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PODZOLS AND PODZOLIZATION

BY

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COPENHAGEN 1976

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2000-11-75. K.&W.

Dr. J. H. V. van Baren
with compliments from
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Denne afhandling er af Den kgl. Veterinær- og Landbohøjskoles fagråd for grundvidenskab antaget til offentligt at forsvares for den jordbrugsvidenskabelige doktorgrad.

København, den 9. december 1975.
Søren Kjeldsen-Kragh
Formand for fagrådet for grundvidenskab

PREFACE

This book contains the results of research which I have carried out during several years at the Department of Soils and Agricultural Chemistry of the Royal Veterinary and Agricultural University, Copenhagen. The final treatment of the material and the writing of the book were done while I was a faculty member of the Asian Institute of Technology, Bangkok.

The research was initiated following a suggestion by Professor, dr. agro. Kjeld Rasmussen, and he has constantly encouraged and adviced me during the progress of the investigations. I wish to express my sincere gratitude for the support I in these ways received from him. I also wish to thank my colleagues at the Department of Soils and Agricultural Chemistry and at Asian Institute of Technology for valuable help and discussions.

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CHAPTER 1

THE PODZOL CONCEPT

An important task of soil science is to explain the development of characteristic soil properties as these are found in nature. The basic ideas upon which the present concept of this soil formation or soil genesis is founded were laid down by the Russian soil scientist V.V. Dokuchaev in the latter half of the nineteenth century. In one of his major works Dokuchaev stated that the properties of soils were determined by climate, organisms,parent rock, relief and the passage of time. These five parameters have since become universally accepted as the soil forming factors.

Dokuchaev described a number of Russian soils and classified these according to their mode of formation. One of the soils discussed by Dokuchaev was the podzol. From Dokuchaev's point of view the characteristic feature of this soil was the presence of a grey or whitish soil layer (horizon) near the surface.

The designation 'podzol' was not introduced by Dokuchaev himself but was in vernacular use in Russia prior to his era. It is generally assumed to be formed from the preposition 'pod', meaning 'under', and the noun 'zola', meaning 'ashes' (Glinka 1926). Ponomareva (1964) assumes that the preposition 'pod' originates from the fact that the greyish (ashy) soil layer is usually found not at the surface but under some layer or layers with different properties. However, according to Muir (1961) and Ponomareva (1964), Dokuchaev explained the origin of the word as related to the soil layer underlying the ashes after shifting cultivation had entailed the burning of the forest. Muir (1961) also points to the possibility that the prefix 'pod' should not be interpreted as the preposition 'under', but as an ancient Russian noun related to the German 'Boden', the Greek 'pedon' and the Latin 'peda'. According to this assumption the original meaning of 'podzol' was simply 'ashy soil'.

According to Muir (1961) the term 'podzol' was used in some Russian papers translated into English and French at the end of the nineteenth century, but Ramann (1911) seems to be the first Western European soil scientist to have fully adopted the term. However, Ramann (1911) used it in a narrower sense than that in which it was used in Russia.

As stated above, Dokuchaev regarded the grey or whitish soil layer as the main characteristic horizon of podzols, and according to Muir (1961) neither he nor his pupils considered the underlying, sometimes highly coloured, soil layers as an integral part of the podzol profile. Although they assumed weathering and leaching processes to be the main cause of the formation of the bleached (eluvial) layer none of them suggested that a deposition took place in the underlying layers. As a bleached horizon could be found in clayey as well as in sandy soils, although perhaps to a different extent, no preference was given to either textural group in the use of the term 'podzol'.

However, according to Ramann's (1911) definition of 'podzol' it was mainly restricted to soils having a bleached layer as well as an underlying (illuvial) layer in which accumulation of coloured substances such as humus and/or iron oxides had taken place. Such soils were well known in Western Europe and had been subject to a number of investigations prior to the introduction of the term 'podzol'. A substantial contribution to the knowledge of these soils was made by Müller (1879, 1884), whom Muir (1961) regards as the greatest of the early writers on podzols. These investigations had brought out that the compounds removed from the eluvial horizon were, at least partly, deposited in the illuvial horizon. Furthermore, it was well known that this kind of illuvial horizon was mainly limited to sandy soils. Hence, in the nomenclature suggested by Ramann (1911), the clayey soils were not considered podzols but fell into other categories, mainly the so-called 'brown soils' (German: 'Braunerden').

The findings in Western Europe on the relationship between the eluvial and illuvial horizons influenced the Russian soil scientists, of course, but some fundamental differences of opinion concerning the nature and the delimitation of these soils persisted. In the Russian clayey podzols the main characteristic of the illuvial horizon was often an elevated clay content as compared to the eluvial horizon and the parent material. This is illustrated by data presented in Glinka (1926),who was inclined to explain this as a translocation of more or less unaltered clay particles within the profile. However, according to Muir (1961), the early Western European soil scientist mostly thought of translocation, leading to the formation of the illuvial horizon, as taking place in solution. Soil scientists in Western Europe were, therefore, reluctant to accept a mechanical translocation of clay as podzolization. This is most clearly brought out by the later classification systems adopted in Western Europe where a clear distinction is made between soils having an illuvial horizon enriched with clay only and those showing true podzolization (Kubiëna 1953, Mückenhausen 1962, Avery 1965, Aubert 1965, 1968, Duchaufour 1968). The soils with a horizon enriched with clay only and assumed to be formed by a mechanical translocation of clay particles are called 'Parabraunerden' or 'sols lessivés', but not 'podzols'. In these classification systems the term 'podzol' is reserved for soils having an illuvial horizon enriched with humus and/or oxides and hydroxides of iron and aluminium.

Soils showing some characteristics of podzols but not developed to the stage defined as true podzols are frequently called 'podzolic' (Russian: podzolistii, German: podsolig, French: podzolique). The actual characteristics of these soils are of course dependent on the particular definition of the podzol.

In the description of different varieties of podzols and podzolic soils it has of course been necessary to employ a number of different terms in Soviet as well as in Western soil literature. Only one of these will be mentioned here, namely the term 'dernovo-podzolic' which is used extensively in the USSR. The term is usually translated into English as 'sod-podzolic' or 'turf-podzolic'. The main characteristics of this soil are, according to Vilenskii (1957) and Grechin et al. (1964), the presence of a bleached layer and an illuvial horizon enriched with clay. Further, it is distinguished from a true podzol by having a horizon containing well-decomposed organic matter overlying the bleached horizon. The true podzol has a layer consisting almost exclusively of poorly decomposed organic matter resting directly or almost directly on the bleached layer. As stated by Bunting (1965) and Nykvist (1968) a dernovo-podzolic soil seems to have many characteristics in common with a 'Parabraunerde' and a 'sol lessivé'.

The Western European trend towards a rather sharp distinction between soils showing clay migration or 'lessivage' only and those showing liberation of sesquioxides and migration of these and/or humus, and the reservation of the terms 'podzol' and 'podzolic' for the latter group, has caused a debate to arise among present-day Soviet soil scientists. Fridland (1958) suggested that the process of clay migration be distinguished from podzolization and called 'illimerization'. A distinction between the two groups of soils was also supported by Gerasimov and Glazovskaya (1960), Zonn (1969), Zonn, Nechaeva and Sapoznikov (1969), Kremer (1969), Gerasimov (1970), Zonn (1971) and Gerasimov and Zonn (1971). The terminology suggested by these authors varies, but in general they seem to prefer to maintain the term 'lessivage' for clay migration. However, some differences remain between the viewpoints of these authors and the principles used in Western soil classification. The sod-podzolic soils are still considered podzolic soils and seem to be distinguished from lessivé-soils by differences in the variation pattern of the $\frac{Al_2O_3}{Si\ O_2}$ -ratio down the profile. In a comparative study of three profiles specified as podzol, sod-podzolic and gray forest soil respectively, Zonn and Karpachevskii (1964) suggest no changes in nomenclature, although all these profiles are characterized more by a translocation of clay than of sesquioxides and/or organic matter. If the data given in the paper are compared with the modern American and World definitions of spodosols and podzols given later in this chapter, not even the soil called 'podzol' itself would qualify for classification among these soils.

Parfenova and Yarilova (1960) considered micromorphological, chemical and mineralogical properties of different soils and found no reason for separating lessivé-soils from podzols. Rode (1964) examined data published for 58 soil profiles and concluded that in most cases these had been formed without the participation of clay migration. He is of the opinion that the extent of clay migration must be very limited since most soil pores are too small to allow the passage of unaltered clay particles. Similar viewpoints are expressed by Ponomareva (1964). Rode (1970) assumes that the clay removal from the eluvial horizon involves a decomposition of the clay minerals and leaching of the decomposition products. The increased clay content in the illuvial horizon is believed to be due to clay synthesis within that horizon. Zaidelman (1970) found no reason for making a distinction between lessivé-soils and podzols in a study of the over-all composition of the inorganic soil fraction of different soils. He considers anaerobic conditions caused by overmoistening to be the major reason for the development of all the soils in question.

It is rather difficult from available sources to find out how a podzol or podzolic soil is actually defined in present Soviet soil classification.

A study of the papers of Glazovskaya (1966), Grigorev, Rudneva and Ufimtseva (1967), Rozov and Ivanova (1967, 1968), Tyurin (1965), Kovda, Lobova and Rozanov (1967a, 1967b) or Kovda et al. (1968), all dealing with soil classification, gives no answer to the problem in terms of defined soil properties. Perhaps the traditional, and presumably still prevailing, Soviet concept of podzols and podzolic soils is best reflected in the paper by Rode (1970) mentioned above. Rode states that podzolic profiles may be of three types: 1. The eluvial type characterized by the absence of accumulation (compared with the parent material) of both clay and sesquioxides; 2. the eluvial-clay-bearing type characterized by an elevated clay content in the layers below the eluvial horizon, where this clay enrichment is not due to illuviation from above but rather to 'internal soil weathering'; and 3. the eluvial-illuvial type characterized by a simultaneous accumulation of clay and sesquioxides in the illuvial horizon. The last type is the only one in which a horizon has received material from the layers above.

It will be seen that only the last type of podzolic profiles will include some soils compatible with the podzol concept as applied in Western Europe. All three types are characterized by eluviation and the concept is, therefore, closely related to the original description by Dokuchaev and his pupils pertaining to the presence of an eluvial horizon only. The importance of the bleached horizon is also stressed by the fact that this horizon in Soviet soil descriptions is called the 'podzolic horizon'. As will be demonstrated below, this is entirely different from the rules of the new American and World classification systems which assign major importance to the properties of the illuvial horizon.

In the USA there is a long tradition of soil classification and several systems have been employed in which the podzols and podzolic soils have occupied different positions. In the system used up to 1960 a number of rather different soils were classified as true podzols, brown podzolic, gray-brown podzolic, yellow podzolic or red podzolic (Baldwin, Kellogg and Thorp, 1938). Except for the true podzols and the brown podzolic soils these soils seem to be characterized more by a clay translocation than by a translocation of sesquioxides and/or humus, and they will, therefore, correspond more closely to the Soviet concept of podzolic soils than that represented by the present British, German and French soil classification schemes.

However, this was changed drastically in 1960 when an entirely new soil classification system was introduced in the USA (Soil Survey Staff 1960). This system is remarkable for at least two reasons. One of these is that practically all soil designations used previously have been replaced by entirely new expressions formed from Latin and Greek roots. Hence, no soils are classified as 'podzols' or 'podzolic' in this system. The second important feature of the system is that each taxonomic soil unit is to a large extent defined in physical and chemical terms which can be evaluated by objective measurements. The degree of subjectivity in soil classification is, therefore, greatly reduced as compared to previous systems in which the soil entities were mainly defined in morphological, and often comparative, terms. This is an advantage as far as soil classification is concerned but, on the other hand, it implies that soil classification is now removed from soil genesis and, as expressed by Smith (1968), "at least one additional step of reasoning is required to go from the definition of the taxa to the genesis or to the interpretation".

In this new American system (often called the Seventh Approximation) a clear distinction is made between soils showing clay translocation only and those showing translocation of sesquioxides and/or humus. The former are mainly classified in one of the orders alfisols or ultisols. The latter are referred to the order spodosols. The exact definition of spodosols entails that these soils must have a spodic horizon below an eluvial horizon. The spodic horizon has an illuvial accumulation of free sesquioxides and/or organic carbon. As stated by the Soil Survey Staff (1960), the spodic horizon must contain at least 0.29 % organic carbon or 1 % free sesquioxides in some part. Further, the $\frac{SiO_2}{R_2O_3}$ -ratio of the clay fraction must be less than that of the clay fraction of the overlying horizon to ensure that an increased sesquioxide content is not due to an accumulation of crystalline clay. The definition of the spodic horizon has been changed several times. Smith (1965) stated that the illuvial material must be amorphous, and in the definition quoted by Smith (1968) the spodic horizon is specified in terms of the amounts of Fe, Al and C that can be extracted by pyrophosphate-dithionite or citrate-dithionite, and by the change in cation exchange capacity due to this extraction. In the definition given in Soil Taxonomy (1970) major emphasis is placed on the presence in the spodic horizon of organic matter and organic iron and aluminium compounds. The chemical criteria to be met by the spodic horizon are that the amount of iron + aluminium that can be extracted by sodium pyrophosphate at pH 10 exceeds 20 % of the clay content and 50 % of the content of citrate-dithionite extractable iron + aluminium. Sodium pyrophosphate at pH 10 is assumed to extract mainly organic iron and aluminium compounds. Furthermore, the spodic horizon must lose 25% of its cation exchange capacity by shaking with citrate-dithionite and be developed to a certain stage defined by the product of the cation exchange capacity, corrected for the clay content, and the horizon thickness.

