the chromium (III) in stichtite is found to be as stable as in chromian chlorites. Intercalation of silicate anions in stichtite may initiate the formation of a chromian chlorite.*

Keywords: *Tasmania, stichtite, pyroaurite, hydroxy-carbonate, chlorite, chromium (III), cation-ordering.*

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Stichtite is the rhombohedral magnesium-chromium(III) hydroxy-carbonate member of the pyroaurite-sjögrenite group of minerals. This group of minerals comprises layered hydroxy-carbonates consisting of positively charged trioctahedral metal-hydroxide layers $[M_a{}^{II}{}_{(1-x)} M_b{}^{III}{}_x(OH)_2]^{x+}$ alternating with negatively charged interlayers of anions and water molecules, e.g. $[x/2\ CO_3\ .\ 0.5\ H_{2O}]^{x-}$ (fig. 1). Metals of the 1st transition series plus magnesium and aluminium are common constituents of the hydroxide layer.

The fraction of trivalent metals, x, is normally in the range 0.25-0.33 for mineral samples. Substitution among both the trivalent and divalent metal cations of the octahedral layer is often observed. Part of the chromium in stichtite, for example, may be substituted by iron and/or aluminium. The magnesium-chromium end member has been given the formula $Mg_6Cr^{III}{}_2(OH)_{16}$ $CO_3 . 4H_2O$(Frondel, 1941).

The existence of distinct $M_a{}^{II}$ and $M_b{}^{III}$ sites in pyroaurite compounds is not normally observable by diffraction techniques, (Allmann, 1970; Taylor, 1973). Indications of cation ordering have been reported for sjögrenite, takovite, hydrotalcite and carrboydite, (Taylor, 1969; Bish, 1977b), and complete cation ordering has been observed for the pyroaurite-like compounds Al_4Li_2-$(OH)_{12}CO_3$, (Serna et al., 1982) and Ca_4Al_2-$(OH)_{12}SO_4$, (Allmann, 1968a). Based on structural considerations Brindley & Kikkawa (1979) have argued that a cation ordered octahedral layer, i.e. a layer where trivalent cations do not occur as nearest metal neighbours, should be the most stable configuration.

The chromium(III)-containing pyroaurite type compounds may provide further insight into the problem of cation ordering in the hydroxide layer. Due to the inert nature of chromium(III) complexes, hydroxy-bridged, polynuclear chromium(III) species (*μ-hydroxo* complexes) are quite robust. For the double hydroxy bridged chromium(III) dimer, the acid cleavage (1M $HClO_4$,

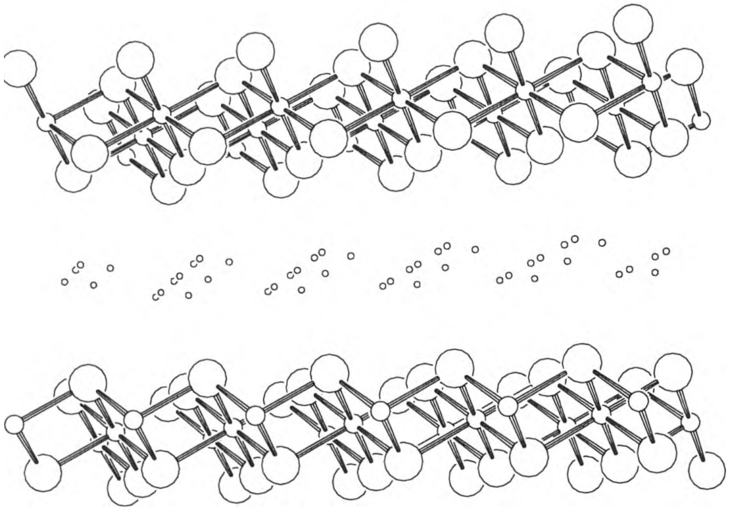

Fig. 1. Structure of pyroaurite type compounds consisting of trioctahedral metal-hydroxide layers (A) alternating with layers of anions and water molecules (B) (only oxygen sites shown). The layers are perpendicular to the c-axis. Drawing based on data from Allmann (1968b, 1969).

25°C) of the first hydroxy bridge is a relative fast reaction; however, cleavage of the remaining hydroxy bridge proceeds slowly, $t_{½} = 6$ days in 2-6 M $HClO_4$ at 25°C, (Thompson, 1964). This allows the hydroxy bridged chromium(III) polynuclear species to be separated by ion exchange chromatography (Laswick & Plane, 1959).

Stichtite dissolves almost instantaneously in dilute mineral acids and any hydroxy bridged chromium(III) polymers present in the structure are assumed to survive through the dissolution step and can thus be separated from the chromium(III) monomers. Previously this technique has been used by Spiccia & Marty (1986) to study the ageing of chromium(III) hydroxide. In the case of stichtite, it is further assumed that chromium(III) hydroxy bonds to other metal cations other than chromium(III) cleave during acid dissolution, and also that the presence in solution of these other metal cations does not influence the robustness of the chromium(III) polymers.

Compounds of the pyroaurite-sjögrenite group are of considerable interest in studies on the formation of phyllosilicates, (Gastuche et al., 1967; Brown & Gastuche, 1967). Ortho-silicate anions may replace carbonate or other anions in the interlayer of pyroaurite type compounds whereby trioctahedral phyllosilicates may form through the polymerisation of interlayer silicate ions, (Schutz & Biloen, 1987; Thomassin & Touray, 1979; Thomassin & Touray, 1982; Crovisier et al., 1983). Hence, in environments where pyroaurite type compounds form, they may occur as shortlived transitory phases only and therefore will not be detected by mineralogical analyses.

Stichtite from Dundas, Tasmania, was originally described by Petterd (1910). Later, other occurences have been reported: Barberton, Transvaal, (Hall, 1922); Cunningsburgh, Shetland Islands, (Read & Dixon, 1933); Black Lake, Quebec, (Poitevin & Graham, 1918); Mount Keith, W. Australia, (Hudson & Bussell, 1981); Teretinsky Ridge, Altay, (Tatarinov et al.,1985; references to other occurrences in the USSR and Eastern Europe are also given); Campo Formoso, Brazil, (Calas et al., 1984). Schumann (1978) refers to an occurrence in Algeria.

At all localities stichtite is present in serpentinites. Stichtite mixed with its hexagonal polytype (barbertonite) may also occur, and normally specimens also contain other mineral impurities such as serpentine and chromite. The only JCPDS card (14-330) (JCPDS, 1964), on stichtite refers to the material from Dundas.

The sample of the Dundas stichtite (no. 1970/137) investigated in the present work, was provided by the Mineralogical Museum of Copenhagen.

Experimental

Chemical analysis

The amount of carbon dioxide evolved during digestion in 2M $HClO_4$ for 30 minutes was determined by absorption in $Ba(OH)_2$, (Larsen, 1949). The concentration of metals in the acid digests was determined by atomic absorption spectroscopy (AAS). The insoluble residue remaining in the acid digest was isolated and washed, and its content of chromium determined after digestion in hydrofluoric acid. A semiquantitative determination of metals in the perchloric acid solution was carried out using an inductive coupled plasma atomizer equiped with a mass spectrometer analyser (ICP/MS).

Solutions for ion exchange chromatographic separation of mononuclear and polynuclear chromium(III) species were prepared by dissolving 20-30 mg of the stichtite sample in 2 ml 2M $HClO_4$ during 30 min. After addition of 1 ml 4M $NaClO_4$ the mixture was filtered and the clear filtrate diluted with water to 50.00 ml. After addition to a 20x1 cm column packed with Sephadex SP C-25 (H^+ form) chromium(III) species were separated by elution according to Stünzi & Marty (1983).

For comparison synthetic samples of stichtite were prepared according to procedures given by Hansen (1990).

All analyses were carried out in triplicate and double deionized water was used throughout the investigation.

X-ray diffraction

Samples, either as unoriented or oriented powdered specimens, were scanned from 6-80°2Θ at 0.5 °2Θ/min using CoKα radiation. Unoriented samples were prepared by tapping and pressing powders against filter paper to minimise preferred orientation; powdered quartz used as an internal standard. Unit cell parameters were obtained by a least squares refinement of diffraction data. Diffractograms were simulated using modified data for the pyroaurite structure (Allmann, 1968b, 1969) as input to the POWD simulation program, (Smith et al., 1982). Glycerol saturation of oriented samples was carried out by exposing the sample to glycerol vapour at 120°C, (Hansen & Taylor, 1990).

Weight (mg)	**Mg^{2+}**	**Cr^{3+}**	**Fe^{3+}**	**Al^{3+}**	**Ni^{2+}**	**CO_3^{2-}**
	µmole					
29.85	**209.4**	**29.85**	**4.93**	**21.50**	**0.62**	**40.89**

Cr(III) monomers 95.5 % **Cr(III) polymers 4.5 %**

Table 1. Chemical composition of the perchloric acid digest of the stichtite and relative a-mounts of Cr(III) monomer and Cr(III) hydroxy polymers. Average values of 3 analyses.

Infrared and visible Spectroscopy

Infrared spectra (IR) from 4000-300 cm^{-1} were recorded on a Perkin Elmer 580 grating spectrophotometer using samples pressed into discs of potassium bromide.

Photoacoustic spectra (PAS) of powdered samples were recorded from 300-750 nm in steps of 1.25 nm using a spectrophotometer equiped with a 150 W Xenon arc lamp, a PTI grating monochromator and Brüel & Kiær detector microphones. At each wavelength the recorded signal was averaged over 20 measurements. The spectra were corrected for wavelength dependent lamp intensity variations by scaling the sample signal relative to the signal from a black sample (lampblack).

Results

The chemical composition of the material dissolved in 2M $HClO_4$ appears from table 1. In addition trace amounts of Mn, Co, Zn, V, Zr and Cu were detected by ICP/MS. Assuming the dissolution extract originated from stichtite only, the formula $Mg_{6.61}Ni^{II}_{0.02}Al_{0.68}Fe^{III}_{0.16}Cr^{III}_{0.94}(OH)_{16}(CO_3)_{1.29}$ is calculated by assuming an overall charge neutrality. The $HClO_4$ residue contained app. 7 % (wt.) of chromium. Only a small fraction (4.5 %) of the total chromium(III) in the perchloric acid digests was present in hydroxy bridged chromium(III) polymer species. These were essentially dimers as indicated by the chromatographic elution behaviour.

Minor amounts of chlorite and chromite and

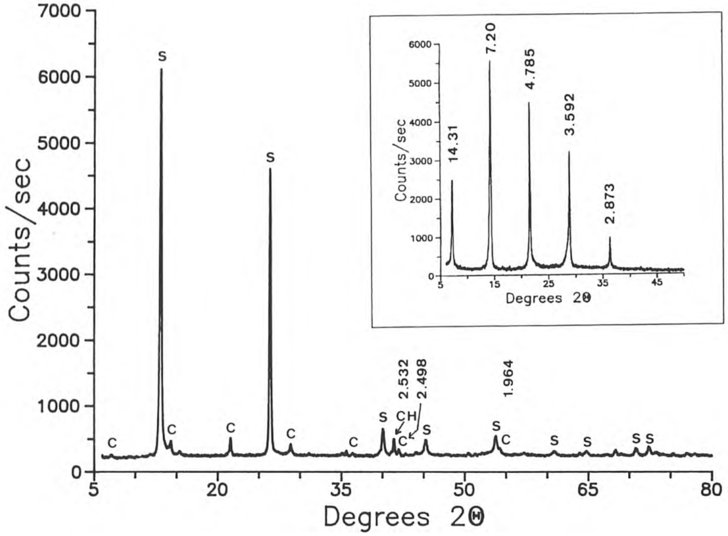

Fig. 2. XRD traces of an unoriented sample of the Dundas stichtite. Insert: XRD trace of an oriented sample of the residue after acid digestion of the stichtite. C = chlorite, S = stichtite and Ch = chromite. d-spacings in Å. (For d-spacings of the stichtite see table 2).

trace amounts of other phases were detected during XRD on unoriented samples (fig. 2). Barbertonite was not detected. XRD of the acid insoluble residue showed chlorite (polytype lib) (fig. 2, insert) and chromite to be present. Table 2 lists the observed and calculated d-spacings and intensities for the stichtite. A least squares refinement of the diffraction data gave $a_o = 3.09$ Å and $c_o = 23.542$ Å for the stichtite unit cell indexed in the hexagonal system. XRD of the oriented sample (fig. 3A) showed chlorite basal reflections and component(s) with diffraction peaks at 11.07, 8.23, 6.72, 5.59 and 4.13 Å in addition to the intense stichtite (003) and (006) peaks. After glycerol saturation (fig. 3B) the position of chlorite peaks remained unchanged, whereas all other peaks broadened and increased to 12.4, 9.3, 8.1 and 4.79 Å. This allowed the 11.07-4.13 Å diffractions of the untreated sample to be assigned to layer structured components which easily degrade in dilute acids and which swell (or degrade) by glycerolation. The diffractions are tentatively assigned to mountkeithite ($(Mg,Ni)_9(Fe,Cr,Al)_3(OH)_{24}(CO_3,SO_4)_{15}(Mg,Ni)_2(SO_4)_2(H_2O)_{11}$)(11.07 and 5.59 Å), (Hudson & Bussell, 1981) and iowaite ($Mg_4Fe(OH)_{10}Cl \cdot xH_2O$) (8.23, 4.13 Å; JCPDS card no. 20,500; JCPDS, 1964).

The main features of the IR trace of the Dun-das stichtite (fig. 4) are those commonly found in pyroaurite type compounds: 3510 cm^{-1} (O-H stretching), 1635 cm^{-1} (H-O-H bending) and 1380 cm^{-1} (CO_3^{2-} ; V_3). No absorptions due to SO_4^{2-} were detected. From IR absorption of the acid insoluble residue, this material (mainly chlorite) contributes to absorptions at 3500-3600 cm^{-1}, 1635 cm^{-1} and 630 cm^{-1}. The three absorptions from 960-1060 cm^{-1} may be ascribed

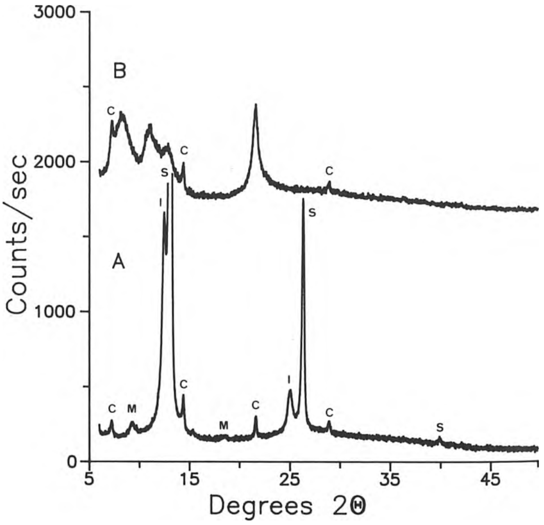

Fig. 3. XRD traces of an oriented sample of the Dundas stichtite before (A) and after (B) glycerolation. C = chlorite, I = iowaite, M = mountheithite, S = stichtite.

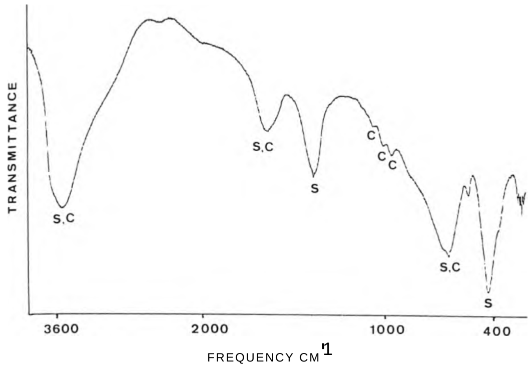

Fig. 4. IR spectrum of the Dundas stichlite. (Scale: < 2000 cm^{-1}: 100 cm^{-1}/.522 cm; > 2000 cm^{-1}: 100 cm^{--1}/0.261 cm) S = stichtite; C = clinochlore.

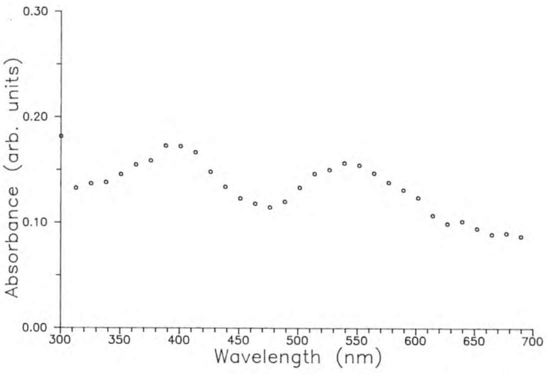

Fig. 5. Photoacoustic spectrum of the Dundas stichtite. (One per each Five points of measurement plotted).

to the acid insoluble residue only.

Two distinct absorptions were observed in the visible region (fig. 5). Both absorptions may be ascribed solely to spin allowed d-electron transitions of octahedrally coordinated chromium(III) (1545 nm (ν_1):$^4T_{2g}$ <— $^4A_{2g}$ and 395 nm (ν_2): $^4T_{1g}$ <— $^4A_{2g}$)$_{-1}$. The crystal field splitting (CFS) D_q = 1835 cm^{-1}, and the Racah B parameter, which is a measure of the covalency of the Cr-OH bond, may be calculated to 685 cm^{-1} according to Poole & Itzel (1963). Due to a small sample amount no PAS spectra could be obtained from the $HClO_4$ insoluble material. It had a grey colour and a silky lustre.

Discussion

From XRD, IR and the acid digestion analysis the Dundas stichtite sample investigated is seen to be reasonably pure, as less than 10 % of the sample is insoluble after 30 min treatment with 2M $HClO_4$. The perchloric acid soluble fraction, however, does contain minor amounts of other layer compounds, probably pyroaurite type compounds resembling iowaite and mountkeithite. The occurrence of the three pyroaurite type minerals together has also been reported from the Mount Keith area, (Hudson & Bussell, 1981). Although the octahedral layer compositions of the three pyroaurite group minerals differ, the composition of the interlayer is primarily responsible for the differences in the respective XRD patterns. Hence, it is possible that the iowaite- and mountkeithite-like phases associated with the Dundas sample have almost identical octahedral layers with compositions almost identical to that of stichtite. However, the very low concentrations of these phases suggest that the errors in the derived composition of the stichtite are small.

The derived formula gives a $M_a(II)$:$M_b(III)$ ratio of 3.72 and a OH:ΣM ratio of 1.90. High $M_a(II)$:$M_b(III)$ ratios were also found in earlier analyses of this Dundas stichtite (Petterd, 1910; Hezner, 1912; Foshag, 1921). The OH/ΣM ratio deviates from 2 which is the theoretical value for octahedral layers without vacancies, c.f. $Mg(OH)_2$. The presence of small amounts of pure metal carbonates or bicarbonates associated with the stichtite sample would not be taken into account in the chemical analysis. Such an impurity would result in OH:ΣM value lower than 2. Moreover, the stichtite from Dundas is characterised by a high aluminium and low iron content.

Chlorite and smaller amounts of chromite constitute the perchloric acid insoluble fraction. Due to the small sample amount available it has not been possible to determine by wet chemical analysis the composition of the chlorite and the chromite. However, appreciable quantities of chromium are present and the possibility of the chlorite being a chromian clinochlore cannot be rejected.

Ion chromatography of the perchloric acid solutions indicates that 4-5 % of the total chromium(III) are present in polynuclear (mainly binuclear) complexes. Hence, for the stichtite 4-5 % of the chromium atoms of the octahedral layer are expected to have at least one chromium atom as its nearest metal neighbour. Assuming a random distribution of the trioctahedral chromium, aluminium, iron, magnesium and nickel, the probability of finding a chromium atom which has at least one chromium atom as its nearest metal neighbour may be calculated as follows:

A: At least one neighbour is Cr

B: One Cr present. $P(B) = P(Cr) = 0.112$

$P(A|B) = [1—(1—0.112)^6] = 0.510$

$P(A \text{ and } B) = P(A|B)\text{-}P(B)$

$= [1—(1—0.112)^6].0.112 = 0.057$

i.e. the probability is 5.7 %. However, considering only the chromium in the octahedral layer, the probability of a chromium(III) being hydroxy bridged to at least one other chromium(III) is equal to P(A|B) = 51.0 %. This figure is 10 times than what has been found experimentally, strongly indicating that chromium(III) cations are distributed in a more or less ordered way in the octahedral layer. According to Brindley & Kikkawa (1979), the charge of +1 created at each trivalent cation site may cause the trivalent cations to be as far apart as possible because of mutual repulsion. If this is the sole cause inhibiting chromium(III) nearest metal neighbours, all trivalent cations in the hydroxide layer are likely to have divalent (magnesium) cations as their nearest metal neighbours. Nevertheless, it may be expected that neither the chromium(III) nor any of the other octahedral cations are randomly distributed.

The XRD of the unoriented stichtite shows low intensities for other than basal reflections. This is quite different from what is expected theoretically (table 2) and from observations of the diffraction of most other pyroaurite type compounds. Hence, the proposed pyroaurite structure model may not apply in all details to the stichtite. For instance a disorder in the octahedral layer stacking in the [001] direction could cancel out other than basal reflections including superstructure diffractions due to cation ordering.

	This investigation				JCPDS 14-330[2]	
(hkl)	d_{obs}[1]	I_{obs}	d_{cal}	I_{cal}	d_{obs}	I_{obs}
(003)	7.87	100	7.85	100	7.8	100
(006)	3.920	57	3.924	25	3.91	90
					2.87	10
(101)			2.656	1		
(012)	2.612	6	2.607	22	2.60	40
(015)	2.326	5	2.325	25	2.32	30
(018)	1.979	6	1.979	24	1.97	30
(10$\underline{10}$)	1.766	2	1.767	6	1.76	10
(01$\underline{11}$	1.671	2	1.671	5	1.66	10
(110)	1.542	3	1.543	8	1.54	20
(113)	1.515	3	1.514	10	1.51	20
(10$\underline{13}$)	1.500	1	1.499	4	1.49	10
(116)	1.437	1	1.436	3	1.43	10
(01$\underline{14}$)	1.424	1	1.423	1		

Table 2. Observed and calculated d-spacings and intensities for stichtite compared with JCPDS data. Indices refer to a hexagonal cell. 1. Quartz used as an internal standard. 2. Original indices has been halved.

The glycerol swelling behaviour of the Dundas stichtite (fig. 3) differs from what has been observed for the CO_3^{2-} forms of pyroaurite and hydrotalcite which expands to give (003) spacings at 10Å and 14.4Å respectively, (Hansen & Taylor, 1990). However, synthetic stichtite is found to swell like hydrotalcite. The 12.41, 9.34 and 4.79Å peaks of the glycerolated stichtite (fig. 3B) sharpened and the 8.1 Å reflection decreased in intensity with increasing time of exposure to glycerol vapour (> 30 days). No reflections occured in the 3-6 °2Θ region. The apparent lack of one rational series of basal reflections may indicate that the stichtite is composed of crystallites which do not swell to the same extent. This may partly be due to different main- and interlayer compositions.

Octahedrally coordinated chromium(III) gives rise to two absorption bands between 300-700 nm resulting in colours from red/violet, gray to green, (Neuhaus & Richartz, 1958; Poole, 1964). In minerals, a lower value of the CFS (and thus green colours) is observed for wider coordination polyhedra or decreasing charge of the oxygens coordinating the chromium(III), e.g. when silicate tetrahedra share ligands (O,OH) with the chromium(III) octahedra, (Neuhaus & Richartz, 1958; Calas et al., 1984). For stichtite the CFS is high (D_q = 1835 cm^{-1} compared with 1740 cm^{-1} for the *aqua* ion $[Cr(H_2O)_6]^{3+}$), so explaining the lilac colour of the mineral. The position of the ν_1 and ν_2 absorptions and the derived D_q and Racah B parameters found in the present study are very similar to the values obtained by Calas et al. (1984) for Brazilian stichtite = 541 nm and ν_2 = 395 nm). Almost the same ν_1 and ν_2 values are observed for chromium(III) of the 'brucitic' layer of chromian clinochlores, (Bish, 1977a; Calas et al., 1984). For most other minerals containing octahcdrally coordinated chromium(III) D_q is smaller and B is higher indicating a lower crystal field stabilisation energy (CFSE = $12 \cdot D_q$) and less covalency of the Cr-O(H) bond. Therefore, in terms of the energy of the octahedrally coordinated chromium(III), the possible incorporation of stichtite-trioctahedral layers in the interlayer of 2:1 phyllosilicates could result in formation of a chromian chlorite.

The reaction sequence leading to a chromian chlorite formation could be initiated by the intercalation of silicate anions in the interlayer of stichtite. During polymerisation of silicate anions and bond formation to the hydroxyl sheets of the chlorite 2:1 subunit, its constituent chromium(III) might be released due to electrostatic repulsion effects and the lower CFSE of octahedrally coordinated chromium(III) which are linked to silicate tetrahedra. This would eventually result in a chlorite consisting of a chromium deficient 2:1 subunit with a chromium rich 'brucitic' interlayer. It is suggested that such reactions might explain the association of chlorite with the Dundas stichtite. However, this is merely speculation and the problem needs further attention. The role of such reactions in this transformation of anionic clays (pyroaurites) to cationic clays (phyllosilicates) should be considered in more detail.

Summary

Selective dissolution of pyroaurite minerals in dilute mineral acids enables their composition to be determined in the presence of more acid re-sistant minerals. A sample of stichtite from Dundas, Tasmania shows aluminium and iron(III) substitution for chromium(III). The stichtite has a divalent: trivalent metal ratio of 3.72 resulting in a low layer charge. 11.2 % of the metal atoms are chromium(III) which show a strong tendency of not to be nearest metal neighbours in the trioctahedral layer of stichtite. Hence the octahedral layer may be regarded as more or less cation ordered. The layer structured minerals swell with glycerol at 120°C, but distinct monolayer or bilayer glycerol intercalates are not formed. The chromium(III) of the stichtite octahedral layer shows a crystal field stabilisation energy of the same magnitude as chromium(III) in chromian chlorites. It is possible that silicate anion interlayering of stichtite may lead to chromian chlorites formation.

Acknowledgments

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References

Allmann, R. (1968a): Die Doppelschichtstruktur der plattchenförmigen Calcium Aluminium-Hydroxisalze am Beispiel die $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$. N. Jahrb. Miner. Mhft.: 140-44.

Allmann, R. (1968b): The crystal structure of pyroaurite. Acta Cryst. B24: 972-77.

Allmann, R. (1969): Nachtrag zu den Strukturen des Pyroaurits und Sjögrenits. N. Jahrb. Min. Mhft.: 552-58.

Allmann, R. (1970): Doppelschichtstrukturen mit brucitahnlichenSchichtionen$[Me(II)_{1-x}Me(III)_x(OH)_2]^{x+}$·Chimia 24: 99-109.

Bish, D.L. (1977a): A spectroscopic and X-ray study of the coordination of Cr^{3+} ions in chlorites. Am. Min. 62: 385-89.

Bish, D.L. (1977b): The occurence and crystal chemistry of nickel in silicate and hydroxide minerals. Ph. D. thesis, The Pennsylvania State University.

Brindley, G.W. & Kikkawa, S. (1979): A crystal-chemical study of Mg, Al and Ni, Al hydroxy-perchlorates and hydroxy-carbonates. Am. Min. 64: 836-43.

Brown, G. & Gastuche, M. C. (1967): Mixed magnesium-aluminium hydroxides. II. Structure and structural chemistry of synthetic hydroxy-carbonates and related minerals and compounds. Clay Min. 7: 193-201.

Calas, G., Manceau, A., Novikoff, A. & Boukili, H. (1984): Comportement du chrome dans les minérauxd'alteration du gisement du Campo Formosa (Bahia, Brésil). Bull. Mineral. 107: 1169-82.

Crovisier, J.L., Thomassin, J.H., Juteau, T., Eberhart, J.P., Touray, J.C. & P. Baillif (1983): Experimental seawater-basaltic glass interaction at 50°C: Study of early developed phases by electron microscopy and X-ray photoelectron spectrometry. Geochim. Cosmochim. Acta 47: 377-87.

Foshag, W.F. (1921): The chemical composition of hydrotalcite and the hydrotalcite group of minerals. Proceedings U.S. Nat. Mus. (No. 2329): 147-53.

Frondel, C. (1941): Constitution and polymorphism of the pyroaurite and sjögrenite groups. Am. Min. 26: 295-315.

Gastuche, M.C., Brown, G. & Mortland, M.M. (1967): Mixed magnesium-aluminium hydroxides. I. Preparation and characterization of compounds formed in dialysed systems. Clay Min. 7: 177-92.

Hall, A.L. (1922): Trans. Geol. Soc. S. Africa 24: 182.

Hansen, H.C.B. (1990): Synthesis of double metal hydroxy-carbonates with pyroaurite structure. Evaluation of their geochemical significance. Ph.D. thesis. Copenhagen (in prep.)(in Danish).

Hansen, H.C.B. & Taylor, R.M. (1990): The use of glycerol intercalates in the exchange of CO_3^{2-} with SO_4^{2-} NO_3^- or Cl^- in pyroaurite type compounds. Submitted for publication in Clay Min.

Hezner, L. (1912): Ueber en neues chromhaltiges Magnesiumhydroxy carbonat. Cbl. Min.: 569-71.

Hudson, D.R. & Busell, M. (1981): Mountkeithite, a new pyroaurite-related mineral with an expanded interlayer containing exchangeable $MgSO_4$. Min.Mag. 44: 345-50.

JCPDS; Joint Comittee on Powder Diffraction Standards. Inorganic Data Cards. Pensylvania.

Larsen, S. (1949): An apparatus for the determination of small quantities of carbonate. Acta Chem. Scand. 3: 967-70.

Laswick, J.A. & Plane, R.A. (1959): Hydrolytic polymerisation in boiled chromic solutions. J. Am. Chem. Soc. 81: 3564-67.

Neuhaus, A. & Richartz, W. (1958): Absorptionsspektrum und Koordination allochromatisch durch Cr^{3+} gefärbter natürlicher und synthetischer Einkristalle und Kristallpulver. Angew. Chem. 70: 430-34.

Petterd, W.F. (1910): Catalogue of the minerals of Tasmania. Hobart p. 167-70.

Poitevin, E. & Graham, P.D. (1918: Contributions to the mineralogy of Black Lake area, Quebec. Can. Geol. Surv., Mus. Bull. no. 27, Geol. Ser. no. 35: 26-30.

Poole, C.P., Jr. (1964): The optical spectra and color of chromium containing solids. J. Phys. Chem. 25:1169-82.

Poole, C.P., Jr. & J.F. Itzel, Jr. (1963: Optical reflection spectra of chromia-alumina. J. Chem. Phys. 39:3445-55.

Read, H.H. & Dixon, B.E. (1933): On stichtite from Cunningsburgh, Shetland Islands. Min. Mag. 23: 309-16.

Schumann, W. (1978): Ædelstene. Dansk bearbejdelse ved Ove Dragsted. G.E.C. Gad, Kbh.

Schutz, A. & Biloen, P. (1987): Interlamellar chemistry of hydrotalcites. I. Polymerisation of silicate anions. J. Solid State Chem. 68: 360-68.

Serna, CJ., Rendon, J.L. & Iglesias, J.E. (1982): Crystal-chemical study of layered $[AU_2Li(OH)_6]^+X^- nH_2O$. Clay Min. 30: 180-84.

Smith, D.K., Nichlols, M.C. & Zolensky, M.E. (1982): A fortran IV program for calculating X-ray powder diffraction patterns-version 10. Pensylv. St. Univ., Pensylv.

Spiccia, L. & Marty, W. (1986): The fate of "active" chromium hydroxide, $Cr(OH)_3.3H_2O$, in aquoues suspension. Study of the chemical changes involved in its ageing. Inorg. Chem. 25: 266-71.

Stünzi, H. & Marty, W. (1983): Early stages of the hydrolysis of chromium(III) in aqueous solution. I. Characterization of a tetrameric species. Inorg.Chem. 22:2145-50.

Tatarinov, A.V., Sapozhnikov, A.N., Produkin, S.G. & Frolovo, L..P. (1985): Stichtite in serpentinites of the Terehtinsky Ridge (Altay). Zapiski Vses. Mineral. Obshchestva 114: 575-81 (in Russian).

Taylor, H.F.W. (1969): Segregation and cation-ordering in sjögrenite and pyroaurite. Min. Mag. 37: 338-42.

Taylor, H.F.W. (1973): Crystal structures of some double hydroxide minerals. Min. Mag. 39: 377-89.

Thomassin, J.-H. & Touray, J.-C. (1979): Etude des premiers stades de l'interaction eau-verre basaltique: donné de la spectrométrie de photoélectrons (XPS) et de la microscopie électronique à balayage. Bull. Mineral. 102: 594-99.

Thomassin, J.-H. & Touray, J.-C. (1982): L'hydrotalcite, un hydroxy carbonate transitoire précocement formé lors de l'interaction verre basaltique - eau de mer. Bull. Mineral. 105: 312-19.

Thompson, G. (1964): C.S.J., Ph.D. thesis. Lawrence Radiation Laboratory Report UCRL-11410, University of California, Berkeley, California.

Cadmium in Danish agricultural soils

Thomas H. Christensen and Jens Chr. Tjell

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The cadmium content of Danish agricultural soils range from 10 to 500 µg kg^{-1} with an average of 215 µg kg^{-1} soil for the plough layer. Soil samples collected at Danish Agricultural Experimental Stations at different times show that the cadmium content of the plough layer has increased over the last 50-60 years at a rate of 0.5 % per year, or 1 µg kg^{-1}y^{-1} due to atmospheric deposition and use of phosphate fertilizers. Since the behaviour of cadmium in the soil is mainly governed by reversible sorption processes, increasing soil concentrations will lead to higher plant uptake and consequently higher and presumably deleterious human exposure to cadmium. In order to sustain or even improve the current situation, the inflow of cadmium to agricultural soils has to be reduced to about 1 g ha^{-1}y^{-1} which is the estimated average outflow by leaching in Danish soils.

Keywords: *cadmium, Cd, accumulation in soils, sorption, soil content, leaching.*

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The behaviour of the toxic metal cadmium (Cd) in agricultural soils has attracted much attention during the last 20 years. Partly because of society's interest in disposing of waste containing Cd as a contaminant on land, and partly because of an increasing understanding of the role of atmospheric deposition and phosphate fertilizers as contributors to the Cd load on the terrestrial environment (Tjell et al, 1983).

The concern for Cd relates to the fact that human exposure to Cd in food and water (table 1) in many parts of the world has reached a level close to what is considered critical (CEC, 1981).

Food class	Human Cd intake	
	%	µg p^{-1}d^{-1}
Vegetables (& fruit)	15	4
Potatoes	20	5
Cereals	25	6
Animalia	20	5
Other (beverage, water, fish etc.)	20	5
Total	100	25

Table 1. Estimated amounts of Cd in human food in Denmark (after Tjell, 1985).

The concern is that higher soil concentrations of Cd will lead to more Cd in agricultural produce and drinking water and thereby to increased Cd exposure of the population.

This paper presents current knowledge on Cd concentrations in Danish agricultural soils in terms of concentration levels with depth, monitored long-term trends in plough layer concentrations, and sorption processes governing the behaviour of Cd in soils. Finally, the implication of this current knowledge is considered in relation to the sustainability concept of avoiding further accumulation of Cd in agricultural soils.

Development of Cd concentration in Danish soils

Cd concentrations have been determined in 193 samples from the Danish Soil Library (Lamm, 1971; Hansen, 1976) representing typical Danish agricultural soils at 0-20, 20-50, and 50-100 cm depths. The results are summarized in table 2. The soil Cd concentrations range from 10 to 500 *µg* kg^{-1}, and although the variability is substantial it is consistent that concentrations in the plough layer are twice as high as in the deeper soil

Depth	Number of observations	Average	Standard diviation	Range
0 - 20 cm	65	215	100	12-494
20 - 50 cm	64	107	90	6-351
50 -100 cm	64	95	110	10-408

* 5g of soil extracted for 24h in 20 ml 6M hot HNO$_3$, diluted to 50 ml and solvent extracted (by NaDDC in MIBK) before determination by graphite oven AAS.

Table 2. Cd concentrations in 3 depth intervals in Danish agricultural soils from the Danish Soil Library.

Results	Number of series	Average rate µg kg^{-1}y^{-1} of Cd
Increase, > 95% significance level	7	+1.17
Increase, 95-80% significance level	7	+0.86
Visual increase, non-significant	8	
Visual constant	9	-

Table 4. Result of statistical analysis of long-term fertilization field series. In some cases only visual assessments have been made.

layers. The average Cd concentration in the plough layer of 215 *µg* kg^{-1} is very close (within 10 %) to reported values for the other Nordic countries (Øien 1975; Anderson, 1977; Sippola & Mäkelä-Kurtto, 1986). The long-term development in Cd concentrations in Danish agricultural soils has been examined at 4 Danish agricultural experimental stations.

The plough layer samples originate from long-term fertilizer experimental plots receiving either 16-20 kg ha^{-1} of phosphorous, plus nitrogen and potassium in fertilizer or manure, and compared with no treatment. The crop rotational pattern is: grain, clover, grain and beet (or potatoes). The oldest experiments (Askov) began 1893, although the samples found only date back to 1923. The basic characteristics of the field soils are shown in table 3.

The time series for the 32 experimental plots were subject to a statistical analysis (table 4). Significant increases in soil Cd concentrations of around 1 *µg* kg^{-1}y^{-1}, were observed in 14 series. For the remaining 18 series, either too short time spans were available, or the variability was too large to give significant trends. Visual inspection further indicated increase for 8 series and constancy for 9 series, mostly sandy and acid soils. Samples from one plot (Tylstrup) showed significant decrease in Cd concentrations over time, but from a much higher initial concentration of 235 *µg* kg^{-1}, in contrast to 70-90 *µg* kg^{-1} for neighbouring plots. Fig. 1 shows the longest available time series from Askov.

The observed increases in soil Cd concentrations are the result of higher inflow of Cd, mainly from the atmosphere and phosphate fertilization, than outflow through downward percolation and removal with crops. However, an increase in ploughing depth from 18 cm to 24 cm in the fifties when mechanization was introduced caused a temporary decrease in soil Cd concentrations as subsoil low in Cd was incorporated into the plough layer.