In Canadian soil classification, similar trends may be observed towards an exact definition of taxonomic units in physical and chemical terms, and towards a separation of soils with a clay translocation from those with a sesquioxide and/or humus translocation. Up to 1968 the two kinds of soils were classified within one order, the podzolic (Leahey 1965, 1968). The soils with clay translocation were called textural podzols by Stobbe (1965). However, in the revised system now used in Canada (Proceedings of the Seventh Meeting of the National Soil Survey Committee of Canada 1968) these soils have been referred to a new order, the luvisolic, and the podzolic order now consists entirely of soils with an illuvial horizon enriched with sesquioxides and/or humus. To be classified within the podzolic order the soil must contain at least one of the horizons Bh, Bhf, Bfh or Bf. The requirements of these horizons appear in Table 1.

Table 1. Definitions of Podzolic B Horizons in the Canadian Soil Classification System

Horizon symbol	Organic matter content	$\Delta Fe + \Delta Al$ 1)	$\frac{OM}{Fe}$ 2)
Bh	> 2 %	normally < 0.8 %	> 20
Bhf	> 10 %	> 0.8 %	< 20
Bfh	5-10 %	> 0.8 %	< 20
Bf	< 5 %	> 0.8 %	< 20

1) Difference in oxalate-extractable iron + aluminium between the horizon in question and the C horizon.

2) Ratio between organic matter content and oxalate-extractable iron.

In the international soil classification system adopted by FAO/UNESCO for the compilation of a soil map of the World (Definitions of Soil Units for the Soil Map of the World, with addendum, 1968, Supplement to Definitions of Soil Units for the Soil Map of the World 1968), a distinction is also made between the two kinds of soils. Those with a clay illuvial horizon are classified as acrisols or luvisols while those with an illuviation of sesquioxides and/or humus are classified as podzols. Even though the terminology is different the definition of a podzol soil in this system is practically identical to the definition of the order spodosol in the American system and even the term 'spodic horizon' is taken over from the American system.

Except for the Soviet concept, there seems to be a high degree of consistency among the definitions of podzols ('spodosols' in the American terminology) in the remaining contemporary soil classification systems. The basic feature of podzols and podzolic soils in all these systems is a liberation of sesquioxides and a downward translocation of these compounds and/or humus within the profile. Although the Soviet concept of these soils is somewhat broader it seems possible to specify a group of podzols which correspond closely to the Western definition. These are the so-called sandy humus-illuvial podzols described, amongst others, by Gerasimov and Glazovskaya (1960), Vilenskii (1961), and Ponomareva (1964).

The terminology of the different systems varies, and soils with properties intermediate between those of podzols or podzolic soils and some other kind of soil may well be classified in different ways in the different systems. However, this seems to be without importance for the present study, and it would furthermore be undesirable to limit the discussion to some narrow, arbitrarily defined group of soils.

A definition largely compatible with those of the systems mentioned will therefore be adopted here, but the arbitrary limits of the American, Canadian and World systems will not be observed. Hence, by a podzol is to be understood in what follows as a soil with signs of downward migration of sesquioxides and/or humus, giving rise to an eluvial horizon impoverished in sesquioxides and an illuvial horizon enriched with sesquioxides and/or humus. It is further understood that these phenomena are not due to a translocation of silicate clay only. From this definition the definition of podzolization is derived as the processes resulting in a podzol.

CHAPTER 2

ENVIRONMENT AND SOME GENERAL PROPERTIES OF PODZOLS

2.1 Horizontation

The profile of a well-developed podzol has a number of rather distinct horizons. Since the podzolization involves a migration of highly coloured substances such as humus and iron oxides the horizons are recognized visually more easily than in most other soils.

The upper horizon of a typical virgin podzol consists of poorly decomposed organic matter with only a small admixture of mineral material. In strongly podzolized soils this organic horizon may rest directly upon a layer of strongly bleached mineral material containing only minute amounts of humus. More often, however, a mineral layer with a dark colour originating from a considerable humus content is found between the upper organic layer and the bleached layer. Together these three layers form the eluvial horizon. The mineral material of all the layers of the eluvial horizon is bleached owing to the removal of iron compounds by leaching.

It is common practice to use capital letters as symbols for the so-called master horizons and to denote subhorizons within each of these by adding lower-case letters or numbers as subscripts to the capital letter of the master horizon. No universal convention exists on the use of such symbols. In Table 2 the symbols used by some of the major soil classification systems discussed earlier have been applied to an idealized podzol profile. These symbols should be regarded merely as examples, since other possibilities exist in some of the systems and the proper symbol to be applied will depend on the actual properties of the horizons in question. This applies especially to the symbols of the subhorizons.

Since the use of the symbols is mainly conventional, there are really no important reasons to prefer one system to another. In this text symbols similar to those used in the USSR and France will be adopted. This is mainly because these symbols represent the original principles according to which A denotes the eluvial horizon, B the illuvial, and C the parent material. Similar symbols are also applied by Joffe (1936), and they correspond closely to those applied by Rice and Alexander (1938) and Byers et al. (1938). When discussing podzol soils it seems undesirable to regard the subhorizons of the eluvial horizon as different master horizons. Fur-

Table 2. Horizon Symbols of Major Soil Classification Systems Applied to an Idealized Podzol Profile

	USA 1)	Canada 2)	USSR 3) and France 4)	World 5)
Horizon consisting mainly of poorly decomposed organic matter	0	L or F	A_o	0
Humus-containing mineral horizon	A1	Ah	A_1	A
Bleached horizon	A2	Ae	A_2	E
Humus illuvial horizon	B2h	Bh	B_1	B
Iron illuvial horizon	B2ir	Bf	B_2	B
Parent material	C	C	C	C

1) Soil Survey Staff (1960).

2) Proceedings of the Seventh Meeting of the National Soil Survey Committee of Canada (1968).

3) Grechin et al. (1964).

4) Duchaufour (1965).

5) Bulletin of the International Society of Soil Science No. 31 (1967). Supplement to Definitions of Soil Units for the Soil Map of the World (1968).

thermore, the symbols used by the other soil classification systems are sharply, but arbitrarily, defined in terms of the chemical and physical properties of the soil layers. Largely similar horizons might therefore require different symbols, and this seems rather artificial. To establish the proper symbols according to one of these systems a number of analyses would be required for this purpose only. For the present study the symbols based on morphological properties only seem satisfactory. The three subhorizons of the eluvial horizon will, therefore, be denoted A_o, A_1 and A_2 respectively.

Below the A horizon an illuvial horizon, or B horizon, is found. This is usually not homogeneous but may be subdivided into a number of subhorizons. The upper part will often have a dark colour due to an illuviation of humus compounds. This subhorizon will be called the B_1 horizon. As will be seen in subsequent chapters, humus is not the only material precipitated in this subhorizon but the colour is mostly due to humus compounds.

The lower part of the B horizon, B_2, is usually brownish or reddish-brown in colour, due to iron compounds. Other substances are precipitated in the subhorizon besides these, but the colour is mostly due to the iron compounds. The subhorizons of the B horizon will not usually be homogeneous throughout. The B_2 horizon especially may often be mottled or streaky, and usually tongues will extend downwards into the parent material. Sometimes these tongues may be of appreciable length and in each tongue a core of B_1 horizon may be present.

The material below the B horizon is usually considered to be fairly unaltered parent material. Its appearance will therefore depend on the character of this parent material. In most of the profiles investigated here, the parent material is rather coarse sand with a yellowish colour due to a coating of the sand particles with iron oxides. The parent material will here be denoted by the symbol 'C', and there is usually no reason for a subdivision.

The symbols mentioned are sufficient for the description of most of the soils investigated in this study. In a few cases some of the subhorizons have been further subdivided, and these sub-subhorizons will be symbolized by adding lower case letters after the subscript number indicating the subhorizon. The only significance of these letters is an indication of the vertical sequence. The uppermost layer of a given subhorizon will be denoted by 'a' (e.g. B_{2a}), the second layer by 'b' (e.g. B_{2b}), etc.

2.2 Climate

Being highly leached soils, podzols only occur in a humid climate where the precipitation considerably exceeds the actual evapotranspiration and hence leaves a considerable quantity of water to leach through the soil profile.

No definite relationship seems to exist between the temperature and the formation of podzols. In the earlier American soil classification system podzols and brown podzolic soils were considered zonal soils characteristically found in cool humid climates (Baldwin, Kellogg and Thorp 1938). Duchaufour (1968) and Scheffer and Schachtschabel (1970) also state that podzols are typically found in such climates. Duchaufour is of the opinion that podzols are typically formed only in a cold climate such as that prevailing in the northern parts of the USSR, Finland, Scandinavia and Canada. Whenever these soils are found outside these areas it is always due to specific local conditions and podzols will never, again according to Duchaufour, extend over larger areas in an Atlantic climate, while in the tropics they are extremely rare.

However, these statements seem to need some modifications. According to Soil Survey Staff (1960) spodosols may be found in all humid climates from boreal forests to the tropics. Podzols have been described in practically all European countries from Yugoslavia (e.g. Racz 1968) to Norway (e.g. Låg 1970). A number of authors, e.g. Barshad and Rojas-Cruz (1950), Bleackley and Khan (1963), Dudal and Moorman (1964), Klinge (1965) and Andriesse (1968, 1969), have described podzol soils in tropical areas. Some earlier descriptions are quoted by Mohr and van Baren (1959), and Klinge (1971) has given a review of the literature on podzols in the tropics. He concludes that podzols cover quite extensive areas in the humid tropics. They are found in lowlands as well as at higher elevations. Although some of the soils mentioned by Mohr and van Baren and Klinge may not meet the requirements of the definition of podzols applied here, there seems to be no doubt that podzols are quite common in the tropics.

Podzols have also been described in very cold climates. Kubota and Whittig (1960) and Stevens (1963) give descriptions of such soils from Alaska, and humus-illuvial podzols occur, according to Gerasimov and Glazovskaya (1960) and Ponomareva (1964), immediately south of the tundra zone in the USSR.

It may well be so that a cool climate favors some of the causes of podzolization, e.g. the accumulation of a mor-type humus (see chapter 4) through a reduced breakdown of organic matter, and possibly also a vegetation liable to promote podzolization. However, this does not mean that high temperature itself prevents or impedes podzolization. Evidence may in fact be produced to support the opposite trend as many of the podzols in the tropics have thick bleached horizons (Barshad and Rojas-Cruz 1950, Bleackley and Khan 1963, Andriesse 1969), while those in cold climates often have a very thin bleached horizon (Kubota and Whittig 1960, Stevens 1963, Ponomareva 1964).

Tonkonogov (1969, 1971) has shown that the occurrence of humus-illuvial podzols is governed to a larger extent by the texture and mineralogy of the parent material than by the climatic conditions. In conclusion it may be stated that podzols are found in all humid climates, although they seem to occur most frequently in cool humid climates.

2.3 Texture

It has already been mentioned that early West-European soil scientists found the most pronounced podzols on sandy soils, while a number of Russian soils classified as podzols or podzolic soils are developed on clayey parent materials. However, according to Gerasimov and Glazovskaya (1960), Vilenskii (1961), and Ponomareva (1964), the humus-illuvial podzols are found on sandy parent materials. The studies of Tonkonogov (1969, 1971) also clearly show that these soils are most highly developed on coarse, sandy parent materials.

In Denmark it has long been established that the majority of the coarse textured soils of glacial outwash plains have a horizon with an accumulation of sesquioxides and/or humus at some distance below the surface and that such horizons are generally absent in the soils developed on clayey moraines. This has been demonstrated by a number of authors, probably most clearly by Bornebusch and Milthers (1935). Although this may be partly due to a somewhat higher rainfall in the regions where most of the glacial outwash plains are situated, as compared to that in the regions where the moraines are dominant, it seems well established that the difference in the soil cover is related to differences in the textural composition.

According to Soil Survey Staff (1960) spodosols do not form in clayey parent materials. The term 'clayey' in this context probably means that the clay content is above 35 % (Soil Survey Staff 1951 and Soil Survey Staff 1960 Appendix 1). A podzol with a very thick A_2 horizon developed on extremely coarse water-sorted moraine has been described by Låg (1970).

Spodosols in the tropics seem, according to Soil Survey Staff (1960), to be limited to nearly pure quartz sand. Klinge (1971) also states that most tropical podzols are developed on quartz sand, but he adds that podzols may also be formed as secondarily developed soils on old latosolic soils. This secondary podzolization is also discussed by Mohr and van Baren (1959).

2.4 Vegetation

Many of the authors quoted earlier (e.g. Duchaufour 1968) and others (e.g. Ganssen 1957) state that the typical vegetation of podzol soils is coniferous forest, often combined with a herb vegetation of mosses. Also Soil Survey Staff (1960) states that most spodosols have had a coniferous forest vegetation while the spodosols of warmer regions are found under savannah or rain forest. According to the Proceedings of the Seventh Meeting of the National Soil Survey Committee of Canada (1968) podzol soils are developed under coniferous and mixed-forest vegetation and under heath vegetation. Scheffer and Schachtschabel (1970) and Bridges (1970) identify coniferous forest and Erica-species as the predominant vegetation of podzol soils.

In Denmark, where natural coniferous forests are at present hardly ever found, podzols occur mainly under heath vegetation. This appears for example from the works of Müller (1924) and Weis (1929, 1932). The dominant plant species of the heath is Calluna vulgaris, but Deschampsia flexuosa, mosses, and lichens are also very common. Müller (1879) also found podzols under Fagus sylvatica forest, and this is also demonstrated in the present study, see chapter 3.