The decrease in soil Cd concentrations due to the admixing of subsoil, is calculated as an apparent outflow of Cd from the plough layer using the measured Cd concentrations and the weight

	Fields	Years of existing samples	Clay < 2 *µ*m %	Silt 2-20 *µ*m %	Organic matter %	pH range in the period	Approximate Cd-content, µg kg^{-1} 0-20 cm	25-50 cm	K$_d^{Cd*}$
Askov	B-3	1923-80	11.5	12.1	3.3	6.0-7.1	175	50	1500 (pH=7)
Lundgaard	H1-3	1942-80	2.4	4.2	2.1	5.1-6.7	125	50	450 (pH =5.5)
Virum	3	1934-61	10.7	18.6	**2.2**	6.0-6.4	200	110	1000 (pH=6.2)
Tylstrup	C-1	1942-70	2.9	5.2	2.3	5.5-6.5	100	15	100 (pH=5)

* K$_d^{Cd:}$ Cd distribution coefficients determined by laboratory batch experiments (soil Cd concentration (µg kg^{1}) divided by solute Cd concentration (µg l^{-1}) at equilibrium at the listed pH-value).

Table 3. Some characteristics of soils in long-term experimental plots at Danish Agricultural Experimental Stations.

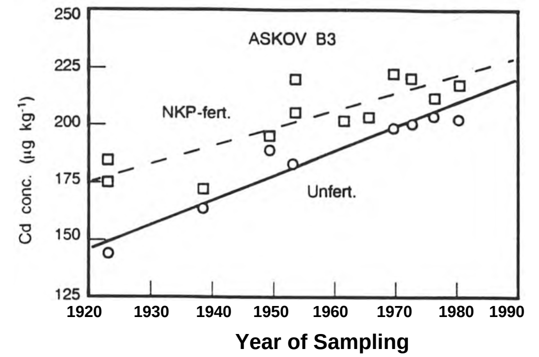


Fig. 1. Cd soil contents of NPK and manure fertilized and unfertilized plots at Askov Agricultural Experimental Station.

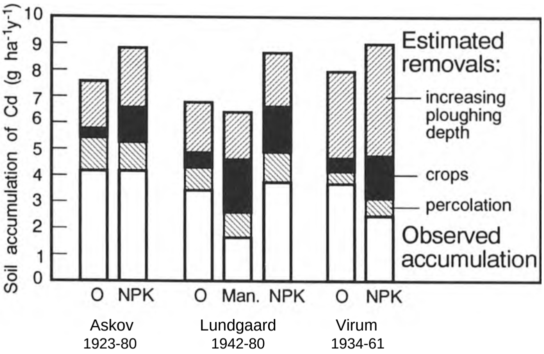


Fig. 2. Observed Cd accumulations (white lower columns) and calculated outflows of Cd from the plough layer of experimental plots subjected to different fertilization schemes. To the observed accumulation is added calculated removal of Cd by percolation and crops and the apparent loss when subsoil low in Cd is incorporated in the expanding plough layer.

ratios of the two soil layers. It is further possible to calculate the outflow of Cd with crops from plots, as yields of all plant parts removed have been recorded. These figures are considerably higher than for normal agricultural fields where most crop residues normally stay behind.

The outflow loss of Cd from the plough layer through downward percolation is estimated from measured distribution coefficients K_d^{Cd}, soil Cd concentrations, and estimated water percolation through the plough layer.

From the observed changes in soil Cd concentrations and the calculated outflows as shown in fig. 2, the residual increase in Cd concentrations is presumed to have been caused by inflow with fertilizer and from the atmosphere. The total average annual inflow of Cd appears to have been in the range 6.5-9 g $ha^{-1}y^{-1}$, of which 1.5-2 g $ha^{-1}y^{-1}$ is due to the P-fertilizer. The calculated atmospheric inflow of 6.5-8 g $ha^{-1}y^{-1}$ is of the same magnitude as measured in bulk precipitation monitored in Denmark since 1972/73, but is higher than the presently recorded inflow of around 1-2 g $ha^{-1}y^{1}$.

The long-term time series show that the Cd concentrations in Danish soils have increased during the last 50-60 years at an average rate of 1 *μg* $kg^{-1}y^{-1}$, corresponding to an annual increase of around 0.5 %. A slightly higher rate of increase in normal agricultural soils may be expected as less crop residues containing Cd are removed in normal farming practice.

Attenuation of Cd in soils

The distribution of Cd between the soil solid phase and soil solution is considered to be a key factor in evaluating the environmental consequences of Cd accumulation in soils. An increase in Cd concentration in the soil solution apparently leads to increase in Cd plant uptake and leaching of Cd. Gerritse et al. (1983) showed for 20 Dutch soils that plant uptake of Cd is highly correlated to Cd concentration in the soil solution.

The dominant mechanism governing the distribution of Cd between soil solids and soil solution is sorption, which here includes physical adsorption, chemisorption, ion exchange and surface complexation. Precipitation processes for Cd, e.g. as carbonates, phosphates and sulphides, are supposedly not likely at environmentally relevant concentrations; only sulphide precipitation may be of significance in strongly anaerobic environments (Christensen, 1989a).

From an environmental point of view Cd sorption in soil is a fast process reaching equilibrium within one hour (Christensen, 1984a). The sorption isotherm showing soil concentrations as a function of solute concentration may provide an estimate of the distribution of Cd between soil solids and solute. Such isotherms are shown in fig. 3 for two soils at different pH values. The

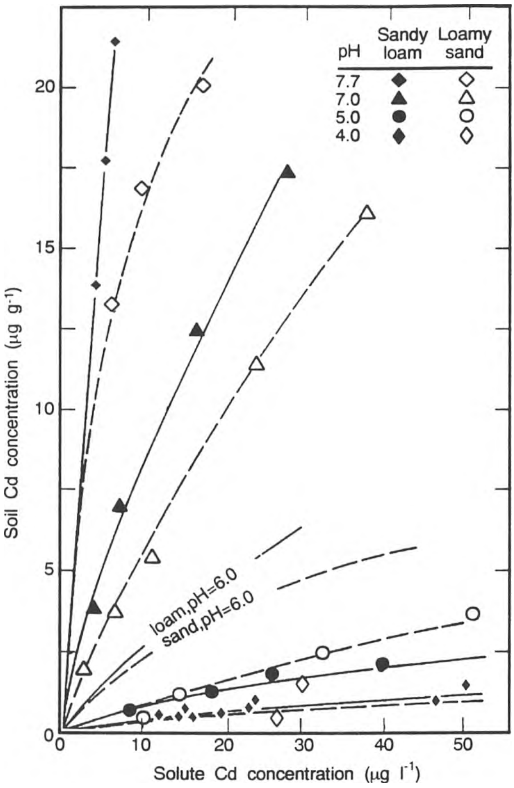


Fig. 3. Sorption isotherms for two mineral soils determined in 10^{-3} M $CaCl_2$ at different pH-values (Christensen, 1984a).

isotherm is usually slightly curvilinear to linear and a linear approximation is usually employed at low concentrations of Cd in soils. The isotherm is described by the slope, equal to the distribution coefficient K_d. The K_d may be used as a rough estimate of the Cd migration velocity (V_{Cd}) relative to the water velocity (V_{water}), through the equation:

$$V_{Cd}(V_{water})^{-1} = (1 + 5.k_d)^{-1} \quad \text{(Christensen, 1985)}$$

Desorption experiments (Christensen, 1984 b) indicate that the sorption process is almost fully reversible and that the distribution of Cd between soil solids and solute is independent of the origin of the Cd, and how long it has stayed in the soil. This indicates that although the soil may have a significant capacity to sorb Cd, the soil is not a permanent sink and previously sorbed Cd may be released upon changes in soil solution composition. This is strongly supported by Cd plant uptake experiments on soils sampled from below houses up to 200 years old. The plant uptake here was similar to uptake from normal exposed soils adjacent to the sampling spots (Jensen & Mosbæk, 1990).

The main factors affecting the distribution of Cd between soil solids and solute are calcium concentration and pH of the solute. At high concentrations other ions may also influence the distribution, e.g. zinc.

The effect of pH on sorption of Cd is evident from the data presented in fig. 3: a one unit increase in pH increases the distribution coefficient (equal to the slope of the curves) approximately 3 times. This shows that keeping up the soil pH is important in limiting the mobility and availability of Cd in the soil environment.

Calcium is the major cation in solution in most Danish soils and is probably the major competitor towards Cd for sorption sites on the soil solids (Christensen, 1984a). Zinc as an example of another competitor is usually present in the soil solution at much higher concentrations than Cd and may at concentrations above 0.3 mg l^{-1} in the soil solution compete with Cd for sorption sites. The effect has been explained as a competitive Langmuir equation (Christensen, 1987). However, in most cases under normal field conditions in Denmark the zinc solution concentration in the soil solute is too low to cause significant competition for Cd sorption sites.

Many soil components are able to sorb Cd e.g. clay minerals, sesquioxides, organic matter and calcite. Estimation of Cd distribution coefficients from soil parameters may be useful for predictive purposes. Such estimations should, however, be based on investigations involving pertinent soil solute concentrations. An investigation of 63 Danish soils at different depths down to 100 cm showed K_d values in the range of 15 - 2450 l kg^{-1}. About 40 % of the soils had K_d values below 200 l kg^{-1}. Correlating the observed K_d values to pH, texture, contents of humus, reactive organic matter, iron- and manganese oxides and other soil properties showed that soil pH was the

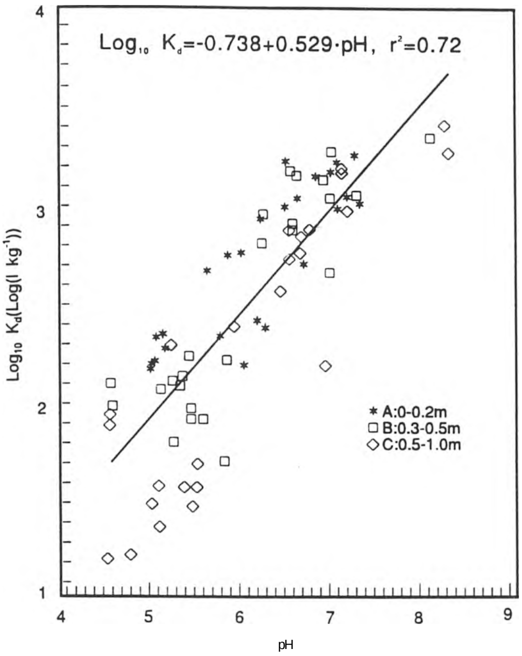


Fig. 4. K_d for Cd as function of soil solution pH (10 M $CaCl_2$) for 63 Danish agricultural soils representing various sampling depths (Christensen, 1989b).

dominating factor accounting for 72 % of the total variation in K_d (Christensen, 1989b). Fig. 4 shows the relationship between $\log_{10} K_d$ and pH (pH is here the soil solution pH estimated as the soil pH (in 10^{-2} M $CaCl_2$) + 0.4). The estimative regression equation improved slightly by including additional soil characteristics. Organic matter was identified as the second most important factor, e.g. an increase of organic matter from 0.5 % to 2.5 % only doubled the K_d value for the soil.

It should be noted that the 63 soils studied were loaded with only minor amounts of Cd. Prior to addition of Cd the soils contained from 12 to 490 μg kg^{-1} of Cd. After addition the Cd concentrations varied between 49 and 1100 μg kg^{-1}. At equilibrium the soil solute concentrations ranged from 0.25 to 3 μg l^{-1}. After equilibration the soil Cd content corresponded roughly to 0.01 % of the soil CEC, showing that Cd occupied only a very small fraction of the sites available for cation exchange. Since many soil compounds do not sorb Cd efficiently and since Cd at low concentrations may only react with the most favourable sorption sites, it is understandable that bulk parameters such as e.g. CEC and clay content do not correlate strongly with the Cd distribution coefficients.

Fig. 4 shows that at pH 5, K_d for Cd is of the order of 50 l kg^{-1} with a corresponding migration velocity of 0.004 times the water flow velocity. At pH 7, the K_d value is about 900 l kg^{-1} with a corresponding migration velocity of 0.0002. These estimates indicate that the mobility of Cd in soils is very restricted, thus high inflows of Cd to agricultural soils is a problem of accumulation rather than of increased leaching.

Based on the determined K_d values and Cd concentrations in Danish agricultural soils the soil solute concentration is estimated to range from 0.01 to 1.6 μg l^{-1} with an average of about 0.4 μg l^{-1}. This value is in fair agreement with measured Cd concentrations of 0.2 μg l^{-1} in drainage water from 15 Danish agricultural fields measured over a four-year period (Jensen, 1978). A net leaching from the plough layer of 3-400 mm per year and estimated soil solution concentrations ranging between 0.1-0.4 μg l^{-1} correspond to losses of 0.3-1.6 g ha^{-1}y^{-1} of Cd, with a likely average of approximately 1 g ha^{-1}y^{-1}.

Management of Cd in agriculture

In Denmark the average human intake of cadmium is of the order of 25 μg d^{-1} per person (table 1) which is only a factor of 2 or 3 below the corresponding PTWI (Provisional Tolerable Weekly Intake) set by the World Health Organisation (CEC, 1981). In order to protect the more vulnerable population groups from long-term effects any increase in the human intake is not warranted. Since agricultural produce is the predominant source for human Cd intake, and since increase in soil concentration will lead to increase in plant uptake of Cd, further accumulation of Cd in Danish agricultural soils should be prevented. A similar approach is apparently under consideration in the EEC (Jensen & Bro-Rasmussen, 1990), partly based on Danish data as presented in this paper.

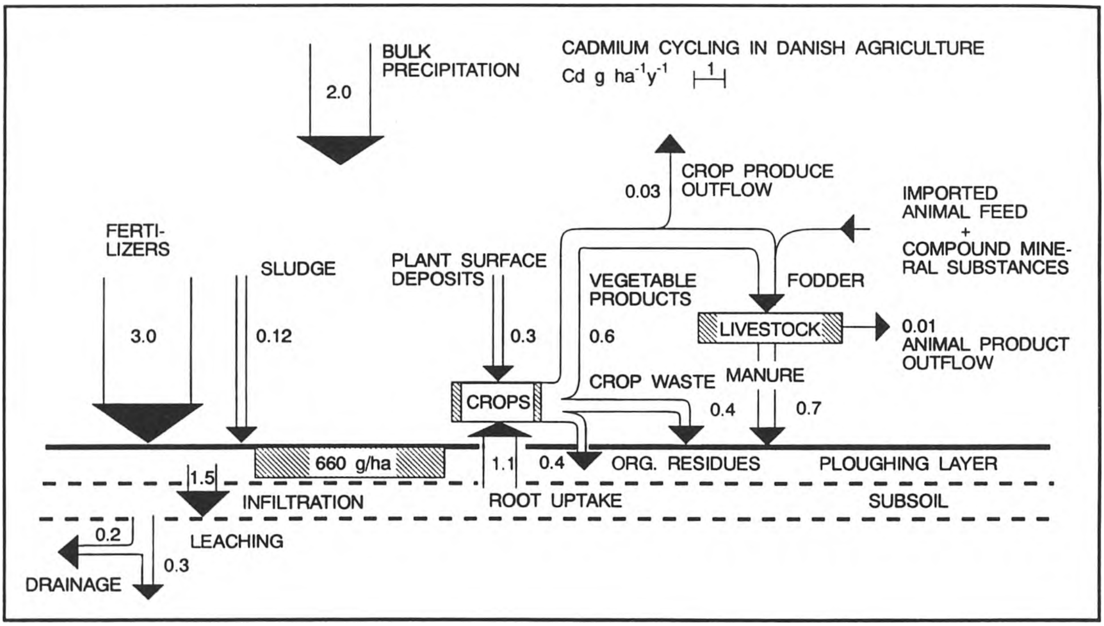


Fig. 5. Average balance of cadmium for the plough layer of Danish agricultural land (Hovmand, 1981).

The average balance for Cd in Danish agricultural land was estimated by Hovmand (1981) as shown in fig. 5. The main conclusion is that phosphate fertilizers and atmospheric deposition are the main inputs and leaching is the only significant outflow, as most Cd in harvested crops is returned to the land via manure.

The Cd inputs to soils with phosphate fertilizers and from the atmosphere may be controlled. The situation is not yet critical and time is available to implement such controls. For instance phosphate fertilizers low in Cd can be produced and advanced stack gas cleaning technology can be established for reduction of atmospheric deposition of Cd.

To adhere to a sustainability concept the inputs of Cd to soil must be reduced to a level not exceeding the outputs. This means that a precise estimate of the loss of Cd from the soil is a key factor in this context. Table 5 presents estimates of the leaching loss of cadmium from the plough layer for three Danish soils considered to differ in pH, cadmium content and hydrological conditions. The variation in Cd losses is substantial: From 1.5-3.5 g ha^{-1}y^{-1} in the more humid western part of Jutland with relatively acid, sandy soils to 0.3-1 g ha^{-1}y^{-1} in the eastern part of Denmark with moderate rainfall and neutral soils. A substainability concept based on these data would suggest a maximum acceptable input of Cd between 0.5 and 1.5 g ha^{-1}y^{-1} for Denmark on average. This would lead to a slow decrease in the Cd content of sandy soils in humid regions and a slow increase in loamy soils in drier regions. Assuming that the plant uptake is directly correlated to soil solution concentration of Cd, this seems acceptable since the plant uptake from loamy neutral soils seems to be half of that from more sandy soils at the same soil concentration. It should be remembered that the estimates are based on laboratory experiments, and field measurements are badly needed.

Summary

The cadmium concentrations in Danish agricultural soils range from 10 to 500 µg kg^{-1} with an average of 215 *µg* kg^{-1} in the plough layer. The subsoil contains only half of

Region in Denmark	Estimated water percolation from plough layer mm/year	Sandy soils [a] at [Cd] µg kg^{-1}		Loamy soils [b] at [Cd] µg kg^{-1}	
		110	170	160	320
Zealand	250	-	-	0.3	0.55
Jutland, north & east	400	1.6	2.5	0.5	1.0
Jutland, west & south	500	2.0	3.2	-	-

a. Assuming: soil solution pH equal to 6.0 and a K_d value of 350 l kg^{-1}.

b. Assuming: soil solution pH equal to 7.3 and a K_d value of 1350 l kg^{-1}.

Table 5. Estimated leaching losses of cadmium (g ha $^{-1}y^{-1}$) from the plough layers in different regions of Denmark.

this. The cadmium concentrations in the plough layer have increased during the last 50-60 years according to analyses of archive soils from Danish Agricultural Experimental Stations. The average accumulation rate of cadmium in soils is around 1 *µg* $kg^{-1}y^{-1}$ or approx. 0.5 *%* per year. The main sources for cadmium are phosphate fertilizers and atmospheric deposition contributing together about 5 g $ha^{-1}y^{-1}$ of cadmium, while about 1 g $ha^{-1}y^{-1}$ is removed through leaching. This shows, that the soil cadmium content will continue to increase over time unless inputs are reduced substantially. As cadmium is retained in the soil, soil solution concentrations will increase and hence an increased plant uptake of cadmium will result. This is undesirable as agricultural produce is the major source for the human intake of cadmium which is already rather high. This indicates that inputs of cadmium to agricultural soils should not be allowed to exceed the average cadmium output of around 1 g $ha^{-1}y^{-1}$ from through leaching.

References

Andersson, A. (1977): Heavy metals in Swedish soils. On their retention, distribution and amounts. Swedish Journal of Agricultural Research, 7:7-20.

CEC (1981): Ecotoxicology of cadmium. Commission of the European Communities & Gesellschaft für Strahlen- und Umweltforschung mbH. (EUR 7499 EN) (GSF-Bericht Ö-629).

Christensen, T.H. (1984a): Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium. Water, Air, And Soil Pollution, 21:105-114.

Christensen, T.H. (1984b): Cadmium soil sorption at low concentrations: II. Reversibility, effect of changes in solute composition and effect of soil ageing. Water, Air, and Soil Pollution, 21:115—25.

Christensen, T.H. (1985): Cadmium soil sorption at low concentrations: III. Prediction and observation of mobility. Water, Air, and Soil Pollution, 26:255-64.

Christensen, T.H. (1987): Cadmium soil sorption at low concentrations: VI. A model for zinc competition. Water, Air, and Soil Pollution, 34:305-14.

Christensen, T.H. (1989a): Cadmium soil sorption at low concentrations. Dr.Agro. Thesis. Polyteknisk Forlag, Lyngby, Denmark.

Christensen, T.H. (1989b): Cadmium soil sorption at low concentrations. VIII. Correlation with soil parameters. Water, Air, and Soil Pollution, 44:71-82.

Gerritse, R.G., van Driel, W., Smilde, K.W. & van Luit, B. (1983): Uptake of heavy metals by crops in relation to their concentration in the soil solution. Plant and Soil, 75: 393-404.

Hansen, L. (1976): Jordtyper ved statens forsøgsstationer. (Soil types at the Danish state experimental stations; in Danish). Tidsskrift for Planteavl, 80:742-58.

Hovmand, M.F. (1981): Cirkulation af bly, cadmium, kobber, zink og nikkel i dansk landbrug. (Cycling of lead, cadmium, copper, zinc, and nickel in Danish agriculture; in Danish). In: Slammets jordbrugsanvendelse, Vol. II. Fokusering, pp. 85-118. Polyteknisk Forlag, Lyngby, Denmark.

Jensen, A., Bro-Rasmussen, F. (1990): Review of Environ mental Fate and Exposure of Cadmium in the European Environment. Final Report No. 90.102 to DG XI of the EEC Commission. To be obtained from: The Danish Isotope Centre, Park allé 345, DK-2605 Brøndby.

Jensen, H., Mosbæk, H. (1990): Relative Availability of 200 Years Old Cadmium from Soil to Lettuce. Chemosphere 20: 693-702.

Jensen, J. (1978): Indhold af B, F, Mn, Cd, Pb og Zn i drænvand. (Concentrations of B, F, Mn, Cd, Pb and Zn in Drainage; in Danish). Tidsskrift for Planteavl 82: 540-48.

Lamm, C.G. (1971): Det danske jordarkiv. (The Danish soil library; in Danish). Tidsskrift for planteavl, 75:703-20.

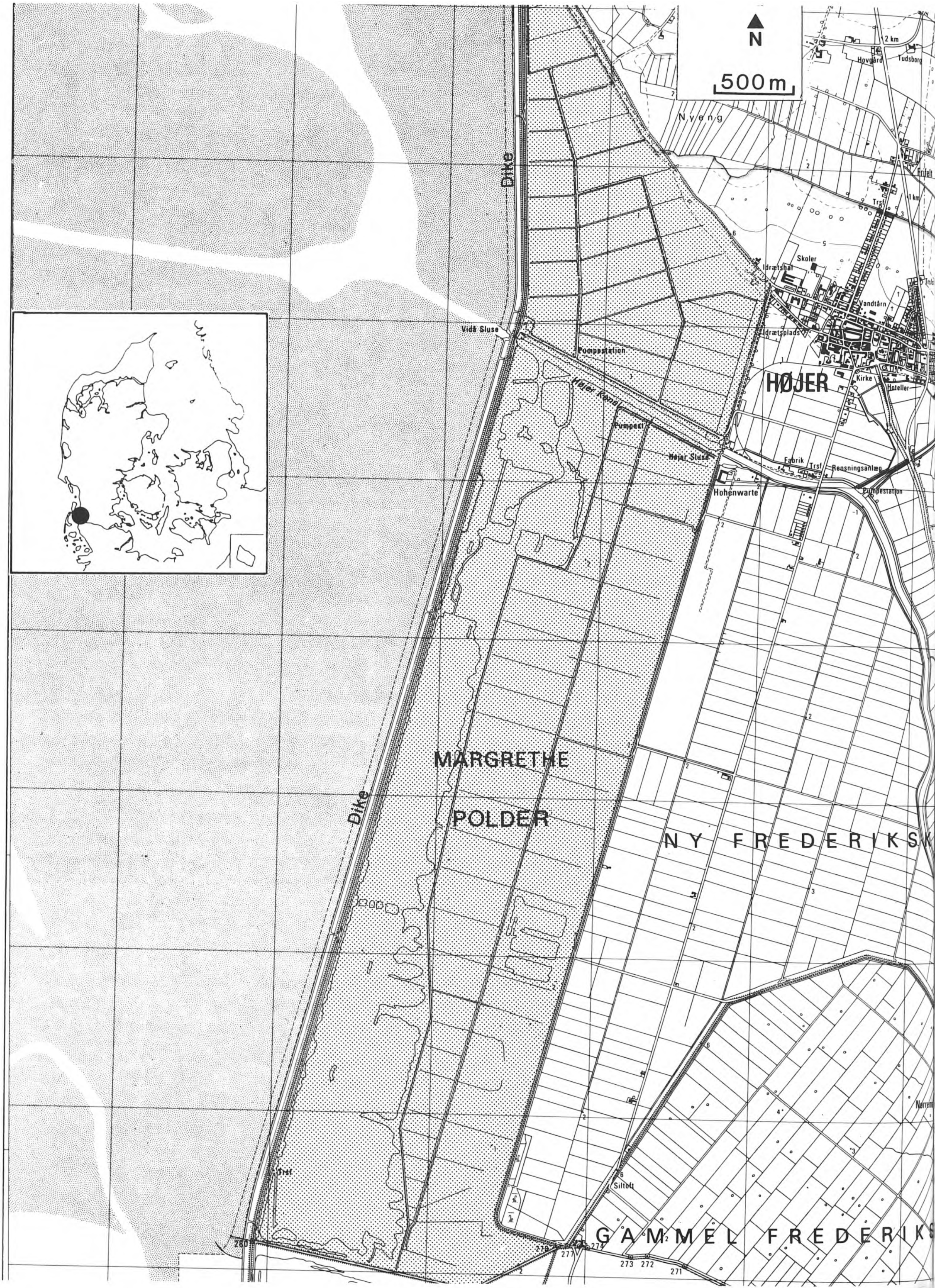
Sippola, J. & Mäkelä-Kurtto, R. (1986): Cadmium in culti vated Finnish soils. Annales Agriculturae Finniae, 25: 255-63.

Tjell, J.C. (1986): Trace metal regulations for sludge utiliza tion in agriculture; A critical review. In: Processing and use of organic sludge and liquid agricultural wastes. Proc. of the 4th Int. Symp., Rome, 1985, pp. 348-60. D. Reidel Publishing Company, Dordrecht.

Tjell, J.C., Christensen, T.H. & Bro-Rasmussen, F. (1983): Cadmium in soil and terrestrial biota with emphasis on the Danish situation. Ecotoxicology & Environmental Safety, 7:122-40.

Øien, A. (1975): Bestemmelse av bly, kadmium og kviksølv i jord ved atomabsorption. (Determination by atomic absorption of lead, cadmium and mercury in soils, in Norwegian). NJF Seminar om Tungmetaller, Sirkulasjon i Jordbruket. Ladelund, Danmark, 21-23 October. Ås-Trykk, Norway.

XIX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Initial soil formation in a salt marsh area of the Margrethe polder

Vibeke Ernstsen

Ernstsen, Vibeke: Initial soil formation in a salt marsh area of the Margrethe polder. Folia Geographica Danica, Tom. XIX, Copenhagen 1991.

The Margrethe polder was constructed in 1981 and is the last one constructed in the Tønder marsh. The main part of the land was reclaimed in 1943-1979. The salt marsh deposits consist mainly of fine-grained stratified sediments. In 1981 and 1983 investigations showed that only few detectable physical, chemical and biological changes had taken place in the soil.

Keywords: *Recently poldered salt marsh, Margrethe polder, initial soil formation, ripening, n-factor.*

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The construction of the Margrethe polder in 1981 is the last construction of polders in the Tønder salt marsh area (fig. 1). The Margrethe polder, which covers an area of about 1,000 hectares, is situated in the western, exposed, marine region of the Tønder salt marsh area (Jacobsen, 1964) and includes the former foreland of the Ny Frederikskog (polder). The polder is intersected by the Vidå river, which has influenced the deposition in the area.

On exposed coasts natural salt marsh formation first begins when vegetation - especially Puccinellia - gains footing on the higher lying parts of the tidal flats situated at mean high-tide level. On the seaward part of the new salt marsh erosional cliff and gullies (land priel) are formed by wave actions. They are both characteristic morphological elements of such a salt marsh (Jakobsen, 1964).

The marsh deposits forming the Margrethe polder was formed during the last c. 120 years. In 1881 the foreland in front of the Ny Frederikskog covered an area of about 120 hectares (fig. 2). As late as in 1935 the main part of the foreland was still a tidal flat covering a total area of 320 hectares. The foreland was widest close to the Vidå river. In 1943-1978 a multi-stage land reclamation project was carried out. Rapid deposition was ensured by effective drainage and growth of Puccinellia. In 1978 this species of plant covered an area of about 750 hectares (fig. 2). The rest of the foreland area was covered mainly by Salicornia. The invasion of the Puccinellia ensured rapid sedimentation, because this plant with its many long and closely set leaves is effectively able to filter out suspended material which is in the water (Jakobsen, 1964). A survey of the area where reclamation started in 1958 and 1965 respectively (fig. 3), showed a deposition of about 60 cm thick layers in 1954-79 and of about 20 cm in 1972-79. By comparison the growth in areas with no Puccinellia was only 5 cm in the period 1972-79.

When the Margrethe polder was constructed the area contained a number of erosion cliffs and gullies (fig. 4).

Field and laboratory studies

This paper is based on two field studies of characteristic morphological elements made shortly after the construction of the polder. In 1981 an investigation was carried out on the six soil profiles 304-309. In 1983 an additional investigation was carried out on seven soil profiles, N1-N4 and N7-N9. The position of the pits are shown

Fig. 1. The Margrethe polder situated in the south-western part of Jutland. • Kort- og Matrikelstyrelsen (A86).

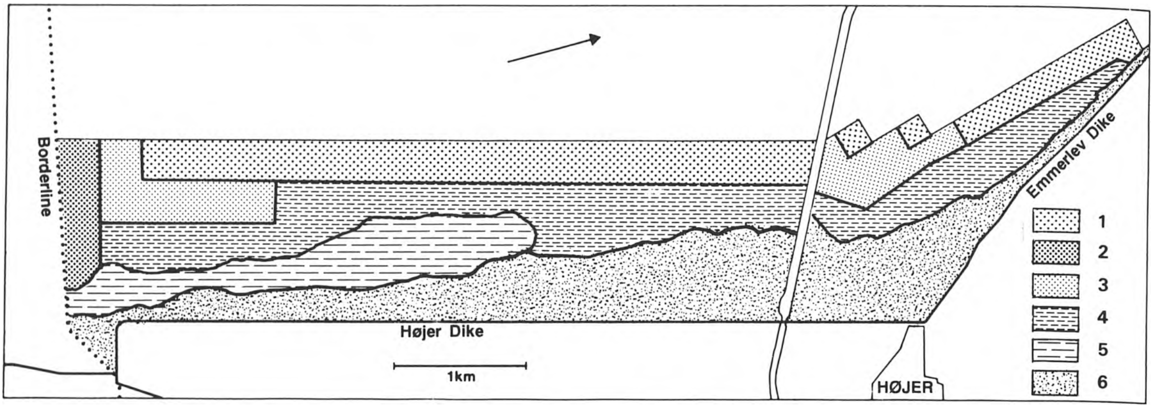


Fig. 2. Salt marsh formation at Højer. Land reclaimed 1: In 1965, 2: In 1963-64, 3: In 1960, 4: In 1958, 5: Foreland 1943-54, 6: Foreland in 1935. (Partly from Jespersen & Rasmussen, 1989).

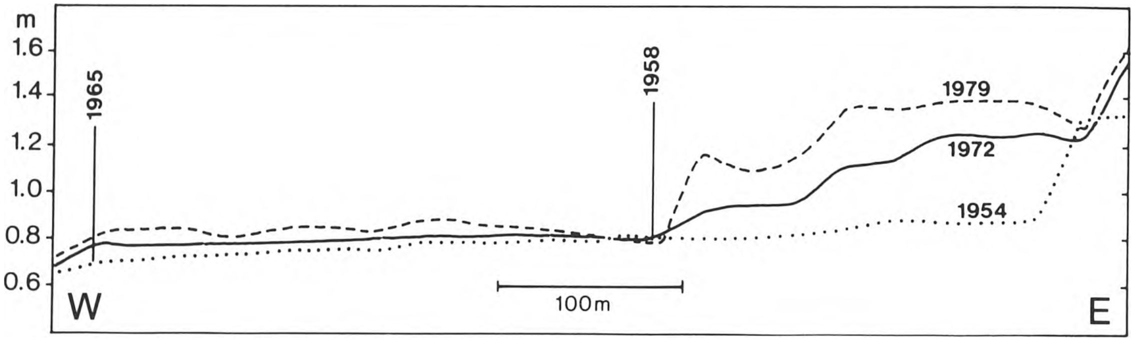


Fig. 3. A vertical view of the sedimentation in the land reclamation fields established in 1958 and 1965 respectively - approx. 2.5 km south of the Vidå river (Jespersen & Rasmussen, 1989).

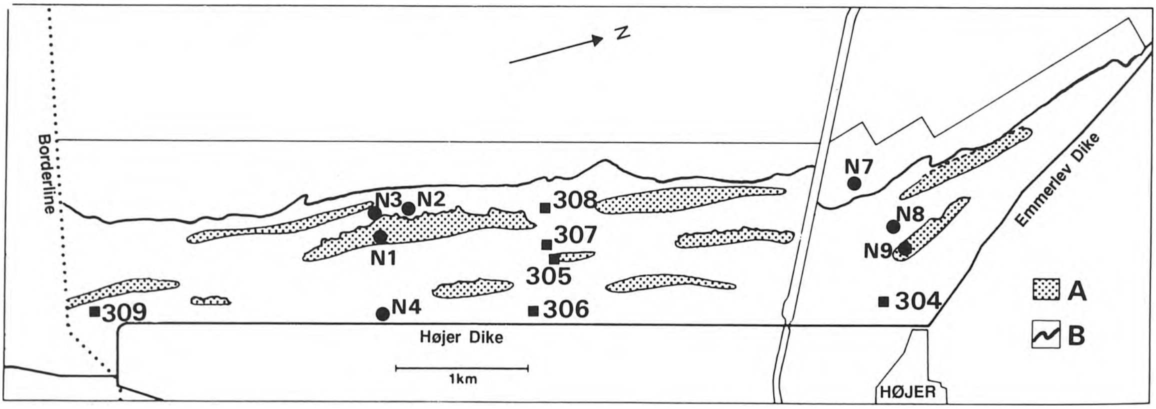


Fig. 4. The morphology in the land reclamation area at Højer in 1972. A: The highest and westernmost part of the cliff marsh. B: The western limit for Puccinellia in 1978 (partly from Jespersen & Rasmussen, 1989). The 304-309, N1-N4 and N7-N9 were investigated in 1981 and 1983 respectively.

in fig. 4. Selected samples were analysed in order to determine the distribution of sand, silt, clay, organic matter and $CaCO_3$ (table 1), pH_{CaCl2}, cation exchange capacity (CEC) and exchangeable cations (Ca^{++}, Mg^{++}, K^+, Na^+) (tables 2 and 3) (Ernstsen, 1984; Ernstsen-Hansen, 1982).

Soil formation - soil ripening

Here geogenesis is considered to include origin and transport of the sediments, whereas pedogenesis is considered to cover the actual soil formation. In practice such a destinction is difficult to make, which is why geogenesis is assumed to stop when the originally saturated sediment is drained or oxidised (Pons & Zonnenveld, 1965). In the last stage of salt marsh formation, when only a few high tides cause sedimentation, geogenesis and initial soil formation - ripening - may overlap. Soil ripening is the name given to the pedological processes which transform soft saturated and reduced sediments into soil. This takes place before more advanced soil formation is detectable. Normally, ripening is divided into physical, chemical, and biological ripening processes. In practice it may be impossible to separate these processes as they proceed simultaneously and influence each other (Pons & Zonnenveld, 1965).

Physical ripening

Physical ripening of the soil comprises mainly the processes which are direct results of the withdrawal of water from the sediments. The decrease in water content leads to formation of soil aggregates as the result of crack formation and disintegration of the sediment mass into small structure elements (Pons & Zonnenveld, 1965). Physical ripening is believed to be irreversible in contrast to chemical and biological ripening, which are generally believed to be reversible (Pons & Zonnenveld, 1965; Smits, et al., 1962). Already during land reclamation and polder construction, as in the Margrethe polder, the hydrological conditions may be improved.

Before a more extensive physical ripening can take place the presence of a vegetation cover is essential, because a well-developed rootsystem is needed for dehydration of the deeper layers. In sediments without vegetation dehydration takes place only in the upper c. 20 cm due to evaporation (Smits, et al., 1962). Sediments with a low content of colloidal particles will not exhibit ripening phenomena. The borderline between sediments poor in colloids and sediments rich in colloids is normally put at 8 % clay or 3 % organic matter, or a combination of the two (Pons & Zonnenveld, 1965). The degree of physical ripening of a sediment may be expressed by the n-value. Morphologically identical elements are assumed to show similar degrees of physical ripening in different depositional environments (salt, brackish or fresh water) and to have the same n-value. Therefore, in the Margrethe polder the physical ripening is not affected by the fresh water brought in by the Vidå river but may be influenced by the sediments it brings in. The physical ripening in the Margrethe polder, expressed by the n-value, was determined for characteristic layers in the profiles N1-N4 and N7-N9 (table 1). The values express the situation 3-4 years after the polder was constructed. The n-value varied between 0.8 and 2.1 which, according to Pons & Zonnenveld (1965) corresponds to a ripening stage of nearly ripe to unripe (table 4). There seems to be no sharp differences in n-value in different parts of the polder due to time of formation and morphology. Possibly, the effect of the improved drainage in connection with the land reclamation methods used here is dominant in soil ripening. In two profiles examined in former gullies, N3 and N8, the n-values are lower than in those of N4, and also lower than the n-value of 4.6 found in recently deposited mud in an active gully in the Ballum salt marsh (Ernstsen, 1984).

In 1979, before the polder was constructed, an investigation of six pits in three generations of erosion cliff—gully systems gave largely the same results. The same investigation showed that the foreland from 1953 and an associated gully were

PROFILE & LAYER	DEPTH (cm)	CaCO3 (%)	PARTICLE SIZE DISTRIBUTION (%)			ORGANIC MATTER (%)	n-VALUE
			CLAY < 2um	SILT 2-63 um	SAND 63-1000 um		
N1.1	4- 9	1.7	18	70	12	7.1	1.45
N1.2	26-30	1.6	14	55	31	2.1	1.33
N1.3	47-52	1.8	16	51	33	3.3	1.24
N1.4	69-74	1.6	10	36	54	1.9	
N2.1	2- 7	3.0	32	53	15	3.0	0.97
N2.2	25-30	1.9	4	43	53	1.9	1.81
N2.3	45-50	1.2	10	18	72	1.0	1.32
N2.4	64-67	1.2	4	12	84	0.7	
N3.1	5-10	1.7	42	50	8	5.3	0.82
N3.2	33-38	1.6	17	56	27	5.0	1.43
N3.3	55-64	1.8	9	39	52	1.8	2.14
N3.4	72-77	1.6	10	14	76	1.6	
N4.1	6-11	1.0	16	61	23	2.7	1.48
N4.2	35-40	1.7	25	55	20	1.3	1.00
N4.3	70-75	3.6	18	63	19	2.0	1.69
N4.4	82-85	1.8	3	38	59	0.4	
N7.1	1- 6	2.5	12	46	42	3.2	1.58
N7.2	15-17	0.6	4	14	82	0.7	
N7.3	29-33	0.9	4	25	71	0.7	
N8.1	6-11	2.5	34	39	27	5.1	0.92
N8.2	23-28	0.8	14	49	37	4.5	1.77
N8.3	54-58	1.0	5	25	70	0.5	
N9.1	3- 8	0.7	4	25	71	3.2	1.51
N9.2	15-20	1.4	8	45	47	1.3	0.80
N9.3	34-38	1.0	6	50	44	1.3	1.72

Table 1. Particle size distribution, $CaCO_3$ content in %, and n-values of N-profiles.

physically ripened to depths of 80 and 40 cm respectively. This old foreland forms less than 10 % of the total area of the Margrethe polder.