There seems to be great uniformity among the authors quoted that podzol soils of the temperate regions occur mainly under coniferous forest or heath vegetation.

2.5 Drainage Conditions

Podzol soils have no universal drainage characteristics. Most authors (e.g. Duchaufour 1968, Scheffer and Schachtschabel 1970) state that podzols may develop on well drained sites as well as on sites where the drainage for some reason is restricted. This is also specified in the Canadian soil classification system (Proceedings of the Seventh Meeting of the National Soil Survey Committee of Canada 1968).

The characteristics of the podzols will, however, depend on the prevailing drainage regime. If the drainage is restricted and the ground water table high during part of the year, reducing conditions may be created below the ground water table. These reducing conditions will cause gleying of the soil. Such soils will often be mottled and may have concretions of iron and manganese compounds. Other morphological and chemical properties will also be affected by the drainage characteristics as shown by Tamm (1931).

All the authors quoted above, and the Canadian and World (Definitions of Soil Units for the Soil Map of the World 1968) soil classification systems separate gleyic podzols from those without this characteristic. Although Soil Survey Staff (1960) does not apply the term 'gley', a distinction is made between spodosols with mottling in some horizon and those without it. The soils with mottling are referred to as 'aquods', a suborder within the spodosol order. The term 'aquod' refers to the wetness of these soils.

2.6 Acidity

Podzol soils are always acid. In fully developed podzols, the pH of the upper horizons will be about 4, often even somewhat below 4. This appears from all the sources quoted earlier and it is also demonstrated in the profile descriptions in chapter 3. As appears from these descriptions the lowest pH values are found in the upper horizons and an increase in pH is normally encountered with depth.

The low pH is due to a very low base-saturation percentage. According to the general relationship between pH and base-saturation percentage (S. Tovborg Jensen 1963) soil with pH about 4 will have a base-saturation percentage close to 0 and hence hardly contain any 'bases'. Used in this context the term 'bases' is often interpreted by soil scientists as the adsorbed cations exclusive of hydrogen and aluminium ions. This expression is in conflict with the chemical definition of a base, which is a molecule or radical capable of accepting a hydrogen ion (Bjerrum 1956, Tyree and Knox 1961). It is difficult to suggest a term to replace the word 'base' and it would seem undesirable since this term has won general acceptance and since it gives a proper description of the phenomenon in question. However, the term 'base' may be interpreted in a way which is compatible with the chemical definition. If 'base' is understood to denote the negative site on the cation exchange complex which has adsorbed a cation other than hydrogen or aluminium, and not the cation itself, then the 'base' will correspond to its chemical definition. This implies, however, that it is not possible to use the expression 'adsorbed bases' but one may speak simply of the 'base content' of the soil. To avoid confusion, e.g.

with a content of calcium or sodium carbonate, the term 'exchange base content' or another term might be proposed. The expression 'base-saturation percentage' can be retained and it has exactly the same practical significance as in its traditional use and exactly the same methods may be used for its determination. In this study the proposed interpretation will be adhered to throughout.

Although the base-saturation percentage of podzols may not actually be 0 it will always be low, as illustrated by Joffe and Wattson (1933), Låg and Mork (1959) and Soil Survey Staff (1960), and for humus-illuvial podzols by Ponomareva (1964).

As the podzols have a sandy texture a substantial part of the cation exchange capacity will be due to organic matter. This will apply especially to the upper horizons which have lost inorganic material that might otherwise make a small contribution to the cation exchange capacity. But since the cation exchange capacity of the inorganic compounds translocated, i.e. mainly sesquioxides, is very low as compared to that of organic matter, the latter will be responsible for a very large fraction of the cation exchange capacity, in the illuvial horizon as well. This has also been shown by Barshad and Rojaz-Cruz (1950), Franzmeier, Hajek and Simonson (1965), Clark and Nichol (1968), and Stephens (1969).

When the pH of the eluvial horizon and particularly of the A_0 horizon is often well below 4, it must be assumed to be due to a content of relatively strong organic acids.

CHAPTER 3

PODZOL SOILS INVESTIGATED IN THE PRESENT STUDY

3.1 Extent of the Investigation

The experimental part of this study has included investigations of 10 soil profiles. Soil samples drawn from the profiles have been subject to a number of analyses and experiments. Most of the analyses and all the experiments will be described later in the appropriate chapters. In this chapter a general description of the soils and data on pH of the individual horizons will be given.

3.2 Sample Preparation and pH-Measurements

The soil samples were brought directly from the field to the laboratory in polyethylene bags. In the laboratory the samples were air-dried and passed through a 2 mm sieve, the primary particles not passing this sieve being discarded. This sieving caused no problems in the case of the mineral horizons, including those with fairly completely disintegrated organic matter. However, in the case of the A_0 horizons which to a large extent consist of organic matter representing all stages of decomposition, from fresh plant material to material without any recognizable structure, the separation obtained was rather arbitrary. Some of the partly decomposed organic material disintegrated easily when treated on the sieve while other fractions had very little tendency to disintegrate. An attempt was made to subject all samples to similar gentle treatment with a large rubber stopper on the sieve, and the material not disintegrating to a size below 2 mm by this treatment was discarded. The material not disintegrating was generally rather fresh plant material, but it must be admitted that this method of separation is not very accurate. However, any method of separating material of this character must necessarily be arbitrary and inaccurate, but it is not considered to have any bearing on the conclusions drawn from the analyses and the experiments.

All analyses and experiments, except those on the soil solution (see chapter 9), were made on the air-dried samples passed through the 2 mm sieve. Most of the analyses required fairly small amounts of soil, sometimes 1 g or less. Samples consisting of sand and organic matter have a strong tendency to separate and representative samples of this small size are difficult to take. To overcome this problem, successively smaller and smaller samples were thoroughly homogenized by treatment in a porcelain mortar until the results of the analyses could be reproduced. All analyses were made in duplicate and repeated if the discrepancies were considered too large.

The pH-values reported in this chapter were measured in a soil-water suspension (pH_{H_2O}) or soil-0.01 M $CaCl_2$ suspension (pH_{CaCl_2}). In both media a soil-liquid ratio of 1:2.5 was employed except in some A_0 horizons where the soil absorbed so much water that measurements were not possible using this ratio. In these cases a soil-liquid ratio of 1:5 was employed. After adding the liquid to the soil the suspensions were left for one hour under frequent stirring and their pH measured with a Radiometer pH-meter equipped with glass and calomel electrodes.

3.3 Profile Descriptions

In the following descriptions the soils will be identified by the Danish name of the locality where the profile is situated. Their locations are shown on the map in Fig. 1. In later chapters the individual soil horizons will be identified by the name of the locality and their horizon symbol.

GØRDING HEDE

Parent Material: Glacial outwash from the Würm glaciation. Coarse sand.
Vegetation: The profile is located in a glade within a young spruce (Picea abies) plantation. The locality of the profile, as far as could be ascertained, has not been disturbed, either during the planting of the trees or on any other recent occasion. The vegetation on the profile site is Calluna vulgaris with some mosses and lichens.
Horizontation:

0-5 cm. A_0. Strongly cohesive dark-brown mor-layer consisting mainly of residues of Calluna vulgaris in various stages of decomposition. On the whole,little decomposed. pH_{H_2O} 3.6, pH_{CaCl_2} 3.0.

5-8 cm. A_1. Black humus-containing mineral layer. Organic matter mainly in a state where no structure of the

Fig. 1. Location of the profiles investigated.

plant material may be recognized, but a small amount of fresh and partly decomposed roots of Calluna vulgaris is present. Sand particles strongly bleached. pH_{H_2O} 4.2, pH_{CaCl_2} 3.1.

8 -13 cm. A_2. Grey layer of bleached sand with some humus admixture. Hardly any plant residues with recognizable structure. pH_{H_2O} 4.3, pH_{CaCl_2} 3.3.

13-23 cm. B_{1a}(13-18 cm), B_{1b}(18-23 cm). Black layer with a metallic lustre. The black colour is due to a content of precipitated humus. The humus has cemented the sand particles into a compact layer. Sand grains bleached. The layer contains some rounded pebbles. Towards the lower boundary the colour changes to dark-brownish. pH_{H_2O} 4.5(B_{1a}) and 4.7 (B_{1b}), pH_{CaCl_2} 3.8(B_{1a}) and 4.0(B_{1b}).

23-43 cm. B_{2a}(23-33 cm), B_{2b}(33-43 cm). Layer with a dark-brown matrix colour, containing a network of still darker streaks. Towards the lower boundary of the layer a number of wavy, approximately horizontal, streaks are found. Tongues extend from this layer to a depth of up to 80 cm. These tongues originate from the B_1 horizon and have the same appearance with a thin surrounding layer of $B_{2a/b}$. pH_{H_2O} 4.7 (B_{2a}) and 4.8(B_{2b}), pH_{CaCl_2} 4.3 (B_{2a}) and 4.6(B_{2b}).

43-86 cm. B_{2c}(43-62 cm), B_{2d}(62-86 cm). Brown-yellow layer of sand coarser than that of the horizons above. The wavy streaks also present in this layer. Sharp lower boundary towards the C horizon marked by a dark-brown horizontal streak. pH_{H_2O} 4.6(B_{2c}) and 4.9(B_{2d}), pH_{CaCl_2} 4.6(B_{2c}) and 4.8(B_{2d}).

86 cm- (investigated until 130 cm) C. Yellowish sand, colour due to a coating of the quartz sand grains with ferric compounds. The sand is finer than that of the $B_{2c/d}$ horizon. In this horizon a few vertical faintly brown streaks are present. pH_{H_2O} 5.0, pH_{CaCl_2} 4.8.

SKARRILD

Parent Material: Glacial outwash from the Würm glaciation. Sand.

Vegetation: Calluna vulgaris with mosses and lichens.

Horizontation:

0-4 cm. A_0.	Strongly cohesive dark-brown mor-layer consisting mainly of residues of Calluna vulgaris in various stages of decomposition. On the whole, little decomposed. pH_{H_2O} 3.9, pH_{CaCl_2} 3.2.
4-12 cm. A_1.	Black layer, colour due to heavily decomposed organic matter. Some admixture of fresh and partly decomposed residues of Calluna vulgaris. Sand particles bleached. pH_{H_2O} 4.1, pH_{CaCl_2} 3.1.
12-26 cm. A_2.	Light-grey layer of bleached sand with small content of structureless humus. pH_{H_2O} 4.4, pH_{CaCl_2} 3.5.
26-31 cm. B_1.	Black layer with sharp lower boundary. Sand grains bleached. pH_{H_2O} 4.4, pH_{CaCl_2} 3.5.
31-62 cm. B_2.	Brown layer with a network of dark-brown streaks. Lower boundary marked by an almost black horizontal streak. pH_{H_2O} 5.0, pH_{CaCl_2} 4.4.
62 cm- C. (investigated until 100 cm)	Yellowish sand, colour due to a coating of the sand grains with ferric compounds. In this horizon some reddish-brown mottles are found. pH_{H_2O} 4.7, pH_{CaCl_2} 4.6.

STAVSHEDE

Parent Material: Glacial outwash from the Würm glaciation. Very coarse sand with some gravel and pebbles.

Vegetation: The profile is located in a glade within a spruce (Picea abies) plantation. The profile does not seem to have been disturbed. The vegetation on the profile site is Calluna vulgaris with some mosses and lichens.

Horizontation:

0-3 cm. A_{oa}. Dark-brown cohesive mor-layer. Very little decomposed plant residues, mainly of Calluna vulgaris. pH_{H_2O} 3.5^*, pH_{CaCl_2} 2.9^*.

3-7 cm. A_{ob}. As above, but decomposition more advanced. The original plant structure may be recognized in a large proportion of the material. pH_{H_2O} 3.1^*, pH_{CaCl_2} 2.6^*

7-11 cm. A_1/A_2. Dark-grey layer, the colour due to a high content of structureless organic matter in grey bleached sand. pH_{H_2O} 3.8, pH_{CaCl_2} 3.2.

11-25 cm. B_{2a}. Layer consisting of dominating reddish-brown parts alternating with more faintly coloured parts. Humus content not very great. No expressed B_1 horizon present. pH_{H_2O} 4.7, pH_{CaCl_2} 4.3.

25-35 cm. B_{2b}. Continuation of layer above, but the more faintly coloured parts dominate this layer. pH_{H_2O} 4.7, pH_{CaCl_2} 4.7.

35-65 cm. B_{2c}. Horizon consisting of faintly brown horizontal layers alternating with streaky, wavy, reddish-brown horizontal layers. The sand of this layer and of the underlying C horizon coarser than that of the horizon above. pH_{H_2O} 4.9, pH_{CaCl_2} 4.8.

65 cm- (investigated until 100 cm) C. Yellowish sand with coating of iron compounds. pH_{H_2O} 4.9, pH_{CaCl_2} 4.9.

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* Soil-liquid ratio, 1 : 5.

KLELUND

Parent Material: Glacial outwash from the Würm glaciation. Sand with some gravel and pebbles, probably affected by later sand-drift.

Vegetation: Calluna vulgaris with some mosses and lichens.