A description of aggregate type and size in the Margrethe polder showed that angular, subangular or platy structural forms were predominant and that the size of the aggregates was mainly coarse to very coarse. Well developed crumbs were only found in the surface horizon of soils in areas reclaimed before 1958, i.e. which had been covered by vegetation for a long time.

Already in the summer of 1981 considerable crack formation had taken place in the soil of the western part of the polder, because the sediments were suddenly drained (Ernstsen, 1984). In this part of the Margrethe polder land reclamation started after 1958. At the time of polder construction it was not covered by vegetation. The clay to silty clay deposits are thin in this part of the polder (< 50 cm) (Jacobsen, non publ.) and the physical ripening has happened quickly. In the rest of the polder cracks were seen only in newly constructed deep channels. An increased formation of soil structure will improve the aeration of the soil and the condition for plant growth in the soil because normally, marsh deposits do not contain textural particles larger than 2 mm. Usually the number of macropores are small, less than 10-15 volume-% which correspond to the limit normally necessary to ensure reasonable plant growth (Madsen, 1983).

Chemical ripening

The chemical ripening starts when air enters the soil and causes all kinds of reactions, depending on the chemical properties of the sediments. Polder contruction followed by adjustment of the hydrological conditions may result in improved aeration and oxidation. This intensifies the pro-

PROFILE & LAYER	DEPTH (cm)	PH CaCl2	EXCHANGEABLE CATIONS Ca++	Mg++	K+	Na+	CEC
			meq./100 g / %				
N1.1	4- 9	7.2	24.7 / 74	6.5 / 20	1.3 / 4	0.5 / 2	33
N1.2	26-30	7.5	12.4 / 67	4.2 / 23	0.9 / 5	0.9 / 5	18
N1.3	47-52	7.7	9.5 / 56	4.1 / 24	1.2 / 7	2.2 / 13	13
N1.4	69-74	7.9	3.4 / 40	1.9 / 23	0.8 / 10	2.2 / 27	8
N2.1	2- 7	7.4	19.7 / 80	3.2 / 13	1.4 / 6	0.3 / 1	25
N2.2	25-30	7.5	9.3 / 71	2.9 / 22	0.7 / 5	0.3 / 2	13
N2.3	45-50	7.4	3.8 / 47	2.6 / 33	0.7 / 9	0.9 / 11	8
N2.4	64-67	7.3	2.5 / 52	1.1 / 22	0.4 / 8	0.9 / 18	5
N3.1	5-10	7.6	35.9 / 77	6.8 / 15	2.1 / 5	1.2 / 3	46
N3.2	33-38	7.7	24.1 / 60	7.1 / 18	1.8 / 5	6.7 / 17	40
N4.1	6-11	5.9	18.0 / 61	7.4 / 25	1.6 / 6	2.4 / 8	24
N4.2	35-40	7.8	19.0 / 65	4.7 / 16	1.5 / 5	4.2 / 14	29
N4.3	70-75	8.1	19.1 / 59	5.9 / 19	1.7 / 5	5.6 / 17	32
N4.4	82-85	7.9	2.3 / 38	1.6 / 27	0.5 / 8	1.6 / 27	6
N7.1	1- 6	7.6	8.4 / 45	4.9 / 27	1.1 / 6	4.0 / 22	18
N7.2	15-17	7.5	0.2 / 4	2.2 / 39	0.5 / 9	2.8 / 48	6
N8.1	6-11	7.6	20.1 / 64	5.7 / 18	1.1 / 4	1.1 / 14	31
N8.2	23-28	7.0	7.2 / 27	7.4 / 27	1.2 / 4	1.2 / 42	27
N9.1	3- 8	6.0	14.0 / 77	3.6 / 20	0.3 / 2	0.1 / 1	18
N9.2	15-20	6.9	6.6 / 61	3.6 / 34	0.4 / 4	0.1 / 1	11
N9.3	34-38	7.1	5.2 / 50	4.6 / 44	0.5 / 5	0.1 / 1	10

Table 2. Some chemical properties, N1-N4 and N7-N9.

cesses of 1) oxidation and humification of organic matter, 2) oxidation of inorganic compounds which are only stable under reducing conditions, 3) changes in distribution of adsorbed ions, and 4) changes in composition of the soil solution (Pons & van der Molen, 1973).

Chemical ripening is reflected visually in change of colour from the originally grey to reddish brown. In N1 and N2 the oxidised layer was 30 cm thick, whereas it was only 10 cm thick in the rest of the profiles. Below 10-30 cm depth the hue varied from 2.5Y to 5Y with low chroma (1-2). In almost all layers brown/reddish mottles were present.

The content of calcium carbonate ($CaCO_3$) varied between 1-3 weight-% (table 1). It occurred mainly as powder and larger fragments, e.g. shells from mussels and snails. The content does not seem to depend on the clay content. For example, thin layers with clay contents of 8 and 47 % contained 1.9 and 2.7 weight-% of calcium carbonate respectively, (table 5). The difference is not great compared with the variations caused by the distribution of larger fragments. The low content of $CaCO_3$ in combination with the variation found down through the profiles make it difficult to estimate the extent of decalcification. The pH_{CaCl2} values of about 6 in the upper layers of N4 and N9 (table 2) and 304 and 306 (table 3) indicate a beginning decalcification in the oldest parts of the polder which have been covered by vegetation for a number of years. In these layers larger fragments of $CaCO_3$ may still be present (Ernstsen, 1984).

The amount and types of exchangeable cations influence soil formation processes to a high degree. Before the polder was constructed frequent floodings of the area below the mean high-tide level caused sodium saturation. Rasmussen (1956) found sodium saturation (ESP) of 30-50 % in sediment samples from tidal flats and salt marshes. The high content of sodium ions in the sediment solution secures good structural properties. When the polder was constructed the salt marsh was no longer under influence of the Sea and gradually, the salt in pores and cavities

PROFILE & HORIZON	DEPTH (cm)	PH CaCl2	EXCHANGEABLE CATIONS meq./100 g / % Ca++	Mg++	K+	Na+	CEC
304							
A1	5- 9	5.1	9.2 / 22	8.2 / 20	0.9 / 2	9.9 / 24	41
B2vor	17-21	6.6	9.7 / 27	10.3 / 28	1.5 / 4	12.1 / 33	37
305							
A1	2- 7	6.8	12.4 / 35	12.8 / 36	1.7 / 5	2.6 / 7	36
B21o	15-20	6.7	3.1 / 27	3.8 / 33	0.5 / 5	2.0 / 18	12
306							
A1ho	6-10	5.7	7.2 / 18	11.2 / 29	1.6 / 4	7.4 / 19	39
B2vor	25-29	6.8	6.2 / 24	8.3 / 32	1.4 / 5	8.2 / 31	26
C1ro	45-49	7.5	15.1 / 43	7.3 / 21	1.7 / 5	9.8 / 28	35
307							
A1o	10-15	6.6	10.7 / 20	12.1 / 22	16.1 / 3	25.7 / 46	54
C1r	28-33	7.4	15.3 / 51	3.3 / 11	1.0 / 3	10.0 / 33	30
308							
A1o	3- 5	7.4	17.8 / 78	3.0 / 13	0.6 / 3	0.4 / 2	23
B22vo	28-32	8.4	12.8 / 69	2.0 / 11	0.6 / 3	2.9 / 16	19
309							
Apho	6-11	7.7	10.8 / 17	13.2 / 21	2.2 / 4	31.9 / 51	62
B2vor	22-27	7.0	11.2 / 19	11.3 / 20	1.8 / 3	31.3 / 54	58

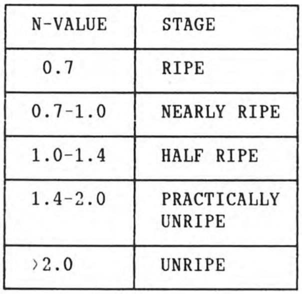
Table 3. Some chemical properties, 304-309.

will be washed out and be replaced by fresh water. This creates an unbalance between the adsorbed ions and the soil solution resulting in dispersion of the aggregated sediments. If free $CaCO_3$ is present the adsorbed Na^+ may be replaced by Ca^{++} under proper drainage conditions.

A quite uniform distribution of adsorbed calcium (Ca^{++}) was found in N1-N4. Ca^{++} made up 45-80 % of the adsorbed cations in the upper c. 30 cm below surface but from there and downwards the percentage decreased sharply. Already at a depth of approx. 15 cm in N7, which at the time when the polder was constructed was below mean high-tide level and N8, which represents a former gully, had a very low calcium saturation (4 %) and a high ESP (40-50 %). This corresponds to the values in non-poldered salt marsh deposits (Rasmussen, 1956). In N9 (an old erosion cliff from 1954) the ESP is very low. This may be due to the more coarse-grained texture and its position close to the Vidå river. Compared with the results from the profiles investigated in 1981 (table 3) a considerable exchange of sodium with calcium seems to have taken place already in the period up to 1983.

In the older parts of the polder, the foreland from 1938, a sodium dispersed layer occurs at a depth of 40-80 cm, e.g. in the profiles 304 and N4. In this layer the soil structure is destroyed and it is almost impermeable to water (Jacobsen, 1981).

Also magnesium (Mg^{++}) forms a substantial part of the adsorbed bases (15-44 %), and often the share increased with depth. Similar results were obtained during the 1981 investigation, which mainly dealt with the upper 40 cm of the soil. To some extent the brackish sediments de-



N-VALUE	STAGE
0.7	RIPE
0.7-1.0	NEARLY RIPE
1.0-1.4	HALF RIPE
1.4-2.0	PRACTICALLY UNRIPE
>2.0	UNRIPE

Table 4. Classification of soil material according to physical ripening (Pons & Zonnenveld, 1965).

Table 5. Particle size distribution and $CaCO_3$ content in two layers from the C2ro horizon from profile 305.

PROFILE 305 HORIZON: C2ro	% CLAY < 2 um	% SILT 2-63 um	% SAND 63-100 um	% CaCO3
Coarse grained layer	7.9	55.2	36.9	1.9
Fine grained layer	46.8	42.0	11.2	2.7

posited close to the Vidå river had a different distribution of Mg^{++} as shown in N7 and N9. Here the content was higher than in N1, which represents sediments deposited in salt water environment.

In comparison with the other bases potassium constituted only 4-10 % of the CEC, often increasing with depth. Compared with the results obtained in 1981, it is possible that a certain exchange and removal of the potassium had taken place from 1981 to 1983 (Ernstsen, 1984; Ernstsen-Hansen, 1982).

Biological ripening

The biological ripening comprises aspects of the ripening process which is influenced by organisms (Pons & Zonnenveld, 1965). The organisms, i.e. soil flora and fauna, mix and loosen the originally stratified sediment, and thereby accelerate the physical and chemical soil forming processes.

During the investigations in the Margrethe polder in 1981 and 1983 no visible soil faunal activity was observed so the biological ripening may depend mainly on the microfauna and -flora and on the vegetation. Apart from N7, all soils were covered by Puccinellia (fig. 3). The largest amounts of roots and the most intensive mixing were observed in the upper 20 cm. Deeper down the amount of roots decreased considerably, and below 30-40 cm only a few roots were found, assumably due to reduced conditions and lack of coarse pores.

During the last stages of geogenesis the vegetation has caused an increase in organic matter in the top soil (table 1). Together with increased microbiological activity the higher content of organic matter has resulted in well developed crumbs or a strong angular/subangular blocky structure. Without vegetation the content of organic matter is typically less than 2 weight-% (Ernstsen, 1984; Ernstsen-Hansen, 1982).

Classification of the soils in the Margrethe polder

The physical ripening can be expressed by the n-value and therefore it is used in soil classification. Calculations of the n-values of characteristic soil layers showed that the ripening was not very advanced in large parts of the polder. Using the Dutch soil classification system (Pons & van der Molen, 1973) all profiles proved to belong to the class of unripe soils and only N1 could be described as "semiripe" at a subgroup level. According to a Danish system the studies in ,1981 showed that wet gley is the dominating soil type in the polder (Madsen, 1983). According to Soil Taxonomy the soils are Fluvents and Fluvepts at suborder level (Soil Survey Staff, 1975).

Summary

The Margrethe polder was constructed in 1981 and is the last one of the polders constructed in the Tønder salt marsh. The polder covers approx. 1,000 hectares. The deposits consist of fine-grained sediments which, in major parts of the polder, occur as alternating layers of sand and silt/clay. Thicker layers of clayey sediments are found in gullies and more protected basins. Some $CaCO_3$ and organic matter occur in the deposits.

By means of profile studies carried out in 1981 and 1983, the initial soil formation or the soil ripening in the Margrethe polder was described immediately after the polder was constructed. Both physical, chemical and biological processes were found to be involved in this soil ripening. The physical ripening involved mainly dehydration of the sediments. The so-called n-value gave an impression of the extent of this process. As to the profiles N1-N9 which represent about 90 % of the polder the n-values were found to vary between 0,8-2.1, thus corresponding to a ripening stage of nearly ripe to practically unripe. For the rest of the polder the n-value was found to be <0.7 corresponding to a stage of ripe soils. Other signs of physical ripening were observed as crack formation in the western low-lying part of the polder in the summer of 1981. In this part of the polder the layers of clayey sediments are quite thin (<0.5 m) so ripening may be expected to happen rather fast here.

In case of chemical ripening the reddish brown colouring of the soil due to oxidation was observed only in the upper 30 cm of the profiles investigated. It is also in this part of the soil that exchange of sodium with calcium has taken place (45-80 % exchangeable Ca^{++} versus about 10 % exchangeable Na^{+}). Normally, the ESP is between 33-55 % in samples from tidal flats. Also former gullies appear to have high ESP. In the part of the polder which was foreland in 1935 a layer of highly dispersed sodium clay occurred, which made it almost impervious to water.

The content of $CaCO_3$ varied between 1-3 weight-% except in the oldest part of the polder where the presence of vegetation seems to have resulted in decalcification and a pH_{CaCl2} drop to about 6.

The biological ripening seemed to be limited to the upper 30-40 cm, where the root activity was found to be high. In some places the biological ripening has resulted in an intense mixture of the stratified sediment and in formation of a well developed soil structure.

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References

Ernstsen, V. (1984): Initiale jorddannende processer i et marskområde - Margrethe kog. Thesis. Geographical Institute, University of Copenhagen.

Ernstsen-Hansen, V. (1982): Margrethe kog - en foreløbig pedologisk undersøgelse. Intern rapport. Geographical Institute, University of Copenhagen.

Jacobsen, N. Kingo (1964): Tøndermarskens Naturgeografi med særligt henblik på morfogenesen. Summary in English. Folia Geographica Danica, Tom. VII, No. 1.

Jacobsen, N. Kingo (1981): Natriumproblemer i Tønder marsken. Internt notat.

Jakobsen, B. (1964): Vadehavets Morfologi. Folia Geographica Danica, Tom XI, No. 1. (in Danish).

Jespersen, M. & Rasmussen, E. (1989): Margrethe Koog - Landgewinnung und Küstenschutz im südlichen Teil des dänischen Wattenmeeres. Die Küste: 97-154.

Madsen, H. Breuning (1983): Himmerlands Jordbundsforhold. Folia Geographica Danica, Tom XVI. (in Danish).

Pons, L.J. & Zonnenveld, J.S. (1965): Soil ripening and soil classification. Int. Inst. for Land Reclamation and Improvement. Pub. 13: 1-95.

Pons, L.J. & Molen, W.H. van der (1973): Soil genesis under dewatering regimes during 1000 years of polder development. Soil Sci. 116: 228-35.

Rasmussen, K. (1956): Investigations on the marsh soils and Wadden Sea sediments in the Tønder region. Geografisk Tidsskrift, 55: 147-69.

Soil Survey Staff (1975): Soil Taxonomy. A basic system of soil classification for making and interpreting soil surveys. Agriculture Handbook No. 436. Soil Conservation Service, U.S. Department of Agriculture.

Smits, H., Zuur, A.J., Schreven, DA. van & Bosma, W.A. (1962): De fysische, chemische en microbiologische rijping der gronden in de Hseelmeer polder. Van zee tot land, 32: 1-110.

Soil variation in a sandy till landscape of Weichselian age in the northern part of Jutland, Denmark

Kristian Dalsgaard, Mogens H. Greve & Peter Sørensen.

Dalsgaard, Kristian, Greve, Mogens H. & Sørensen, Peter: Soil variation in a sandy till landscape of Weichselian age in the northern part of Jutland, Denmark. Folia Geographica Danica, Tom. XIX, Copenhagen 1991.

Based on data from pit or auger hole examinations, a soil map of a 262 ha large area was made in a part of Himmerland, Jutland. The area shows a large variation in soil types, 13 subgroups of Alfisols and Spodosols were found. The soils varied from Arenic Hapludalf to Typic Fragihumod. The best developed spodic horizons were found in sheets of wind-blown sand of the coversand type. A well-developed fragipan was found in sandy till containing from 2 to 10 % clay. The epipedon in this former Calluna heath area was found to be heavily influenced by cultivation. Antropic epipedons were found close to farms established less than 100 years ago.

Keywords: *Sandy till, coversand, Spodosols, Alfisols, fragipan, human influence, Calluna heath.*

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The main distribution of soil types in Denmark has been known since Bornebusch and Milthers (1935) published their soil map at the scale 1: 500,000. This is mainly a map of the parent material with an indication of the distribution of podzols. Description and classification of soil profiles along the main gas pipe line (Madsen & Jensen, 1985) has increased our knowledge of soil types and their relation to different landscapes and parent materials. Madsen (1983) has given a regional description of soils based on selected toposequenses and parent materials in Himmerland in the northern part of Jutland. In the present study the distribution of soil types was more closely studied in a 262 ha area in a young morainic landscape in the Aars area of Himmerland. The soil types were classified at the subgroup level according to Soil Taxonomy (Soil Survey Staff, 1990). The study was part of the Danish Nature and Forest Agency project with the purpose of developing a site mapping system for re-afforestation of marginal agricultural land (Greve & Sørensen, 1990).

Geology and topography

The most recent map of Quaternary deposits in Denmark, 1:200,000, (DGU, 1989) indicates that

Fig. 1. Location of the study area.

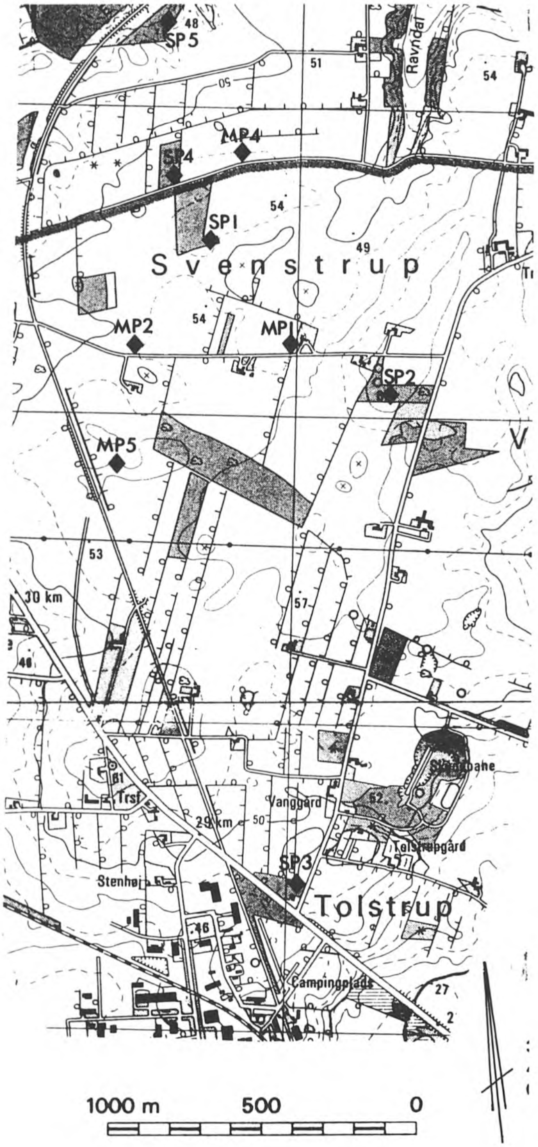


Fig. 2. Part of the topographical map 1216 I SV and 1216 II NV from 1978 and 1979, original scale 1:25,000. • Kort- og Matrikelstyrelsen (A 413-90). The location of the soil pits is indicated, Sp marks pits in forest, Mp marks pits on arable land.

the survey area consists of Glaciofluvial sands and gravels, but the area has not yet been mapped intensively. The soil survey revealed that the area (figs. 1 and 2) is in a morainic landscape largely composed of sandy till deposited by the main Weichselian glacial advance about 18,000 years B.P. The relief is weakly undulating, and the elevation varies from 47 m to 62 m above OD. The survey further showed that 33 % of the area is covered by a number of isolated sheets of well-sorted fine sand (fig. 3). The thickness of the sheets varies between a few decimeters to more than 2 metres, and they show no signs of dune morphology. The distribution of the sand sheets reveals no obvious relation with the morphology of the landscape. They are most probably of the coversand type described by Kolstrup (1982) and Kolstrup and Jørgensen (1982) from the southern part of Jutland. Coversand has not been described in this part of Denmark before, but the morphology of the sand sheets, together with the lack of dune topography and internal dune-foreset cross-bedding, indicate that these deposits are coversand. This view is further supported by presence of alternating horizontal beddings, and, in some instances, of a relatively high content of silt, neither characteristics are normally found in dunes. In the following the sand sheets are therefore referred to as coversand. The coversand is thought to have been deposited in the Dryas time at the end of the Weichselian glaciation. The typical particle size distribution of the coversand illustrated by the upper metre of profile Mp1 is shown in table 1. The silt content of the coversand varies greatly; the highest amount was found in the C horizon of Sp3, which contained 38 % silt. The relatively high content of coarse sand, and especially silt, in the sandy tills, is illustrated by profile Mp5 (table 1).

The survey showed that a well-developed fragipan is found in 33 % of the area. The fragipan is only developed in the sandy tills and not in the coversand, but in some instances the fragipan is found in sandy tills covered by coversand. Fragipans are supposed to be developed as a result of soil compaction due to freeze-thawing processes in areas with permafrost regimes (Van Vliet & Langohr, 1981). In Denmark fragipans have previously been described in individual soil profiles e.g. Baastrup, et al. (1977) and Madsen (1983). Müller (1884, 1887) gave an early description of 'leral' (in English 'clay ortstein'). Later investigations have revealed that an 'leral' described by

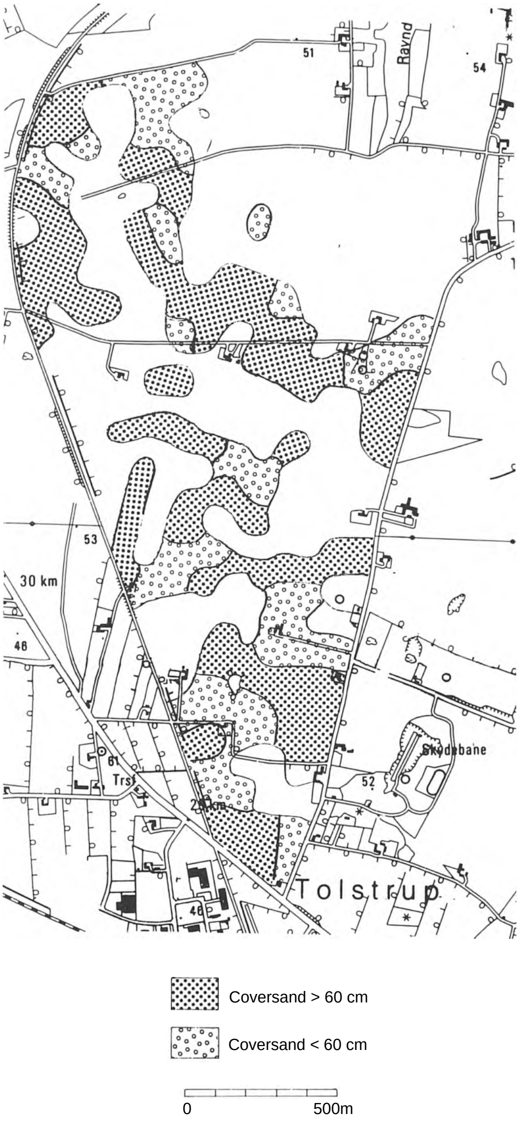


Fig. 3. Distribution of and thickness of coversand. Thin layers of coversand incorporated in the plough layer are not shown. • Kort- og Matrikelstyrelsen (A 413-90).

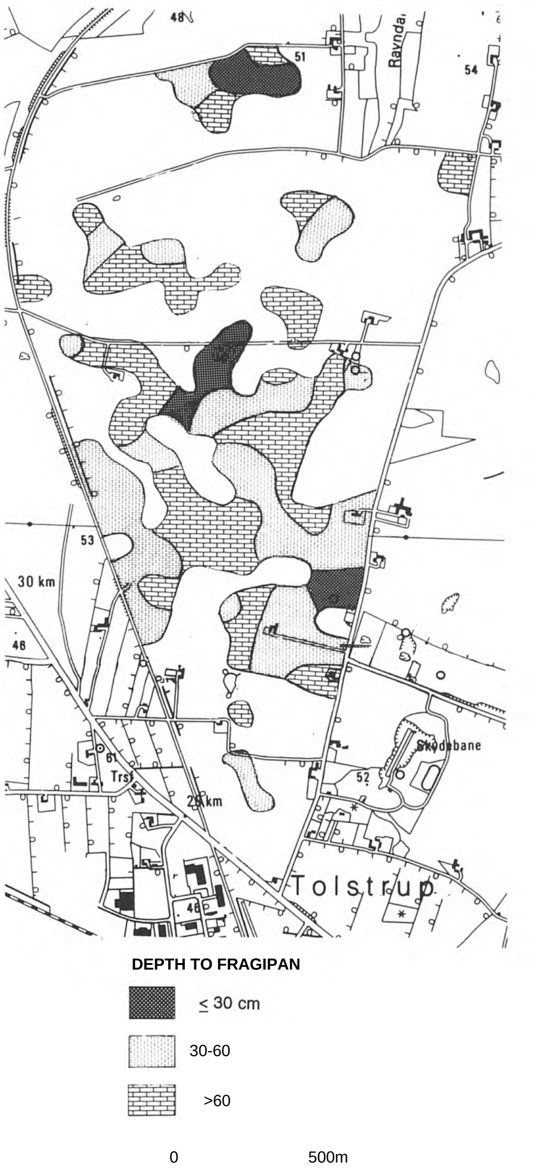


Fig. 4. Distribution of and depth to fragipan. • Kort- og Matrikelstyrelsen (A 413-90).

Müller (op.cit.) could be identified as a fragipan (Øvig, 1986). It was surprising to find the fragipan so widely distributed in the survey area as it is considered to be present only in soils with a higher clay content.

Climate

The climatic data were supplied by the Danish Meteorological Institute (Lysgaard, 1969). The nearest station is Aalestrup 15 km south of the area. For the period 1931-60 the annual mean air temperature was 7.7 °C, the coldest month was Febuary -0.5 °C, and the warmest month was July 16.1 °C. Average precipitation was at Hornum 4 km west of the area 705 mm, ranging from 461 to 959 mm. The climatic data imply that the well-drained soils have udic moisture regimes and the temperature regime is mesic, close to the frigid one.

Vegetation and former land use

The natural vegetation in the area about 4000 BC. before man introduced agriculture in Denmark, was probably a mixed open forest composed of oak, lime, hazel, and birch. This was the forest type on well drained, sandy soils described by Odgaard and Rostholm (1985) from Central Jutland and by Aaby (1985) from the Djursland peninsula.

Iron age fields are found in the northeastern part of the area, as well as just outside the western border. The remains of a big iron age village dating from around 0 AD. with stables forming parts of the houses, has been found approximately 1 km south of the area. These iron age findings suggest intensive human activity at that time, including large stocks of grazing cattle. This might be the origin of the introduction of the Calluna heath, which in 1810 covered most of the area, with only a minor area under cultivation.

Judging from the age of the village names, the land-use pattern shown in fig. 5 probably dates back at least to medieval times (about 1200 AD.). The southern part of the mapped area belongs to a village just outside the area. In an earlier analysis (Dalsgaard, 1989) it was found that only one third of the land belonging to these villages was arable land, the rest being Calluna heath and a few percent meadow. The land use pattern in the northern part of the area seems to have been the same. The heath played a major role in the farming system and was part of a vegetation system created and maintained by man. (Dalsgaard, 1990; Nielsen, et al. 1987).

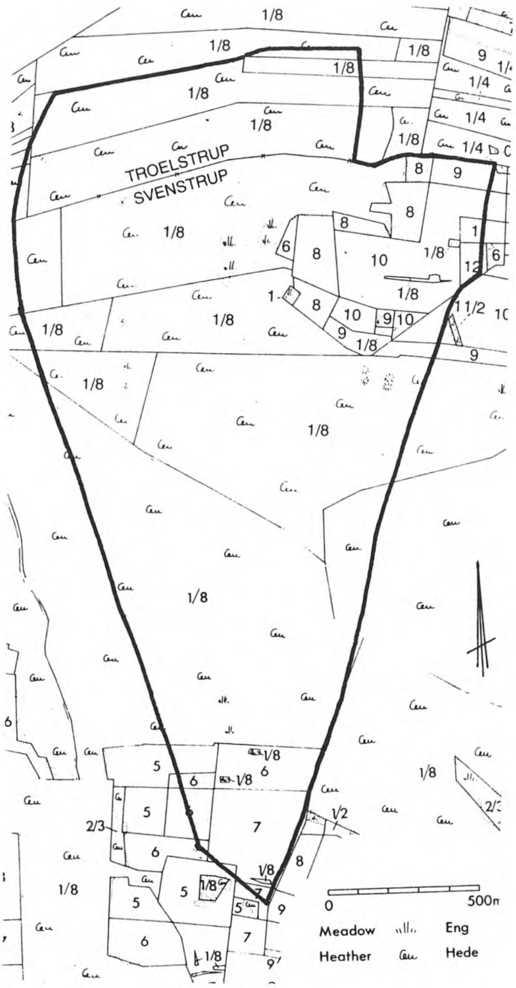


Fig. 5. A scale down version of land registration map from 1810, original scale 1:4000. • Kort- og Matrikelstyrelsen (A 413-90).

The vegetation pattern on the first topographical map from 1880 was nearly the same as in 1810, but in 1920 about one third of the heath area was cultivated in connection with the establishment of new farms. In 1960 the whole area was cultivated, apart from a few small plots of spruce planted on the poorest soils.

Field methods

The soil map is based on data from 10 soil pits representing the major soil types in the area and on one auger hole per hectar. The soil descriptions are in accordance with Soil Taxonomy (Soil Survey Staff, 1975). The naming of soil horizons and the classification were made in accordance with Soil Survey Staff (1990). The pits were 2 m long and 1.5-2 m deep, and horizontal sections were exposed in order to study the distribution of roots and vertical cracks. The auger holes were made with a 3 cm semi-cylindrical auger, down to two metres' depth where possible. Identification of fragipan is done in the field. The sandy type of fragipan found in the survey area does not fulfil all the requirements for a typical fragipan according to Witty and Knox (1989). Therefore we have used the following 5 criteria for the identification of fragipans in soils with less than 8-10 % clay:

1. The fragipan is brittle when moist.
2. The fragipan has a lenticular or lenticular - platy structure (Lindbo & Weneman, 1989).
3. Roots are absent in the fragipan, except in worm galleries and cracks.
4. The fragipan has a relative high bulk density compared to the horizon above it.
5. A dry fragment from the fragipan slakes or fractures when placed in water.

Identification of the fragipan in the soil pits was based on the above criteria. Identification of the fragipan by augering was more difficult and required field experience. It was mainly identified by its hardness and brittleness. The type of fragipan found in the area is present in profile Sp2.

Laboratory methods

Soil samples were taken with a known volume. The soil was air-dried and passed through a 2 mm sieve. A subsample was ground to less than 125 *µm* and used for all analyses except particle size and pH. Particle size analyses were made on a 60 g soil sample. The organic matter was oxidized by 6 % H_2O_2. Afterwards the mineral soil was dispersed with 0.002 M Na-pyrophosphate, and the sample was separated at 38 *µm* by wet sieving. The coarse fraction was sieved 20 minutes using ASTM standard sieves. The 20 *µm* and 2 *µm* fractions were determined by Andreasen pipette. The percentage values used in the USDA particle size nomenclature were found by graphic interpolation. Total carbon content was determined by dry combustion, and nitrogen by the Kjeldal method. pH was measured in 1:1 soil/liquid mixture with destilled water and with 1 M KCl.

Iron and aluminium were extracted by dithionite-citrate-bicarbonate (Fe_d and Al_d (Mehra & Jackson, 1960) and by Sodium pyrophosphate at pH 10 (USDA 1972) and centrifuging at 22,000 g (Fe_p and Al_p). The contents of Fe and Al in the supernatant solution were determined by AAS. Phosphorus was extracted from samples ignited for 2 hours at 550 °C (total P) and from untreated samples (inorganic P) by boiling with 1 M HCl. Samples were boiled for 20 minutes or until all red stains had disappeared. The P concentrations were determined by the molybdenum blue method at 710 nm. All data are based on own dry weight.

Main soil types

The main soil types found in the area are shown in figs. 6 and 7. Four typical soils and an atypical one representing different parent materials and with different types of soil horizons, are described below.

Profile Mp1 is an "Antropic" Haplohumod (fig. 6, table 1, and photo 1) was selected to represent both the soils on thick coversand and soils with

MP1

Classification	"Antropic" Haplohumod.
UTM	NH 310992.
Terrain	Weakly undulating
Parent material	Coversand above sandy till
Slope	0°
Vegetation	1880: Heather, from 1920 arable land

Horizons

Ap 0-20 cm	Black (5YR 2,5/1 m) with many pale sand grains; fine sand; structureless, single grain; non sticky; very friable; many very fine roots; few worm galleries; artefact, chalk from liming fragments of wall bricks; clear and smooth boundary.
Ap2 20-40 cm	As Ap, but contains more organic carbon.

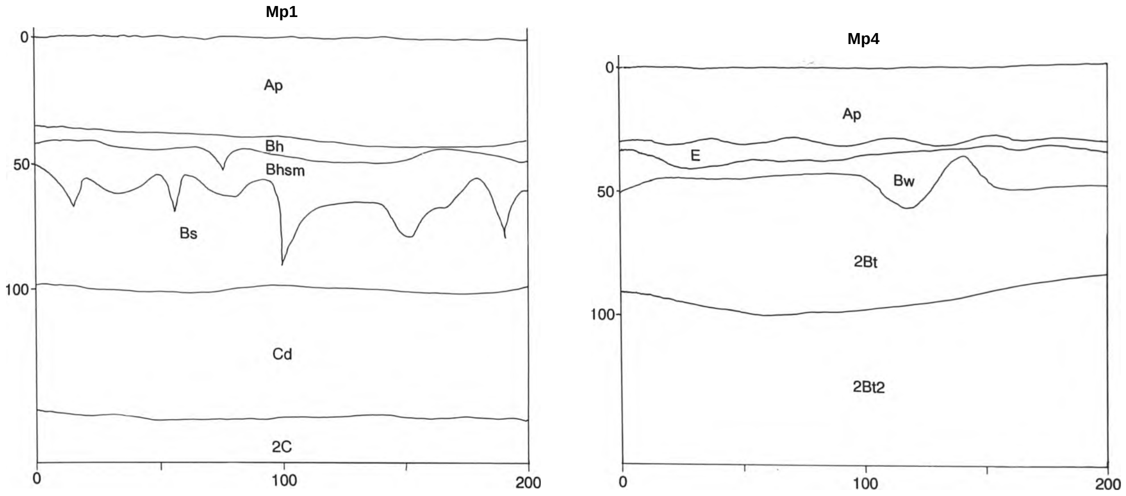
Bh 40-45 cm	Black (10YR 2/0 m) with a few pale sand grains; fine sand; structureless, massive; slightly sticky, very friable; humus between sand grains; fine roots are common; no gravel; few worm gallerys; clear and smooth boundary.
Bhms 45-65 cm	Dark brown (10YR 3/3 m) with many 2-3 cm Φ dark yellowish brown (10YR 4/6 m) distinct mottles; fine sand; coarse platy structure in the upper part of the horizon, elsewhere structureless, massive; strongly cemented; no pores; few very fine roots in the worm galleries; no gravel; few worm galleries; diffuse irregular boundary.
Bds1 65-100 cm	Yellowish brown (10YR 5/6 m) with many 2-3 cm Φ brownish yellow (10YR 6/6 m) distinct round mottles, two 5 cm wide dark brown illuviation bands at 95 and 100 cm; fine sand; structureless, massive; non sticky; no pores; no roots; no gravel; diffuse and smooth boundary.
Bds2 100-150 cm	Light yellowish brown (2,5Y 6/4 m) with weak dark streaks, 5-10 cm wide kryoturbated loamy bands; fine sand; structureless massive; non sticky; no pores; no gravel; no stones; sharp and smooth boundary.
2C 150-180 cm	Light yellowish brown (2,5Y 6/4 m) with yellowish brown (10YR 5/8 m) mottles; gravelly coarse sand; structureless; non sticky; no pores no roots; some rounded and subrounded gravel in the upper 20 cm of the horizons.

Photo 1. Profile Mp1, "Antropic" Haplohumod. Scale division in cm.

an antropic epipedon. The soil is developed in a 150 cm thick layer of coversand above sandy till. The particle size distribution shows well-sorted fine sand, with a low silt content. The silt content decreases with depth. The bulk density was high below 65 cm, indicating a dense packing of the sand grains. Roots are only found in worm galleries and cracks in the spodic horizon. The spodic horizon is strongly developed with a black organic matter-rich Bh horizon and a cemented Bhsm horizon.

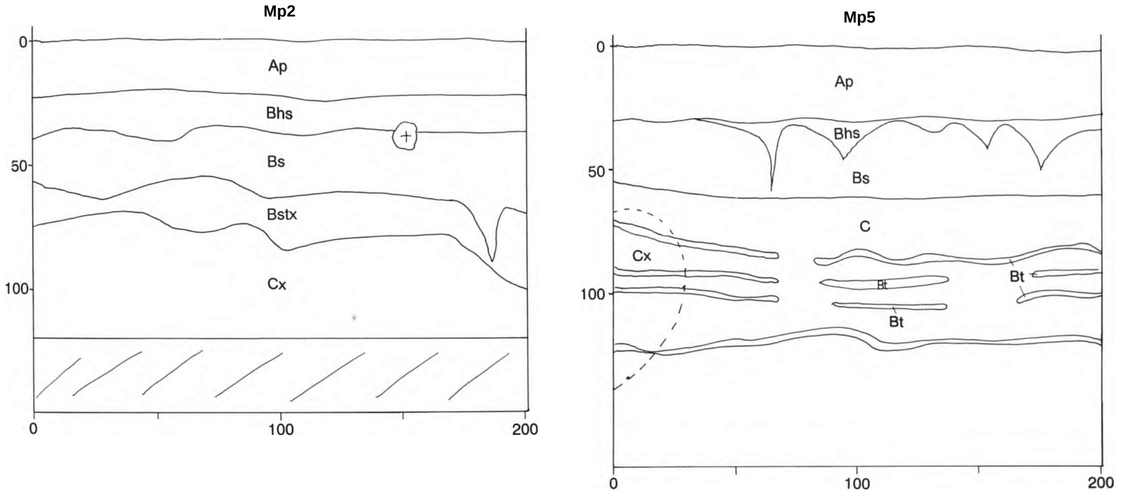
The area around the profile is former heathland, which was brought under cultivation between 1880 and 1920. Since then a thick dark phosphate-rich plough layer has developed. Even though the hydrochloric acid method extracts more phosphate than the citric acid method used by Soil Survey Staff (1975) we assumed that the epipedon fulfils the criteria for an anthropic epipedon.

Profile Mp5 (fig. 6, table 1, and photo 2) is a Typic Haplorthod with weakly developed Bt bands developed on sandy till with a low clay



"Antropic" Haplohumod
coversand on sandy till

Arenic Hapludalf
thin coversand on sandy till



"Antropic" Fragiumbrept
sandy till

Typic Haplorthod
sandy till

Fig. 6. Drawings of the soil profiles in arable land. Classification and parent material are indicated.

			Particle size distribution Mikro meter % of < 2 mm								Bulk dencity	Poro-sity
Profile	Hori-zon	Depth (cm)	<2	2-20	20-63	63-125	125-250	250-500	500-200	>2mm	g/cm3	%
Mp1	Ap	0-40	1.3	1.5	7.6	20.4	51.0	16.7	1.4	0.0	1.62	39
	Bh	40-45	1.0	2.4	5.5	16.2	51.0	21.4	2.5	0.0	1.49	44
	Bhsm	45-65	1.6	1.4	2.2	14.1	52.8	24.9	3.1	0.0	1.59	40
	Bsd1	65-100	0.1	0.1	0.7	19.9	56.4	20.9	1.9	0.0	1.72	35
	Bcd2	100-150	0.2	0.1	0.2	10.3	72.8	15.7	0.7	0.0	1.86	30
	2C	150-180	0.6	0.1	0.8	8.1	43.4	34.2	12.9	32.5	1.93	27
Mp2	Ap	0-25	3.5	6.1	12.1	22.5	32.8	18.1	4.9	0.8	1.30	51
	B(hs)	25-40	3.6	5.5	10.7	19.8	35.6	19.6	5.1	2.6	1.35	50
	B(s)	40-65	6.0	5.6	11.8	20.5	30.7	19.2	6.3	10.2	1.35	50
	Bx(t)	65-80	3.4	8.3	13.7	21.0	27.8	18.3	7.5	2.5	1.70	36
	Cx	80-150	4.9	9.0	13.6	19.7	28.0	18.0	6.8	5.3	1.71	35
Mp4	Ap	0-30	2.8	8.1	19.4	24.2	25.7	14.6	5.5	1.9	1.18	56
	Bw	30-40	4.5	12.5	16.9	23.5	25.6	13.5	3.6	0.5	1.58	41
	2Bw	40-50	2.7	3.3	5.0	21.7	38.3	22.4	7.8	1.2	1.83	31
	2Bw	40-50	2.8	4.1	6.7	21.2	35.7	22.7	5.7	0.0	1.59	40
	2B/E	50-90	5.0	3.6	8.2	16.4	27.2	23.2	14.8	9.3	1.75	34
	2B/E	50-90	4.1	4.7	12.4	18.9	29.7	19.8	11.8	10.7	1.70	36
	2Bt	135	7.7	7.0	15.5	19.3	25.6	17.2	7.0	7.9	1.69	36
	2Bt	175	11.1	11.1	11.1	19.9	24.9	14.5	7.9	3.1	1.86	30
Mp5	Ap	0-30	3.0	7.3	11.4	21.4	32.5	18.0	6.5	5.2	1.27	52
	Bhs	30-35	2.1	6.3	12.1	24.4	29.5	17.7	7.9	4.6	1.48	44
	Bs	35-60	1.1	5.0	14.0	24.5	32.0	17.2	6.2	3.0	1.74	34
	C	60-150	0.7	5.6	13.7	25.3	30.2	19.4	5.1	1.9	1.90	28
	Bt-band	80	2.6	8.1	13.8	24.1	29.5	16.2	5.6	1.5		
Sp2	Ap	0-20	1.7	3.2	11.6	25.6	40.4	15.0	2.4	4.4	0.98	63
	Bhs	20-40								1.4	1.20	55
	Bs(t)x	40-65	1.8	7.8	15.3	21.0	29.5	17.8	6.9	5.5	1.62	39
	C(t)x	65-150	2.6	7.8	14.0	19.1	28.9	20.0	7.6	5.2	1.64	38

					P			pH		Fe		Al	
			Org. C %	C/N	Total mg/kg	Inorg	C/P	1120 1:1	KCl 1:1	PYR %	DCB %	PYR	DCB
Mp1	Ap	0-40	1.62	16.2	524	424	162	6.87	5.91				
	Bh	40-45	3.13	26.0	992	702	108	6.35	5.52				
	Bhsm	45-65	1.37		368	295	187	6.51	5.16	0.15	0.21	0.36	0.41
	Bsd1	65-100	0.21					7.14	5.34	0.02	0.05	0.09	0.10
	Bcd2	100-150	0.13					6.74	9.94	0.02	0.04	0.05	0.08
	2C	150-180	0.09					6.77	5.07				
Mp2	Ap	0-25	3.49	18.8	675	441	149	6.10	5.29				
	B(hs)	25-40	1.14		282	98	62	5.33	4.29	0.18	0.28	0.23	0.23
	B(s)	40-65	1.49		320	128	78	5.09	4.19	0.25	0.38	0.32	0.32
	Bx(t)	65-80	0.35					5.13	4.25				
	Cx	80-150	0.29					4.95	4.22				
Mp4	Ap	0-30	2.00	16.0	500	271	89	6.21	5.50				
	Bw	30-40	0.44	15.7	159	120	113	6.46	3.91				
	2Bw	40-50	0.20					6.71	5.27				
	2Bw	40-50	0.20					6.42	4.28	0.08	0.22	0.10	0.13
	2B/E	50-90	0.04					5.43	3.87	0.09	0.24	0.07	0.09
	2B/E	50-90	0.10					4.84	5.48	0.03	0.20	0.05	0.06
	2B/t	135	0.11					5.20	3.90				
	2Bt	175	0.10					5.60	3.90				
Mp5	Ap	0-30	2.90	22.3	517	265	115	5.58	4.92				
	Bhs	30-35	0.88		446	235	41	5.17	4.42	0.13	0.32	0.22	0.26
	Bs	35-60	0.23		258	150	21	5.14	4.54	0.04	0.17	0.10	0.12
	C	60-150	0.13					5.17	4.50				
	Bt-band	80	0.14					5.10	4.26				
Sp5	Ap	0-20	1.54	20.8	217	87	118	4.01	3.63				
	Bhs	20-40	1.56					4.45	4.07	0.15	0.24	0.34	0.36
	Bs(t)x	40-65	0.60					4.60	4.21	0.13	0.29	0.34	0.37
	C(t)x	65-150	0.22					4.55	4.22				

Table 1. Analytical data from samples from five of the profiles.

MP5

Classification	Typic Haplorthods.
UTM	NH 304989
Terrain	Weakly undulating
Parent materiel	sandy till
Slope	0°
Vegetation	1880 and 1920 Calluna heath, probably arable land since around 1950

Horizons

Ap 0-30 cm	Black (10YR 2/1 m); fine sand; Weaksubangular structure; slightly sticky; many pores of all sizes; many small roots; 5-10 % gravel and stones; small pieces of chalk; worms are present; sharp and smooth boundary.
Bhs 30-35 cm	Dark brown (10YR 3/3 m); fine sand; weak platy structure; non sticky; many pores of all sizes; many fine roots; less than 5 % stones smaller than 5 cm Φ; sharp and irregular boundary.
Bs 35-60 cm	Dark yellowish brown (10YR 4/4 m); fine sand; weak platy structure; many pores of all sizes; many fine roots; less than 5 % stones smaller than 5 cm Φ; sharp and smooth boundary.
C 60-170 cm	Light yellowish brown (10YR 6/4 m) bands of Bt materiel, description stated below; fine sand; structureless; non sticky; few worm galleries down to 110 cm; few roots; less than 5 % gravel and stones smaller than 5 cm Φ; water is coming out of profile in 160 cm.
Cx	As described above except; weak platy structure; brittle.
Bt-streaks	Yellowish brown (10YR 5/6 m); fine sand; structureless, massive; non sticky; accumulated thickness is 10 cm in some parts up to 15 cm; the boundary to the C horizons is abrupt.

Photo 2. Profile Mp5, Typic Haplorthod. Svale division 10 cm.

content (about 3 %) and with no or weak fragipan development. Despite high bulk density roots are seen down to 110 cm depth. The horizontal bands of illuvial clay (marked Bt in fig. 6) reflect clay movement before the podzolization started. Meanwhile, neither the difference in clay content between the illuvial and elluvial zones, nor the accumulated thickness of the clay bands, satisfy the requirements of an argillic horizon. The spodic horizon has fragments of a Bhs horizon and a pronounced Bs horizon.

The area around the profile was brought under cultivation shortly after 1950. Judging from the lower pH (5.6 versus 6.9), the plough layer has received less lime than the plough layer in profile Mp1. The higher C/N ratio probably also reflects the shorter time of cultivation and the lower pH.

Classification	Typic Fragiorthod
UTM	NH 313991
Terrain	Weakly undulating
Parent materiel	Thin coversand above sandy till
Slope	0°
Vegetation	1880: Heather 1920: Coniferus, at present 25 years old Norwegian Spruce

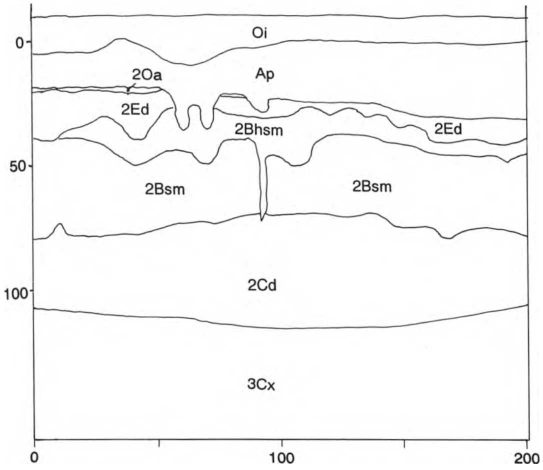
Horizons

Oie -5-0 cm	Poor to moderate decomposed needles
A(p) 0-20 cm	Very dark grayish brown (10YR 3/2 d) with 10 % 1-2 cm Φ dark grayishbrown (10YR 4/2 d) distinct sharp mottles, loamy fine sand; structureless porous massive; non sticky; very friable; few fine and coarse pores, the coarse ones are vertical, the fine ones are random oriented; common roots of all sizes; few active worm galleries; sharp and smooth boundary.
Bhs 20-40 cm	Dark reddish brown (10YR 3/3 d) with 1-2 cm Φ distinct sharp and diffuse, medium very dark brown (10YR 2/2 d) mottles, loamy sand; structureless porous massive; non sticky; friable; few fine pores; common roots of all sizee; stones are more commen in the upper part of the horizon; clear wavy boundary.
Bs(t)x 40-65 cm	Dark yellowish brown (10YR 4/6 m) loamy sand; moderate coarse platy structure; non sticky; hard, brittle (m); in some part of the horizon clay illuviation as bridging between the sand grains is seen; common very fine to fine unconnected pores; few fractures some with roots; no roots outside fractures; diffuse wavy boundary.
CB(t)x 65->150	Light olive brown (2,5Y 5/4 m) loamy sand, weak coarse to very coarse platy structure; non sticky; hard, brittle (m); clay bridging as in the Bs(t)x horizon; many fine unconnected pores; few fractures with roots; no roots outside fractures; the structure gets coarser and weaker downwards.

Photo 3. Profile Sp2, Typic Fragihumod. Scale division 10 cm.

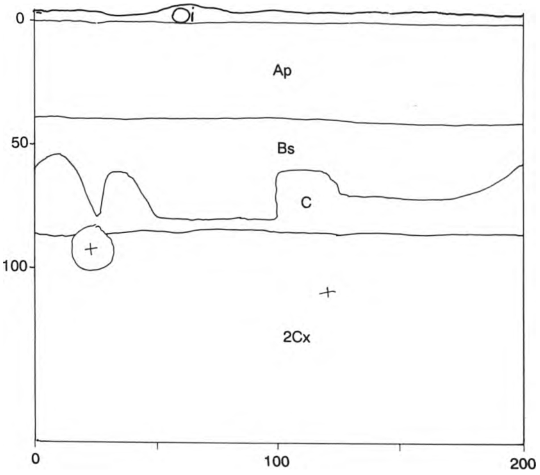
Profile Sp2 (fig. 7, table 1, and photo 3) is a Typic Fragihumod, and represents soils with fragipan developed on sandy till. The particle size distribution shows a relatively high silt content (23 %) and a low clay content. In Ap the higher 125-250 *µm* sand fraction and the lower silt content might indicate that coversand and till are mixed together in this horizon by the ploughing. The bulk densities of the Bsx and Cx horizons are relatively low for a fragipan, just above 1.6 g/cm^3. Still roots were only seen in the vertical cracks of the fragipan, and in photo 3 a vertical

SP1



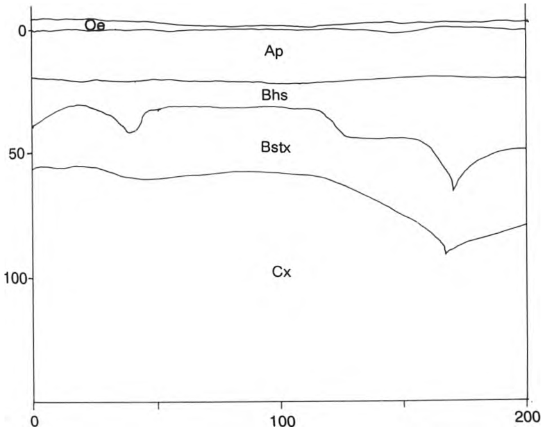
Typic Fragihumod
windblown sand over
coversand on sandy till
Picea glauca app. 40 years

SP3



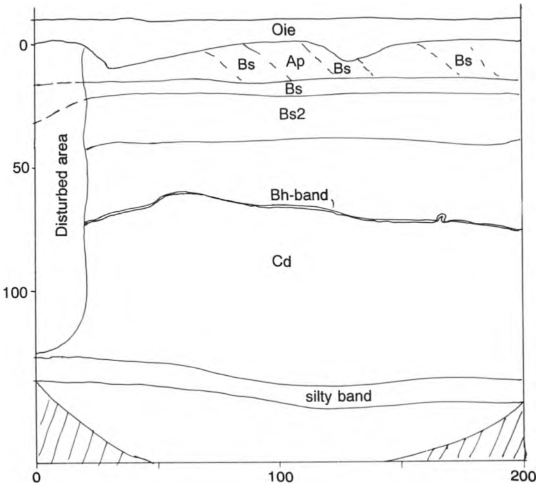
"Plaggeptic" Fragihumod
coversand on sandy till
Picea abies app. 35 years

SP2



Typic Fragiorthod
thin coversand on sandy till
Picea abies 20 years

SP4



Entic Haplohumod
coversand
Picea abies 26 years

Fig. 7. Drawings of the soil profiles in forest land. Classification, parent material and tree species are indicated.

crack with roots is seen to the left of the measure tape.

The spodic horizon is divided into a Bhs horizon with many roots and a Bs horizon, which is developed in the fragipan. It only contained a few roots in the cracks. Both the Bs and Cx horizon show only weak signs of clay illuvation in form of cutans forming bridges between the sand grains.

Profile Mp4, an Arenic Hapludalf (fig. 6, table 1), represents the Alfisols. The plough layer in this profile most probably consists of coversand. At least a layer of coversand (Bw) is present underneath. As shown in table 1 the clay content increases with depth. The Ap horizon is black (10 YR 2/1 m) with 2 % organic carbon and a pH of 6.2 in water. This indicates that base saturation might be above 50 % and therefore the epipedon would be mollic. The nearly neutral pH values found in the upper horizons are due to liming of the soils. For example in the lower part of the 2BE horizon the pH is only 4.8.

Profile Mp2 (fig. 6 and table 1) is more problematic, it has a very dark brown (10YR 3/2 m) Bhs horizon with well-developed spodic features. The ratio of Fe_p + Al_p to Fe_d + Al_d is (0.8), but the clay content is 3.0 %, so that the (Fe_d + Al_d) to clay ratio is 0.14, which is not enough to fulfil the requirements of a spodic horizon. The profile is therefore classified as a Typic Fragiumbrept, because no Antropic subgroup is established in the Fragic great group. As Antropic Haplohumod the "Antropic" Fragiumbrept (Mp2), and the (MP1), Plaggeptic Fragihumod (Sp3), only cover very small areas they are not shown on the soil map.

The distribution of soil types

The distribution of soil types classified at subgroup level according to Soil Survey Staff (1990) is shown in fig. 8. As already mentioned the soil map is based on a total of 10 soil pits and on one auger hole per hectare. Inclusions, i.e. cases where a single auger hole indicated the presence of a different subgroup, are only shown on the map when the soil may have properties deprimental to forest growth. This ensures that the soil map can be used as a basis for choosing tree species or deciding the placing of the individual forest stands for re-afforestation of the area, without danger of introducing any destabilizing effects in the future forest. For example an Alfic Haplorthod is allowed in a Typic Fragiorthod, but not vice versa. This is because the fragipan is root restrictive, in contrast to the uncemented spodic horizon, and therefore a possible source of windthrow in spruce stands.

The dominant soil order is Spodosols, Alfisols are only present in the north-eastern part of the area. The two main orders of Spodosols, Humods and Orthods, cover nearly equal percentages of the total area. Aquods are only found in 2 % of the area, and only in depressions where most of them have been covered with peat. Today most of the peat has decomposed due to drainage. Some of the Aquods might therefore have been covered by Histosols, at the time the drainage was undertaken, since it has been found that peat decomposes at a rate of about 2 cm per year after drainage (Dalsgaard, 1985). The Aquods have not been studied in detail due to the small area they cover.

Humods are almost exclusively found on coversand. Where fragipan is present in the sandy till underneath the coversand the Humods are classified in the Fragic great group, while the rest are classified in the Haplic great group.

The Orthods are present on the sandy tills with the low clay content. This means that the irregular distribution of the coversand is reflected in the distribution of the Orthods. The Orthods with fragipan are classified in the Fragic great group, while the rest has been classified in the Haplic great group. Clay illuviation, which has led to formation of an argillic horizon, is observed in both great groups, and leads to placement of the soils in the Alfic subgroups. The usual argillic horizon is non-banded, and not of the lamellar type seen in profile Mp5 (fig. 6). The difficulties in augering through the fragipan might have lead to an underestimation of the area covered with Alfic Fragiorthods.

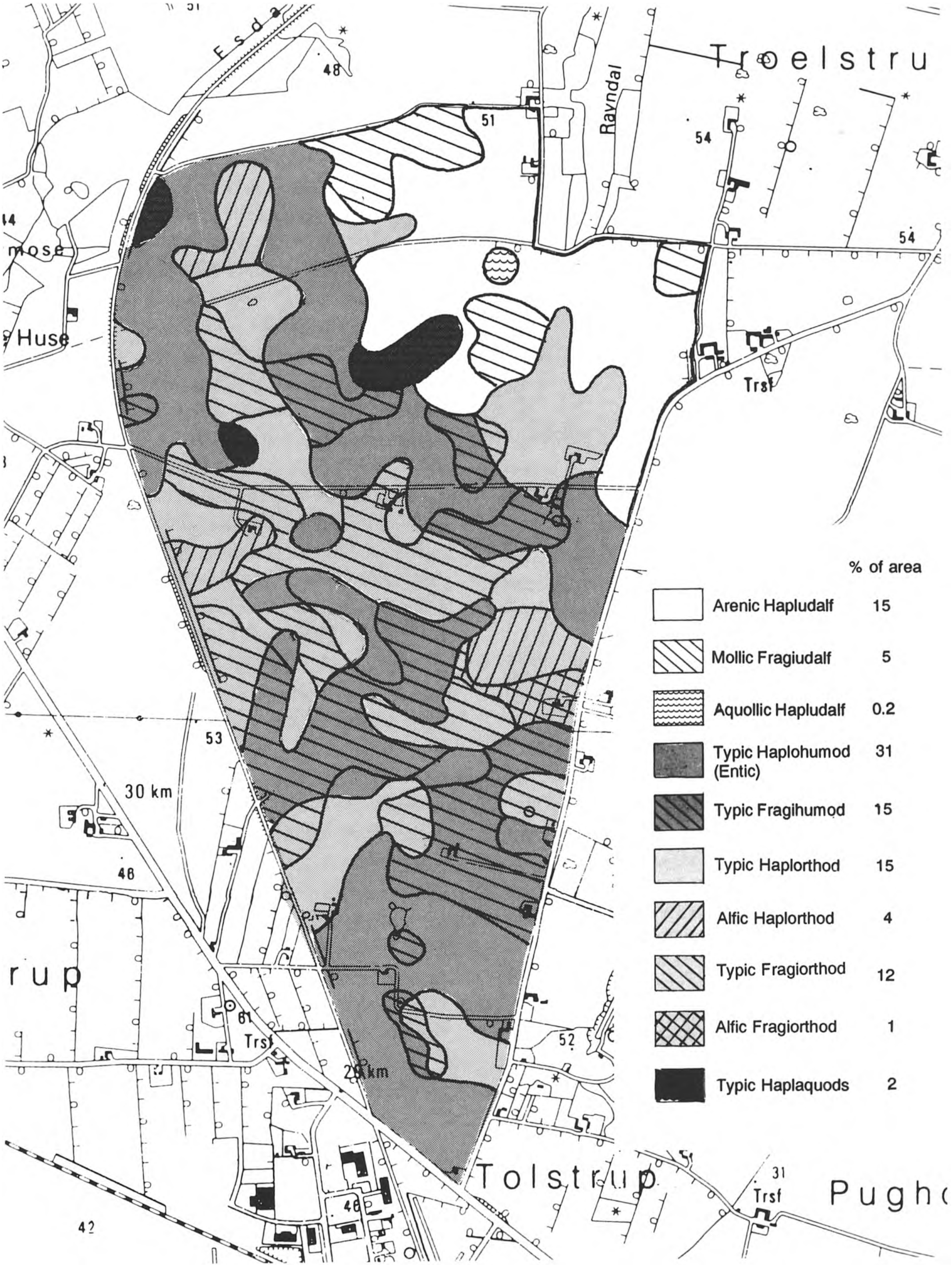


Fig. 8. Soil map of the investigated area. The soils are classified at suborder level according to Soil Taxonomy. • Kort- og Matrikelstyrelsen (A 413-90).

The Alfisols are found in the north-eastern part of the area, where the sandy till has a higher clay content between 5 and 10 %. The Alfisols with fragipan are classified as Mollic Fragiudalfs due to a dark thick plough layer. The rest of the Alfisols are classified as Arenic Hapludalfs. There is a small, wet area covered by Alfisols, which most probably should be classified as an Aquollic Hapludalf, but this area was not studied in detail.

Discussion

Parent material

The area was located on supposed glaciofluvial material (DGU, 1989) but turned out to be sandy till with sheets of coversand. The sandy till generally has a low content of gravel and stones. The one exception, the high amount found in profile Mp1 in the 2C horizon, wasmost probably caused by wind erosion removing the finer material before the coversand was laid on top.

Coversand has not been described in this part of Denmark before, but the morphology, the internal structure, and the particle size distribution strongly support the interpretation that the sand sheets are coversand.

The study showed that some of the critera for identification of a fragipan (Witty & Knox, 1989) cannot be applied to the sandy fragipans in the area. For example, the dominant structure is not coarse or very coarse prisms, but lenticular or lenticular-platy. The great extension of the fragipan (33 % of the area), and the irregularity of its occurrence, is considered to be of importance for planning the re-afforestation in the area because of its root-restrictive properties.

The soils

Podzolization dominates the soil morphology of the area. It follows from the theory (Petersen, 1976; de Coninck, 1980), that this implies the presence, or former presence, of a mor-producing vegetation, which in this area was the Calluna vulgaris heath introduced by man. The date of introduction of the Calluna heath is difficult to establish. But iron age findings in the area implies that the Calluna heath could be at least 2000-3000 years old. That the Calluna-dominated vegetation, which covered most of the area in 1810, had been maintained for about 2000 years or more is also supported by the degree of development of the spodic horizons examined in the area.

There is a strong correlation between distribution of the Humods and the coversands. The reason for this is a low free-iron content, rather than a high carbon content, in the spodic horizons present in the coversand. The ratio between Fe_d and organic carbon is less than 0.2. The highest value of free-iron content found in the Humods, was 0.21 % in the Bhsm horizon in profile Mp1.

The Orthods developed in the sandy tills have slightly higher contents of free iron and aluminium (0.5-0.7 %) than the Humods.

Cultivation of the heath during the last hundred years has caused changes in the soils, especially the epipedons. Liming has raised pH in the Ap horizons to a value between 5.6 and 6.9. The pH in the upper mineral horizons of the forest soils is from 3.7 to 4.1. As a result of ploughing before planting the forest soils today have thick, dark epipedons. Profile Sp3 is the only profile with an ochric epipedon, while the other forest profiles and Mp5 have umbric epipedons. Mp4 might have mollic epipedons as discussed earlier. Profile Mp2 has the same high level of phosphorus as profile Mp1 and they have probably both antropic epipedons.

The influence of cultivation on the Spodosols seems to be limited to mixing, of the O, A and E horizons, and possibly in many instances the upper B horizons as well. Worm galleries are formed in the cemented spodic horizon and deeper in the uncemented spodic horizons. Apart from this, the spodic horizon is well preserved in the soils of the survey area, and the depodzolizing effect of cultivation seems to be less powerful than that caused by a 70 year old oak invasion on the Calluna heath in central Jutland described by Nielsen et al. (1987). Possibly, because roots of annual crops are less effective in loosening up the spodic horizon, than the roots of the oak trees and the associated perennual grasses.

From fig. 5 it can be seen that in 1810 the cultivated soils belonging to the farms in Svenstrup were mainly located on Alfisols, but that the western part of the Alfisol area was covered with Calluna heath. The introduction of the heath vegetation in this area has left no signs of podsolization in the Alfisols, probably because of the higher clay content in these soils than in the soils which are podzolized.

Classification

Classification of the soils at subgroup level results in a soil map with many small subareas. 10 subgroups are shown on the map, while 3 are not shown. The 13 subgroups reflect different characteristics in the soils, caused by differences in parent materiel and human influence. The most obvious human-caused factor was the destruction of the natural forest leading to establishment of Calluna heath followed by cultivation with liming and manuring. The study has shown, that the Soil Taxonomy classification scheme is insufficient at the subgroup level, because it does not make possible to differentiate Spodosols, which are strongly influenced by cultivation. It is important that these are classified in the Spodosol order, because the podzolization process will no doubt start again if the area is once again covered by a mor-producing vegetation such as Calluna vulgaris or Norwegian spruce (Picea abies).

Summary

The soils of a 262 ha area were mapped in detail in order to develop a soil map system for re-afforestation of marginal agricultural land. Examination by means of a combination of profile pits and auger holes gave a good picture of the soil variation in the survey area. The soil map Fig. 8 shows the great variation: 10 subgroups in 3 soil orders of Soil Taxonomy reflecting the variation in parent materials, vegetation history and land-use patterns.

5 % clay in the parent material seems to determine the boundary between Alfisols and Spodosols. The cause for the podzolization is the man introduced Calluna vulgaris heath. Orthods are found on sandy till with low clay content, whereas Humods are present on coversands with low free-iron and aluminium contents. The coversands, which has not been described in this part of the country before, covered 36 % of the area. At great group and sub group levels the soils were differentiated in terms of presence or absence of a fragipan (33 % of the area), by an argillic horizon, and by limed and manured epipedons.

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References

Aaby, B. (1985): Norddjurslands landskabsudvikling gennem 7000 år, Fortidsminder. 60-84.

Baastrup, E., Dalsgaard, K & Petersen, T.H. (1977): Jorde på Bording Bakkø. Geo-rapport nr. 4, Geologisk Institut, Aarhus Universitet, 47 p.

Bornebusch, C.H. & Milthers, K. (1935): Soil Map of Denmark. DGU III række, nr. 24. 68 p.

Coninck, F. de (1980): Major mechanisms in the formation of Spodic horizons. Geoderma 24:101-28.

Dalsgaard, K. (1985): A reconstruction of the pre-medieval landscape with aid of the 1844 land registration maps. Aarbøger for nordisk Oldkyndighed og Historie, 1984:301-03.

Dalsgaard, K. (1989): Udviklingen i landbrugslandskabet fra Stavnsbåndets tid til idag. In: Bondefrigørelsen. (Andersen, J., Bekker-Nielsen, T. & Fenger, O. ed.) Acta Jutlandica LV, 3:87-102.

Dalsgaard, K. (1990): Spodosols of Denmark. Procedings, V International Soil Correlating Meeting (in press).

DGU (1989): Jordartskort over Danmark 1:200.000, (Map of the quaternary deposits in Denmark). Danmarks Geologiske Undersøgelse, Miljøministeriet.

Greve, M.H. & Sørensen, P. (1990): Lokalitetskortlægning på marginaljord - et pilotprojekt. Thesis, Geologisk Institut. Aarhus University, 158 p. + Appendices.

Kolstrup, E. (1982): Cover sand and cover sand stratigraphy in Denmark. Geografisk Tidsskrift 82:88-91.

Kolstrup, E. & Jørgensen, J.B. (1982): Older and Younger Cover-sand in southern Jutland (Denmark). Bull. Geol. Soc. Denm., 30:71-77.

Lindbo, D.L. & Veneman, P.L.M. (1989): Fragipans in the Northern U.S. In Fragipans: Occurrence, classification, and genesis: Proceedings of a symposium. Eds.: Niel E. Smeck & Edward J. Ciolkosz. (SSSA special publication: No. 24)

Lysgaard, L. (1969): Foreløbig oversigt over Danmarks klima 1931-1960. Det Danske Meteorologiske Institut Meddelelser Nr. 19.

Madsen, H. Breuning (1983): Himmerlands jordbundsforhold. Folia Geographica Danica Tom XVI, 329 p.

Madsen, H. Breuning & Jensen, N.H. (1985): Jordprofilundersøgelsen, Landbrugsministeriet, Arealdatakontoret.

Mehra, P.O. & Jackson, M.L. (1960): Iron oxide removal from soils and clays by the dithionite-citrate system buffered with sodium bicarbonate. Clay Mineralogy, Monogr. Earth Sci., Ser. 5: 317-27.

Müller, P.E. (1884): Studier over Skovjord som Bidrag til Skovdyrkningens Theori II. Om Muld og Mor i Egeskov og paa Heder. Tidsskrift for Skovbrug 7:1-232.

Müller, P.E. (1887): Studien über die natürlichen Humusformen und deren Einwirkung auf Vegetation und Boden, Springer, Berlin, 324 p.

Nielsen, K.E., Dalsgaard, K. & Nørnberg, P. (1987): Effects on Soils of an Oak Invation of a Calluna Heath, Denmark, I: Morphology and Chemistry, Geoderma 41: 79-95.

Odgaard, B.V. & Rostholm, H. (1988): The Single Grave barrow at Harreskov, Jutland: Excavation and Pollen analysis of a fossil soil. Journal of Danish Archaeology, vol. 7.

Petersen, L. (1976): Podzols and Podzolization. De Studerendes Råd, Copenhagen 293 p.

Soil Survey Staff (1975): Soil Taxonomy: A Basic system of Soil Classification for Making and Interpreting Soil Surveys. U.S. Department of Agriculture Handb. No. 436, 754 p.

Soil Survey Staff (1990): Keys to Soil Taxonomy, 4th edition. SMSS techn. monogr. no. 6. Blacksburg, Virginia.

U.S.D.A. (1972): Soil Survey Laboratory methods and procedures for collecting soil samples. Soil Survey investigation report No. 1. U.S. Department of Agriculture, Washington, D.C. 63 p.

Van Vliet, B. & Langohr, R. (1981): Correlation between fragipans and permafrost with special reference to silty Weichselian deposits in Belgium and northern France. Catena 8: 137-54.

Witty, J.E. & Knox, E.G. (1989): Identification, role in soil Taxonomy, and the Woldwide Distribution of fragipans. In Fragipans: There occurence, classification, and genesis. Proceedings of a symposium. Eds.: Niel E. Smeck & Edward J.: Ciolkosz. (SSSA special publication: no. 24).

Øvig, L. (1986): Fragipan, en pedologisk undersøgelse af en fragipan i Sophie Amaliegaard Skov. Thesis, Geologisk Institut Aarhus University. 109 p.

Aspects of soil geography in South Greenland

Bjarne Holm Jakobsen

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Soils in subarctic Greenland have been studied with special emphasis on their pedogenetic variation. Due primarily to the climatic gradient from maritime coastal areas to the more continental interior, zonal soils range from strongly leached and acid Spodosols to only weakly acid Inceptisols. Chemical analyses evidenced a multiple process system in the formation of soils in the area and a probable general sequence of intensity of pedogenetic processes. The study provided a better understanding of variations within the group of podzolized soils.

Keywords: *Greenland. Subarctic. Soils.*

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In South Greenland extensive soil studies were initiated in the mid-1980s to evaluate the impact of agricultural land use on soils, and especially the effects of intensified grazing due to expansion of the sheep-breeding industry.

Modern sheep-breeding in subarctic South Greenland is primarily based on grazing of the natural vegetation during the summer period. Stall-feeding takes place from October through May mostly with hay produced on small home-field plots.

Carrying capacity, critical thresholds of the environmental system, soil-degradation and erosion processes have earlier been considered by Jacobsen & Jakobsen (1986) and Jakobsen (1990a). Furthermore, studies of specific translocation processes in subarctic Spodosols by using energy dispersive X-ray techniques for analyses of thin sections from B horizons have been presented by Jakobsen (1989, 1990b). In the present paper an outline of the geography of soils in parts of South Greenland is presented, and dominating soil-forming processes are discussed.

Most zonal soils in the area show more or less distinct morphological eluvial and illuvial features, indicating that podzolization is taking place. The properties of E and B horizons vary markedly, and especially the chemical characteristics within the illuvial horizons indicate an active system of multiple processes. The soil geography probably reflects different intensities of processes within the multiple process system.

Multiple processes in soil genesis, a classic idea presented by e.g. Marbut (1951) and Simonson (1978) are discussed in relation to podzolization as observed in South Greenland. Podzolization both involves organic translocation of metal cations by water-soluble organic acids (Ponomareva, 1964; Petersen, 1976; De Coninck, 1980) and inorganic translocation mainly involving positively charged, mixed aluminium- and iron-silicates (Farmer et al., 1980; Anderson et al, 1982; Childs et al, 1983; Ugolini et al, 1987).

Geographical conditions

The study area comprises the ice-free landscape from the Davis Strait coast to the present margins of the Inland Ice (fig. 1). The coastal region is of the skerries type with only sporadic, thin covers of fine-grained deposits. In the middle region - a subalpine type - the hilly landscape contains tills and glaciofluvial materials with only small areas of barren rock on wind exposed higher positions in the landscape. To the east a narrow alpine zone near the Inland Ice is characterized by glaciers, glaciofluvial material on valley floors, and scree covered valley sides.

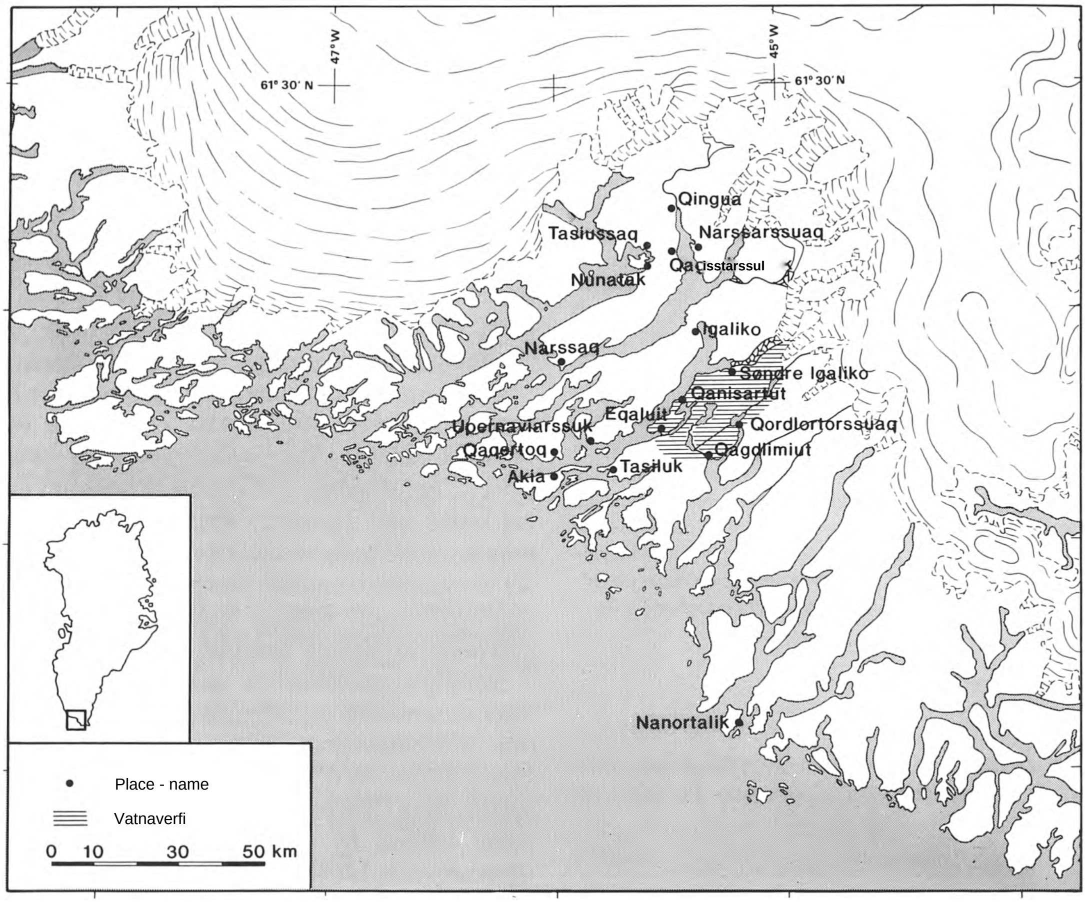

Fig. 1. The study area, South Greenland.