Horizontation:

0-3 cm.	A_{oa}.	Dark-brown cohesive mor-layer. Very little decomposed plant residues, these mainly of Calluna vulgaris. pH_{H_2O} 3.6*, pH_{CaCl_2} 3.1*.
3-8 cm.	A_{ob}.	As above, but decomposition more advanced. The original plant structure may be recognized in a large proportion of the material. pH_{H_2O} 3.4, pH_{CaCl_2} 2.9.
8-18 cm.	A_2.	Grey bleached layer, some humus content. No A_1 horizon present. This layer contains a great amount of gravel and pebbles mixed with the sand. pH_{H_2O} 4.3, pH_{CaCl_2} 3.2.
18-23 cm.	B_1.	Almost black layer with high content of precipitated humus. Sand grains bleached. pH_{H_2O} 4.2, pH_{CaCl_2} 3.5.
23-45 cm.	B2a.	Reddish-brown matrix with network of darker streaks. Some almost black horizontal wavy streaks. pH_{H_2O} 4.8, pH_{CaCl_2} 4.1.
45-75 cm.	B_{2b}.	More faintly brownish layer with some brown horizontal wavy streaks. pH_{H_2O} 4.8, pH_{CaCl_2} 4.5.
75 cm - (investigated until 100 cm)	C.	Faintly yellowish sand, coated with iron compounds. pH_{H_2O} 5.1, pH_{CaCl_2} 4.7.

* Soil-liquid ratio, 1 : 5.

TINGHEDEN

Parent Material: Deposit from the Riss glaciation. Very fine sand with few pebbles.

Vegetation: Calluna vulgaris with some mosses and lichens. Scattered remains of Pinus mugo, some of which seem to have been cut, others to have died naturally.

Horizontation:

0-8 cm.	A_o.	Thick brown, cohesive mor-layer. Mostly remains of Calluna vulgaris in various stages of decomposition. pH_{H_2O} 3.3*, pH_{CaCl_2} 2.7*.
8-15 cm.	A_1.	Dark layer, colour due to structureless organic matter. Sand bleached. pH_{H_2O} 3.7, pH_{CaCl_2} 3.1.
15-30 cm.	A_2.	Thick layer with a light-grey matrix in which some extremely bleached, almost white, spots averaging about 3 cm in diameter are found. Humus content small. pH_{H_2O} 4.3, pH_{CaCl_2} 3.4.
30-35 cm.	B1.	Compact, almost entirely black layer. Sand grains bleached. pH_{H_2O} 4.1, pH_{CaCl_2} 3.5.
35-55 cm.	B_2.	Compact, reddish-brown, streaky layer. pH_{H_2O} 4.5, pH_{CaCl_2} 4.3.
55 cm - (investigated until 100 cm)	C.	Yellowish very fine sand, extensively mottled. This layer also rather compact. pH_{H_2O} 4.4, pH_{CaCl_2} 4.1.

TREHØJE

Parent Material: Deposit from the Riss glaciation, perhaps subject to wind erosion in the distant past. Rather coarse sand.

Vegetation: Calluna vulgaris with some mosses and lichens.

Horizontation:

0-5 cm.	A_o.	Dark-brown, almost black, cohesive mor-layer. Mainly remains of Calluna vulgaris in various stages of decomposition. pH_{H_2O} 3.6, pH_{CaCl_2} 3.0.

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* Soil-liquid ratio, 1 : 5.

5-12 cm. A_1. Dark layer with bleached sand. Colour due to high humus content. Some partly decomposed residues of Calluna roots. pH_{H_2O} 4.0, pH_{CaCl_2} 3.1.

12-20 cm. A_2. Grey bleached layer with some organic matter. pH_{H_2O} 4.7, pH_{CaCl_2} 3.4.

20-25 cm. B_1. Black, somewhat cemented layer with a metallic lustre; sand grains bleached. pH_{H_2O} 4.6, pH_{CaCl_2} 3.8.

25-32 cm. B_1/B_2. Transitional layer with alternating dark brown-black and reddish-brown parts. Rather compact. pH_{H_2O} 4.9, pH_{CaCl_2} 4.5.

32-50 cm. B_{2a}. Dark-brown layer with still darker horizontal streaks. Rather compact. pH_{H_2O} 4.7, pH_{CaCl_2} 4.7.

50-75 cm. B_{2b}. Fainter brown layer with a few darker horizontal streaks. Sharp lower boundary but some tongues extend into the underlying horizon. pH_{H_2O} 4.8, pH_{CaCl_2} 4.7.

75 cm - (investigated until 100 cm) C. Yellowish sand, coated with iron compounds pH_{H_2O} 4.9, pH_{CaCl_2} 4.8.

LØWENHOLM

Parent Material: Moraine from the Würm glaciation. Fine sand.

Vegetation: Open stand of old (about 100 years) Fagus sylvatica. Herb vegetation: mainly mosses, and some Deschampsia flexuosa.

Horizontation:

0-5 cm. A_{oa}. Brown, cohesive mor-layer consisting of poorly decomposed litter, mainly residues of leaves of Fagus sylvatica. pH_{H_2O} 4.1*, pH_{CaCl_2} 3.7*.

5-12 cm. A_{ob}. Dark-brown cohesive mor-layer, more decomposed than the layer above, with a concentration of living Fagus roots. pH_{H_2O} 3.6, pH_{CaCl_2} 3.0.

* Soil-liquid ratio, 1 : 5.

12-23 cm. A_2. Grey bleached layer with small humus content. Practically no roots in this layer. Lower boundary irregular. pH_{H_2O} 4.3, pH_{CaCl_2} 3.3.

23-43 cm. B_1. Layer almost entirely black due to a humus illuviation. pH_{H_2O} 4.4, pH_{CaCl_2} 3.6.

43-55 cm. B_{2a}. Layer consisting of a brown matrix with still darker streaks. Very compact. At the time investigated (April 13, 1971) almost water saturated. The layer seems to be almost impervious. pH_{H_2O} 4.7, pH_{CaCl_2} 4.1.

55-90 cm. B_{2b}. Mottled layer, somewhat more faintly coloured than that above, in some parts greyish. Probably reducing conditions, at least temporarily. pH_{H_2O} 4.7, pH_{CaCl_2} 4.1.

90 cm - (investigated until 100 cm) C. Greyish fine sand, no signs of oxidation, probably reducing conditions. At the time of investigation this layer was entirely below the ground water level. pH_{H_2O} 5.2, pH_{CaCl_2} 4.3.

TRINDERUP

Parent Material: Moraine from the Würm glaciation. Fine sand. Profile site located on a small hill. Possibly affected by sand-drift.

Vegetation: Young spruce(Picea abies) plantation. Herb flora: mosses and some grasses. Profile site may have been disturbed during the planting of the trees.

Horizontation:

0-8 cm. Ao. Brownish, rather loose mor-layer with much undecomposed and partly decomposed plant material. pH_{H_2O} 3.7, pH_{CaCl_2} 3.3.

8-20 cm. A_1/A_2. Bleached layer with a high content of black organic matter without recognizable plant structure. pH_{H_2O} 3.9, pH_{CaCl_2} 3.3.

20-35 cm.	B_1.	Dark-brown layer with appreciable humus illuviation. pH_{H_2O} 4.6, pH_{CaCl_2} 4.0.
35-45 cm.	B_1/B_2.	Transitional layer with a dark-brown colour in the upper part changing to a lighter brown colour towards the lower boundary. pH_{H_2O} 4.7, pH_{CaCl_2} 4.3.
45-70 cm.	B_2.	Brown layer. Colour fading towards the lower boundary. pH_{H_2O} 4.6, pH_{CaCl_2} 4.4.
70 cm- (investigated until 100 cm)	C.	Yellowish sand, coated with iron compounds. pH_{H_2O} 5.0, pH_{CaCl_2} 4.7.

STØTTRUP HEDE

Parent Material: Inland sand dune. No recent sand drift. Sand.

Vegetation: Profile site located in a glade in a spruce (Picea abies) plantation. Probably undisturbed. Covered with Calluna vulgaris, mosses and lichens.

Horizontation:

0-8 cm.	A_o/A_1.	Cohesive brown mor-layer. In the upper part with much undecomposed plant material. In the lower part decomposition of plant material more advanced, with an appreciable content of bleached sand. Not possible to separate A_o and A_1. pH_{H_2O} 3.8, pH_{CaCl_2} 3.1.
8-25 cm.	A_2.	Grey, strongly bleached layer with small humus admixture. pH_{H_2O} 4.5, pH_{CaCl_2} 3.5.
25-35 cm.	B_1.	Dark-brown layer with some humus illuviation. Colour not homogenous. Dark-brown parts alternating with more faintly coloured parts. pH_{H_2O} 4.6, pH_{CaCl_2} 4.0.
35-70 cm.	B_2.	Streaky layer. The colour fades from dark-brown at the upper boundary to yellowish brown near the lower boundary. pH_{H_2O} 4.9, pH_{CaCl_2} 4.4.
70 cm- (investigated until 100 cm)	C.	Yellowish sand, coated with iron compounds. pH_{H_2O} 5.0, pH_{CaCl_2} 4.7.

SKARPHOLT

Parent Material: Late-glacial marine deposit. Possibly affected by sand-drift. Sand.

Vegetation: Old, rather open spruce (Picea abies) plantation. Dominating herb: Deschampsia flexuosa.

Horizontation:

0 - 5	cm.	A_o.	Grey-brown mor-layer of largely undecomposed plant material. pH_{H_2O} 4.5, pH_{CaCl_2} 3.6.
5-10	cm.	A_1.	Light-grey, bleached layer with a transitional change to the underlying horizon. pH_{H_2O} 3.9, pH_{CaCl_2} 3.2.
10-15	cm.	A_2.	Very strongly bleached layer. pH_{H_2O} 4.3, pH_{CaCl_2} 3.7.
15-22	cm.	B_1.	Dark reddish-brown layer with some humus illuviation. pH_{H_2O} 4.2, pH_{CaCl_2} 4.0.
22-55	cm.	B_{2a}.	Layer with alternating reddish-brown and yellowish-brown parts. pH_{H_2O} 4.4, pH_{CaCl_2} 4.3.
55-90	cm.	B_{2b}.	Layer with a number of almost horizontal red-brown streaks in a yellowish-brown matrix. pH_{H_2O} 4.6, pH_{CaCl_2} 4.5.
90 cm- (investigated until 100 cm)		C.	Yellowish sand, coated with iron compounds. pH_{H_2O} 4.6, pH_{CaCl_2} 4.5.

CHAPTER 4

THE ORGANIC MATTER CONTENT OF PODZOLS, AND ITS PHYSICAL AND BIOLOGICAL PROPERTIES

4.1 Determination of Soil Organic Matter

The determination of the exact content of organic matter in soils is a somewhat complex operation. In principle, it may be done by measuring the weight loss of a sample subjected to ignition or to wet combustion by means of an oxidating agent that can be entirely removed from the soil after the oxidation, e.g. hydrogen peroxide. However, these methods will rarely give accurate results due to a contribution to the weight loss by the inorganic soil constituents in the case of ignition, and due to incomplete oxidation in the case of wet combustion.

To eliminate these difficulties it is usually considered more satisfactory to calculate the organic matter content from a determination of the carbon content, which latter can be made with a high degree of accuracy, at any rate in soils such as podzols that do not contain inorganic carbon compounds. The carbon content is calculated from the amount of carbon dioxide produced when the soil is subjected to dry or wet combustion. Since, at least in the dry combustion method, total combustion can be easily ensured, these methods will give an accurate carbon content. However, the calculation of the organic matter content from the carbon content is somewhat more problematical. In this calculation it is traditionally assumed that organic matter contains 58 % carbon, and accordingly the factor 1.724 is usually employed for converting percent carbon into percent organic matter. The conversion factor is based on only one preparation of humus extracted from peat with ammonia (Sprengel 1826), and it is very unlikely that it will hold for all soil organic matter. It has been proved by many investigations on extracted humus (e.g. Ponomareva 1964, Kononova 1966, Schnitzer and Skinner 1968a) that the carbon content may deviate substantially from 58 %. As shown by Broadbent (1953) it will usually be lower and hence the calculation will require a larger conversion factor. Broadbent (1953) also showed that the carbon content of the organic matter usually decreases with depth within a given profile, also in podzols. He therefore suggested that factors around 1.9 and 2.5, for surface and subsoils repectively, would be more satisfactory.

Another group of methods of organic matter determination is based on a measurement of the amount of oxidating agent consumed during a wet combustion (Jackson 1958, Allison 1965, Agrokhimicheskie Metody Issledovaniya Pochv 1965, Orlov and Grindel 1968, and many others). The results of these methods are all directly or indirectly calibrated against the results of the methods mentioned above and hence have the same inherent drawbacks. Furthermore, the results will depend on the oxidation state of the carbon and on the more or less complete combustion of the organic matter. Hence, these methods must be assumed to give still more unreliable results and their main advantage is that they are comparatively rapid.

For most practical purposes the errors arising from the factors above may be without importance, but since the organic matter of the various horizons in podzols seems to differ in composition it is considered more correct to report the results of the analyses carried out in this study as percent organic carbon.

The method employed here was dry combustion, using the equipment and technique described in Spithost (1933). This method makes use of a catalyst consisting partly of PbO_2. It is difficult to obtain commercial PbO_2 sufficiently low in carbonate to avoid a high blank value. To overcome this difficulty the PbO_2 was treated with 2 n HNO_3 and washed with water prior to being used in the catalyst. Each time a fresh catalyst was prepared a blank analysis was run. In no case was carbon dioxide in excess of 1 mg registered during the blank test. This is considered satisfactory, since the carbon dioxide produced by samples with a high or medium organic matter content was 100-300 mg per analysis. In these cases the relative error caused by the blank value is below 1 %. In the samples low in organic matter the relative error is, of course, larger. Of these samples more than 2 g of soil was employed in each analysis and the error will therefore be less than 0.02 % C. No attempts were made to correct the results for the blank value.