Due to the drift-ice from the Polar Sea with the East Greenland Current around Cap Farvel the low-arctic climate shows a trend from an oceanic para-arctic type in the outer coast areas to a more continental para-boreal type in the inner regions (fig. 2). The foggy and moist climate found in the areas close to the Davis Strait is characterized by a mean annual temperature of about +0.5 °C, mean temperatures of the warmest and coldest month of about +7 °C and about -5 °C, respectively, and a mean annual precipitation of about 900 mm. Mean summer month temperatures increase to slightly above +10 °C at the heads of the fjords, but as the mean temperature of the coldest month is as low as about -7 °C, the mean annual temperature only reaches about +1 °C. The annual precipitation here is about 600 mm. Generally, the precipitation in South Greenland is distributed evenly throughout the year with slightly higher values during July-December.

From measurements made 1985-89 the mean annual evapotranspiration rate was found to increase from about 150 mm to about 300 mm from the outer coast area to inland areas. Daily evapotranspiration rates normally range from 1 to 3 mm during the growing season.

Both long- and short-term climatic oscillations characterize the area. Different kinds of historical information and oxygen isotope analyses of ice cores from the Greenland Inland Ice (Dansgaard, 1975) indicate a relatively warm

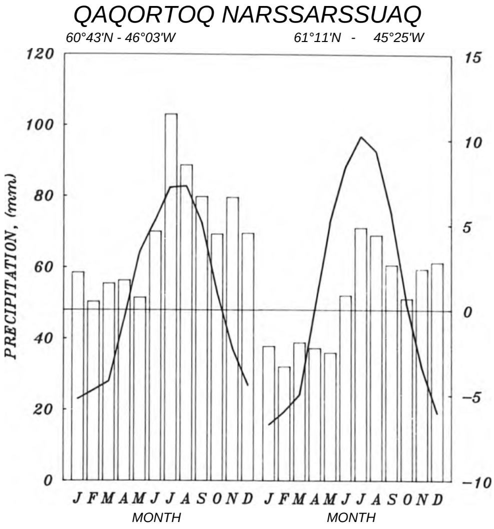

Fig. 2. Annual variation in temperature and precipitation (1960-1989) at Qaqortoq and Narssarssuaq.

medieval period followed by a cold period, the *Little Ice Age.* Even though the *Little Ice Age* is reckoned to be the coldest period since the last glaciation, ice core analyses show that such long-term climatic changes are not unique but are a general phenomenon during the Holocene.

The climate also varies markedly from year to year, especially as regards the length and warmth of the growing season, the wind climate, and the water balance. Climatic extremes, such as heavy daily rainfalls (70-90 mm), are observed in some years. During periods of strong, dry foehn winds from the Inland Ice the evapotranspiration rate, measured as soil water loss, may reach 15 mm/day. The yearly, highly varying frequency and duration of foehn situations during the summer periods therefore crucially control the water balance of soils in the area.

According to the Soil Taxonomy (Soil Survey Staff, 1975) the soil temperature regime is classified as cryic. The soil moisture regime is udic in well drained positions whereas aquic regimes are found in poorly drained areas.

In the continental sub-alpine regions with relatively warm summer periods luxuriant subarctic vegetation types dominate. Subarctic birch forest and copses of willow are here interspersed with birch heath and open grassland communities. Fens and bog areas are found around lakes and along streams. In the high-lying inland areas towards the Inland Ice, on top of high-lying, wind-exposed ridges and in some of the tracts with intrusive geological formations, the landscape is mostly barren, in some places interspersed with fell—field vegetation. The peninsulas and islands of the skerries landscape are covered by dwarf shrub heath, rich in mosses and lichens.

Methods

In the field soils were described according to FAO (1977). Fine earth samples from the major horizons were analysed using the following methods: Particle size distribution was determined by sieve and pipette methods; pH was measured in 0.01 M $CaCl_2$ (1:2.5). Organic carbon was determined by combustion in a LECO induction furnace, and nitrogen was analysed by Kjelddahl digestion. Total and inorganic phosphorus was determined spectrophotometrically after extraction with 12 N sulfuric acid of fine earth heated to 550 °C, and by extraction of unheated fine earth. Exchangeable bases were extracted by NH_4OAc and determined by Atomic Absorption Spectrophotometry (AAS). Exchangeable acidity was determined at pH 8.1 by Pipers method (Borggaard et al., 1983), and the Cation Exchange Capacity (CEC) calculated as the total amount of cations. Soluble Al, Fe and Mn were extracted by dithionite-citrate (Mehra & Jackson, 1960) and by pyrophosphate (McKeague, 1967). Acid-oxalate-extractions of Al, Fe, Mn and Si were carried out according to McKeague et al. (1966). Al, Fe and Mn were determined by AAS, Si was determined spectrophotometrically (Morrison et al., 1963).

Soil geography

The soil-forming factors, and especially the climatic and vegetational zonation, are clearly reflected in the geography of soils. Generally, the zonal soil type changes from a strongly leached, very acid Spodosol in the humid outer coast areas

	Hor.	Depth (cm)	Colour (moist)		Morphological features
P1	O	+5-0	2.5YR	2/3	Organic mat (LFH-layer).
	A	0-1	7.5YR	2/2	Humose, silt loam, weak thin platy, very friable.
	E	1-12	10YR	5/2	Slightly gravelly sandy loam, weak medium platy, friable.
	Bs	12-20	7.5YR	3/4	Slightly gravelly sandy loam, weak medium platy, friable.
	R	20-			Granitic bedrock.
P2	A	0-2	10YR	2/2	Humose, silt loam, moderate fine crumb, very friable.
	E	2-8	2.5Y	7/1	Slightly gravelly silt loam, moderate medium platy, friable.
	Bhs	8-16	2.5YR	3/3	Gravelly sandy loam, moderate fine subangular blocky, friable.
	Bs	16-24	7.5YR	3/4	Gravelly loamy sand, moderate fine subangular blocky, friable.
	BC	24-40	10YR	4/6	Gravelly sand, weak very thick platy, firm, weakly cemented.
	C	40-	10YR	5/2	Gravelly sand, structureless (single grain).
P3	A	0-0.5	10YR	2/2	Humose,gravelly silt loam, weak very fine granular, very friable.
	E	0.5-7	10YR	5/2	Gravelly sandy loam, weak fine subangular blocky, very friable.
	Bs1	7-15	7.5YR	4/4	Gravelly sandy loam, weak medium subangular blocky, friable.
	Bs2	15-30	10YR	5/3	Gravelly sandy loam, weak medium subangular blocky, friable.
	C	30-	2.5Y	6/2	Gravelly sand, structureless (massive).
P4	A	0-6	7.5YR	3/2	Humose, gravelly loamy sand, weak fine granular, very friable.
	E	6-12	10YR	5/3	Gravelly loamy sand, weak medium granular, very friable.
	Bs1	12-20	5YR	3/4	Gravelly loamy sand, structureless (single grain).
	Bs2	20-33	2.5YR	2/2	Gravelly loamy sand, moderate fine subangular blocky, very friable.
	Bs3	33-47	7.5YR	4/4	Gravelly sandy loam, strong medium granular, weak fine subangular blocky, friable.
	Bs4	47-58	10YR	4/3	Gravelly sandy loam, strong medium granular, weak medium platy, (pisolitic), friable.
	BC	58-90	2.5YR	5/3	Gravelly sandy loam, strong medium granular, moderate medium platy (pisolitic), friable.
	C	90-	7.5GY	6/1	Gravelly loam, strong fine angular blocky, moderate thick platy (fragic).
P5	A	0-6	7.5YR	2/1	Gravelly sandy loam, strong fine crumb, very friable.
	AB	6-13	7.5YR	4/2	Gravelly sandy loam, moderate fine crumb, very friable.
	B	13-20	7.5YR	4/6	Gravelly loamy sand, moderate fine subangular blocky, very friable.
	BC	20-40	7.5YR	3/3	Gravelly sand, moderate medium subangular blocky, very friable.
	C	40-	7.5YR	2/2	Gravelly sand, structureless.

Table 1. Morphological features of the five soils studied.

to moderately leached Inceptisol in the warmer and driest continental areas.

The most important intrazonal soils are found in small inclusions, on carbonate-rich sandstone parent material, on parent material rich in vulcanic material, and in areas with poor drainage. Both Andepts and Eutrochrepts with calcic horizons are found in the Qagssiarssuk inland region (fig. 1), whereas Aquents, Aquepts, Fibrists, Hemists and Saprists are found all over South Greenland in poorly drained landscapes. Permafrost was observed in some of the organic soils, especially in areas with restricted solar radiation.

Azonal soils as e.g. Lithic Orthents and Psamments are found in barren and sparsely vegetated landscapes. These soils, which show only rudimentary soil formation, occur on very young parent material close to the Inland Ice margins, at high altitudes, on steep slopes, on intrusive parent material showing very restricted plant growth, and in areas affected by active erosion or deposition processes, primarily caused by wind.

The geography of soils in the hilly landscape of the middle subalpine region also shows a gradient from south to north in regard to intensity of leaching. To the south and in the Vatnaverfi area (fig. 1) strongly leached, very acid and moderately acid Cryorthods and Cryopsamments dominate. To the north, the area around Qagssiarssuk generally shows moderately leached soils, e.g. Typic and Dystric Cryochrepts and Typic Cryopsamments. This distribution of soils indicates that annual precipitation values are relatively high in Vatnaverfi as compared with the interior farther north. This gradient in humidity is probably controlled by the proximity to and the topographical protection from the Davis Strait.

Allmost all soils are developed on a two-sequential parent material. Tills and glaciofluvial materials are covered by a mantle of late-glacial loess. The thickness and mean grain size of these fine-grained, windblown deposits vary according to position in the landscape. In the late-glacial period strong winds from easterly directions deposited aeolian sediments eroded from barren areas close to the Ice Margin. The thickness of the deposits generally decreases from more than 0.5 m in some inland areas to few centimetres in outer coast areas. Roughly, the median grain size decreases from 80 *μm* in the eastern part of Vatnaverfi to 30 *μm* at Akia, and from 140 *μm* north of Qingua to 50 *μ*m in the Qagssiarssuk- region. In regard to susceptibility by soil erosion, it is an important factor that the nutrient-rich and biologically most active part of many soils has developed in fine-grained windblown material (Jakobsen, 1990).

Soil profiles

The five soils presented in this paper give an outline of the range of zonal soils in South Greenland. The main morphological features of the soils are listed in table 1.

Profile 1, a Lithic Cryorthod from the outer-coast island Akia (fig. 1), is formed on coarse-textured glacial till covered by a very thin mantle of loess. It was examined in a hilly landform covered by dwarf shrub, on a slightly concave slope (12°) facing west.

Fig. 3. Typic Cryoorthod (profile 2) with distinct eluvial and illuvial horizons.

Profile 2 (fig. 3) from Vatnaverfi, northeast of Qordlortorssuaq is classified as a Typic Cryorthod. It is formed on loess-covered till on a south-facing, gently sloping hillform (3°). The vegetation is an open birch forest/grassland community.

Profile 3, a Typic Cryopsamment, has also characteristic spodic features. It is situated just east of Tasiluk in the outer coastal region. The landform is hilly and the parent material is glacial till covered by loess. The profile was examined on a convex south-facing slope (10°) having a very sparse birch shrub/grassland vegetation. Compared to the other four soils, which are well drained, this site is somewhat excessively drained.

Profile 4, a Typic Cryorthod some 40 km northeast of Nanortalik in an open grassland area is formed on till material on a southwest facing convex slope (2°).

Profile 5 is from the dry continental interior a few kilometres north of Tasiussaq. This Typic Cryochrept is formed on till and situated on a slightly convex south facing slope (7°). An open

	Hor.	%< 2 µm	%C	%N	%org.P	C/N	C/P
P1	A	8.7	29.94	0.255	0.068	117	440
	E	3.9	3.32	0.145	0.018	23	184
	Bs	5.7	3.75	0.020	0.019	188	197
P2	A	3.2	14.62	0.773	0.038	19	385
	E	2.7	2.55	0.139	0.009	18	283
	Bhs	6.1	4.70	0.256	0.021	18	224
	Bs	3.7	1.91	0.102	0.013	19	147
	BC	1.6	0.29	0.020	0.003	15	97
P3	A	4.6	4.83	0.311	0.043	16	112
	E	3.9	2.60	0.179	0.032	15	81
	Bs1	5.1	1.35	0.089	0.011	15	123
	Bs2	5.6	0.43	0.032	0.006	13	72
	C	3.2	0.08	0.008	0.001	10	67
P4	A	5.6	3.93	0.267	0.030	15	131
	E	5.2	2.08	0.103	0.014	20	149
	Bs1	6.8	2.08	0.097	0.014	21	149
	Bs2	7.8	2.91	0.155	0.026	19	112
	Bs3	8.2	2.63	0.150	0.024	18	110
	Bs4	8.7	1.95	0.128	0.024	15	81
	BC	8.7	0.68	0.044	0.007	15	97
	C	9.8	0.27	0.015	0.003	18	90
P5	A	6.8	18.84	1.346	0.113	14	167
	AB	7.9	4.00	0.311	0.068	13	59
	B	5.7	0.93	0.070	0.023	13	40
	BC	4.7	0.75	0.054	0.023	14	33

Table 2. Analyses of soil horizons. Content of particles <2µm, organic carbon and nitrogen, organic P, and C/N and C/P of the organic matter.

	Hor.	CEC	K	Na	Ca	Mg	B.S.%
P1	A	90.26	0.82	0.57	2.99	2.98	8.2
	E	14.63	0.03	0.06	0.20	0.14	3.0
	Bs	31.74	0.03	0.07	0.20	0.14	1.4
P2	A	45.30	0.75	0.18	4.74	1.73	16.3
	E	10.91	0.06	0.05	0.77	0.23	10.2
	Bhs	53.57	0.03	0.06	0.92	0.26	2.4
	Bs	23.48	0.02	0.04	0.32	0.10	2.0
	BC	4.42	0.01	0.02	0.07	0.02	2.7
P3	A	24.30	0.17	0.07	0.50	0.29	4.2
	E	14.47	0.08	0.05	0.30	0.14	3.9
	Bs1	13.90	0.02	0.03	0.12	0.03	1.4
	Bs2	5.24	0.02	0.03	0.07	0.02	2.7
	C	0.92	0.02	0.02	0.07	0.01	13.0
P4	A	18.98	0.22	0.12	1.05	0.64	10.7
	E	12.61	0.07	0.09	0.35	0.15	5.2
	Bs1	20.63	0.04	0.06	0.30	0.08	2.4
	Bs2	32.93	0.03	0.08	0.52	0.10	2.2
	Bs3	32.97	0.03	0.12	0.45	0.07	2.0
	Bs4	25.88	0.04	0.13	0.40	0.06	2.4
	BC	13.12	0.06	0.10	0.32	0.04	4.0
	C	9.72	0.10	0.15	0.55	0.12	9.5
P5	A	98.26	0.56	0.29	55.14	8.27	65.4
	AB	29.22	0.08	0.08	16.47	2.09	64.1
	B	11.69	0.06	0.04	6.69	0.90	65.8
	BC	9.60	0.07	0.04	5.09	0.70	61.5

Table 3. Analyses of soil horizons. Cation exchange capacity in meq./100g (CEC), exchangeable bases and base saturation (B.S.%).

birch forest interspersed with willow shrubs and grassland characterizes the area.

Apart from profile 5 the soils had a bleached eluvial horizon under the A horizon giving the soils a clear podzolic signature. The illuvial zone in these four soils exhibits different morphological properties, but none of them showed any cementation of the Bs horizon. In profile 5 a cambic horizon is seen under a relatively thick, humus-rich A horizon.

Chemical analyses are shown in tables 2-3 and figs. 4-8. Very low pH values (< 4) and high C/N (> 100) and C/P (>400) ratios are characteristic of the A horizons of strongly developed subarctic Spodosols (profile 1). Almost all bases have been leached from the soil, showing only a very slight accumulation of bases in the A horizon.

At favourable sites in the continental interior near-neutral soil reaction, relatively low C/N ratios (13-14) and a C/P ratio of 50-150 indicate high biological activity and rapid mineralization, resulting in formation of up to 10 cm thick, well structured A horizons, rich in basic ions. Inceptisols (profile 5) are found in here.

The transitional soil types - Typic Cryorthods and Typic, nearly Spodic, Cryopsamments - have medium to strong acid reactions and are strongly depleted of basic ions apart from a slight accumulation in the A horizons.

CEC values in A and B horizons are generally high in proportion to the content of humus and clay. In the A horizon the CEC is primarily due to organic matter. Humus compounds in these soils presumably have a high total acidity, because exchange sites are not blocked or tied up in complexes with e.g. clay minerals. In the B horizon both humus and translocated Al- and Fe-rich silicate material contribute to the high variable charge found in these horizons.

The distribution of Fe and Al extracted by dithionite-citrate (d), pyrophosphate (p) and acid oxalate (o) treatments, the content of acid oxalate extractable Si and of inorganic phosphorus in the two characteristic zonal soils (profiles 1 and 5) and in the transitional soils (profiles 2-4) exhibits characteristic patterns which provide some evidence for the genetic origin of soils, epecially Spodosols. These patterns are the basis for the discussion of soil formation.

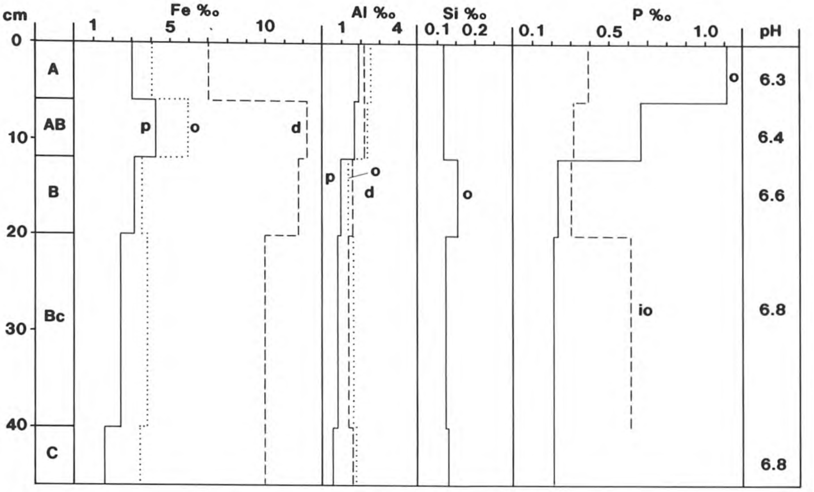

Fig. 4. Chemical characteristics of profile P5. pH-values, extractable Fe, Al and Si, and the content of organic (o) and inorganic (io) P. p (pyrophosphate extractable), o (oxalate extractable) and d (dithionite extractable).

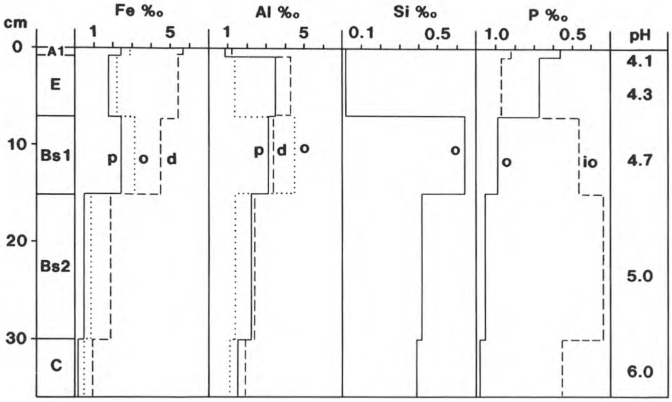

Fig. 5. Chemical characteristics of profile P3. pH-values, extractable Fe, Al and Si, and the content of organic (o) and inorganic (io) P. p (pyrophosphate extractable), o (oxalate extractable) and d (dithionite extractable).

Soil formation

Each of the different stages in soil formation, examplified by the five presented soil profiles, causes the soils to get some unique features reflecting a specific combination of soil-forming factors. Most of the range of active processes are the same, but their intensity has differed greatly.

In the Typic Cryochrept, profile 5 (fig. 4) very little translocation has taken place. In the only slightly acid soil environment, orthosilicate and phosphate materials have been translocated to deeper-lying horizons probably to some extent in complex form with reactive and mobile hydroxy-(Al, Fe) compounds. An early translocation of Si has also been observed in chronosequence studies of young soils e.g. in Canada by Wright (1959) and in eastern Greenland (Jakobsen, 1990b).

Contrary to aluminium, iron is probably - in this soil - at an early stage of soil formation periodically mobilized in the organic-rich A horizon by redox-controlled processes. A slight accumulation of both amorphous and well crystallized iron oxides is observed in the B horizon. The local maximum of Fe_p in the AB horizon possibly reflects an in situ reaction of reactive iron oxide material with humus compounds already present in the horizon. No appreciable formation and translocation of mobile metal-organic complexes are expected in the present soil environment.

In the somewhat excessively drained and sparsely vegetated Typic Cryopsamment, profile 3 (fig. 5) the initial inorganic translocation processes have been more intense than observed in

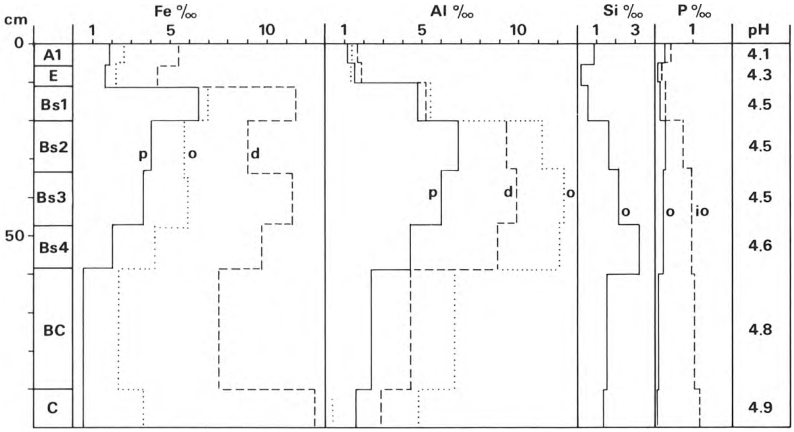

Fig. 6. Chemical characteristics of profile P4. pH-values, extractable Fe, Al and Si, and the content of organic (o) and inorganic (io) P. p (pyrophosphate extractable), o (oxalate extractable) and d (dithionite extractable).

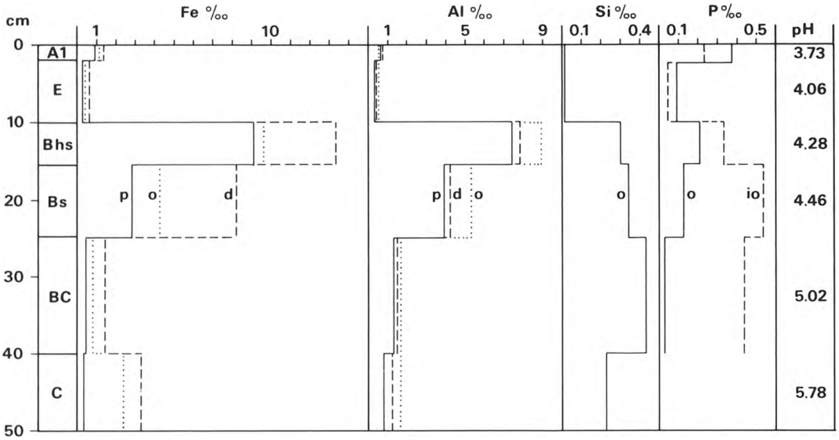

Fig. 7. Chemical characteristics of profile P2. pH-values, extractable Fe, Al and Si, and the content of organic (o) and inorganic (io) P. p (pyrophosphate extractable), o (oxalate extractable) and d (dithionite extractable).

the Inceptisol. Hydroxy compounds of mainly Al, and some Fe, have been translocated into the B horizon as mobile complexes with silicate and phosphate. A marked local maximum in Si_O and a Al_{o-p}/Si_o ratio close to 2 in the Bs1 horizon indicate a pronounced accumulation of allophane-like material. Due to good drainage conditions and very low organic matter content at this site, redox-controlled translocation of Fe has been impeded and the limited formation of mobile metal-organic complexes in the strongly acid A horizon has presumably only involved aluminium.

A higher intensity of weathering and translocation processes induced by reactive organic complexants is seen in the Typic Cryorthod, profile 4 (fig. 6). A separation is observed of the B horizon in an upper part dominated by organic complexes and a lower part still containing considerable amounts of allophane-like material (Al_{o-p}/Si_o ratios of 2-3). At this stage too, analyses show a local maximum in the organic carbon content in the upper B horizon. Both Fe and Al are translocated as acidic organic complexes, which upon reaching the upper B horizon react with imogolite and allophane-like material releasing silica-rich material. Insoluble metal-organic complexes accumulate, whereas the silica-rich material moves downwards and accumulates in the lower-lying B horizon.

In the Typic Cryorthod, profile 2 (fig. 7) intense translocation processes controlled by organic complexants characterize the spodic horizon. The upper part of the spodic horizon con-

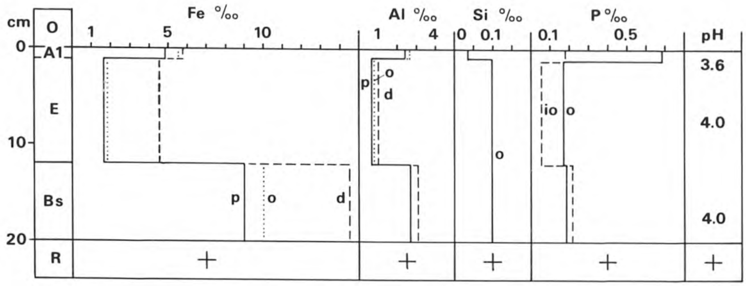

Fig. 8 Chemical characteristics of profile P1. pH-values, extractable Fe, Al and Si, and the content of organic (o) and inorganic (io) P. p (pyrophosphate extractable), o (oxalate extractable) and d (dithionite extractable).

tains about 5 % organic C and has morphological features characteristic of a Bhs horizon. Still some allophane-like material is found in the B horizons, probably mostly in the central parts of structural elements now covered by metal-organic complexes (Jakobsen, 1989). The illuviation of remobilized silica has caused a weak cementation of the BC horizon.

The mostly "Lithic" Cryorthods, profile 1 (fig. 8), which are found in the skerries landscape at the outer coast, are the only Spodosols which show regular Mor-formation. A very strong acid, about 5 cm thick O horizon is normally found. The spodic horizons in these soils, and present translocation processes, are strongly dominated by a very high activity of acidic organic complexants. Evidence, from common chemical analyses, of early stages in Spodosol formation has been obliterated, and most of the early stage illuvial material have changed in composition, whereby silica-rich phases probably left the profile.

The different mechanisms in translocation processes in these subarctic soils clearly reflect a multiple process system, where a range of processes change over longer periods and probably also show short-term variations in intensity. Short-term changes and seasonal variations have been reported by Milnes and Farmer (1987), Ugolini and Dahlgren (1986), and Stoner and Ugolini (1988). Evidence for long-term intensity changes are given by Farmer (1979). Due to the complex origin of morphological and chemical characteristics of soils the interpretation of soil genesis based on common chemical analyses of soil horizon material only may lead to misleading interpretations. Studies involving some kind of soil sequence may help to avoid this. Soil solution studies from beneath genetic horizons give information on current processes and their short-term changes, whereas micro-analyses of thin sections from soil horizons may give some information on long-term changes of processes.

Studies by Ugolini et al. (1987) show the activity of multiple soil-forming processes in the Arctic Tundra. Direct evidence is given for seasonal variations in intensity of brunification, particle migration and both inorganic and organic translocation of Fe and Al containing complexes. Thin section analyses of spodic horizons in subarctic Spodosols (Jakobsen, 1989, 1990c) show zonation in the chemical composition of monomorphic cutan material in the larger aggregates. Indirect evidence is given for a general shift from illuviation of Si-dominated material, followed by a mostly inorganic translocation of Al, Fe and Si to processes mainly controlled by acidic organic complexants.

Acknowledgements

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References

Anderson, H. A., Berrow, M.L., Farmer, V.C., Hepburn, A., Russel, J.D. & Walker, D. (1982): A reassessment of Podzol formation processes. Journal of Soil Science, 33: 125-36.

Borggaard, O.K., Møberg, J.P. & Petersen, L. (1983): Øvelsesvejledning til Geologi og Jordbundslære I. D.S.R. Copenhagen, 85 p.

Childs, C.W., Parfitt, R.L. & Lee, R. (1983): Movement of aluminium as an inorganic complex in some podzo-lized soils, New Zealand. Geoderma, 29: 139-45.

Dansgaard, W. (1975): Indlandsisen. Grønland (Ed. by P. Koch). Gyldendal, Copenhagen.

De Coninck, F. (1980): Major mechanisms in formation of Spodic horizons. Geoderma, 24(2): 101-28.

FAO (1977): Guidelines for soil profile description. FAO, Rome, 66 p.

Farmer, V.C. (1979): Possible roles of a mobile hydroxy-aluminium orthosilicate complex (proto-imogolite) and other hydroxy-aluminium and hydroxy-iron spe-cies in podzolization. Colloques intemationaux du C.N.R.S., 303: 275-79.

Fanner, V.C. Russel, J.D. & Berrow, M.L. (1980): Imogolite and proto-imogolite allophane in spodic horizons: evidence for a mobile aluminium silicate complex in Podzol formation. Journal of Soil Science, 31: 673-84.

Jacobsen, N. Kingo & Jakobsen, B. Holm (1986): C^{14} datering af en fossil overfladehorisont ved Igaliku Kujalleq, Sydgrønland, set i relation til nordboernes landnam. Geografisk Tidsskrift, Bd. 86: 74-77.

Jakobsen, B. Holm (1989): Evidence for translocations into the B horizon of a subarctic Podzol in Greenland. Geoderma, 45: 3-17.

Jakobsen, B. Holm (1990a): Soil Resources and Soil Erosion in the Norse Settlement Area Østerbygden in Southern Greenland. Acta Borealia (in print).

Jakobsen, B. Holm (1990b): Soil formation as an indication of relative age of glacial deposits on the Angmagssalik Island, Eastern Greenland. Geografisk Tidsskrift Bd. 90: (in print).

Jakobsen, B. Holm (1990c): Multiple processes in the formation of subarctic Podzols in Greenland. Soil Sci-ence (submitted).

Marbut, C.F. (1951): Soils: Their genesis and classification (Lectures to U.S. Dept. Agr. Grad. School, 1927): Madison, Wisc., Soil Sci. Soc. America, 25 p.

McKeague, J.A. & Day, J.H. (1966): Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci., 46: 13-22.

McKeague, J.A. (1967): An evaluation of 0.1 M pyrophosphate-dithionite in comparison with oxalate as extractants of the accumulation products in podzols and some other soils. Can. J. Soil Sci., 47: 95-99.

Mehra, O.P. & Jackson, M.L. (1960): Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium-bicarbonate. Clays and Clay Minerals, 7: 317-27.

Milnes, A.R. & Farmer, EC. (1987): Micromorphology and analytical studies of the fine matrix of an Australian humus iron Podzol. J. of Soil Science, 38: 593-605.

Morrison, J.R. & Wilson, A.L. (1963): The absorptiometric determination of silicon in waters. Analyst, 88: 100-104.

Petersen, L. (1976): Podzols and Podzolization. Doctoral Thesis, D.S.R., Copenhagen, 293 p.

Ponomareva, V.V. (1964): Theory of Podzolization. Nauka, Moskva-Leningrad, 1964. Israel, Program for Scientific Translation, Jerusalem, 1969, 309 p.

Simonson, R.W. (1978): A multiple-process model of soil genesis. In: Quarternary Soils (ed. W.C. Mahaney): 3rd Conference on Quarternary Research, 1976. Geo Abstract Ltd. Norwich, England, p. 1-25.

Soil Survey Staff (1975): Soil Taxonomy. U.S. Dept. Agr., U.S. Govt. Print Office, Washington, D.C.

Stoner, M.G. & Ugolini, F.C. (1988): Arctic pedogenesis: 2. Threshold-controlled subsurface leaching episodes. Soil Science, 145(1): 46-51.

Ugolini, F.C. & Dahlgren, R. (1986): The mechanism of podzolization as revealed by soil solution studies. In: Podzols and Podzolization. Comptes Rendu de la Table Ronde Internationale, Université de Poitiers, France, 10 et 11 avril 1986.

Ugolini, F.C., Stoner, M.G. & Marrett, D.J. (1987): Arctic pedogenesis: 1. Evidence for centemporary podzolization. Soil Science 144(2): 90-100.

Wright, J.R., Leahey, A. & Rice, H.M. (1959): Chemical, morphological and mineralogical characteristics of a chronosequence of soils on alluvial deposits in the Northwest Terrritories. Can. J. Soil Sci., 39: 32-43.

Dystric Cambisol from Tierra del Fuego - the contribution of soil micromorphology

Peter Frederiksen

Frederiksen, Peter: Dystric Cambisol from Tierra del Fuego - the contribution of soil micromorphology. Folia Geographica Danica, Tom. XIX, Copenhagen 1991.

Standard analytical methods and thin section analysis were used in a study of a Dystric Cambisol from Tierra del Fuego. Standard methods established the main physical, chemical and mineralogical parameters of the soil. They indicated that biological activity had been limited, that transformation of interstratified clay minerals may have occurred, that Fe and Al had been liberated by weathering and possibly translocated downwards, and that base leaching and possibly base recycling had occurred. Thin section analysis mainly helped to characterize the sand and coarse silt petrology and to better understand the formation of structure and clay cutans.

Keywords: *Soil micromorphology. Dystric Cambisol. Tierra del Fuego. Pedogenesis.*

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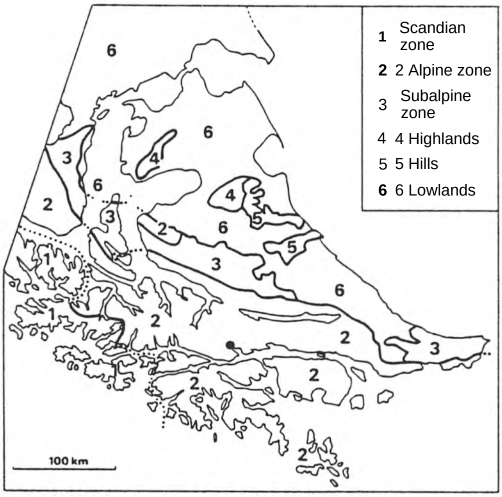

Fig. 1. Relief zones of Tierra del Fuego showing location of the profile in the alpine zone (dot).

In a study of the physical geography of Tierra del Fuego, southernmost South America (Frederiksen, 1985, 1988) soil micromorphological descriptions were used to complement standard analytical methods, particularly for identifying pedological features in the weakly developed soils. This article reports on how thin section analysis contributed to a better understanding of the pedogenesis of a Dystric Cambisol.

The soil is located in Argentina in Territorio Nacional de Tierra del Fuego, Antartida e Islas del Atlantico Sur on the main island of Tierra del Fuego, close to ruta nacional 3 at Ushuaia's southern city limit towards Bahia Lapataia (fig. 1). It is situated in an alpine landscape of interconnected U-valleys (fig. 2). A glacier deposited a marginal moraine arc west of Ushuaia during the Pleistocene that was deglaciated 8000 BP (Auer, 1956, 1970) and covered by a thin loess sheet during early Holocene.

Holocene changes between drier/moister and cooler/warmer periods (Auer, 1933, 1958, 1965) most probably resulted in changing soil temperature and moisture conditions. At present the climate is cool (ET according to Köppen, 1931) and humid. The mean annual air temperature is 5.7 °C and the mean annual rainfall (548 mm/yr) is evenly distributed throughout the year (Servicio Meteorologico Nacional, year not given). Deciduous Nothofagus pumilio forest covered the soil until the area was deforested a few years ago, and it is at present covered by Nothofagus pumilio shrubs, Chiliotrichum diffusum bushes and

Fig. 2. Aerial photograph of the alpine zone with interconnected U-valleys.

herbs. The landform is undulating and the profile lies on a 16° slope oriented 260° N. The soil is developed in silty loess over silty till, possibly with some tephra in the loess, it was well drained and moist at the time of description.

Methods

Thin section preparation (Stoops, 1978) *and analysis* (microstructure and porosity pattern, pores and coarse material: Stoops, 1978; pedological features: Brewer, 1976), *profile descriptions* (FAO, 1974,*1985),particle size distribution* (Andreasen, 1965; Hansen, 1961), *organic carbon* (Tabatabei & Bremner, 1970), *total nitrogen, pH*($CaCl_2$ *and pH*(H_2O) (Borggaard et al. 1973), *pH(NaF)* (Fieldes & Perrott, 1966), *extractable cations* (Møberg et al. 1980), *exchangeable acidity* (Borggaard et al. 1979), and *Fe and Al dithionite and X-ray analysis of the clay and silt fractions* (de Coninck of ITC-Gent, personal communication) were carried out.

Results and discussions - standard analytical methods

The profile description (see below) and the particle size distribution analysis (table 1) - each fraction given as a percentage of the 0-8 mm interval - show that the soil is silty and that the Au1, Au2 and Bw horizons are characterized by a near absence of fractions > 2 mm (loess), whereas the 2Bw1, 2Bw2 and 2C horizons (till) have about 20 % gravel. The 2C horizon has less clay and fine silt and more coarse silt than the 2Bw1 and 2Bw2 horizons.

The profile description only gives a general idea of structural development, i.e. that the degree of structural development decreases with depth.

Au1 0-6 cm, 10YR 4-3/2 dry, very dark to dark greyish brown, no mottling, silty loam, weak subangular blocky, loose, no cutans, very few rounded gravel, clear and smooth boundary.

Au2 6-11 cm, 10YR 4/2 dry, dark greyish brown, no mottling, silty loam, weak subangular blocky, loose, no cutans, very few rounded gravel, gradual and smooth boundary.

Bw 11-25 cm, 10YR 6-5/6 dry, brownish yellow to yellowish brown, no mottling, silty loam, moderate subangular blocky, very friable, very few rounded gravel, gradual and smooth boundary.

2Bw1 25-35 cm, 2.5Y 7/4 dry, pale yellow, no mottling, gravelly silty loam, moderate subangular blocky, very friable, no cutans, frequent rounded gravel, gradual and smooth boundary.

2Bw2 35-70 cm, 5Y 7/2-3 dry, light grey to pale yellow, no mottling, gravelly silty loam, weak angular blocky, very friable, no cutans, frequent rounded gravel, clear and wavy boundary.

2C 70-90 cm, 5Y 7/3 dry, pale yellow, no mottling, gravelly silt, massive, very friable, frequent rounded gravel, clear and wavy boundary.

The clear and smooth boundary between Au1 and Au2 and the paler Au2 with a more intimately mixed organic and mineral matter and a lower organic carbon content (20.3 % vs. 7.5 %) justify their separation in two subhorizons. The high organic carbon (20.3 %) and low N content (1.26 %) of Au2 the thinness of both indicate a low biological activity. Temperature was probably the major factor limiting biological activity (the mean annual air temperature is 5.7 °C) and possibly a low nutrient availability. Moisture or oxygen availability were not limiting - monthly rainfall ranges from 30 to 60 mm and hydromorphic properties were absent.

The X-ray diffraction (XRD) analysis of the clay fraction (fig. 3) showed in all horizons the following reflections, interpreted as follows: 14.5 Å after K treatment at 550 °C where the reflections become more pronounced with depth *(chlorite increasing with depth),* 10 - 5 - 3.33 A after K treatment at 550 °C *(illite), 12* Å except after K treatment at 550 °C *(kaolinite),* 4.26 Å after K treatment *(quartz)* and 3.2 Å after K treatment *(feldspar).* A 10-14.5 Å bridge or 12.5 Å peak is present in Al, Bw, 2Bw1 and 2Bw2 after K treatment and possibly in 2C *(interstratified clay minerals). Smectite* is present in 2Bw2 (18 Å reflection after Mg and glycerol treatment). Chlorite, mica, kaolinite, feldspar, quartz and amphibole are present in the silt fraction.

	Grain-size distribution (%)						Org.C	Total N	(Fe_2O_3.%)/
	<2um	2-20	20-63	63-250	250-2000	>2000	%	%	(clay-% x 0.1)
Au1	15.5	42.0	24.0	11.1	7.0	0.0	20.3	1.26	1.2
Au2	16.6	36.6	26.8	10.4	9.4	0.0	7.5		1.5
Bw	15.2	45.1	14.3	11.7	10.5	2.7	2.8		2.3
2Bw1	12.6	34.4	10.0	13.1	12.4	17.1	1.7		1.4
2Bw2	13.0	44.7	6.0	6.9	8.2	20.7	0.6		0.8
2C	7.9	20.2	44.5	3.8	3.3	20.0	0.3		2.7

	pH (CaCl2)	pH (NaF)	Fc %	Al %	CEC	Ca	Mg	K	Na	Base sat. %
					(meq / 100 g soil)					
Au1	5.1	7.1	13.1	1.9	76.4	23.5	7.8	1.1	0.6	43
Au2	4.6	7.2	17.0	2.3	43.6	10.1	4.0	0.1	0.4	33
Bw	4.1	9.6	25.7	6.6	28.5	0.9	0.3	0.2	0.2	5
2Bw1	4.5	10.1	14.3	6.3						
2Bw2	4.5	10.4	9.6	4.2						
2C	4.3	8.7	19.2	1.9	8.1	0.5	0.1	0.0	0.1	11

Table 1. Soil physical and chemical data.

Since chlorite, mica, kaolinite, quartz, feldspar and amphibole may all be expected to have been deposited as part of the loess and till. The displacement of the 10-14 Å bridge towards the 14 Å reflection with depth suggests an increasing chlorite component of the interstratified clay mineral with depth.

The Fe and Al dithionite and Fe_2O_3/clay-% values are highest in the B horizons. One explanation may be higher weathering intensity in the B than in the A horizons as indicated by the XRD analyses of the clay fraction - illite has changed into other 2:1 layer silicate clay minerals. A second possibility is liberation of Fe and Al in the topsoil due to weathering followed by downward translocation, which is supported by the presence of a Fe_2O_3/clay-% maximum in the B horizons. How Fe and Al moved is, however, obscure. Podzolization understood as formation, translocation, and precipitation of organo-metallic complexes (Petersen, 1976) is probably not a likely explanation, because the complexes would tend to precipitate in the A horizons due to the high Fe and Al content. Formation of Al_2O_3-Fe_2O_3-SiO_2-H_2O sols followed by translocation not associated with organic matter and transformation to allophane, imogolite or like substances in situ was suggested as precursor to podzolization by Farmer (1982). Such a mechanism could account for the Fe and Al variation, and for the

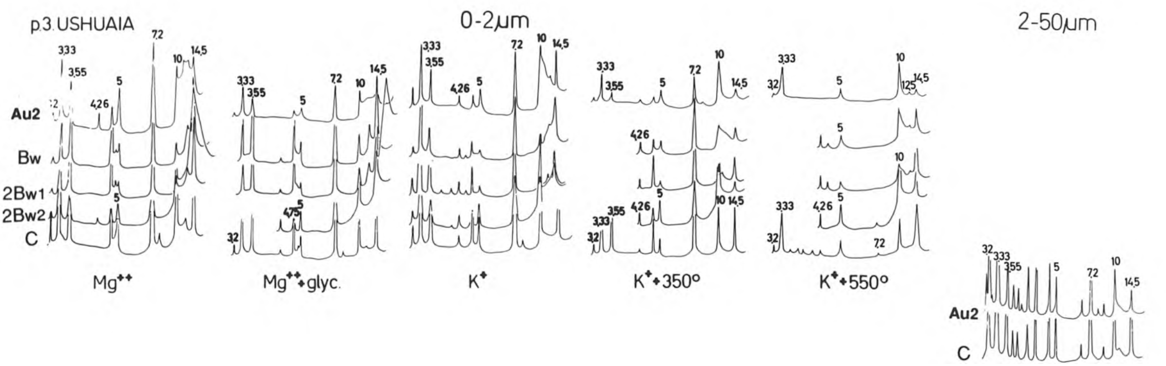

Fig. 3. X-ray diffractograms of oriented samples of the clay and silt fractions.

pH(NaF) maximum in the B horizons. Fieldes et al. (1966) related high pH(NaF) values to the presence of significant amounts of allophane and imogolite. Holocene tephras overlie sandy till and glaciofluvial gravel close to the present profile, but volcanic glasses were not identified in thin sections of the light mineral fraction of the loess and till. Tephras may therefore not be part of the loess and till. The high pH(NaF) values may therefore not be related to allophane, but possibly to poorly crystalized Fe and Al oxides and hydroxides.

The cation exchange capacity decreases from 76.4 meq/100 g soil in Au1 to 8.1 meq/100 g soil in 2C, which is mainly related to the organic carbon which decreases with depth. The base saturation decreases from 43 % in Au1 to 5 % in Bw and 11 % in 2C. This may be caused by 1) base leaching followed by nutrient uptake by roots, leaf fall and subsequent release of nutrients in the A horizons (base recycling), 2) nutrient release from ashes in the topsoil (charcoal is present in A), and/or 3) a decreasing weathering intensity and nutrient release with depth. The exchange complex is dominated by Ca and Mg and a Ca/Mg ratio of 2.4-3.0.

Clay illuviation features were not observed in the field, which may be explained by the evenly distributed rainfall throughout the year probably resulting in a moist soil most of the year.

Result and discussions - thin section analysis

The sand and coarse silt fractions consist in Au2 of few mudstones and volcanic rocks, common quartzites and oxides, in Bw a few schists, arkoses and volcanic rocks, common mudstones, quartzite and oxides, in 2Bw1 a few schists, greywackes and oxides and common mudstones, in 2Bw2 of common mudstones, quartzite, arkose and oxides, and in 2C common mudstones, quartzite, arkose and oxides. This indicates that the loess and till is derived from metamorphic, sedimentary and volcanic rocks. The thin section analysis thus complements the XRD analysis of the clay and silt fractions by supplying information on the composition of the sand and coarse silt fraction.

The macroporosity mainly shows the secondary poresystem (the coarse pores), and is consequently a good measure of the degree of break up of the parent material. The decrease from a very high macroporosity in the A horizons to a very low macroporosity in 2C indicates the decreasing break up of the parent material with depth.

The basic building blocks of structure in Au2 are pellets. A pellety microstructure is found in a third of the thin section, pellets are aggregated into partially separated crumbs in another third (fig. 4), and the partially separated crumbs into completely separated crumbs in the last third. Three levels of aggregation are thus present in Au2. An ortho-infilled megachannel (probably produced by a worm or some other being) has a

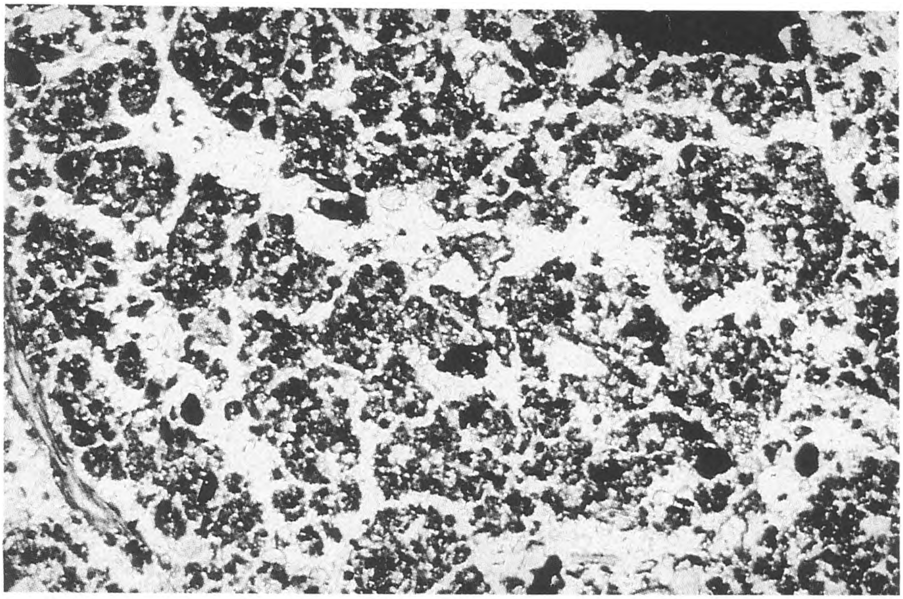

Fig. 4. A pellety and crumbly microstructure in Au2.

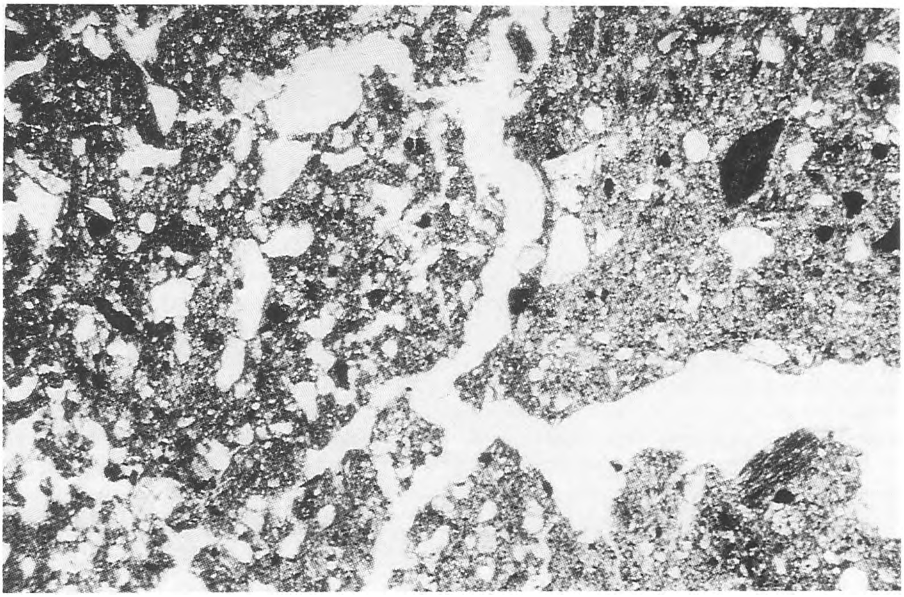

Fig. 5. A spongy and jointed microstructure in Bw.

porosity pattern, microstructure, and soil material (resembles subsoil material) that differ from the surrounding A horizon, which clearly illustrates the effect of bioturbation. The pellety and crumbly microstructure surrounded by a network of channels in Au2 indicates that bioturbation dominated the formation of structure. Fissures may have formed in the early phase of pedogenesis, but they have then been disrupted by bioturbation.

All types of microstructure in the profile are present in 2Bw1. The fissured, jointed (fig. 5) and fragmented microstructures most probably reflect an increasing break up of the parent material in that sequence due to repeated swelling and shrinking of the soil material (increasing produc-

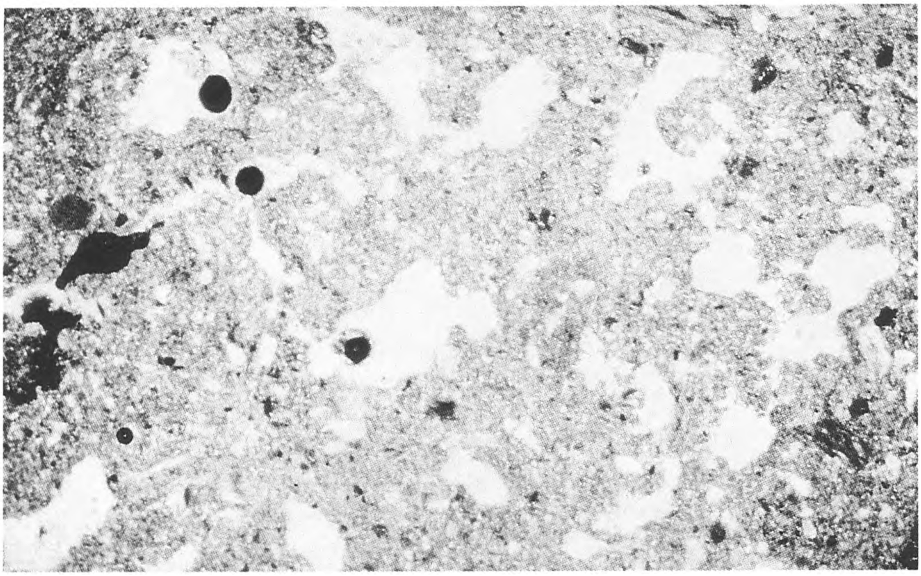

Fig. 6. A cavitied microstructure in 2C.

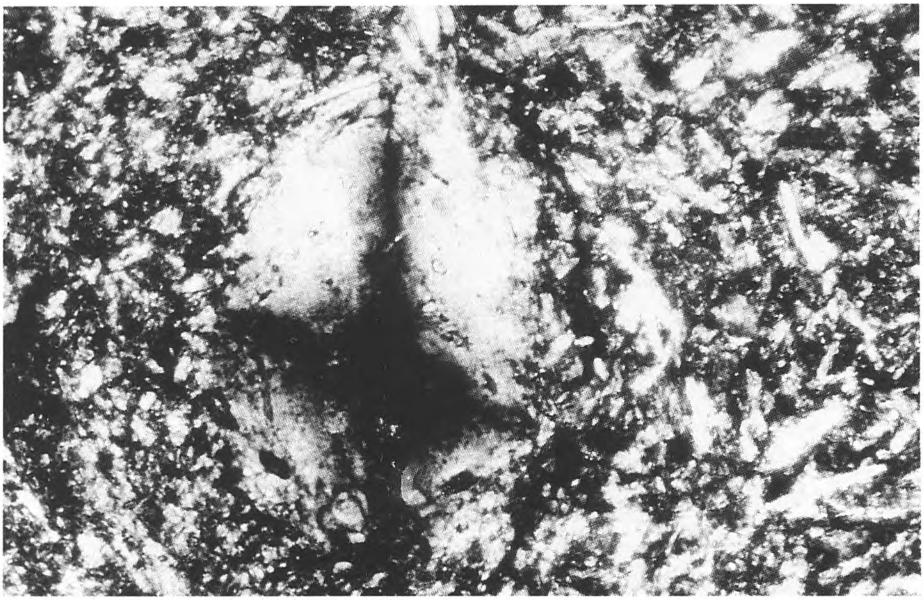

Fig. 7. A strongly oriented argillan with isogyre.

tion of fissures). Similarly the cavitied, spongy (fig. 5), crumbly and pellety microstructures reflect the increasing break up produced by roots and animals (increasing production of channels). Aggregation into more complex secondary structures has also taken place. That some parts have a fissured or cavitied microstructure (typical of 2C) and others a pellety microstructure (typical of A) indicate the variation in intensity of swelling/shrinking and of roots/animals within short distance in Bw. That channels and fissures in Bw are equally frequent indicate, that bioturbation and repeated swelling and shrinking were equally important. The cavitied microstructure in 2Bw1 and 2Bw2 and the cavitied (fig. 6) and fissured microstructure in 2C indicate a low degree of

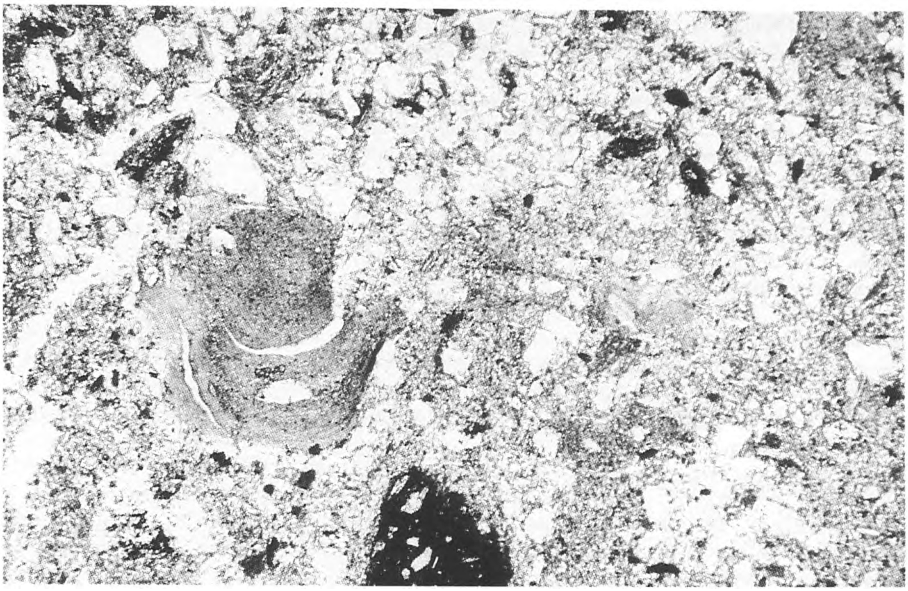

Fig. 8. A complex argillan/silargillan.

break up of the parent material.

Few clay and silt cutans were observed indicating limited clay illuviation, probably due to the continuously moist climate. The cutans were not observed in the A horizons, they were most frequent in 2Bw1 and decreased in frequency towards 2C. The cutans may be due to clay dispersion in the A horizons followed by translocation to and deposition in lowerlying horizons, mainly in Bw.

The thin section analysis permitted a detailed description of clay illuviation features. The presence of strongly oriented argillans (fig. 7) indicates, that the clay particles must have sedimented slowly one on top of the other. This requires slow infiltration of water from the pore into the soil matrix, whereby the dispersed particles have more time to become oriented before settling. More rapid infiltration of water would produce less oriented argillans. The silargillan is less oriented, which may be related to a rapid infiltration of water into the matrix, and/or the result of a more rapid deposition of the coarser silt particles. The complex argillan/silargillan (fig. 8) could have formed the same way. Hence the increasing fineness of texture from the porewall to the pore interior of the complex feature. The papules are probably reworked argillans.

Summary

In this study it was found, that soil micromorphological analysis complemented standard analytical methods on investigations of a Dystric Cambisol from Tierrra del Fuego, southernmost South America. Standard analytical methods provided information on physical, chemical and mineralogical parameters and provided a basis for understanding humus accumulation, clay mineral transformations, weathering, leaching, and possibly recycling. Thin section analysis complemented this with a characterization of sand and coarse silt petrology and provided a better understanding of the formation of structure and argillans and silargillans.

References

Andreasen, A.H.M. (1965): De faste stoffers finhed samt finhedens teknologiske betydning. Akademisk Forlag. København.

Auer, V. (1933): Verschiebungen der Wald- und Steppengebiete Feuerlands in post-glazialer Zeit. Acta Geograph., 5.

Auer, V. (1956): The Pleistocene of Fuego-Patagonia. Part I. The Ice and Interglacial Ages, Ann. Acad. Sci. Fennicae, A.III, 45.

Auer, V. (1958): The Pleistocene of Fuego-Patagonia. Part II. The History of the Flora and Vegetation. Ann. Acad. Sci. Fennicae, A.III, 59.

Auer, V. (1959): The Pleistocene of Fuego-Patagonia. Part IV. Bog Profiles. Ann. Acad. Sci. Fennicae, A.III, 80.

Auer, V. (1965): The Pleistocene of Fuego-Patagonia. Part V. Quaternary problems of South America. Ann. Acad. Sci. Fennicae, A.III, Geologica-Geographica, 100.

Borggaard, O.K. & Møberg, J.P. (1973): Øvelsesvejledning til geologi og jordbundslære I. DSR, København.

Brewer, R. (1976): Fabric and mineral analysis of soils. Krieger. New York.

FAO-Unesco (1974): Guidelines for Soil Profile Descriptions. FAO, Rome.

FAO-Unesco (1985): Soil map of the world. 1:5,000,000. Revised legend. Unesco, Paris.

Fieldes, M. & Perrott, K.W. (1966): The nature of allophane in soils. Part 3 - Rapid field and laboratory test for allophane. N.Z.J.Sci., 9, 623-29.

Frederiksen, P. (1985): Soils of Tierra del Fuego - A Satellite-based Land Survey Approach. Ph.D. thesis. Institute of Geography, University of Copenhagen.

Frederiksen, P. (1988): Soils of Tierra del Fuego - A Satellite-based Land Survey Approach. Appendix: Methods and Soil Data - Annex with 5 plates. Folia Geographica Danica, Tom. XVIII. København, C.A. Reitzel. 159 p.

Hansen, L. (1961): Hydrometermetoden til bestemmelse af jordens tekstur. Grundforbättring, 3, 177-88.

Köppen (1931): Grundriss der Klimakunde. Berlin.

Møberg, J.P. & Petersen, L. (1980): Øvelsesvejledning til Geologi og Jordbundslære II. DSR. København.

Petersen, L. (1976): Podzols and Podzolization. DSR. Copenhagen. 293 p.

Servicio Meteorologico Nacional (year of publication not given): Estadisticas Climatotologicas 1951-60., Serie B, No. 6., Buenos Aires. Quinta Edicion.

Stoops, G. (1978): Provisional Notes on Micropedology. State University of Gent (Geologisch Instituut/ITC).

Soil Survey Staff (1975): Soil Taxonomy. Agriculture Handbook no. 436. United States Department of Agriculture. 754 p.

Tabatabei, M.A. & Bremner, J.M. (1970): Use of the Leco-automatic 70 - second carbon analyzer for total carbon analysis of soils. Soil Sci. Soc. Amer. Proc., 34, 608-10.

Soils of Kalimantan, Indonesia

Leif Petersen

Petersen, Leif: Soils of Kalimantan, Indonesia. Folia Geographica Danica, Tom. XIX, Copenhagen 1991.

The Indonesian part of the island of Borneo, Kalimantan, covers 549,000 km^2 and extends from 4° 23' N to 4° 11' S and from 108° 49' E to 117° E. It includes four provinces: South, East, West and Central Kalimantan. The interior of Kalimantan is sparsely populated and weakly developed.

The climate is humid equatorial with a mean rainfall varying from about 2000 mm/year in the coastal lowlands to more than 4000 mm/year in the central mountain areas. Mean daily temperatures at low altitudes are about 25°C throughout Kalimantan with monthly variations less than 2°C and diurnal variations of 10-15°C.

A large part of West Kalimantan and the western part of Central Kalimantan are covered by metamorphosed and deformed clastic sediments, silicic volcanic rocks and granitic intrusions of an age varying from Carboniferous to Eocene. Areas with a complex mixture of rocks occur along subduction zones in southeast Kalimantan and at the border to the Malaysian part of Borneo. Large areas of East and South Kalimantan are covered by late Tertiary and early Quaternary sediments including limestone, sandstone and shales. Late Tertiary and Quaternary deposits of sands and peat occur along the west and south coasts and in places they extend several hundred km inland.

The dominant soils in all parts of Kalimantan are brown to yellowish brown, highly leached Acrisols with an extremely low base saturation percentage and a low content of all major plant nutrients. The sand and silt fractions of these soils consist almost exclusively of quartz, and kaolinite is dominant in the clay fraction. Ferralsols seem to be limited to areas with ultrabasic rocks occurring in a subduction zone in southeast Kalimantan. These soils are also extremely low in exchangeable bases and the dominating minerals in both coarse and fine particle size fractions are iron oxides and hydroxides. Podzols and Arenosols are the typical soils of sandy terraces, and Luvisols occur in areas with limestone. The coastal swamps and flood plains along major rivers are covered by Histosols, Gleysols and Fluvisols.

The majority of the land in Kalimantan is covered with tropical rain forest. Some areas are used by the local population for shifting cultivation. Limitations to agricultural utilization of the land include steep slopes, sandy soil texture and poor soil drainage. Where these limitations are less pronounced, the agricultural potential is limited by low soil fertility. Therefore, agricultural systems based on permanent cultivation will require regular applications of lime and fertilizers.

Keywords: *Soil development in Kalimantan, physical and chemical properties of Kalimantan soils, soil fertility in Kalimantan, agricultural potential of Kalimantan soils.*

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Borneo, the third largest island in the World, is administratively divided into three parts. The southern and largest part belongs to Indonesia while the northern part consists of the Malaysian states Sarawak and Sabah and the country of Brunei (fig. 1).

The Indonesian part, Kalimantan, covers 549,000 km^2 and extends from 4° 23' N to 4° 11' S and from 108° 49' E to 117° E. It includes four provinces: South, East, West and Central Kalimantan. The total population of Kalimantan is about 9 million and the average population density is about 16 persons per km^2. The major part of the population lives in cities and towns near the coast and the interior is sparsely populated and weakly developed.

Climate

Being located close to the Equator, Kalimantan has a humid equatorial climate with high rainfall, high temperature and light winds. Variations in climate occur due to differences in distance from the coast, altitude and prevailing winds. Although the rainfall is not evenly distributed over the year there is no distinct dry season and throughout the area the average monthly precipitation exceeds the potential evapotranspiration which is 100-150 mm/month. However, the precipitation is rather unreliable and periods of up to a few months with a rainfall lower than the potential evapotranspiration are common in many areas

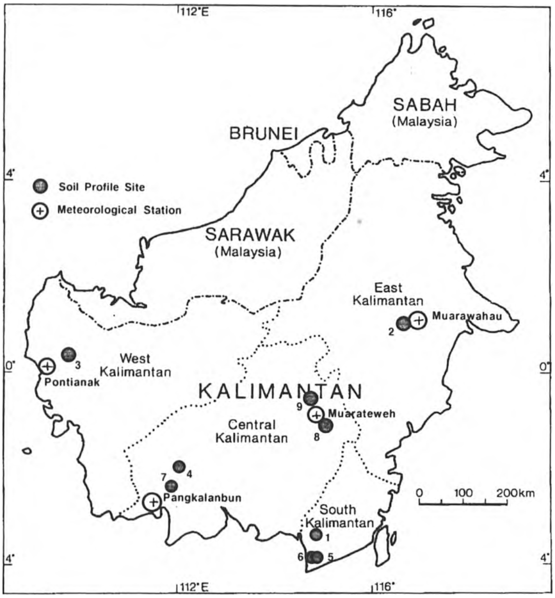


Fig. 1. Map of Borneo with locations of soil profile sites and meteorological stations.

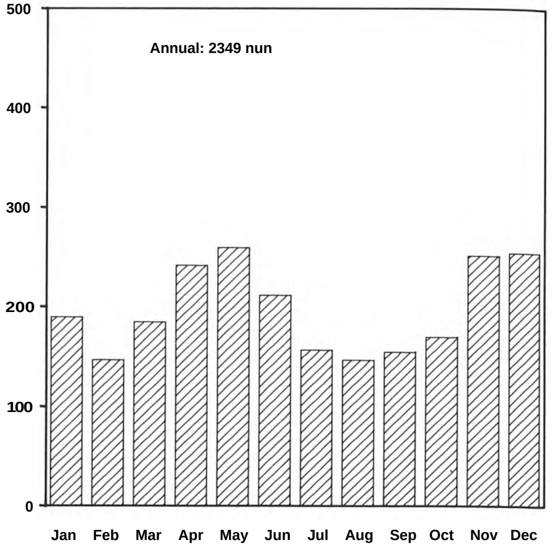


Fig. 2. Mean annual and monthly precipitation (mm) at Muarawahau, East Kalimantan.

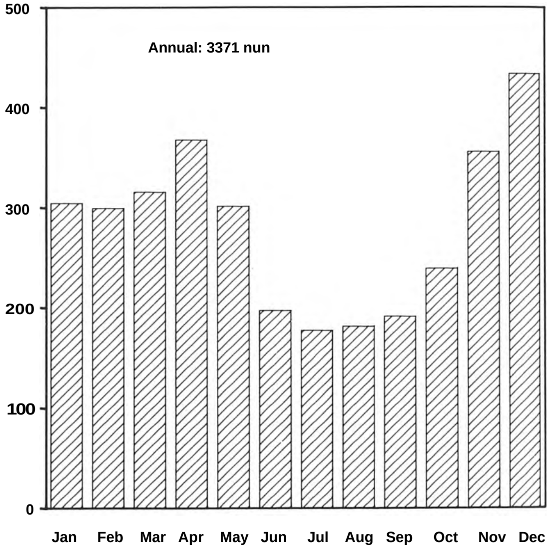


Fig. 3. Mean annual and monthly precipitation (mm) at Muarateweh, Central Kalimantan.

during the driest months, i.e. from June through October.

The mean annual and monthly precipitation at four locations (fig. 1) are shown in figs. 2-5. The rainfall pattern is rather similar at the four locations with two maxima in December and April-May and a rather low rainfall from June through October. The mean annual rainfall varies from 2349 mm at Muarawahau to 3371 mm at Muarateweh. By comparison with the potential evapotranspiration, which is about 1500 mm/year, it is obvious that a considerable surplus of water must be removed by run-off. The meteorological stations, where the rainfalls given in figs. 2-5 have been measured, are all located at low altitude. At higher altitude in the central parts of Borneo the rainfall is considerably higher and may exceed 4000 mm/year (Koteswaram, 1974). The rain usually occurs as high intensity thunder storms. At low altitudes the mean daily temperature is 25-26°C throughout Kalimantan. The temperature fluctuations over the year are small. The differences between the mean temperature of hottest and coldest months are usually less than 2°C and the diurnal variation is 10-15°C.

Geology and geomorphology

The geology of Kalimantan has been described by van Bemmelen (1949) and Hamilton (1979). A

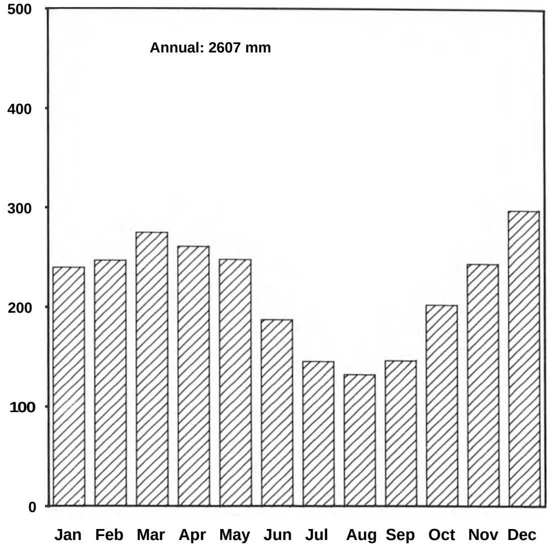


Fig. 4. Mean annual and monthly precipitation (mm) at Pangkalanbun, Central Kalimantan.

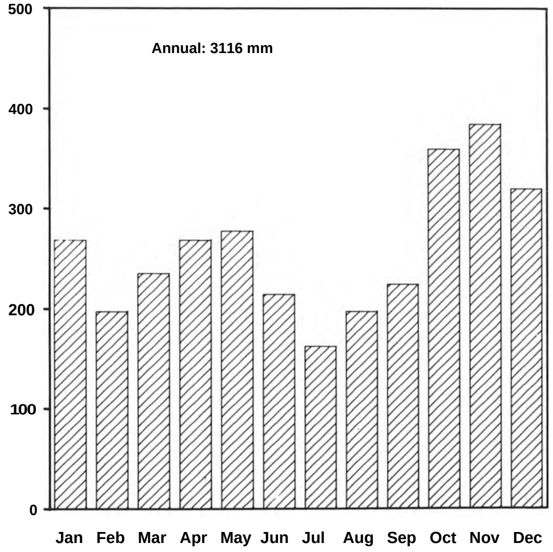


Fig. 5. Mean annual and monthly precipitation (mm) at Pontianak, West Kalimantan.

geological sketch map is shown in fig. 6. The oldest rocks occur in an area extending from near the west coast across the central part of West Kalimantan and beyond the boundary between West and Central Kalimantan. These rocks constitute a variety of deformed and metamorphosed clastic sediments, silicic volcanic rocks and granitic intrusions. Their age varies from Carboniferous to Eocene. The volcanic rocks and the granitic intrusions are mainly of Cretaceous age.

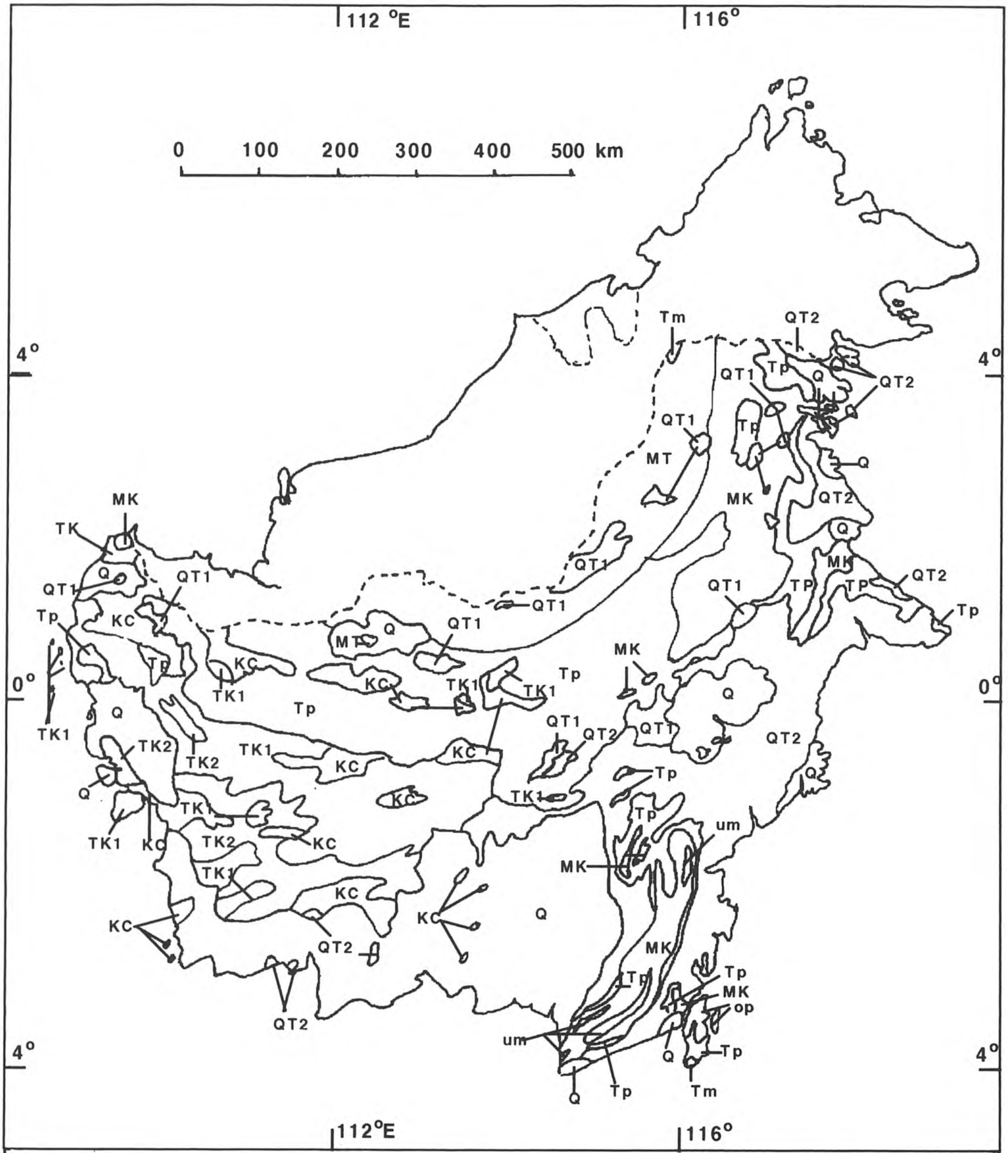
The mountains in southeastern Kalimantan were formed by subduction of a plate from the west beneath an eastern plate in late Cretaceous and early Paleogene (Paleocene through Oligocene). The rocks in this area are a complex mixture of Cretaceous sediments overlain by Eocene strata. The area along the border to the Malaysian part of Borneo is dominated by broken clastic sediments folded by subduction of the South China Sea floor beneath Borneo in Eocene. South of this area a rather broad region covering the northern parts of East, Central and West Kalimantan is dominated by more or less folded Paleogene and middle Tertiary sedimentary rocks including sandstone and shales.