4.2 Organic Matter Content in Individual Horizons

From the way the term 'podzol' is interpreted in this study it follows that at least some podzols will have a significant content of organic matter in the illuvial horizon. They will, of course, in addition usually have a large content of organic matter in the upper subhorizons of the eluvial horizon. The actual amount present in each subhorizon will depend entirely on the conditions and on the degree of podzolization. Large variations are found among the numerous results of analyses of the organic matter content of individual podzol horizons reported in the literature.

Since an accumulation of sesquioxides in the B horizon is sufficient to qualify a soil as a podzol it should be possible to find podzols with no or insignificant organic matter accumulation in the B horizon. It is, however, the impression of the author that such soils are rarely found, at any rate in the absence of permanent or temporary ground water influence. In the American soil classification system such soils would be referred to the suborder ferrods (Soil Taxonomy 1970). In the description of this suborder it is stated that these soils are unknown in the United States. In the Canadian soil classification system (Proceedings of the Seventh Meeting of the National Soil Survey Committee of Canada 1968) no subgroup of podzols is described where the soils have zero or very low content of organic matter in the B horizon. In the humo-ferric podzols, which is the subgroup of podzolic soils characterized by the lowest illuviation of organic matter as compared with that of iron compounds, the organic matter content is allowed to be as high as 10 % and the ratio of organic matter to oxalate-extractable iron may be as high as 20. In the World system (Definitions of Soil Units for the Soil Map of the World 1968) a group of ferric podzols is described as having a B-horizon with a ratio of 'free (elemental) iron' to organic carbon above 6. However, it is not clear how the expression 'free (elemental) iron' should be interpreted, and no information on the actual occurrence of such soils is given.

All the podzols analyzed by Weis (1929, 1932), Cann and Whiteside (1955), Schnitzer and Wright (1957), McCracken and Weed (1963), Franzmeier, Hajek and Simonson (1965), Jacquain, Juste and Dureau (1965), McKeague, Schnitzer and Heringa (1967), Tamm and Holmen (1967), Bouma et al. (1969), Gonzalez and Hubert (1972) as well as results published by many other authors show a significant organic matter accumulation in the B horizon. This also applies to the soils designated as 'iron podzols' by Tamm (1931). The tropical podzols described by Barshad and Rojaz-Cruz (1950), Bleackly and Khan (1963), Klinge (1965) and Andriesse (1969) have an appreciable humus illuviation in the B horizon. This is also true of the two 'humus-podzols' in Sarawak described by Andriesse (1968) but the profile called 'grey-white podzolic' by Andriesse (1968) is characterized more by clay translocation than by podzolization.

In Soviet soil literature, results of analyses of so-called podzolic soils often show insignificant organic matter contents in the B horizon. However, as discussed earlier these soils would not be called podzols in the sense this expression is used here. As examples the results published by Abramova (1961) and Belchikova (1961) may be mentioned. The main feature of the soils discussed by these authors is an appreciable clay removal from the eluvial horizons. The soils are developed on rather clayey parent materials, and no significant illuviation of either organic matter or sesquioxides is proved in the analyses reported by the authors. On the other hand the results given by Ponomareva (1964) and Tonkonogov (1969, 1971) for humus-illuvial podzols show appreciable organic matter content in the B horizon.

In the soils described in the previous chapter organic carbon determinations have been made on samples from all the horizons. The results are quoted in Table 3. The patterns of organic matter distribution in the profiles investigated are very similar. A large fraction of the material of the A_o horizons consists of organic matter. In some of the profiles this fraction exceeds half of the total material. The actual values found are, of course, influenced by the difficulties encountered in separating the fresh plant material from the more or less decomposed organic matter but the general impression of organic matter forming the main constituent of the A_o horizons is not affected.

The organic matter content of the A_1 horizons is still appreciable, although much smaller than in the A_o horizons, varying from about 3 to about 9 % C. A further decline in the organic matter content is noted in the A_2 horizons, where 0.5 to 1.5 % C is found in the profiles investigated.

The organic matter content of the B_1 horizon is invariably higher than that of the overlying A_2 horizon in the profiles where a clear A_2 horizon is present. Below the B_1 horizon the organic matter content declines fairly rapidly with depth. Generally the B_2 horizons still contain appreciable amounts and in the C horizons small to very small amounts of organic matter are present in all the profiles.

4.3 Physical Properties

In the preceding text the term 'organic matter' has been preferred but the term 'humus' has also been used frequently. Before entering a discussion of the properties of the organic matter of podzol soils it seems

Table 3. Contents of Organic Carbon and Nitrogen, and Colour of Sodium Dithionite-EDTA Extracts, of the Soils Investigated

Profile	Horizon	C,%	N,%	$\frac{C}{N}$	Colour of sodium dithionite-EDTA extract
Gørding Hede	A_o	23.8	0.643	37	brown
	A_1	3.79	0.103	37	brownish yellow
	A_2	1.32	0.037	36	brownish yellow
	B_{1a}	5.70	0.219	26	almost black
	B_{1b}	4.57	0.149	31	very dark brown
	B_{2a}	1.19	0.038	31	yellow
	B_{2b}	0.99	0.032	31	faint yellow
	B_{2c}	0.29	0.012	24	almost colourless
	B_{2d}	0.08	0.005	16	colourless
	C	0.05	0.001	50	colourless
Skarrild	A_o	22.6	0.496	46	brown
	A_1	8.93	0.230	39	brown
	A_2	0.48	0.018	27	faint yellow
	B_1	7.78	0.268	29	almost black
	B_2	0.61	0.028	22	yellow
	C	0.23	0.012	19	almost colourless
Stavshede	A_{oa}	40.3	1.14	35	yellow
	A_{ob}	40.6	1.09	37	brownish yellow
	A_1/A_2	3.56	0.137	26	yellowish brown
	B_{2a}	1.56	0.070	22	light yellow
	B_{2b}	0.54	0.016	34	almost colourless
	B_{2c}	0.18	0.008	23	almost colourless
	C	0.10	0.002	50	colourless
Klelund	A_{oa}	42.7	1.45	29	yellow
	A_{ob}	31.6	0.983	32	yellowish brown
	A_2	1.40	0.054	26	yellow
	B_1	9.04	0.294	31	almost black
	B_{2a}	0.24	0.010	24	very faint yellow
	B_{2b}	0.14	0.008	18	almost colourless
	C	0.04	0.004	10	colourless

Table 3. Continued

Profile	Horizon	C,%	N,%	$\frac{C}{N}$	Colour of sodium dithionite-EDTA extract
Tingheden	A_o	44.1	1.26	35	yellowish brown
	A_1	4.56	0.093	49	yellowish brown
	A_2	0.46	0.014	33	faint yellow
	B_1	4.76	0.135	35	dark brown
	B_2	1.59	0.047	34	faint yellow
	C	0.21	0.021	18	faint yellow
Trehøje	A_o	31.0	1.13	27	brown
	A_1	9.01	0.241	37	brown
	A_2	1.52	0.035	43	yellowish brown
	B_1	7.58	0.260	29	dark brown
	B_1/B_2	0.90	0.039	23	yellow
	B_{2a}	0.24	0.010	24	light yellow
	B_{2b}	0.13	0.005	26	almost colourless
	C	0.03	0.007	4	colourless
Løwenholm	A_{oa}	38.3	1.87	20	yellow
	A_{ob}	26.2	0.970	27	dark brown
	A_2	1.48	0.025	59	yellowish brown
	B_1	2.11	0.074	29	dark brown
	B_{2a}	1.53	0.035	44	yellow
	B_{2b}	0.77	0.022	35	faint yellow
	C	0.16	0.013	12	almost colourless
Trinderup	A_o	25.9	0.945	27	brown
	A_1/A_2	6.82	0.207	33	brown
	B_1	3.77	0.099	38	dark brown
	B_1/B_2	1.77	0.063	28	yellowish brown
	B_2	0.34	0.031	11	faint yellow
	C	0.18	0.013	14	colourless
Støttrup Hede	A_o/A_1	15.1	0.232	65	yellowish brown
	A_2	0.96	0.033	29	light brown
	B_1	1.44	0.055	26	light brown
	B_2	0.80	0.038	21	faint yellow
	C	0.16	0.012	13	colourless

Table 3. Continued

Profile	Horizon	C,%	N,%	$\frac{C}{N}$	Colour of sodium dithionite-EDTA extract
Skarpholt	A_o	33.1	1.56	21	yellowish brown
	A_1	4.24	0.105	40	-
	A_2	1.53	0.025	61	faint yellowish
	B_1	1.64	0.077	21	yellow
	B_{2a}	1.79	0.051	35	-
	B_{2b}	0.43	0.021	36	-
	C	0.33	0.008	41	almost colourless

appropriate to pay attention to the proper use of these terms. Some authors and schools of soil science use the expression 'soil organic matter' to designate all kinds of living and dead vegetable and animal matter in the soil while they restrict the term 'humus' to dead soil organic matter which has entirely lost its original plant or animal structure (Scheffer and Schachtschabel 1970, Buckman and Brady 1969). From a theoretical point of view such a distinction has many advantages since the decayed structureless organic matter lends a number of important properties to the soil which are not imposed by fresh or partly decomposed plant and animal residues.

However, it is usually difficult or impossible to devise an analytical method capable of distinguishing between the two groups of organic matter. In the case of soils where a rapid turn-over of organic matter is taking place the amount of partly decayed plant and animal residues may be small compared with the amount of structureless organic matter. In such soils the results of total carbon determinations may be assumed to be a good estimate of the content of well decomposed, structureless organic matter or of 'humus' in its narrowest sense.

This is, however, not the case in podzol soils. As may be seen from the profile descriptions in the previous chapter a great part of the organic matter of the A horizons, and especially of the A_o horizons, is present in a partly decomposed state and the amount of 'humus' in its narrow sense will be small in these horizons. Furthermore, all transitional stages between the fresh plant material and structureless organic matter will be represented. It seems, therefore, rather artificial and also very difficult to try and separate a particular fraction of well-decomposed humus from the bulk organic matter fraction. In this text the term 'humus' will be used synonymously with the term 'soil organic matter' and it will not be limited to the structureless dark-coloured fraction unless specified. This should be regarded merely as an explanation of the designation 'humus' as it is applied here, and it should not be inferred from this that the properties which the organic matter lends to the soil are independent of the stage of decomposition.

The partly decomposed organic matter present in the upper horizons and especially in the A_o horizons of podzols is the type of humus for which Müller (1879) introduced the term 'mor'. The term is (like the other 'mull', which was also introduced into scientific soil literature by Müller) of Danish vernacular origin and both have since become universally adopted as designations for humus with particular properties. Müller distinguished between these two humus forms only, although he stated that intermediate forms existed. Further classification of humus forms has been done by a number of authors, for instance Kubiëna (1953) who in his soil classification scheme assigned major importance to the properties of the humus. Detailed schemes of classification of humus with special reference to that of forest soils are also given by Bernier (1968) and Wilde (1971). These schemes outline a fairly high number of different humus forms but the basic divisions of the schemes are closely related to the ideas of Müller. A scheme involving the separation of three different humus forms is quite often employed and described for example by Scheffer and Schachtschabel (1970) and by Duchaufour (1965). The three humus forms are the two described by Müller, although Scheffer and Schachtschabel prefer the expression 'raw humus' to 'mor', and an intermediate form called 'moder'.

It should be noted that as the terms 'mor' and 'mull' are described here, and used by the authors mentioned, they are not entirely identical to those introduced by Müller. Müller meant the terms to designate the entire soil layer containing one of the humus forms and not the humus only. The meaning assigned to the terms by Müller is in accordance with common previous and present use of the terms in Danish.

The properties of mor have been described by Müller (1879, 1884), Waksman (1936) and many others including the authors quoted above. The mor is characterized by plant debris in a partly decomposed stage and an incomplete mixing of the organic matter with the inorganic soil constituents. Hence a mor-layer is situated as a mainly organic layer on top of the mineral soil and containing only a limited admixture of inorganic material. The topmost part of the mor-layer will often be composed of relatively unaltered plant residues. The decomposition of these increases with increasing depth within the mor-layer but in a typical mor-layer the original plant structure may be recognized in a large proportion of the material.

The character and the colour of the mor-layer will to a certain extent depend on the kind of plant residues and hence on the vegetation of the area. In most of the profiles described in the preceding chapter the dominant vegetation is Calluna vulgaris and hence the mor-layers to a large extent consist of remains of this plant species. In the deeper parts of the mor-layer the colour is usually dark-brown.

The mor-layer is always very cohesive. This is partly due to the great content of partly decomposed plant material, but probably still more due to the huge number of fungal hyphae which make the plant residues adhere to each other. This was clearly demonstrated by Müller (1879) in his studies of mor formed from litter of Fagus sylvatica, and it has also been found by Jensen (1963a). In podzols developed under poorly drained conditions the organic matter of the A_o horizon may have the appearance of peat (Låg and Mork 1959).

The humus of the A_1 horizon and the small amount present in the A_2 horizon probably originates mainly from plant roots and constituents of the A_o horizon mixed with the mineral soil, although this mixing is limited compared with that of other humus-containing layers, i.e. mull-layers. It is not to be excluded that a part of the organic matter in the A_1 and A_2 horizons has been brought there by leaching. The organic matter of the A_1, and especially the A_2 horizons, is somewhat more decomposed than that of the A_o horizon although a fraction may be present as partly decomposed plant roots and other plant residues.