Large areas of East and South Kalimantan are covered by late Tertiary and early Quaternary sediments including limestone, sandstone and shales. Late Tertiary and Quaternary unconsolidated sediments occur along the west and south coasts. In the depression formed by the subduction in late Cretaceous and early Paleogene and located in the eastern part of Central Kalimantan these deposits are several km thick in places and extend several hundred km inland from the south coast. In this area subsidence is still in progress and large areas are swamps. Further inland, the swamps change into sandy terraces.

The landforms change from mountains in the area bordering the Malaysian part of Borneo over hilly, rolling and undulating to almost flat on the sandy terraces and the coastal plains.

Soils

A soil map of Kalimantan adapted from the Soil Map of the World 1:5,000,000 (FAO-Unesco, 1979) is shown in fig. 7. The map is based on general information and sporadic soil observations since a systematic soil survey covering Kalimantan has not been carried out. In recent years a number of soil surveys have been made in



LEGEND

KC	Igneous, metamorphic and sedimentary rocks, Early Cretaceous through Carboniferous
TK1	Granitic rocks, Eocene through late Cretaceous
TK2	Silicic volcanic rocks, Eocene through Late Cretaceous
MK	Melange, broken formations or imbricated terrain, Cretaceous
MT	Melange, broken formations or imbricated terrain, Eocene
um	Ultramafic rocks
op	Ophiolite
Tp	Sedimentary rocks, Oligocene through Paleocene
Tm	Sedimentary (in East Kalimantan) and volcanic (in South Kalimantan) rocks, Middle Miocene through Oligocene
QT1	Intermediate and basic volcanic rocks, Early Quaternary through Miocene
QT2	Sedimentary rocks, Early Quaternary through Miocene
Q	Sediments, Quaternary through Miocene

Fig. 6. Geological map of Kalimantan, adapted from Hamilton (1979).

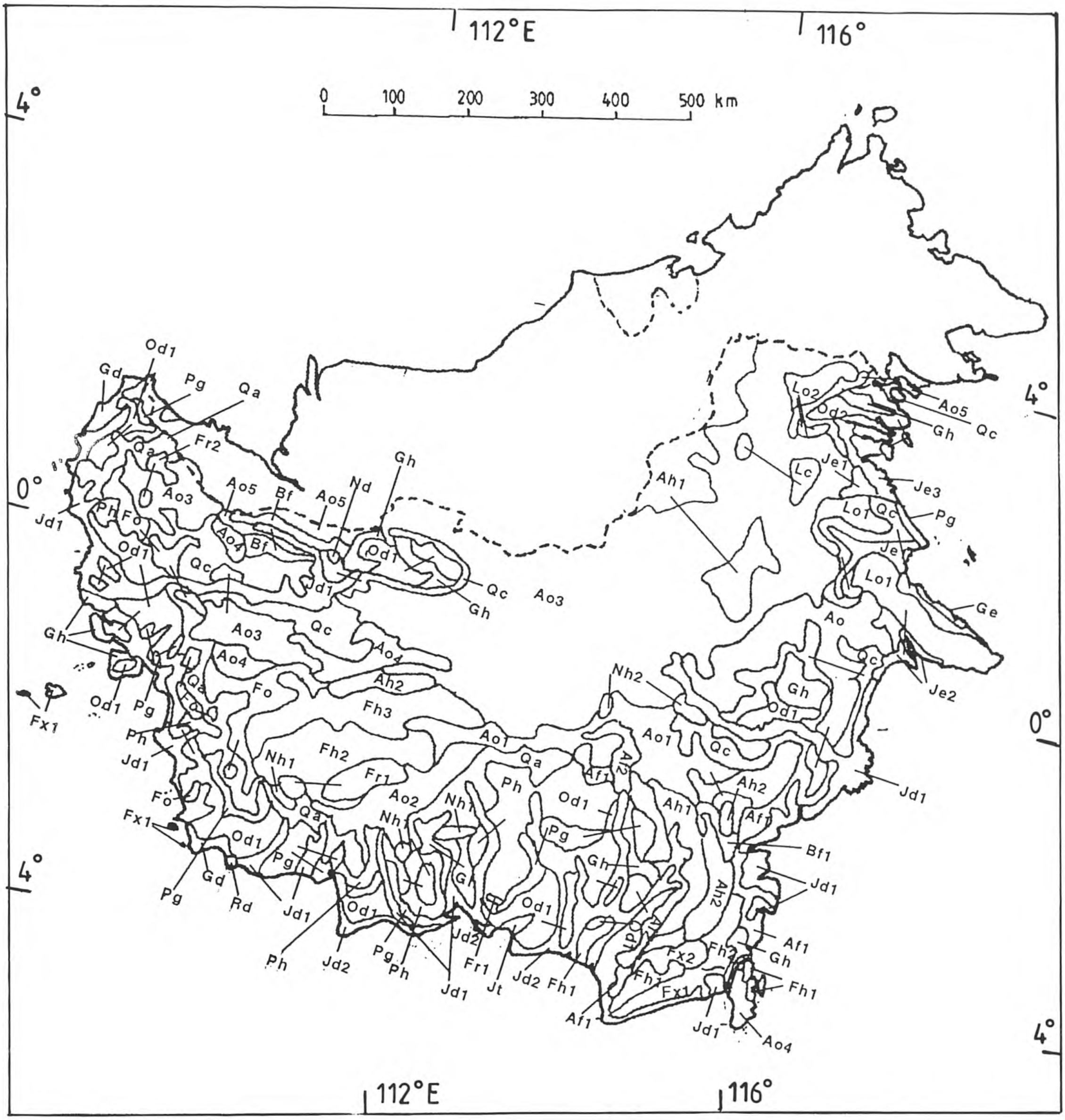


Fig. 7. Soil map of Kalimantan, adapted from the FAO-Unesco Soil Map of the World (FAO-Unesco, 1979). Legend is described in table 1.

connection with the Transmigration Programme which is sponsored by the Indonesian Government. The Transmigration Programme is concerned with moving of people from densely populated regions in Indonesia, mainly Java and neighbouring islands, to sparsely populated regions such as Kalimantan. The soil surveys form a part of the investigations carried out in order to identify suitable settlement areas for the transmigrants. However, the soil information collected during these surveys has to a large extent remained unpublished.

It appears from fig. 7 that the dominant soils in upland areas with mountains, hilly, rolling or

Table 1. Legend to Figure 7 (Symbols and terms are defined in Table 2).

Map Symbol	Dominant soils	Associated soils	Inclusions	Phase	Texture	Topography
Af1	Af		Fx Jd		Medium/fine	Level to undulating
Af2	Af	Ag Od	Qf Ap	Petric	Medium	Level to undulating
Ah1	Ah		Ao Fh I		Medium	Steep to mount.
Ah2	Ah	I	Nd	Lithic	Medium/ fine	Steep to mount.
Ao1	Ao	Bd	Jd Ag Af		Medium/fine	Rolling to hilly
Ao2	Ao	Ah	Fx Jd		Fine	Level to hilly
Ao3	Ao	Ah Bd	Be Ag		Medium/fine	Steep to mount.
Ao4	Ao	I	Ah	Lithic	Medium/fine	Steep to mount.
Ao5	Ao	Af L	Gd		Medium/fine	Rolling to hilly
Bf	Bf		Ah Fo		Medium/fine	Rolling to hilly
Fh1	Fh		Ah I	Petroferric	Medium/fine	Steep to mount.
Fh2	Fh	Qf	Jd	Petric	Medium	Rolling to hilly
Fh3	Fh	Ah	I	Petroferric	Medium/fine	Steep to mount.
Fo	Fo		Qf	Petroferric	Medium	Rolling to hilly
Fr1	Fr		Jd Ag	Petric	Medium/fine	Rolling to hilly
Fr2	Fr		Ao	Petroferric	Medium/fine	Steep to mount.
Fx1	Fx	Of	Jd Ag	Petric	Medium	Level to hilly
Fx2	Fx	Fh	Ah I	Petric	Medium	Steep to mount.
Gd	Gd	Gh Bg	Jd Od		Fine	Level to undulating
Ge	Ge	Gh	Je Re		Fine	Level to undulating
Gh	Gh	Jd	Od Jt		Fine	Level to undulating
Jd1	Jd	Gd	Bd Rd Od		Medium/fine	Level to undulating
Jd2	Jd	Rd	Od Gh		Coarse	Level to undulating
Je1	Je	Be	Ge Vp		Medium/fine	Level to undulating
Je2	Je	Ge	Re Vp		Medium/fine	Level to undulating
Je3	Je	Gh	Oe Re		Fine	Level to undulating
Jt	Jt	Od	Gd R P	Saline	Fine	Level to undulating
Lc	Lc	Ne	Th I		Fine	Steep to mount.
Lo1	Lo		Lc Je I		Medium/fine	Steep to mount.
Lo2	Lo	Fo Lc	Be I Nd		Medium/fine	Steep to mount.
Nd	Nd		Ah I		Fine	Rolling to hilly
Nh1	Nh		Jd Nd Vp		Fine	Level to undulating
Nh2	Nh		Th Be		Fine	Rolling to hilly
Od1	Od		Jd Gh			Level to undulating
Od2	Od	Gh	R Jd Jt			Level to undulating
Pg	Pg		Gh Od		Coarse	Level to undulating
Ph	Ph	Qa	Pp		Coarse	Rolling to hilly
Qa	Qa	Po	Jd		Coarse	Level to undulating
Qc	Qc	Bd	Ah Jd		Coarse	Level to hilly
Rd	Rd	Gd Od	Gh Jt S		Coarse	Level to undulating

Table 2. Symbols and Terms Used in Table 1.

Soil Units

Af	Ferric Acrisols	Ge	Eutric Gleysols	P	Podzols
Ag	Gleyic Acrisols	Gh	Humic Gleysols	Pg	Gleyic Podzols
Ah	Humic Acrisols	I	Lithosols	Ph	Humic Podzols
Ao	Orthic Acrisols	Jd	Dystric Fluvisols	Po	Orthic Podzols
Ap	Plinthic Acrisols	Je	Eutric Fluvisols	Pp	Plinthic Podzols
Be	Chromic Cambisols	Jt	Thionic Fluvisols	Qa	Albic Arenosols
Bd	Dystric Cambisols	L	Luvisols	Qc	Cambic Arenosols
Be	Eutric Cambisols	Lc	Chromic Luvisols	Qf	Ferralic Arenosols
Bf	Ferralic Cambisols	Lo	Orthic Luvisols	R	Regosols
Fh	Humic Ferralsols	Nd	Dystric Nitosols	Rd	Dystric Regosols
Fo	Orthic Ferralsols	Ne	Eutric Nitosols	Re	Eutric Regosols
Fr	Rhodic Ferralsols	Nh	Humic Nitosols	S	Solonetz
Fx	Xanthic Ferralsols	Od	Dystric Histosols	Th	Humic Andosols
Gd	Dystric Gleysols	Oe	Eutric Histosols	Vp	Pellic Vertisols

Phases

Petric	A 25 cm thick soil layer with 40% or more of oxidic concretions, hardened plinthite, or limestone occurs within 100 cm of the surface.
Petroferric	The upper part of a continous layer indurated by iron oxides occurs within100 cm of the surface.
Lithic	Continuous rock occurs within 50 cm of the surface.
Saline	A soil layer with an electric conductivity of the saturation extract higher than 4 mmho/cm occurs within 100 cm of the surface.

Texture

Coarse	Less than 18% and more than 65% sand.
Medium	18-35% clay, or less than 18% clay and less than 65% sand.
Fine	More than 35% clay.

Topography

Level to undulating	Dominant slopes 0-8%.
Level to hilly	Dominant slopes 0-30%.
Rolling to hilly	Dominant slopes 8-30%.
Steep to mount.	Dominant slopes over 30%.

undulating topography are Acrisols and Ferralsols. However, the investigations referred to above, which have been carried out in connection with identification of suitable transmigration settlement sites, have revealed that the occurrence of Ferralsols is more limited than shown on the map. Ferralsols have not been observed in several soils surveys carried out in the large area in the southwestern part of Kalimantan shown in fig. 7 to be dominated by Ferralsols, and the area is probably dominated by Acrisols. Hence, the only important area with Ferralsols seems to be that located in the southeastern part of Kalimantan (fig. 7). It is also doubtful whether all the soils classified as Acrisols actually meet the definition of this soil unit. Many or perhaps most of these soils should possibly be classified as Nitosols since only a small decrease in clay content occurs below the argillic horizon. However, in order to avoid discrepancies with the soil map in fig. 7, the classification as Acrisols has been maintained, and the soils, for which descriptions and data are given below, are classified as Acrisols even if the correct classification might be Nitosols. In order to ensure conformity with the soil map in fig. 7, the classification according to the FAO-Unesco system is based on the legend from 1974 (FAO-Unesco, 1974) although a revised legend was published in 1988 (FAO, 1988). The classification according to the Soil Taxonomy system is based on *Keys to Soil Taxonomy* (Soil Survey Staff, 1988).

In a few small areas the soils are developed on limestone. These soils usually have an argillic horizon which may have a high base saturation and accordingly they are classified as Luvisols.

On the sandy terraces the dominating soils are Podzols and Arenosols, and the swamps are dominated by Gleysols and Histosols. Fluvisols occur on alluvial deposits along rivers and streams.

Acrisols

Profile descriptions and analytical data for four profiles classified as Acrisols are given below (profiles No. 1-4). The locations of the profile sites are shown in fig. 1. Profiles, for which no source has been given, have been investigated in connection with the present study.

Despite the fact that these profiles are located far apart and developed on different parent materials they have quite similar physical and chemical properties. All are medium to fine textured and the colours are brown to yellowish brown except in the deeper horizon of profile No. 2 where colours are yellowish red.

There are some variations among the soils in content and distribution of humus. The lowest humus content is found in profile No. 2 while profiles No. 1, 3 and 4 have rather high content of humus. In profile No. 1 the humus content is so high that it warrants classification as a Humic Acrisol (Humult), and profile No. 4, which is under primary forest, has a shallow A horizon containing about 15 % humus.

One of the most striking features of all the soils is a low content of exchangeable bases and, consequently, a low base saturation percentage, a low pH and a high content of exchangeable aluminium. This is due to a severe leaching caused by the high surplus of precipitation and the fact

Profile No. 1 (Verheye and Tessens, 1977).

Location: Martapura, South Kalimantan (3° 25’ S, 114° 49’ E)
Parent Material: Old alluvial deposit derived from an acid volcanic complex.
Classification: FAO-Unesco, Humic Acrisol.
Soil Taxonomy, Typic Haplohumult.
Horizontation:

0-17 cm	Ah1	Very dark greyish brown (10 YR 3/2), clay, clear boundary.
17-24 cm	Ah2	Dark greyish brown (10 YR 4/2), clay, clear boundary.
24-34 cm	AB	Brown (10 YR 5/3), clay, medium subangular blocky, clear boundary.
34-63 cm	Bt1	Dark yellowish brown (10 YR 4/6), clay, medium angular blocky, clear boundary.
63-90 cm	Bt2	Brownish yellow (10 YR 6/6), clay, fine angular blocky, patchy clay cutans.

Profile No. 1. Analytical Data

Depth	Texture *(%)*			pH		C	N	C/N
(cm)	Sand	Silt	Clay	H_2O	KCl	*(%)*	(%)	
0-17	43	16	41	4.6	3.5	5.2	0.30	17
17-24	43	17	40	4.7	3.6	2.3	0.17	13
24-34	41	18	41	4.8	3.6	2.6	0.12	22
34-63	37	15	48	4.8	3.6	0.7	0.09	8
63-90	34	15	51	5.2	3.7	-	-	-

Depth	Exchangeable cations (me/100g)							
(cm)	Ca	Mg	K	Na	Al	a	b	c
0-17	0.6	0.8	0.2	0.1	-	20.7		8
17-24	0.1	0.2	0.1	0.1	-	12.5		4
24-34	0.1	0.1	0.1	0.1	-	11.2		2
34-63	-	-	-	-	-	11.0		-
63-90	-	-	-	-	-	10.9		-

a: CEC at pH 7 (me/100 g)
b: CEC at soil pH (me/100 g)
c: Base saturation (%)

Profile No. 2 (Grüneberg et al., **1983).**

Location: Muaramarah, East Kalimantan (1° 3’ N, 116° 42’ E)
Parent Material: Miocene sediment.
Slope: 6-7%
Vegetation: Recently cleared Dipterocarp forest.
Classification: FAO-Unesco, Orthic Acrisol.
Soil Taxonomy, Typic Paleudult.
Horizontation:

0-4 cm	Ah	Yellowish brown (10 YR 5/6). silt loam, weak fine subangular blocky. few line pores, many roots.
4-28 cm	Bt1	Strong brown (7.5 YR 5/8), silt loam, weak subangular blocky, many fine and few medium pores, many fine and few medium roots.
28-54 cm	Bt2	Yellowish red (5 YR 5/8), silty clay loam, moderate subangular blocky, common fine and medium pores, few fine and medium roots.
54-94 cm	2BCt	Yellowish red (5 YR 5/8), silty clay, strong brown (7.5 YR 5/6) mottles, moderate fine to medium subangular blocky, few fine pores, few fine roots.
94-110 cm	2C	Yellowish red (5 YR 5/8), silty clay, red (2.5 YR 5/8) mottles, medium to strong, very fine to fine subangular blocky, few fine pores, few fine roots.

Profile No. 2. Analytical Data

Depth	Texture *(%)*			pH		C	N	C/N
(cm)	Sand	Silt	Clay	H_2O	KCl	(%)	(%)	
0-4	19	70	11	4.5	4.1	1.3	-	-
4-28	15	62	23	4.1	3.9	0.4	-	-
28-54	15	56	29	4.1	3.8	0.3	-	-
54-94	12	46	42	4.2	3.9	0.2	-	-
94-110	10	45	45	3.8	3.7	0.2	-	-

Depth	Exchangeable cations (me/100							
(cm)	Ca	Mg	K	Na	Al	a	b	c
0-4	0.3	0.5	0.3	0.0	2.1	11.1	3.2	10
4-28	0.3	0.5	0.1	0.0	5.5	10.6	6.4	8
28-54	0.2	0.5	0.3	0.0	7.2	15.2	8.3	7
54-94	0.2	0.5	0.3	0.0	8.6	14.0	9.6	7
94-110	0.3	0.5	0.2	0.0	11.4	16.2	12.4	6

a, b. c: see Profile No. 1

Profile No. 3 (Buurman and Subagjo, 1980).

Location:	Anjungan, West Kalimantan (0° 19' N, 109° 15' E)
Elevation:	40 m a.s.l.
Parent Material:	Granodiorite.
Slope:	Gently sloping
Vegetation:	Rubber trees with fern undergrowth.
Classification:	FAO-Unesco, Orthic Acrisol. Soil Taxonomy, Typic Kandiudult.

Horizontation:

0-10 cm	Ah	Brown (10 YR 5/3), sandy clay loam, weak coarse subangular blocky, very friable, slightly sticky, many pores, clear smooth boundary.
10-41 cm	ABt	Yellowish brown (10 YR 5/4), sandy clay loam, weak coarse subangular blocky, friable, slightly sticky, plastic, common pores, patchy clay coatings, gradual smooth boundary.
41-89 cm	Bt1	Brownish yellow (10 YR 6/6), sandy clay, massive, firm, slightly sticky, very plastic, common pores, patchy clay coatings, diffuse smooth boundary.
89-135 cm	Bt2	Brownish yellow (10 YR 6/8), clay, massive, few pores, diffuse smooth boundary.
135-210 cm	BC	Brownish yellow (10 YR 6/8), clay, many fine clear strong brown (7.5 YR 5/6) mottles, massive, few pores.

Profile No. 3. Analytical Data

Denth (cm)	Texture (%) Sand	Silt	Clay	PH H_2O	KCl	C (%)	N (%)	C/N
0-10	63	12	25	5.4	4.4	3.9	-	-
10-41	60	12	28	5.4	4.4	1.5	-	-
41-89	50	12	38	5.1	4.2	0.4	-	-
89-135	45	12	43	5.4	4.3	0.4	-	-
135-210	44	15	41	5.3	4.3	0.2	-	-

Depth (cm)	Exchangeable cations (me/100g) Ca	Mg	K	Na	Al	a	b	c
0-10			0.8*)		0.9	13.8	2.8	6
10-41			0.9*)		0.7	6.2	2.2	15
41-89			0.7*)		0.6	4.7	2.1	15
89-135			0.5*)		0.6	4.2	1.6	12
135-210			0.3*)		0.6	3.9	1.3	8

a, b, c: see Profile No. 1

*)Total exchangeable bases

Profile No. 4 (Petersen, 1987).

Location:	Rantaupulut, Central Kalimantan (1° 55' S, 111° 59' E)
Elevation:	38 m a.s.l.
Parent Material:	Sandstone.
Land form:	Undulating plain.
Slope:	5%.
Vegetation:	Mixed Dipterocarp forest.
Drainage:	Well drained.
Classification:	FAO-Unesco, Orthic Acrisol. Soil Taxonomy, Typic Kandiudult.

Horizontation:

-2-0 cm	O	Forest litter; abrupt smooth boundary.
0-6 cm	Ah	Brown to dark brown (10 YR 4/3), silty clay loam, moderate fine to medium granular, friable, abrupt smooth boundary.
6-25 cm	ABt	Brownish yellow (10 YR 6/6), silty clay loam, moderate fine to coarse subangular blocky, friable to firm, gradual smooth boundary.
25-53 cm	Bt1	Yellowish brown (10 YR 5/8), silty clay, moderate medium to coarse subangular blocky, friable to firm, gradual smooth boundary.
53-100 cm	Bt2	Strong brown (7.5 YR 5/6), clay, brownish yellow (10 YR 6/6) mottles, moderate medium to coarse subangular blocky, firm, thin cutans, clear wavy boundary.
100-125 cm	Bt3	Reddish yellow (7.5 YR 6/6), silty clay. very pale brown (10 YR 7/3) mottles, moderate coarse subangular blocky, very firm, thin cutans.

Profile No. 4. Analytical Data

Depth (cm)	Texture (%) Sand	Silt	Clay	PH H_2O	KCl	C (%)	N (%)	C/N
0-6	15	55	30	3.8	3.1	9.0	0.58	16
6-25	16	45	39	4.5	3.5	1.3	0.12	11
25-53	19	40	41	4.6	3.6	0.7	0.07	9
53-100	19	38	43	5.0	3.8	0.3	0.04	9
100-125	9	47	44	4.9	3.7	0.2	0.04	6

Depth (cm)	Exchangeable cations (me/100g) Ca	Mg	K	Na	Al	a	b	
0-6	1.1	<0.1	0.3	0.1	6.6	23.7	8.1	7
6-25	0.1	0.2	0.1	<0.1	4.3	7.8	4.8	6
25-53	0.1*)		<0.1	<0.1	3.6	5.4	3.9	6
53-100	0.1*)		<0.1	<0.1	2.9	4.1	3.3	7
100-125	0.1*)		<0.1	<0.1	2.9	4.6	3.3	7

a, b, c: see Profile No. 1

Ca + Mg.

that the soils are very old and leached for an extensive period of time.

Mineralogical investigations have been carried out on profile No. 3 by Buurman and Subagjo (1984) and on profiles located close to profile No. 2 by Grüneberg et al. (1983). Larsen (1989) made mineralogical investigations of the clay fraction of two profiles from Central Kalimantan developed on sedimentary rocks and having properties similar to profile No. 4.

The results of these investigations showed that the sand and silt fractions in all the soils studied consisted almost exclusively of quartz. Other minerals such as feldspars and micas were present in trace amounts only.

The clay fraction in all the soils investigated was dominated by kaolinite. In addition Buurman and Subagjo (1984) identified gibbsite in the clay in profile No. 4, and Grüneberg et al. (1983) found quartz, illite, chlorite, mixed-layer minerals, goethite and feldspars in the clay fraction of the profiles studied. Besides kaolinite, which accounted for about half of the clay fraction in the soils studied by Larsen (1989), quartz, illite, vermiculite, goethite and traces of feldspars were identified in the clay fraction. Hematite and gibbsite were not detected.

Ferralsols

Descriptions and analytical data for two profiles classified as Ferralsols are given below (profiles No. 5-6). Both profile sites are located in the area in South Kalimantan shown in fig. 7 to be dominated by Ferralsols.

The two profiles, which are located close to each other and probably developed on identical parent materials, differ in texture. However, it was observed during the texture analysis of profile No. 6 that the sand fraction consists of rounded particles resembling a kind of concretions rather than of mineral particles. The particles were hard and did not disintegrate even by a sonic treatment. Hence, the estimated textural composition is not comparable to that of soils consisting of mineral particles.

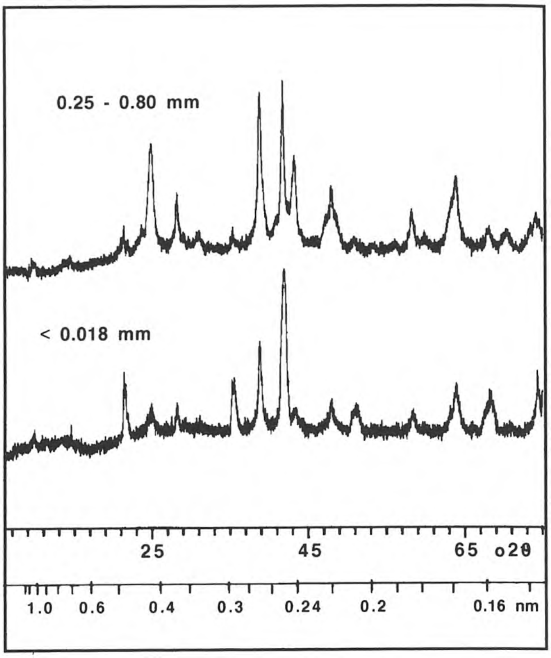


Fig. 8. X-ray diffractograms of unoriented samples of two particle size fractions from the Bws horizon in profile No. 6 (Co-Ka radiation).

The soils have a medium to low humus content in the surface horizons but the subsurface horizons have rather high humus contents. In profile No. 6 the humus content exceeds 1 % at a depth of more than 1 m. Actually this profile should probably be classified as a Humic Haploperox according to the Soil Taxonomy classification since the particle density was measured to be about 4.0 g/cm^3 in all horizons, indicating a bulk density of about 2.0 g/cm^3. Assuming a bulk density of 2.0 g/cm^3 the total content of organic carbon to a depth of 1 m is about 19 kg/m^2 justifying classification as a Humic Haploperox and perhaps as a Humic Ferralsol according to the FAO/Unesco classification. Both soils have low cation exchange capacities. Assuming a cation exchange capacity of 200 me/100 g for humus at pH 7, the cation exchange capacity of the clay in profile No. 6 is as low as 7-9 me/100 g. The soils also have low base saturation percentages.

Preliminary mineralogical investigations by means of X-ray diffractometry have been carried out on the particle size fractions <0.018 mm (clay and fine silt) and 0.25 - 0.8 mm (coarse

Profile No. 5	(Verheye and Tessens, 1977)
Location:	Peleihari Extension Station, South Kalimantan (3° 48’ S, 114° 48’ E)
Parent Material:	No information, probably ultrabasic rock.
Classification:	FAO-Unesco, Rhodic Ferralsol. Soil Taxonomy, Rhodic Haploperox.
Horizontation:	
0-17 cm Ah	Dusky red (10 YR 3/3.5), clay, granular.
17-68 cm AB	Dark red (10 R 3/6), clay, weak granular, gradual boundary.
68-170 cm Bws1	Dark red (10 R 3/6), clay, very weak granular, friable, diffuse boundary.
170- cm Bws2	Dark red (10 R 3/6), clay, very weak granular, friable.

Profile No. 5. Analytical Data

Depth (cm)	Texture *(%)* Sand	Silt	Clay	PH H₂O	KCl	C (%)	N (%)	C/N
0-17	10	12	78	5.2	4.3	0.71	0.04	18
17-68	9	11	80	5.0	4.0	0.73	0.05	15
68-170	9	8	83	4.8	4.0			
170-	9	8	83	4.8	4.0	-		

Depth (cm)	Exchangeable cations (me/100g) Ca	Mg	K	Na	Al	a	b	c
0-17	tr.	0.1	tr.	tr.		4.6		2
17-68	tr.	tr.	tr.	0.1		4.4		2
68-170	tr.	tr.	tr.	0.1		10.2		1
170-	tr.	tr.	tr.	0.1		10.2		1

a, b , c: see Profile No. 1

Profile No. 6.	
Location:	Peleihari Sugar Estate, South Kalimantan. (3° 47’ S, 114° 44’ E)
Parent Material:	Ultrabasic rock
Slope:	4% towards East.
Vegetation:	Secondary growth with 5 m tall trees.
Classification:	FAO-Unesco, Rhodic Ferralsol. Soil Taxonomy, Rhodic Haploperox.
Horizontation:	
-2-0 cm O	Litter.
0-18 cm Ah	Dark reddish brown (2.5 YR 2.5/4), clay loam, moderate very fine to fine angular blocky, friable, few coarse and many fine roots, diffuse boundary.
18-66 cm AB	Dark reddish brown (2.5 YR 2.5/4), clay loam, weak medium subangular blocky breaking to strong fine granular, very friable, few medium and common very fine roots, diffuse boundary.
66-123 cm Bws	Dark reddish brown (2.5 YR 2.5/4). clay, weak medium subangular blocky breaking to moderately strong fine granular, very friable, few medium and line roots.

Profile No. 6. Analytical Data

Depth (cm)	Texture *(%)* Sand	Silt	Clay	pH H₂O	KCl	C (%)	N (%)	C/N
0-18	36	35	29	6.4	5.0	1.84	0.15	13
18-66	34	30	36	6.4	5.4	0.88	0.05	19
66-123	32	28	40	6.6	5.5	0.64	0.03	21

Depth (cm)	Exchangeable cations (me/100g) Ca	Mg	K	Na	Al	a	b	
0-18	0.5	0.2	0.06	0.2	0.3	8.9	1.3	10
18-66	0.4	0.04	<0.01	0.07	0.3	5.5	0.8	9
66-123	0.3	0.03	<0.01	0.1	0.2	4.9	0.6	8

a, b, c: see Profile No. 1

sand) of the Bws horizon of profile No. 6. No pretreatment except grinding in an agate mortar was applied. Diffractograms of unoriented samples are shown in fig.8.

It is not possible to identify any silicate minerals from either diffractogram. The minerals identified in both samples include magnetite (and/or maghemite), haemetite, goethite and gibbsite, but as judged from the size of the gibbsite peak at 0.485 nm the content of this mineral seems to be low. Hence, both particle size fractions are dominated by iron(III) oxides and hydroxides. This is in agreement with results of determinations of the amounts of iron, aluminium, titanium and silicium dissolved by an 8 hour extraction with 20 % HCl at 120°C as shown in table 3, which also include weight losses on heating at 350 and 900°C. Most of the weight loss on heating occurred at temperatures below 350°C supporting the presence of goethite and/or gibbsite in the samples.

The presence of Ferralsols on these ultrabasic rocks and their apparent absence on most other

Table 3. Composition of two particle size fractions of the Bws horizon in Profile No. 6 (% by weight at 110°C).

Fraction	Fe_2o_3	Al_2O_3	SiO_2	TiO_2	Insoluble residue	Loss on heating 110-350°C	350-900°C
<0.018 mm	72.50	9.54	0.24	0.27	6.21	8.02	2.13
0.25 - 0.80 mm	48.77	4.74	0.28	0.12	42.20	2.68	0.36

parent materials indicate that they have developed only on parent materials very low in silica.

Podzols and Arenosols

The typical soils of the sandy terraces covering rather large areas, especially in Central Kalimantan Province, are Podzols and Arenosols. Descriptions and analytical data for a profile belonging to each of these soil units are given below (profiles No. 7-8).

The description and analytical data of profiles No. 7 and 8 do not need many comments. Both profiles are coarse textured with low cation exchange capacities and low base saturation percentages. Profile No. 7 has been subject to shifting cultivation which has caused mixing of the upper horizons, but the spodic horizon is clearly expressed. The correct classification of profile No. 8 according to Soil Taxonomy is probably Typic Tropopsamment since the only parameter excluding this classification is a slightly too high content of silt (and/or clay) in the Bw horizon.

Luvisols

Luvisols are limited to areas where the parent material is limestone or other basic rocks and even in these areas most of the soils are leached to an extent that they are classified as Acrisols (Ultisols). Description and analytical data of a soil developed on limestone and having a high base saturation percentage is given below (profile No. 9).

In addition to a high base saturation percentage all horizons in profile No. 9 have a rather high cation exchange capacity indicating the presence of clay minerals with a cation exchange capacity higher than that of iron and aluminium oxidhydroxides and kaolinite. In agreement with the soil being developed on limestone the adsorption complex is strongly dominated by adsorbed calcium.

Histosols, Fluvisols and Gleysols

No descriptions or data are presented for Histosols, Fluvisols and Gleysols. With the exception of some Fluvisols, they are poorly drained. Histosols are common in coastal swamps but in some areas such as the eastern part of Central Kalimantan Province they extend several hundred km inland. Histosols also occur in local inland depressions. Most of the Histosols are classified as Dystric Histosols due to a low base saturation percentage. Many Histosols, especially in coastal areas, contain iron pyrites.

Profile No. 7.

Location:	Pangkalanbanteng, Central Kalimantan. (2° 25’ S, 111° 53’ E)
Parent Material:	Sandy terrace
Slope:	2%
Vegetation:	Secondary growth
Classification:	FAO-Unesco, Gleyic Podzol. Soil Taxonomy, Typic Tropaquod.
Horizontation:	
0-10 cm A(p)	Dark reddish brown (5 YR 3/2), sandy loam, moderate fine subangular blocky, friable, many fine, medium and coarse pores, many fine, medium and coarse roots, diffuse smooth boundary.
10-37 cm EA	Very dark gray (10 YR 3/1), sand, common dark gray (10 YR 4/1) mottles, structureless, friable, many fine, medium and coarse pores, common fine, medium and coarse roots, diffuse smooth boundary.
37-45 cm Bh	Very dark gray (5 YR 3/1), loamy sand, moderate medium subangular blocky, friable, many fine, medium and coarse pores, common fine roots, abrupt smooth boundary.
45-53 cm Bms	Dark red (2.3 YR 3/6) (top) and yellowish brown (10 YR 5/8) (bottom), sandy loam, hard, structureless, very firm, common fine, medium and coarse pores, very few fine roots, cemented with iron compounds and organic matter, gradual boundary with tongues extending into Bg.
53-75 cm Bg	Brown (10 YR 5/3), loamy sand, common grayish brown (10 YR 5/2) and yellowish brown (10 YR 5/6) mottles, weak medium angular blocky, friable, common fine pores, very few fine roots, gradual smooth boundary.
75-120 cm Cg	Light gray (10 YR 7/2), sandy clay loam, structureless, non plastic, slightly sticky, common fine pores, very few fine roots.

Profile No. 7. Analytical Data

Depth (cm)	Texture *(%)* Sand	Silt	Clay	pH H_2O	KCl	C (%)	N (%)	C/N
0-10	68	30	2	3.9	3.1	8.6	0.38	23
10-37	92	5	3	4.8	3.9	0.9	0.04	22
37-45	80	10	10	4.6	3.7	3.3	0.10	33
45-53	73	23	4	4.8	4.2	1.6	0.08	20
53-75	80	13	7	5.3	4.8	1.8	0.08	22
75-120	71	7	22	5.4	4.7	0.5	0.03	16

Depth (cm)	Exchangeable cations (me/100e) Ca	Mg	K	Na	Al	a	b	c
0-10	1.3	0.1	<0.1	0.3	7.9	20.7	6.8	9
10-37	0.1*)		<0.1	0.1	1.4	2.8	1.5	11
37-45	0.2	0.1	<0.1	0.1	4.0	11.9	4.2	4
45-53	0.1*)		<0.1	0.1	3.2	13.5	3.5	2
53-75	0.1*)		<0.1	0.1	0.5	2.5	0.8	12
75-120	0.1*)		<0.1	0.1	0.5	2.3	0.8	13

a, b, c: see Profile No. 1

*)Ca + Mg.

Fluvisols also occur in low-lying coastal areas. In addition rather large areas with Fluvisols occur along the major rives. The major part of these soils are acid with low base saturation percentage and they are, accordingly, classified as Dystric Fluvisols.

Gleysols occur mainly in poorly drained areas of the sandy terraces. Like practically all other soils they are acid and classified as Dystric Gleysols, but some qualify for classification as Humic Gleysols due to high organic matter content.

Present and potential land use

Most of Kalimantan is currently under tropical rain forest. Mixed Dipterocarp forest is the typical vegetation in upland, well drained areas. Swamp forest with tree species adapted to poorly drained soils dominate in the low-lying coastal plains and in other poorly drained areas. Small

Profile No. 8.

Location:	Pandran, Central Kalimantan. (1° 06' S, 115° 03' E)
Parent Material:	Eroded sandy terrace
Slope:	20 %
Vegetation:	Mixed Dipterocarp forest
Classification:	FAO-Unesco, Ferralic Arenosol. Soil Taxonomy, Typic Troporthent (Typic Tropopsamment).

Horizontation:

-1-0 cm O	Litter.
0-15 cm Ahl	Dark yellowish brown (10 YR 4/6), loamy sand, weak fine crumb, loose, few fine and medium, many coarse pores, many fine, few medium and coarse roots, gradual smooth boundary.
15-39 cm Ah2	Yellowish brown (10 YR 5/4), loamy sand, weak fine crumb, loose, few fine and medium, many coarse pores, few medium and coarse roots, gradual smooth boundary.
39-104 cm Bw	Very pale brown (10 YR 7/4), sandy loam, weak fine crumb, loose, few fine and medium, many coarse pores, few medium and coarse roots, gradual smooth boundary.
104-146 cm C	Pale brown (10 YR 6/3), loamy sand, weak fine crumb, loose, few fine and medium, many coarse pores, few medium and coarse roots.

Profile No. 8. Analytical Data

Depth (cm)	Texture (%) Sand	Silt	Clay	PH H_2O	KCl	C (%)	N (%)	C/N
0-15	84	9	7	4.2	3.7	1.2	0.06	20
15-39	81	12	7	5.3	4.4	1.3	0.06	22
39-104	76	15	9	5.5	4.8	0.8	0.04	19
104-146	83	8	9	6.0	4.6	0.2	0.02	9

Depth (cm)	Exchangeable cations (me/100g) Ca Mg	K	Na	Al	a	b	c
0-15	<0.1*)	<0.1	<0.1	1.9	3.6	1.9	<8
15-39	<0.1*)	<0.1	<0.1	1.1	3.8	1.3	<8
39-104	<0.1*)	<0.1	<0.1	0.6	2.2	0.8	<14
104-146	<0.1*)	<0.1	<0.1	0.4	1.4	0.6	<21

a, b, c: see Profile No. 1

*)Ca + Mg

areas in the immediate vicinity of the coast have a mangrove or nipa vegetation.