The organic matter of the B horizon is quite different in character. Although occasional plant roots and partly decomposed residues of these may be found in this horizon the bulk organic matter has no recognizable plant structure. It is usually found as coatings on mineral grains as observed by Racz (1968) or as so-called pellets described by Soil Survey Staff (1960). McCracken and Weed (1963) observed that the organic matter was present as dark-brown to black intergranular bridges between the quartz sand grains. Frequently the intergranular bridges were extensive enough to form a matrix. In moist conditions the black B_1 horizon will sometimes have a metallic lustre on freshly cut soil profiles.

4.4 Biological Properties

It has already been mentioned that fungal hyphae are found in great numbers in the mor-layer. It is generally agreed that compared with the mull the mor is low in bacteria and high in fungi. In mor developed under a forest vegetation of Fagus sylvatica Jensen (1962a, 1962b, 1963a, 1963b, 1963c, 1963d, 1965) found that the number of microorganisms per g of dry soil was approximately equal to the number found in mull soils. However, as the mor samples contained much more organic matter than the mull ones the number of microorganisms per g organic matter was about 5 times higher in mull than in mor. Furthermore, the bacterial flora of mull soils were richer in species and more varied than those of mor soils. Although no profile descriptions are given by Jensen the presence of a bleached layer under the mor-layer has been noted in some of the mor soils.

On the other hand the number of microfungi per g of dry soil was 3-4 times higher in mor than in mull, giving approximately equal numbers when calculated on the basis of organic matter. In spite of the higher counts on mor sites the population of microfungi in the mull soils was found to contain a higher number of different genera and species than the population in mor soils. Also the number of yeasts and yeast-like fungi was 3-4 times higher in mor than in mull when calculated on a dry soil basis. However, in the case of these fungi the population of the mor soils contained more different species than that of mull soils.

The most important reasons for the more limited variety and activity of the organisms in the mor soils compared with the mull soils must be assumed to be the higher acidity and the lower content of nutritional elements in the mor soils.

Also, the macroflora and -fauna is very different in the two kinds of soils. In his first paper Müller (1879) noted Deschampsia flexuosa and Trientalis europaea to be the dominant herbs on mor sites with a forest vegetation of Fagus sylvatica. Mosses were also found to a great extent. On the mull sites mosses were rarely found and the herb vegetation was more varied than on mor sites with such species as Asperula odorata, Mercurialis perennis and Milium effusum frequently represented.

The mull sites contain, still according to Müller (1879), a much more varied and active fauna than the mor sites. The most striking difference between the two kinds of soils is the abundance of earthworms, mainly Lumbricus terrestris, in mull soils and their virtual absence from mor soils.

The biological properties of the subsurface horizons are less well known than those of the mor-layer. Generally, the biological activity decreases rapidly with depth (Alexander 1961). Broadbent (1953) quotes an experiment showing that the biological activity of the A_2 horizon of a podzol was reduced to 4 % of that in the upper organic horizon. Crawford (1956) found that the B horizon contained a great number of bacteria belonging to the genera Corynebacterium, especially C. simplex, which is able to precipitate iron from ferric citrate solutions through utilization of the citrate in its nutrition. Iron oxidizing bacteria could not be demonstrated. Mudge (1927) also showed that bacteria capable of precipitating iron from solutions of ferric ammonium citrate were present in podzol B horizons. On the other hand McKenzie, Whiteside and Erickson (1960) found that the number of citrate oxidizing bacteria was much larger in the A horizon than in the B horizon, while they demonstrated the presence of iron oxidizing bacteria in the B horizon.

CHAPTER 5

CHEMICAL PROPERTIES OF THE ORGANIC MATTER OF PODZOLS

5.1 Obstacles in the Investigation of Soil Organic Matter

Despite many investigations, most of the chemical properties of the humus compounds remain rather obscure. This is due to a number of factors, all of which seem to be related to the complicated chemical structure of the humus compounds. Many of the classical and modern methods used in the investigation of simpler organic compounds have been applied to the humus compounds but the results are usually very difficult to interpret. As will be illustrated in the following sections the results are subject to great variation and highly dependent on the actual experimental conditions.

There is, of course, no reason to assume that the humus compounds have a structure or contain functional groups not found in any other known organic substances. However, a thorough characterization of an organic compound usually requires preparation of a reasonable amount of the compound with a reasonable degree of purity, or that it can be broken down into compounds with such properties by processes which are well understood. It has not yet been possible to isolate any considerable humus fraction fulfilling the usual criteria of purity, and although many experiments involving a chemical break-down of humus into simple compounds have resulted in significant yields of well-known compounds the actual processes by which the break-down takes place are usually only partly understood. It is, of course, possible to determine some basic characteristics of the organic matter without employing a purification and/or chemical break-down, for example the elementary composition. However, even this is limited by the fact that the humus compounds are found in an intimate, inseparable mixture with inorganic soil constituents that contain some of the same elements as the humus compounds. In practice the only elements that may be determined directly are carbon, and this will strictly apply only to carbonate-free soils, and nitrogen, which is usually present only in negligible amounts in the inorganic soil fraction. The determination of all other elements is complicated by the fact that these elements are found in comparable or greater amounts in the inorganic soil fraction.

The characterization of functional groups in untreated humus is impeded by the fact that such groups will be found in a practically infinite number of configurations. The chemical methods employed in such investigations are based on some more or less specific properties of the functional groups but, as is well-known from organic chemistry, these properties may be modified or changed by neighbouring similar or different groups and by the steric arrangement, etc. Approaches have, with some success, been made to overcome some of the difficulties and newer physical methods such as infrared spectrometry and nuclear magnetic resonance seem to offer special opportunities in this respect.

For the reasons mentioned above most of the studies made on the humus compounds have employed humus preparations extracted by various reagents from soils. The validity of the results obtained by investigations of extracted organic matter is limited by at least two factors. One of these is the possible change in composition and properties of the organic matter during the extraction, and the other is the fact that no solvent has yet been found that is able to cause a total dissolution of the soil organic matter. The question arises, therefore, as to what extent the extracted fraction is representative of the entire organic matter fraction. As there must be some reasons for the separation into a soluble and an insoluble fraction there must be some differences in the properties of the two fractions of the organic matter. Attempts to reduce the risk of error caused by one of the factors mentioned will often increase the risk caused by the other. For example, if the alteration of the humus compounds is kept low by the application of mild extractants the fraction of humus extracted tends to become low, and vice versa.

In the following sections some of the methods most frequently used for extracting soil organic matter will be examined from these points of view and with special reference to podzol soils.

5.2 Extraction of Organic Matter from Soils

5.2.1 Extraction by Water

From the fact that humus is a natural component of humid soils it follows that it must be largely insoluble in water. Water will, therefore, usually dissolve only negligible amounts of the true humus compounds. However, in the study of the genesis of podzols the water-soluble fraction must be assumed to be of particular importance, and many authors, including Jacquin and Bruckert (1965) and Bruckert (1966, 1970a, 1970b) have studied the properties of the organic matter extracted by water from soils and litters. The purpose of most of these studies was to identify simple organic acids, but unidentified polymeric compounds related to the true humus compounds have also been found in water extracts and natural water leachates (Schnitzer and Desjardins 1969, Bruckert 1970a). In the present experimental investigation it has also been found that some organic matter from different horizons of podzols could be dissolved in water under laboratory as well as field conditions (see chapter 9).

5.2.2 Extraction by Aqueous Solutions of Neutral Salts

Addition of neutral salts containing anions with non-complexing or weak complexing properties such as NaCl, Na_2SO_4, etc. does not significantly improve the ability of the water to disperse organic matter. The failure of such solutions to extract significant amounts of organic matter has been demonstrated by Evans (1959) for a neutral surface soil and by Schnitzer, Wright and Desjardins (1958) for podzol A and B horizons.

5.2.3 Extraction by Alkaline Solutions

It is well known that alkaline solutions can disperse a part of the soil organic matter and cause the formation of a brown or dark-brown extract. Various bases such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, etc. have been employed in these extractions. Sodium hydroxide in concentrations 0.1 n, 0.5 n, or 1.0 n seems to be the most frequently used extractant and schemes employing this extractant are described by many authors, e.g. Waksmann (1936), Kononova (1966), Saurbeck and Führ (1968). The amount of humus extracted varies a great deal and depends on concentration and kind of base, nature of soil and soil horizon, particular properties of the organic matter etc.

As compared to most other extractants alkaline solutions are effective in dispersing soil organic matter. Evans (1959) found that 0.4 n NaOH extracted in two days 18 % of the total content of organic C from a neutral surface soil. For a podzol Schnitzer, Wright and Desjardins (1958) found that 0.5 n NaOH extracted 24.8 % of the total carbon content of the A_0 horizon and 96.3 % from the B_2 (humus illuvial) horizon, while much smaller amounts could be extracted from the corresponding horizons of a clayey grey wooded soil (Schnitzer and Gupta 1964).

While the results of the comparative study by Schnitzer, Wright and Desjardins (1958) are quite consistent, some divergencies are noted with other studies employing the same soil. For example, Levesque and Schnitzer

(1967) found that 0.5 n NaOH extracted only 46.4 % of the organic carbon from the same B horizon.

It is highly debatable to what extent the properties of the organic matter are changed during extraction. It has been shown by many authors, e.g. Bremner (1950) and Choudhry and Stevenson (1957), that oxygen is absorbed during the alkaline extraction. The effect of oxidation on the organic matter is not well known. Bremner (1950) calculated that only a small percentage of the organic matter was oxidized to carbon dioxide. To reduce the oxidation it is often recommended to make the extraction under nitrogen or to add a reducing agent such as $SnCl_2$ to the extractant (Choudhry and Stevenson 1957). Wright and Schnitzer (1959) found only small differences in composition and properties of organic matter extracted with 0.5 n NaOH from a podzol A_o and B_h horizon under air and nitrogen respectively. The main differences were somewhat larger contents of carbonyl and carboxyl and lower contents of phenolic and alcoholic hydroxyl in the organic matter extracted under air compared with that extracted under nitrogen.

Swift and Posner (1972) found that incubation of humic acids for 30 days in 1 n NaOH under oxygen caused a reduction in molecular weight, liberation of aminoacids and a considerable increase in the content of carbonyl and carboxyl groups. Reduction in molecular weight and liberation of amino acids were also noted by incubation made under nitrogen, but not to the extent found by incubation under oxygen.

Hydrolysis and so-called neoformation of humus (Duchaufour and Jacquin 1963) are also usually assumed to take place during alkaline extraction. Compounds with some properties similar to those of extracted humus may even be produced by a similar treatment of fresh plant material or pure carbohydrates with alkaline solutions (Waksman 1936). This should be taken into account when studying organic matter preparations from soil horizons containing a large amount of undecomposed or partly decomposed plant material such as podzol A_o horizons. Schnitzer and Skinner (1968) found no major differences in the elementary composition and content of functional groups of organic matter extracted from a podzol B horizon with 0.5 n NaOH under nitrogen, and with 0.1 n HCl, respectively.

5.2.4 Extraction by Acid Solutions

Various inorganic and organic acids have been found capable of extracting organic matter from soils. The amount extracted depends on kind and concentration of acid as well as on the conditions of extraction. The nature of the soil horizon is also of the utmost importance for the amount of organic matter extracted. In most cases inorganic acids seem to be preferred for this extraction. A major reason for this is that the acid itself does not interfere with the determination of organic matter in the extract.

Ponomareva (1964) used 0.1 and 0.5 n H_2SO_4 and found that a large fraction of the humus of the B horizon of sandy humus-illuvial podzols could be extracted by these solutions, while substantially smaller fractions were extracted from the A horizon of the same soils. Similar results were obtained by Schnitzer and Wright (1957) and Schnitzer, Wright and Desjardins (1958) who used 0.5 % HCl, 0.5 % HF, and a mixture of these acids. All these solutions could extract a substantial fraction of the organic matter from podzol B horizons compared with very small or negligible amounts from the A_0 horizons. HF was considerably more effective than HCl and the efficiency of the mixture of the two acids was similar to that of HF alone. The amount of organic matter extracted from the B horizon by HF was comparable to that extracted by 0.5 n NaOH while the latter extracted about 25 % of the organic carbon from the A_0 horizon compared with trace amounts extracted by HF and HCl (Schnitzer, Wright and Desjardins 1958).

The organic matter extracted by acid solutions is usually considered to belong to the fraction of extracted organic matter classically known as fulvic acids. This fraction is in the traditional separation procedure (see, for example, Saurbeck and Führ 1968, Kononova 1966, Schnitzer and Gupta 1964) obtained by acidification of a neutral or alkaline humus extract. The only criterion used in defining this fraction is that it remains dispersed after the acidification, while the fraction precipitated is known as humic acids. Although frequently referred to as more or less definite fractions the actual size and composition of these fractions depend to a large extent on the modification of the procedure used in the extraction and separation of these groups of organic matter.

According to Kononova (1966) fulvic acids are generally considered less mature than humic acids. However, relying on investigations of muck and peat soils, Schnitzer and Hoffman (1966) and Schnitzer (1967) concluded that increased humification is associated with an increase in the fulvic acid fraction and a decrease in the humic acid fraction. Goh and Stevenson (1971) found that synthetic compounds having infrared spectra and other properties similar to natural humic acids could be changed into compounds more similar to fulvic acids by oxidation with hydrogen peroxide. Using the ^{14}C-dating technique, Scharpenseel, Ronzani and Pietig (1968) found only small age-differences between fulvic and humic acids from podzol A_h and B_h horizons.

In the studies of Ponomareva (1964) the amount of fulvic acids obtained from podzol B horizons by extraction with 0.1 n NaOH followed by acidification with H_2SO_4 did not exceed the amount extracted with 0.1 n H_2SO_4 directly. However, in the case of A horizons, where 0.1 n H_2SO_4 almost failed to extract any organic matter, fulvic acid fractions accounting for 10-25 % of the total organic carbon content were obtained by extraction with 0.1 n NaOH and subsequent acidification with H_2SO_4. This seems to indicate an alteration of the organic matter of the A horizons during the alkaline extraction.

As will be described in the following sections it has been possible to determine some characteristics of the extracted humus fractions, but it has hitherto been impossible to isolate more than minute amounts of well-defined organic compounds from the fulvic and humic acids. The doubt always exists as to what extent the properties of these fractions are artifacts produced by the reactions taking place during the extraction.

5.2.5 Extraction by Complexing Agents

A number of inorganic and organic compounds capable of forming complex compounds with metal ions have been found effective in the extraction of organic matter. As in the case of acids, inorganic compounds are generally preferred to avoid interference with the determination of the organic matter extracted, but organic complexing agents have also been employed, e.g. by Tinsley and Salam (1961) and Martin and Reeve (1957a, 1957b).

Evans (1959) found sodium pyrophosphate and sodium fluoride to be effective in extraction of organic matter from a neutral surface soil. Employing surface samples from four very different soils Aleksandrova (1960) found no major differences between the amount of organic matter extracted by 0.1 n sodium hydroxide and 0.1 m sodium pyrophosphate. However, if the soils were pretreated with 0.1 n sulphuric acid the sodium hydroxide was more efficient than the sodium pyrophosphate.

Schnitzer, Wright and Desjardins (1958) found that sodium pyrophosphate and sodium fluoride extracted organic matter amounts comparable to the amount extracted by a sodium hydroxide solution of equal concentration from a podzol B horizon. Part of the dissolving action of these reagents may be due to their alkalinity but neutralization prior to extraction did not substantially reduce the amount of carbon extracted. It should be added that even if the sodium fluoride solution was neutralized to pH 7 before the extraction, the solution had pH > 10 after extraction. This may be explained as due to the release of hydroxyl ions caused by formation of aluminium fluoride complexes (Fieldes and Perrott 1966). A similar effect was not noted for the sodium pyrophosphate solutions, where the pH declined on contact with the soil as would be expected, since the soil was more acid than the solution. From the A_0 horizon sodium pyrophosphate and sodium fluoride could dissolve only small amounts of organic matter, less than 10 % of the total amount present compared with about 25 % for sodium hydroxide. In this case the pH of the sodium fluoride declined on contact with the soil as was the case with most other reagents. The complexing properties of the fluoride ion may be one of the reasons for the superiority of HF compared with HCl in extracting organic matter, as discussed in section 5.2.4. The ability of sodium pyrophosphate to extract great amounts of organic matter from podzol B horizons compared with rather low amounts from the A horizons has also been demonstrated by Jacquin, Juste and Dureau (1965), McKeague (1968) and Hubert and Gonzalez (1970). This was also found by Bascomb (1968) who used potassium pyrophosphate.

Organic complexing agents such as EDTA (Schnitzer, Wright and Desjardins 1958), cupferrone and acetyl acetone (Martin and Reeve 1957a, 1957b) have been shown to have a similar effect towards the organic matter of podzol A and B horizons respectively.

A method based on a somewhat similar principle is the application of a cation exchange resin. Rosell and Babcock (1968) found repeated extractions of a surface sample from a loamy prairie soil with sodium saturated ion exchange resin to be more effective in extracting organic matter than repeated extractions with 0.5 n sodium hydroxide. For a peat the reverse sequence was found. Besides this, the organic matter extracted with the resin contained a much higher fraction of humic acids than that extracted with sodium hydroxide. Levesque and Schnitzer (1967) found that an ion exchange resin on Na-form extracted about 25 % less organic matter from a podzol B horizon than 0.5 n NaOH. For most other soil samples tested the difference was larger. The results were, however, similar to those of Rosell and Babcock in that the resin extract always contained more humic acids and more non-dialyzable carbon than the NaOH extract. Although the most obvious explanation for this is a partial break-down of the organic matter during NaOH extraction the authors explained it as caused by the greater ability of NaOH to separate low molecular organic compounds from inorganic soil constituents. However, De Serra and Schnitzer (1972) found such strong evidence for a partial decomposition during NaOH extraction compared with extraction with an ion exchange resin that they admitted some decomposition could have taken place, although they did not entirely abandon the other explanation above. Hubert and Gonzalez (1971) found that a strongly acid ion exchange resin on H-form extracted slightly more organic matter from a podzol B horizon than 0.1 m sodium pyrophosphate, and their investigations revealed no major differences in the properties of the material extracted by the two methods.

5.2.6 Extraction by Organic Solvents

A number of organic, non-complexing, solvents have been used in the extraction of soil organic matter, either alone or as part of an extraction scheme aimed at a fractionation of the soil humus. Examples are alcohols, ethers, and hydrocarbons such as benzene (Waksman 1936, Kononova 1966). In general, such reagents are fairly ineffective extractants for true humus compounds. Rather, they must be assumed to dissolve compounds closely related to plant constituents such as waxes, fats, resins, etc. Parsons and Tinsley (1960) found that anhydrous formic acid could extract only 2-3 % of the total organic matter content at room temperature but the amount extracted could be increased almost five times by boiling, and addition of salts increased the amount dissolved still more.

5.2.7 Decomposition of Inorganic Soil Constituents

To avoid the complications involved in the extraction of humus, some authors (Broadbent 1955, Leenheer and Moe 1969, Ivanushkina 1971) have suggested decomposing the most active fraction of the inorganic soil material by means of hydrofluoric acid. Using this technique it would be possible to study the properties of unextracted organic matter with smaller interference from the inorganic soil constituents, mainly clay. Few investigations pertaining to podzol soils using this technique seem to have been made, and it seems likely that this treatment will also cause some alterations in and probably the dissolution of organic matter. As demonstrated above, hydrofluoric acid is capable of extracting a substantial fraction of the organic matter of podzol B horizons.

5.2.8 Interpretation of the Extractability of Organic Matter of Podzols

From the discussion in the previous sections it is obvious that the organic matter of B horizons of podzols is much more easily dispersed than that of A, and especially of A_0 horizons. The only reagent that can extract a substantial part of the organic matter from A_0 horizons is concentrated NaOH. On the other hand, a variety of acids, complex-forming compounds and bases are able to bring about an almost complete extraction of the organic matter of B horizons. These reagents are all capable of removing metals such as iron and aluminium from the organic matter as soluble or insoluble compounds. The results, therefore, strongly suggest that these metals are responsible for the insolubility of the organic matter of the B horizons of podzols. The general assumption, as also pointed out by most of the authors quoted above, is that the metals are found in some insoluble complex compounds with the organic matter. Upon removal of at least a part of the metals most of the organic matter becomes soluble. It is, of course, not to be inferred from this that the various extractions are without any additional effects on the organic matter. The products extracted may well have been subject to some of the alterations discussed in section 5.1. It seems most likely that these effects will be of greatest importance when strongly alkaline or acid solutions are employed in the extractions, while neutral complex-forming compounds would be expected to cause smaller alterations.

One logical conclusion, but not the only one, derived from extending this reasoning to the organic matter of the A horizon is that this needs some alteration in order to become dispersed, since only quite strong bases are effective in the extraction of organic matter from this horizon, and even these extract only a relatively small fraction.

In the present study no attempt has been made to extract humus compounds from the soil samples other than the water extractions discussed in chapter 9. However, some observations were made which confirm the results mentioned above. All the soil samples were heated with a solution containing EDTA,2Na and sodium dithionite with the purpose of determining iron and aluminium as described in chapter 6. The pH of the extraction mixtures was about 5. During the extractions it was observed that there was a great difference in the extent to which the extracts became coloured by dispersed organic matter. An attempt was made to determine the amount of carbon extracted using the gaschromatographic technique described in chapter 9. However, the original carbon content of the solutions due to the EDTA was too great to allow a reasonable accuracy in the analyses. Only a visual evaluation of the colours of the extracts was therefore made. Although there may not be a rigorous correlation between the colour and the organic matter content of the solutions this evaluation gives some impression of the amount of organic matter extracted.

The results are shown in Table 3. Although some exceptions are noted, the extracts from B horizons are generally the most intensively coloured, and hence these extracts may be assumed to contain the largest amounts of dispersed humus compounds. In some profiles a fairly intensively coloured extract is obtained from A_{ob} horizons having a very large content of organic matter in a partly decomposed state. If the extracts from A_1 horizons are compared with those from B_1 horizons of the same profiles the latter are generally more intensively coloured even if the total carbon content is higher in the A_1 horizon.

In what follows some of the chemical properties of the organic matter of podzol A and B horizons will be discussed. These are mostly based on extracted humus, and it must be assumed that the results are more reliable for the humus from the B horizon than for that from the A horizon, since it is often extracted by a milder reagent and since the fraction extracted is much greater, which makes it more representative. Before beginning the discussion of these properties some more limitations should be pointed out. These are connected with the fact that the humus extracted has often been subject to some purification and fractionation. This is usually done by employing techniques like acidification, precipitation by various reagents, redissolution, ion exchange techniques, dialysis and sometimes even long sequences of chemical reactions with the aim of making derivatives, etc. All os these may cause some unknown alterations of the humus compounds and/or an uncontrolled loss of material which may lead to false conclusions, since the extracted material is far from being homogeneous.

The following discussion will to a large extent be based on the investigations made by Schnitzer and co-workers. These investigators have produced the most extensive data pertaining to the organic matter of podzols available in literature. The most serious drawback of the investigations, limiting their application to podzols in general, is that they are, with few exceptions, based on only one soil profile and a great number of the investigations are made on the same humus preparation from this soil.

5.3 Elementary Composition of the Organic Matter

Although organic carbon and nitrogen may be estimated on the untreated soil it is necessary to rely on results obtained from extracted organic matter when estimating the contents of these elements in the organic matter itself. Data on the elementary composition of extracted organic matter are reported for a Canadian podzol by Wright and Schnitzer (1959), Schnitzer, Shearer and Wright (1959) and Schnitzer and Desjardins (1962), for a Danish podzol by Hansen and Schnitzer (1966) and for nine Canadian podzols by Schnitzer (1970). Schnitzer and Desjardins (1969) reported data on the elementary composition of organic matter obtained from a natural leachate of a Canadian podzol.

When the results are fairly consistent the following discussion will mainly take into account the data reported by Wright and Schnitzer (1959) and the results reported in the remaining papers mentioned will be discussed only if they represent important deviations from these.

5.3.1 Carbon Content

In section 4.1 it was stated that the carbon content of the organic matter decreases with depth in most soils including podzols. Wright and Schnitzer (1959) reported that organic matter extracted from the A_o horizon contained almost 57 % C when calculated on the basis of ash-free, dry organic matter. The organic matter extracted from the B_h horizon contained only about 50 % C. However, Hansen and Schnitzer (1966) found more than 56 % C in the organic matter from the B_h horizon of a Danish podzol. The latter study did not include the organic matter of the A horizon. Humic and fulvic acids extracted from a podzol humus-illuvial horizon with 0.1 n NaOH and separated by acidification with HCl to pH 2 by Shurygina et al. (1971) contained 55.56 % and 51.32 % C respectively.

5.3.2 Oxygen and Hydrogen Content

The organic matter extracted from the A_o horizon by Wright and Schnitzer (1959) had a lower oxygen content and a higher hydrogen content than that extracted from the B_h horizon of the same soil. The former contained 5.2 % hydrogen and 35 % oxygen, corresponding to a molar ratio of 2.35, and the latter contained 3.7 % and 44 % of the two elements, corresponding to a molar ratio of 1.35. Hence, the organic matter of the B horizon appears to be considerably more oxidized than that of the A_o horizon. However, Hansen and Schnitzer (1966) found that the organic matter extracted from the Danish podzol contained 5.8 % and 35.7 % of the two elements respectively, corresponding to a molar ratio of 2.56, i.e. even higher than that previously found for an A horizon. As the latter study did not include organic matter from the A horizon it is not possible to draw any conclusions about possible differences in oxidation state within this profile. Shurygina et al. (1971) found fulvic acids from a podzol humus-illuvial horizon to be much more oxidized than humic acids from the same horizon. The molar ratio of hydrogen to oxygen in the two fractions were 1.16 and 2.00 respectively. No information is given on the proportions between the two fractions.

For humus-illuvial podzols Ponomareva (1964) has shown in an indirect way that the organic matter of the B horizon is more oxidized than that of the A horizon. In her experiments, the carbon content determined by a method based on collection and determination of carbon dioxide was compared with the carbon content calculated from the oxygen consumption during wet combustion of the organic matter. In four profiles investigated the carbon content calculated from the oxygen consumption was 7-16 % larger than that based on evolved carbon-dioxide in the A horizons, but 4-14 % smaller in the B horizons. It is not possible from the description given by Ponomareva (1964) to judge whether a complete oxidation has been obtained in the analyses but the relative difference in oxidation state of the organic matter of the two horizons seems well established. As regards the extent to which the results are representative for the entire organic fraction of the horizons in question, they are superior to the results obtained from investigations carried out on extracted organic matter, since they are based on the total organic matter present in the horizons.