The forest, especially the mixed Dipterocarp forest occurring in upland areas, is utilized for timber production which forms the basis for most of the industrial enterprises in Kalimantan, and timber products account for the major part of the export from Kalimantan.

Except for new developments, especially in connection with the Transmigration Programme mentioned above, agriculture in Kalimantan is mainly based on shifting cultivation carried out by the local population living in scattered villages in forested areas. Although different systems of shifting cultivation are used in different areas, the infertility of the soils allows only one or two crops to be cultivated after each land clearing. The most common crop in this system is upland rice, but other crops including maize, cassava, sweet potato and a variety of vegetables are also grown. Fruit trees and trees producing commodities for marketing, such as rubber and coffee, are usually grown during the fallow period.

The fallow period required to restore the fertility to a level facilitating another arable crop is 15-20 years, but due to increasing population pressure in recent years there has been a trend towards a shorter fallow period with a consequent decline in crop production. During the fallow period a regrowth of wooden species is normally established, but overexploitation, especially in areas with poor soils such as those on the sandy terraces, has caused large areas to become covered with grass (alang-alang, *Imperata cylindrica).*

The potential for agricultural systems based on permanent cultivation is limited by a number of factors. In mountainous areas the land is unsuitable due to steep slopes. Sandy soil texture and poor drainage are major limitations on the sandy terraces and in the swamps, respectively, although some of the poorly drained areas may be suitable for cultivation of wetland rice.

In areas with undulating and rolling plains and medium to fine textured soils, the physical conditions are suitable for cultivation of arable and tree crops. However, the acid soil reaction and

Profile No. 9.

Location: Muarateweh, Transmigration Site SKP B SP 2, Central Kalimantan. (0° 33' S, 114° 43' E)
Parent Material: Limestone
Slope: 3%
Vegetation: Agricultural crops, no vegetation when profile description was made.
Classification: FAO-Unesco, Orthic Luvisol.
Soil Taxonomy, Typic Hapludalf.
Horizontation:

0-12 cm A	Brown to dark brown (10 YR 4/3), silt loam, moderate fine subangular blocky, friable, many fine and few medium roots, clear smooth boundary.
12-36 cm Bt1	Dark yellowish brown (10 YR 4/4), silty clay loam, weak fine subangular blocky, friable to firm, few fine roots, gradual smooth boundary.
36-63 cm Bt2	Yellowish brown (10 YR 5/6), silty clay loam, moderate medium subangular blocky, firm, no roots, clear smooth boundary.
63-92 cm Bt3	Yellowish brown (10 YR 5/8), silty clay, strong brown (7.5 YR 5/6) and light grey (10 YR 7/2) mottles, strong coarse subangular blocky, firm, no roots, clear smooth boundary.
92-150 cm BC	Brownish yellow (10 YR 6/8), silty clay loam, light grey (10 YR 7/2) and red (2.5 YR 4/8) mottles, strong coarse subangular blocky, very firm, no roots, some limestone gravel.

Profile No. 9. Analytical Data

Depth	Texture *(%)*			pH		C	N	C/N
(cm)	Sand	Silt	Clay	H_2O	KCl	(%)	(%)	
0-12	24	53	23	5.7	5.3	2.5	0.20	13
12-36	17	45	38	5.3	4.6	0.7	0.10	7
36-63	17	47	36	5.0	4.0	0.5	0.09	6
63-92	15	44	41	4.9	3.8	0.4	0.07	5
92-150	13	48	39	5.1	4.1	0.2	0.08	3

Depth	Exchangeable cations (me/100g)							
(cm)	Ca	Mg	K	Na	Al	a	b	c
0-12	15.2	0.1	0.2	<0.1	0.5	17.7	15.8	88
12-36	17.5	0.2	0.1	0.1	0.4	20.4	18.1	88
36-63	15.4	0.2	0.1	0.1	2.6	20.1	18.2	79
63-92	16.0	0.2	0.1	<0.1	4.0	21.4	20.2	77
92-150	22.1	0.3	0.2	<0.1	0.7	24.9	23.3	91

a, b, c: see Profile No. 1

the low soil fertility are serious limitations. Permanent cultivation of arable crops, therefore, requires regular applications of lime and of all major fertilizer elements, and cultivation of tree crops requires at least fertilizer applications. Furthermore, when planning application of lime and fertilizers, the low cation exchange capacity and the high degree of leaching must be taken into account. The introduction of agricultural systems based on permanent cultivation of the land will also entail a number of problems caused by the weakly developed infrastructure.

References

Bemmelen, R.W. *van* (1949): The geology of Indonesia. Vol. I A. General geology of Indonesia and adjacent archipelagoes. Government Printing Office, The Hague.

Buurman, P. & Subagjo (1980): Soil formation on granodiorites near Pontianak (West Kalimantan). In Red Soils in Indonesia. Agricultural Research Reports 889. Bulletin No. 5, Soil Research Institute, Bogor. Ed.P. Buurmann: 106-118. Centre for Agricultural Publishing and Documentation, Wageningen.

FAO (1988): FAO-Unesco soil map of the World. Revised legend. World Soil Resources Report 60. FAO, Rome.

FAO-Unesco (1974): Soil map of the World 1:5,000.000. Volume I. Legend. Unesco, Paris.

FAO-Unesco (1979): Soil map of the World 1:5,000,000. Volume IX. Southeast Asia. Unesco, Paris.

Grüneberg, F., Hoffmann, R. & Nitsch, M. (1983): Böden der humiden Tropen und Probleme ihrer Nutzung, dargestellt an Beispielen aus der indonesischen Provinz Ostkalimantan. I. Böden aus miozänen Sedimentgesteinen. Giessener Beiträge zur Entwicklungsforschung. Reihe I, 9: 109-28. Tropeninstitut Giessen.

Hamilton, W. (1979): Tectonics of the Indonesian region. Geological Survey Professional Paper 1078. United States Government Printing Office, Washington, D.C.

Koteswaram, P. (1974): Climate and meteorology of humid tropical Asia. In Natural Resources of Humid Tropical Asia. Natural Resources Research XII: 27-85. Unesco, Paris.

Larsen, E. W. (1989): Pedologiske og edafologiske undersøgelser af to Ultisols fra Kalimantan, Indonesien. Hovedopgave. Kemisk Institut, Kgl. Veterinær- og Landbohøjskole, København.

Petersen, L. (1987): Conditions for agricultural development in Central Kalimantan, Indonesia. Geografisk Tidsskrift, 87: 49-56.

Soil Survey Staff (1988): Keys to Soil Taxonomy (fourth printing). Soil Management Support Services. Technical Monograph No. 6. Ithaca, New York.

Verheye, W. & Tessens, E. (1980): The Latosol and Podzolic soil concepts in Indonesia. In Proceedings of the Conference on Classification and Management of Tropical Soils 1977. Ed. K.T. Joseph: 168-74. Kuala Lumpur.

A study of crusts and their effect on water balance of some Nigerian soils

Merete Styczen

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A study of crusts and their effects on physical soil properties and water balance of the soils were carried out at four sites (Samaru, Kwello, Jos, and Ibadan) in Nigeria. The crusts occurred primarily on degraded soils, and were often connected with erosion. Micromorphological studies showed smaller contents of organic matter in the crusting soils, as well as a high degree of compaction and few, if any, continuous pores in the crust. Calculations, taking into account the reduced hydraulic conductivity of the crusted soils, indicated that crusts lead to a shorter potential growth period and an increased risk of crop failure.

Keywords: *crusting soils, structure, water balance, crop failure.*

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One of the effects of land degradation, particularly on soils dominated by fine sand or silt, is crusting. Crusting and water erosion are parts of the same complex. Degraded soils are more susceptible to both erosion and crusting due to their poor structure, and because the hydraulic conductivity of a crust is low, much runoff is generated on these soils. As part of a larger study of physical and chemical consequences of soil erosion in Nigeria, crusts were found to have profound influence on water availability for crops. This article deals with some characteristics of the crusts encountered as well as their physical consequences.

Fig. 1. The location of the chosen sites in Nigeria. Samaru is situated near Zaria and IITA near Ibadan.

Location and soils

The soils are situated near Samaru, Kwello, Jos, and at the International Institute of Tropical Agriculture, IITA, Ibadan, Nigeria (fig. 1). At Samaru and at IITA, the parent material is Precambrian Basement Complex, mainly composed of granite, gneiss, and schist, while at Kwello it is Metasediments, and at Jos it s pyroclastic vulcanic material.

In Samaru, four sites were chosen. Number one did not show signs of accelerated erosion, number two and three were eroded, and number four is an example of a soil which develops, when erosion has truncated the soil. At each of the three other localities, two profiles where chosen. In Jos and at IITA, the profiles representing the "non-eroded" state did not show signs of erosion, while in Kwello, it might have been subjected to accelerated erosion earlier. In Samaru and Jos, the "non-eroded" profiles were under grass, while at IITA it was under forest. In Kwello it was under the first year of cultivation after bush fallow. The remaining profiles were all in or at the edge of cropped areas.

Methods

For each soil a profile was described, and samples were collected for analysis. For the upper two horizons, samples were collected for micromorphological descriptions which were carried out according to Bullock et al. (1985). For detailed descriptions, see Styczen (1988).

Textural analysis, bulk density determination and clay mineralogical analysis as well as different chemical analyses were made (Styczen, 1988, 1990).

Results of field and physical investigations

Soil classification

The soils were classified according to Soil Taxonomy at sub-group level (table 1). Almost all soils are Alfisols, except the recently exposed Samaru 4 soil which is an Entisol. Samaru 2 has plinthite at a depth of 125 cm, so erosion may change its classification to a Plinthustalf. The soils classified as Paleustalfs have a stronger red colour in the lower part of the argillic horizon than the Haplustalfs.

Profile descriptions

From the descriptions of the Samaru soils it appears that the consistency in the upper horizon differs between uneroded and more eroded soils. The classification changes from "slightly hard" for Samaru 1 to "hard" and "very hard" for Samaru 2 and 3. The eroded soils appear to have a surface crust. The consistence of the IITA soils determined under moist conditions changes from "friable" in the non-eroded soil to "firm" in the eroded soil, and both the Kwello soil and the Jos soil develop crust when eroded. The structure of the upper horizon of the Kwello soils changes from granular in the uneroded soil to porous-massive in the eroded soil.

Table 1. Results of classification of ten Nigerian soils (Soil Taxonomy).

Site	Non-eroded	eroded	Strongly	eroded
Samaru	Ultic Haplustalf	Ultic. Haplustalf	Plinthustalf	Typic Ustorthent
IITA	Oxic Paleustalf	Oxic Paleustalf		
Jos	Ultic Haplustalf	Ultic Paleustalf		
Kwello	Ultic Haplustalf	Ultic Haplustalf		

In general, the trend is that the porosity, the number of roots and the termite activity is greatest in the non-eroded soils. The clearest trend, however, is the deteriorated structure in the upper layers of the eroded soils and the greater hardness when the soils are dry.

Thin-section descriptions

For the Samaru soils, the observations in the field are supported by the thin-section studies. The microstructure is clearly different in the non-eroded and the eroded soils. While Samaru 1 is quite porous in both horizons, Samaru 2 has a surface crust. At the top of this surface crust, large vesicles are surrounded by well sorted quarts grains (zone 1). Beneath is a thin, massive layer of finer sand and clay without visible pores (zone 2). The third layer (zone 3) is compact, with bridged grain to intergrain microaggregate structure and a total pore volume of approximately 25 %. The structure known from Samaru 1 (spongy structure) is found at a few cm depth only.

In case of Samaru 3 it could be seen that the hard surface is not a crust but the top of a Bt-horizon which is rather massive in structure. The soil has evidently been truncated by erosion. The pore volume of the surface of this layer is estimated to 10 %[1]

The thin section studies support the horizontal division of the profile and reveals an ongoing enrichment of the soil by aeolian material. The occurrence of easily weathered materials such as feldspar and mica in the topsoil of an otherwise strongly weathered soil can best be explained by supposing that they have been brought with the wind from Sahara.

The IITA-soils in particular are marked by their content of organic material. Different types of egg-shaped excrements are present in large amounts in several of the thin sections, probably from oribatid mites. The mineralogical fraction is uniform in the four sections studied, but the structure of the organic material differs. In the forest soil the fine material seems to be made up of faeces in more or less decomposed form (coalescing and disintegrating). The material appears organized. In the eroded soil, the amount of organic material seems less and the degradation more advanced, although the colouring of the fine material is almost as strong. It is difficult or impossible to distinguish the condensed excrements from the general granular structure of the matrix.

Another indicator of the changes in biological activity is the fact that there are more undecomposed fine roots in the eroded soil than in the forest soil, probably because the biological activity is less in the latter. In thin sections of the eroded soil 15-20 % of the thin section consists of identifiable plant material, while in the forest soil there are 4-10 % identifiable plant material in the upper 7 cm and only 2 % in 8-15 cm depth.

The conclusion is that the biological activity is significantly greater in the forest soil than in the cultivated soil. Plant material degrades quicker and the organization of the soil in "lumps of excrements" seems to create a very stable structure. Only the cropped soil was found to crust.

Also the eroded soils in Jos and Kwello crust easily. In case of the Jos soil, the most visible change was loss of fine material. While the sand grains are embedded in fine material in Jos 1 (porphyric structure), the fine material only creates bridges between the sand grains in Jos 2 (gefüric to chitonic structure).

The changes in the eroded Kwello soil, compared with the uneroded one, resemble very much the changes observed in the Samaru soil. The non-eroded soil has a moderately developed subangular blocky structure in the top layer and a vuggy structure in the deeper ones. As Samaru 2, Kwello 2 contains four zones of which the upper zone consists of very well sorted quarts grains ordered around large vesicles (zone 1), followed by a thin clay enriched layer (zone 2) and a closely packed layer (zone 3) before the structure resembles the structure of Kwello 1 at depth (zone 4). The clay of the crust is dark coloured, either due to humus or to sesquioxides, the last explanation being the most likely. Less fine material surrounds the sand grains in Kwello 2 compared to Kwello 1 (chitonic and gefüric structure, respectively). Furthermore, the content of organic material is higher in Kwello 1 (2-5 %) than in Kwello 2 (less than 1 %).

Physical changes - Discussion

Crust formation is, as phenomenon, described by Kowal (1972) with special reference to Samaru, and in a more general manner by, among others, McIntyre (1958), Chen et al. (1980) and Hoogmoed and Stroosnijder (1984). Hoogmoed and Stroosnijder describe two types of crust:

a) An almost invisible type, which usually is found on soils with a small content of clay and silt (maximum 5 % particles less than 50 μm. The crust is formed when raindrops separate clay and silt particles which are then transported by the infiltrating water. The process, by which the particles clog up the pores between the sand grains are described by Chen et al. (1980).

b) An easily visible type with a thickness of at least some

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[1] The pore volume may be estimated with a high degree of certainty for single thin slides, but it takes a large number of slides to determine the pore volume in the soil and its variability in three dimensions. The pore volumes have been estimated for one or two slides only for each sample.

> millimetres. This type of crust is found on aggregated (loamy or clayey) soils, and it is formed by destruction of aggregates by immersion or direct raindrop impact. When water penetrates the surface which is sealed, air cannot escape, and air bubbles are concentrated beneath the crust. This may create an almost pumice-like appearance. The crust reduces infiltration and may be hard for germinating plants to penetrate.

The description of a crust as a thin massive layer composed of fine material which fills up the space between sand grains (zone 2) over a compact, sometimes horizontally oriented, layer (zone 3) was also given by McIntyre (1958) and by Chen et al. (1980). The upper layer identified in the thin section descriptions (zone 1 in both Samaru 2 and Kwello 2), is, however, not mentioned by the two authors. The zone consists of coarse sand, sometimes mixed with small amounts of fine material. The layering is very characteristic, as the sand surrounds well rounded vesicles. An explanation of the phenomenon could be that air bubbles, perhaps released during infiltration of water, can be caught in the material being transported along the soil surface (bedload). Firstly, it is only the heaviest particles which are transported in this way. This could explain the very fine sorting of the material in zone 1. Secondly, as the particles move in a rolling/jumping manner, air bubbles may be caught. It is easiest to visualize the process taking place in connection with sedimentation. As phenomenon it could be thought to resemble "bubble sand" which forms when waves rolls over a beach and sedimentation takes place rapidly. In this case bubbles are caught in the sediment, and the sand ends up with a spongy structure (Reineck & Sing, 1980). The vesicles, cause the porosity to be high, but with little positive effect on the hydraulic conductivity.

At Samaru Kowal (1972) found that the crust has clearly visible layers of sand in disperse and compact form alternating with thin layers of finer material. Kowal also found that the bulk density in the compact layer was 1.6-1.7 g/cm^3, compared to 1.4-1.5 in the underlying soil. Similarly, the total porosity increased from 35-39 % in the crust to 43-48 % in the underlying soil. From the thin sections is seen an even greater reduction of the pore volume in the most compact layer, where less than 10 % is taken up by pore space. From the pF-curves Kowal finds that the total volume of pores above 17.3 μm in diam. is very small indeed. In the present study, bulk density increases were found only in soils cleared by machines.

Norton (1987) found that the total porosity of the crust was not related to differences in infiltration rates, the amount of splash erosion or the hardness of the crust. The infiltration rate was better correlated to the volume of planar pores.

Infiltration measurements from Samaru show that the hydraulic conductivity decreases from around 50 mm/hr to 10 mm/hr, when the crust is formed over two rain events (Kowal 1972). The hydraulic conductivity of well developed and probably also sesquioxide-stabilized crust in Samaru can be expected to be much lower.

Agassi et al. (1981) found that crusting also depends on the ESP of the soil as well as ion strength and ion composition in the rainwater. The weaker the ion strength and the higher the ESP, the greater the tendency to crust formation. The effect of ion strength may, however, be expected to be of less importance on kaolinitic soils than on the more lime-rich and the mineralogically different Alfisols (Typic Rhodoxeralf, Calcic Haploxeralf) examined in this study.

Effect of crusting on the water balance of the soil

The calculations of water balance

With the aim of estimating the effect of erosion on the water balance and plant growth, a number of calculations were carried out. Only the results from Samaru and IITA will be presented. The effect on crop growth of reduced soil depth due to erosion and increased surface runoff due to crusting is compared.

The calculations for Samaru, Jos and Kwello are made on the basis of meteorological and soil physical data from Kowal and Knabe (1972). Average rainfall and evaporation data are given for periods of 10 days. It is not clear exactly which years form the basis for the average values, and it may be noted that the average rainfall may well be higher than that if the measurement period includes the rainfall-wise anomalously good 1950s. From the end of the 1950s and until 1984 the amount of rainfall has decreased substantially all over West Africa (a.o. Todorov, 1985).

The calculation for IITA is based on daily observations from 1.1.1979 to approximately the 10.10.1985. Data from 1979 to 1983 stems from Lawson: Weather Bulletin (IITA).

For the analysis of water balance the dates of the beginning and the end of the growing period were calculated according to a modified version of the definition given by Kowal and Knabe (1972). For average 10-days-values of rainfall, the beginning of the rainy season is defined as the first 10-day period receiving 25 mm of infiltrated rain or more, which is followed by a 10-day period in which the amount of infiltrated rainfall is at least equal to half of the potential evaporation. For data for individual years (IITA), the variability, even for 10-day periods, is large and the definition needs to be strengthened further. It is assumed that the rainy season cannot start before April 1st and two 10-day-periods in succession receiving a rainfall amount of less than half of the potential evaporation must not occur within the first 50 days. The end of the rainy season is defined as the last 10-day period receiving at least 12.5 mm of rain and with an evaporation in the following period which is greater than the precipitation. The growing period is prolonged beyond the rainy season with the time it takes to evaporate the amount of available water in the profile. Furthermore, for IITA a stress index is calculated as the sum of the moisture deficits, when all available water has been extracted, divided by the daily evaporation at the particular time:

$$\text{Stress index} = \sum^{i} | (P-E+S) | /E$$

where

i is the number of times P-E+S (mm/10-day-period) is negative within the growing period,

Table 2. Rainfall and evaporation at Samaru, calculated for 10-day-periods. The accumulated surplus assuming 0 and 25 % runoff is calculated for a profile containing 100 mm of water. All figures are in mm. Data from Kowal and Knabe (1972).

Month	Period	Evap.	Prec.	Acc. Surpl.	Acc. Surpl., 25 % runoff.
Jan	1-10	36.8	0		
	11-20	37.1	0		
	21-31	41.7	.3		
Feb	1-10	42.2	.3		
	11-20	43.2	.5		
	21-28	35.3	.8		
Mar	1-10	47.2	.3		
	10-20	46.5	4.3		
	21-31	52.8	2.5		
Apr	1-10	51.1	7.1		
	10-20	51.3	9.4		
	21-30	50.8	20.3		
May	1-10	49.3	32.5		
	10-20	50.3	41.4		
	21-31	54.1	58.2	4.1	
June	1-10	45.7	46.2	4.6	
	10-20	40.6	59.4	23.4	3.9
	21-30	45.7	46.2	44.2	9.7
July	1-10	37.3	58.4	65.3	16.2
	10-20	35.6	70.4	100	33.4
	21-31	34.8	92.7	100	68.2
Aug	1-10	32.0	82.5	100	98.1
	10-20	31.8	88.4	100	100
	21-31	33.3	110.5	100	100
Sep	1-10	34.5	94.5	100	100
	10-20	34.3	82.6	100	100
	21-30	38.1	53.3	100	100
Oct	1-10	38.1	22.9	84.8	79.0
	10-20	38.6	9.9	56.1	47.9
	21-31	42.9	3.3	16.4	7.4
Nov	1-10	35.5	.5		
	10-20	36.1	.5		
	21-30	37.1	.3		
Dec	1-10	34.5	0		
	10-20	34.3	0		
	21-31	37.6	0		

S is stored moisture,

P is precipitation, and

E is evaporation (as denominator measured in mm/day).

A large number of stress days means that the plant must have been hampered in its growth, or has died before the end of the growing period.

The date where 10 mm of water is stored in the profile for the first time during the rainy season is also used as an indicator of water status of the soil.

Water balance at Samaru

In table 2 are shown Kowal's data for rainfall and

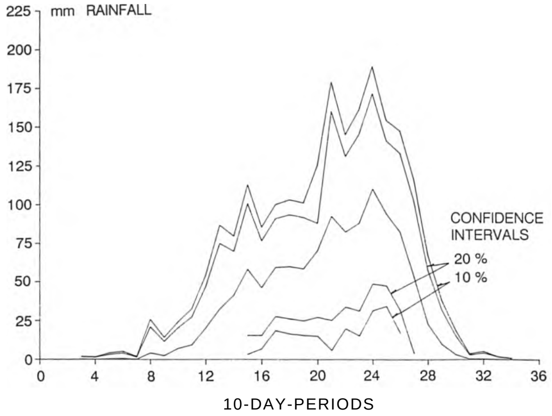

Fig. 2. The average rainfall distribution for Samaru, shown for 10-day-periods. The 10 and 20 % confidence interval-lines should be read vertically. Example: For period 16, there are (100 - 20 =) 80 % probability for receiving between 15 and 77 mm rainfall.

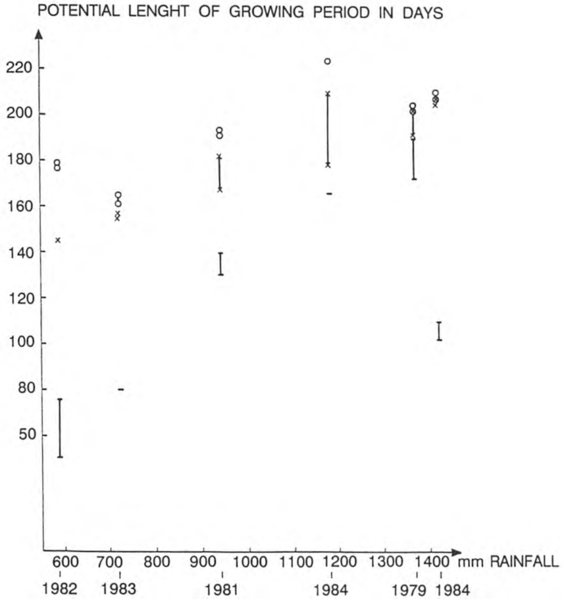

Fig. 3. Dependency of the growing period on rainfall, infiltration, and retention capacity of a soil like IITA-1 in the years 1979-84. The signatures (0) corresponding to 100 %, (x) to 75 % and (-) to 50 % infiltration. The assumed available water content was 35 and 25 mm, 35 mm corresponds to the upper end of the line.

evaporation at Samaru, together with the accumulated surplus (if any) under the assumption of 0 and 25 % surface runoff. Using the above definition, the growing season begins 1-10th of May assuming 0 % runoff and 11-20th May assuming 25 % runoff. 50 % runoff would cause the date to be moved 10 days further. Furthermore, an accumulated surplus of 10 mm occurs 3 weeks later at 25 % runoff than at full infiltration. Taking into consideration the reduced amount of available water in the root zone and the variability of the rainfall (fig. 2), it is clear that the risk of crop failure is increased in the beginning of the growing season. If there is none or only a small amount of stored water in the soil, the crop is highly dependent on the rainfall distribution and the danger of the plants drying out is increased. The variability of the rainfall is shown in fig. 2. Confidence intervals of 10 and 20 % are marked. At the end of the growing season only a few days are lost when the runoff increases from 0 to 25 %.

The beginning of the growing period is independent of the depth of the potential root zone, while the end of the growing period is not. In a well drained area, the depth of the soil is important, when the root growth is restricted downwards. Using a potential rooting depth of 190 cm on Samaru-1 and 80 cm on Samaru-4, the potential growing period may be calculated as 212 and 162 days, respectively.

Reduced entrance of water into the subsoil is another direct effect of the increased runoff amount. In the calculated example, the throughflow in 75 cm depth is reduced by 63 %. Assuming 46 % runoff, no throughflow takes place in 75 cm depth.

Water balance at IITA

For IITA, the available water content was calculated according to Moormann et al. (1975), taking into account field capacity and wilting point, volume weight and gravel content of the soil. The estimates for the soils were 16.5 mm in the forest and 31.1 mm in the cropped area, due to the presence of a gravel layer at shallow depth. As for Samaru, the calculations indicate that the beginning of the growing period is not dependent on the depth of the potential root zone, but on the possibilities of infiltration. This effect becomes more pronounced when less water infiltrates. The difference between the beginning of the growing period at 0 and 25 % and 25 and 50 % runoff is on an average 6 days and approximately 26 days respectively (fig. 3).

If 50 % of the water runs off, two of the growing periods investigated become so short and with so great a moisture deficit that total crop failure must be expected. From fig. 3 it is clear that the longest growing periods are found when full infiltration is possible. A large amount of rainfall does not necessarily compensate for the reduced infiltration, if it is not suitably distributed (i.e. 1980). Fig. 3 should be considered together with fig. 4, which shows the number of stress days. The growing period may, even at 50 % runoff in 1981 and 1984 be rather long, but the number of stress days within the period is also rather large. This is true also at 0 and 25 % runoff in 1982. On the other hand, the growing period at 50 % runoff in 1980 was so short that there are hardly any stress days within that period. From fig. 4 it appears that the number of stress days depend on both the profile depth and the runoff coefficient.

Another way of evaluating the problem of decreasing length of the growing period is shown in fig. 5. It describes the number of seasons out of six, when a harvest can be expected, as a function of the duration of crop growth. If the amount of potentially available water in the root zone decreases from 35 to 25 mm, and assuming 25 % runoff, the number of good seasons for a 200-day crop is reduced from 3 to 1. Likewise, the number of seasons is decreased from 4 to 2 good seasons for a 180 day-crop. In case of a runoff 50 %, a crop of 200 days duration cannot survive at all, while a crop of 120 days can survive in 3 seasons out of 6. Fig. 6 shows the length of the growing period for a number of crops suitable for the study area. The result of increasing runoff is a reduction in choice of 'secure' crops and varieties.

Measured values of erosion at IITA are between 1 and approximately 20 t/ha per year. Assuming 15 t soil loss/year, which equals a loss of 1 cm in a 10-year period, the growing period is reduced with 0.3 days over the 10 years due to loss of soil depth (assuming zero weathering). A crust may, on the other hand, be formed in very short time, e.g. during one storm. A decrease in infiltration to 75 % equals, in average, 17 days

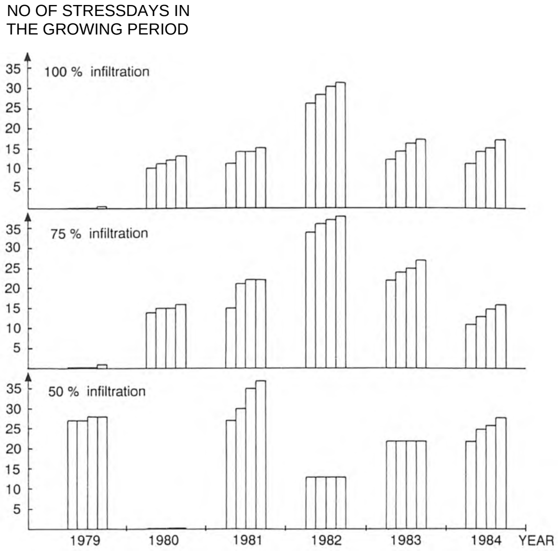

Fig. 4. Number of stress days in the growing period for the years 1979-84 as a function of per cent infiltration and the available water content of the root zone. 1) 35 mm 2) 30 mm, 3) 27.6 mm and 4) 25 mm available water in the root zone.

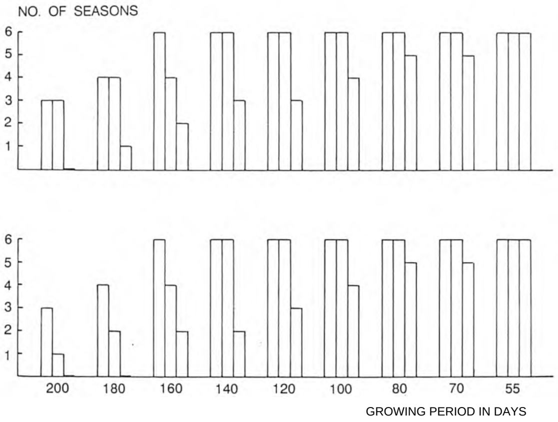

Fig. 5. The number of seasons out of 6 (1979-84), where a crop with a growing period of a given length could finish its development, assuming 1) 100 %, 2) 75 % and 3) 50 % infiltration. In the calculations were assumed a) 35 mm and b) 25 mm available water in the root zone.

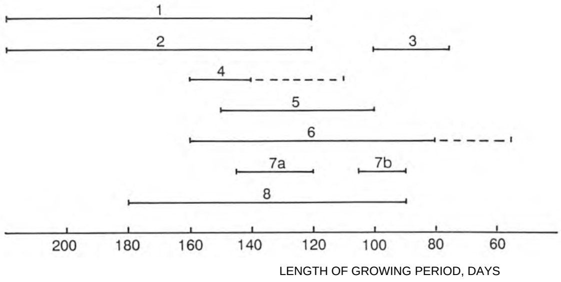

Fig. 6. The length of the growing season for a number of Nigerian crops. 1) Sorghum 2) Maiwa-millet, 3) Geromillet, 4) Maize, 5) Rice, 6) Cowpea, 7) groundnut- a) with alternating branching b) with sequential branching. 8) Soyabean.

shorter growing period. A further decrease of infiltration of 5 % shortens the growing period with a further 13 days. Similar calculations can be made to evaluate the effect of crusting on groundwater recharge. The calculations indicate that the changes of infiltration in these soils have a stronger effect on the growing conditions than any other parameter connected with water balance and erosion. The infiltration changes are partly a consequence of the decreased content of organic material, exposure of the soil surface, less soil faunal activity, unstable aggregates and structure, etc., and partly a consequence of the erosion processes themselves, particularly splash erosion.

Water balance calculations - Discussion

An obvious question to ask is whether the runoff percentages used in the calculations are realistic. For Samaru Kowal (1970) reports an average of 21.4 % surface runoff as percentage of yearly rainfall and 29.3 % surface runoff as percentage of the rainfall in the rainy season. For the same area Lawes (1965) measured up to 70 % runoff. The largest amount of runoff occurs in July-August, when the soil is saturated.

For IITA Lawson et al. (1981) and Lal (1976, 1984) report on the basis of different trials between a few percent and 40 % runoff, depending on the slope and the treatment of the area. Another study reports a decrease in infiltration rate of 40 and 70 % respectively, when the land use is changed from forest to maize and bare fallow (Lal et al. 1974). The effect was due to crust formation. Typical values for surface runoff is 20-30 % in the first season and 11-20 % in the second season for conventional tillage. The distribution is probably due to the fact that the heaviest showers fall in the beginning of the rainy season, while the later part of the rainy season is characterized by less intense storms. During single storms the amount of runoff may exceed the average values. The chosen parameters should therefore be within a realistic range.

It appears from the calculations that the reduced infiltration - with or without a reduced potential root zone means a decrease in the length of the growing period, an increase in the number of days during the growing period where the plant suffers from lack of water, and an increased risk of crop failure. This means a decrease of the possible choice of crops and varieties and a smaller potential yield.

There may be other effects. The root growth may be limited to the topsoil if the soil does not become wet at depth. This means that a smaller soil volume is available for nutrient extraction. Another problem is connected with the photoperiod of the crop. Kassam and Andrews (1975) found that for each week the sowing of sorghum is delayed after the 26th May in the Samaru area meant 360 kg/ha less yield. This should be seen in relation to a maximum yield of approximately 3500 kg/ha. Seen in relation to the increased risk in the beginning of the growing season (fig. 2) it appears that in case of 100 % infiltration the farmer has an average of around 20 days for ploughing and sowing before yield losses occur. In case of 75 % infiltration he has around 10 days and in case of 50 % infiltration, the seed bed preparation can only be carried out after the sowing ought to have taken place.

Hoogmoed and Stroosnijder (1984) have reached similar conclusions during studies of water balance on crust forming soils in Mali. In the study, a growing season at 50 % runoff was found to be 75 days in normal years and 50 days in dry years. This should be compared to a theoretically reachable growing season of 90-105 days in normal years and 70-90 days in dry years with

100 % infiltration. In an observed storm of more than 80 mm, 80 % of the rainfall was lost as surface runoff. The authors estimate the increase per day of growth extra in the period from sowing to flowering to be 10 kg of millet/ha compared with a normal yield of 500 kg/ha.

Conclusion

The calculations indicate that changes of infiltration in these Nigerian soils have a stronger effect on cropping conditions than any other parameter related to water balance and erosion. The changes of infiltration are partly a consequence of the general degradation, that is a decrease in content of organic material, exposure of the soil surface, less soil faunal activity, decreased aggregation and structure, etc., and partly a consequence of the erosion process itself, particularly splash erosion.

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References

Agassi, M., Shainberg, I. & Morin, J. (1981): Effect of electrolyte concentration and soil sodicity on infiltration rate and crust formation. Soil Sci. Soc. Am. J. 45: 848-51.

Bullock, P., Fedoroff, N., Jongerius, A., Stoops, G., & Tursina, T. (1985): Handbook for soil thin section description. Waine Research Publications. 152 p.

Chen, Y, Tarchitzky, J., Brouwer, J., Morin, J. & Banin, A. (1980): Scanning electron microscope observations on soil crusts and their formation. Soil Science, 130: 49-55.

Hoogmoed, W.B. & Stroosnijder, L. (1984): Crust formation on sandy soils in the Sahel. I. Rainfall and infiltration. Soil and Tillage Research 4: 5-24.

Kassam, A.H. & Andrews, D.J. (1975): Effects of sowing date on growth, development and yield of photosensitive sorghum at Samaru, Northern Nigeria. Expl. Agric.: 11: 227-40.

Kowal, J. (1970): The hydrology of a small catchment basin at Samaru, Nigeria. III. Assessment of surface runoff under varied land management and vegetation cover. Nigerian Agric. J., 7 (2): 120-33.

Kowal, J. (1972): Study of soil surface crusts in the loess plain soils of Northern Nigeria. Nigerian J. Sci., 6 (1): 93-100.

Kowal, J. & Knabe, D. (1972): An Agroclimato-logical Atlas of the Northern States of Nigeria. Zaria, Ahmadu Bello University Press, Nigeria.

Lal, R. (1976): Soil erosion on alfisols in Western Nigeria. I. Effects of slope, crop rotation and residue management. Geoderma, 16: 363-75.

Lal, R. (1984): Mechanized tillage systems effect on soil erosion from an alfisol in watersheds cropped to maize. Soil and Tillage Research 4: 349-60.

Lal, R., Kang, B.T., Moormann, F.R., Juo, A.S.R., & Moomaw, J.C. (1974): Soil management problems and possible solutions in Western Nigeria. Paper presented at the seminar on the Soil Management and the Development Process In Tropical America, held at Centro Internacional de Agricultura Tropical, Cali, Columbia, Feb. 1974.

Lawes, DA. (1965): A note on the moisture storage capacity of the Samaru soils, Northern Nigeria. Samaru Miscellaneous Paper, No. 5. Institute of Agricultural Research, Samaru, Nigeria.

Lawson, T.L. (1979-1983): Weather Bulletin Jan-Dee. 1979 (80, 81, 82, 83). International Institute of Tropical Agriculture, Ibadan, Nigeria.

Lawson, T.L., Lal, R., & Oduro-Afriyie, K. (1981): Rainfall redistribution and microclimatic changes over a cleared watershed. In: Tropical Agricultural Hydrology, Lal, R. & Russel, E.W. (Eds.), John Wiley and Sons Ltd, London. p. 141-51.

McIntyre, D.S. (1958): Permeability measurements of soil crust formed by raindrop impact. Soil Sci., 85: 185-89.

Moormann, F.R., Lal, R., Juo, A.S.R. (1975): The soils of IITA. IITA Technical Bulletin no. 3. IITA, Ibadan, Nigeria. 48 p.

Norton, L.D. (1987): Micromorphological study of surface seals developed under simulated rainfall. Geoderma, 40: 127-40.

Reineck, H.-E. & Singh, I.B. (1980): Depositional Sedimen tary Environments. Second edition, Springer Verlag, Berlin. 552 p.

Styczen, M. (1988): Vandforårsaget erosion og jordbunds mæssige ændringer. Part of Ph.D. Thesis. Royal Veterinary and Agricultural University, Copenhagen.

Styczen, M. (In press): Nutrient and water balance on some eroded soils in Nigeria. Paper presented at the 6th. International Soil Conservation Conference, Addis Ababa, Ethiopia, 10—16th of Oct. 1989.

Todorov, A.V. (1985): Sahel: The changing rainfall regime and the "normals" used for its assessment. J. Cli. Appl. Met., 24 (2): 97-107.

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