5.3.3 Nitrogen Content

As shown by many authors including Weis (1929, 1932), Joffe and Watson (1933), Young (1962), Ponomareva (1964), and Gonzalez and Hubert (1972) the $\frac{C}{N}$-ratio of the bulk organic matter of podzols is much higher than the $\frac{C}{N}$-ratio of well-decomposed organic matter of most other soils. Weis (1929, 1932), who worked with podzols from the same areas as some of those studied in this investigation, found $\frac{C}{N}$-ratios as high as 60 although values in the range 25-30 were more common. Weis (1929) found an enormous decrease in the $\frac{C}{N}$-ratio with depth. In some C horizons $\frac{C}{N}$-ratios smaller than 5 were found. In his later study Weis (1932) found this trend to be much less pronounced, and he attributed this to differences in the age of the soils studied. Although it is a general experience that the $\frac{C}{N}$-ratio decreases with depth (Stevenson 1959, Young 1962) a decrease to the extent found by

Weis (1929) seems rather unlikely and the explanation offered by Weis (1932) seems difficult to credit. The reason for Weis's findings is not known but an examination of his data reveals that the low $\frac{C}{N}$-ratios are invariably found where the absolute contents of carbon as well as nitrogen are very small and hence subject to large experimental relative errors.

Joffe and Watson (1933) found an irregular variation with depth of the $\frac{C}{N}$-ratio in two podzol profiles. They explained some high values in the A horizon as being due to a content of charcoal in the soil.

The soils investigated in the present study have been analyzed for nitrogen using the simplified Kjeldahl procedure described by Kjær (1968), and the $\frac{C}{N}$-ratios have been calculated. The results are listed in Table 3. They confirm that the organic matter of all the horizons has a high $\frac{C}{N}$-ratio. If samples with negligible amounts of carbon and nitrogen, where the relative analytical errors may be quite considerable and cause large errors in the $\frac{C}{N}$-ratios, are disregarded, the remaining values are within the range 20-65. The majority of the values are between 20 and 40. The pattern of variation seems rather different from soil to soil and little regularity is noted. The widest $\frac{C}{N}$-ratio is found in the A_o horizon of the profile developed on drifting sand where the vegetation mainly consists of Calluna vulgaris. High values are also found in some A_1 and A_2 horizons. Generally the $\frac{C}{N}$-ratio seems to be slightly lower in the B horizon but this is not without exceptions. In the Trinderup profile the highest $\frac{C}{N}$-ratio (38) is found in the B horizon. It is, therefore, difficult to draw any conclusions about a regularity in the variation of the $\frac{C}{N}$-ratio with depth in the soils studied.

In the organic matter extracted by Wright and Schnitzer (1959) there is a considerable difference in the nitrogen content of the organic matter extracted with 0.5 n NaOH under nitrogen from the A_o and B_h horizons respectively. The former contains about 2.35 % N corresponding to a $\frac{C}{N}$-ratio of 24 and the latter 0.70 % N corresponding to a $\frac{C}{N}$-ratio of 71. It should be noted that there is a remarkable difference in the nitrogen content in the material extracted under air and under nitrogen from the A_o horizon while the effect on the content of all other elements (also on the nitrogen content of the organic matter extracted from the B_h horizon) is negligible. The nitrogen content of the organic matter extracted from the A_o horizon under air is only 1.87 %. The authors offer no explanation for this difference. It could be due to a liberation of free aminoacids and subsequent removal of these during the purification of the material. Swift and Posner (1972) have shown that much larger amounts of aminoacids are liberated from humic acids incubated in alkaline solution under oxygen than from humic acids incubated in alkaline solution under nitrogen.

Sowden and Schnitzer (1967) showed that whereas approximately equal fractions of the organic matter and the nitrogen were extracted by 0.5 n NaOH from the B_h horizon, the nitrogen-containing compounds were preferentially adsorbed by the cation exchange resin used in the purification of the organic matter. Hence, the purified organic matter had a smaller nitrogen content than the original soil organic matter. Since the purification of the organic matter extracted from the A_o horizon in the studies mentioned above was made by dialysis and not by ion exchange technique this may be one of the reasons for the differences in the nitrogen content of the organic matter from the two horizons.

Humic acids extracted with 0.5 n NaOH from a podzol humus-illuvial horizon by Shurygina et al. (1971) contained 3.72 % N, while the fulvic acids from the same horizon contained only 0.87 % N.

5.3.4 Contents of Other Elements

It must be assumed that all the elements found in organic compounds of living organisms will be present in the humus compounds as well. In addition to those discussed already sulphur seems to be the most important. Wright and Schnitzer (1959) found 0.7 % and 1.3 % in the organic matter from the A_o and B_h horizons respectively. However, in studies employing extracted organic matter from the same soil Schnitzer and Desjardins (1962) found only 0.35 % and 0.26 % in the organic matter from the two horizons. The reason for this discrepancy is not known but the latter values seem to be the more probable, since they are of the magnitude usually encountered in soil organic matter (Alexander 1961).

The organic matter must also be assumed to contain various metals in different modes of combination. However, the content of these is usually impossible to determine since the extractants used in extraction of organic matter will extract metals and other elements from the soil inorganic fraction as well. Hence, all humus extracts will contain a high proportion of metals and inorganic anions. The majority of this inorganic material is usually removed by various treatments as described in section 5.2.8. However, it has not yet been possible to obtain an entirely ash-free organic matter preparation, even if strong methods have been employed in the purification. This indicates that some metals, and perhaps other elements as well, are fixed to the organic compounds by strong bonds. This will be discussed further in chapter 7.

5.4 Chemical Structure of the Organic Matter

5.4.1 Molecular Weight

As discussed earlier the humus compounds consist of macromolecular compounds. Several approaches have been made towards establishing actual molecular weights using such techniques as osmometry, cryoscopy, vapor pressure reduction, ultracentrifugation, gel filtration, etc.

Being mixtures of different organic compounds no definite molecular weights can be assigned to any one fraction of the humus compounds except in those few cases where pure compounds have been isolated. In general it is possible to determine an average molecular weight only. The average molecular weight of a heterogeneous mixture is in addition not well defined since it will depend on the nature of the method whether the so-called number average or weight average is obtained. The number average molecular weight $\bar{M}_n$ is given by

$$\bar{M}_n = \Sigma M_x V_x = \frac{1}{\Sigma \frac{F_x}{M_x}}$$

where V_x, is the number fraction and F_x, the weight fraction of molecules having molecular weight M_x (Lansing and Kraemer 1935). Similarly, the weight average molecular weight $\bar{M}_w$ is given by

$$\bar{M}_w = \Sigma M_x F_x$$

Methods dependent on the number of molecules, such as osmometry and similar methods involving a measurement of one of the colligative properties, will yield the number average molecular weight, while some other methods such as ultracentrifugation according to Stevenson, van Winkle and Martin (1953) are likely to yield the weight average.

It follows from the equations given that there will not be a simple relationship between the two molecular weights. The actual ratio of $\bar{M}_w$ to $\bar{M}_n$ depends on the heterogeneity of the material. In addition some of the methods used in the determinations of the molecular weights are subject to certain inherent limitations. If water is used as a solvent in a method involving measurement of a colligative property errors may be introduced by dissociation of the organic material. Gel filtration and ultracentrifugation are also subject to certain limitations as discussed by Posner (1963), Lindquist (1967), Flaig and Beutelspacher (1968) and Cameron et al. (1972a).

The actual molecular weights of extracted humus preparations reported in the literature vary highly. Using gel filtration Posner (1963) found molecular weights ranging from below 4,000 to above 200,000 for humic acids extracted by a sodium carbonate-sodium hydroxide mixture from a red-brown earth. Meisel et al. (1971) found by ultracentrifugation the molecular weight of fulvic and humic acids extracted from peat by 0.1 n NaOH + 0.1 m $Na_4P_2O_7$ to be 600 and 3,000 - 3,400 respectively. By gel filtration Tan and Giddens (1972) obtained two fractions of fulvic acids both with molecular weights below 15,000 and two fractions of humic acids having molecular weights below 15,000 and above 30,000 respectively. Values as high as 1 x 10^6 and 15 x 10^6 have been reported for humic acids by Wershaw et al. (1967) and Cameron et al. (1972b).

For a humus preparation extracted from a podzol B_h horizon by 0.5 % HF and purified by dialysis, Wright, Schnitzer and Levick (1958) found the molecular weight to be 50,800. The determination was made by osmometry in 0.15 m NaCl. For organic matter extracted from the same soil and horizon by 0.5 n NaOH and purified by treatment on a hydrogen-saturated ion exchanger Schnitzer and Desjardins (1962) found the molecular weight to be 669. This determination was made by cryoscopy in sulfolane and cyclohexanol, both solvents giving nearly identical values. However, although Schnitzer and Desjardins (1962) discuss various molecular weights found previously by other authors no mention is made of the large value found in the former study, and hence no explanation is attempted of this almost 100-fold discrepancy. The latter study also included organic matter extracted from the A_o horizon and purified by electrodialysis. The molecular weights determined by cryoscopy in sulfolane and cyclohexanol were 1,684 and 1,100 respectively. The authors attributed the lower value to the organic matter being partly insoluble in cyclohexanol.

In two later papers Schnitzer and Skinner (1968b) and Hansen and Schnitzer (1969b) reported further investigations on the molecular weight of the material extracted from the B_h horizon. Using vapour pressure osmometry in water they found lower molecular weights due to dissociation of the material in aqueous solution. Schnitzer and Skinner (1968b) corrected for this employing a factor found from a study of the relationship between true molecular weight and molecular weight determined by vapour pressure osmometry for benzene carboxylic acids with 1 to 6 carboxyl groups per molecule. This method seems to be without theoretical justification and a more reliable correction factor based on the pH of the solutions was employed by Hansen and Schnitzer (1969b). It is noteworthy that whereas the first correction factor led to a molecular weight in agreement with that determined earlier (Schnitzer and Desjardins 1962), the latter correction factor gave a molecular weight approximately 50 % higher. Both studies mentioned also included a fractionation of the material by gel filtration. Within each paper there is an excellent agreement between the different values, but considerable divergencies are noted between the results of the two investigations although allegedly the same material and the same technique have been employed. In the first study fractions were obtained with corrected number average molecular weights determined by vapour pressure osmometry from 175 to 3,570 while the range in the latter study was 275-2,110. In both cases these molecular weights were 2-10 times smaller than the specifications of the Sephadex gels employed. This may be due to the fact that the authors neglected the effect of the gradient in ionic strength as discussed by Lindqvist (1967). In calculating the number average molecular weight of the original material from the total weight and molecular weight of each fraction obtained by gel filtration, using the equation given in the beginning of this section, the authors in both studies found an excellent agreement only because they neglected the loss of material during the gel filtration. A still more serious objection may be raised against some calculations made by Schnitzer and Skinner (1968b) which led to an excellent, but false, agreement between the molecular weights determined by vapour pressure osmometry and by ultracentrifugation.

Hansen and Schnitzer (1966) found by cryoscopy that organic matter extracted from the B horizon of a Danish podzol had a molecular weight of 551.

5.4.2 Molecular Structure of the Organic Matter

Although a number of pure organic compounds have been isolated from soils, as described by Flaig (1971), the bulk and relatively stable humus seems to be of a complex polymeric nature. In reviews by Bremner (1951), Broadbent (1953) and Felbeck (1971) various possible humus constituents such as carbohydrates and uronic acids, nitrogen compounds including amino acids and amino sugars, and aromatic compounds including single ring as well as polycyclic structures, are discussed.

The prevailing view seems to be that the humic and fulvic acids consist of a mainly aromatic core to which various side chains, mainly of an aliphatic nature with various functional groups, are attached (Kononova 1966, Halworth 1971, Sørensen 1973). The main difference between humic and fulvic acids seems to be more a question of degree than of kind as would be expected from the fact that these concepts represent conventional fractions only. Kononova (1966) states that the fulvic acids have a less condensed structure than humic acids. According to Martin and Haider (1971) the fulvic acid fraction may in addition contain some polysaccharides. Hansen and Schnitzer (1969a) subjected humic and fulvic acids from a podzol B_h horizon to Zn-dust distillation and fusion but found no qualitative differences between the decomposition products from the two humus fractions. The compounds identified were all aromatic hydrocarbons consisting of 2-5 benzene units with few substituents. They accounted for less than 1 % of the original amount of organic matter.

Many authors, including Davies (1971), regard polyphenols as precursors of the stable humus compounds. The polyphenols do not constitute a well-defined group of compounds and few of the authors using this concept have tried to give a definition or delimitation of the group. Comprehensive text- and reference books on organic chemistry such as those by Schmidt and Rule (1947), Noller (1958) and Smith and Cristol (1966) do not describe or define a group of compounds as polyphenols. Most authors describing the presumed reactions of polyphenols in soils and their relation to humus compounds seem to include a varity of compounds ranging from simple polyhydroxybenzenes to complex polymeric compounds among the polyphenols. Most often the chemical constitution of the polyphenols seems to be related to that of the tannins occuring in the leaves and bark of many trees. It has been shown that chemical or biological oxidation of some compounds falling within this broad concept of polyphenols, or mixtures of these with compounds such as amino acids, peptides, amino sugars, or carbohydrates may yield products having many properties in common with humus compounds extracted from soils (Lindqvist and Lindqvist 1969, Goh and Stevenson 1971, Pollack, Lentz and Ziechmann 1971, Bondietti, Martin and Haider 1972).

Schnitzer and co-workers have made a number of investigations to determine the fundamental molecular structure of the organic matter of podzols. Wright and Schnitzer (1961) found that prolonged heating at 170 °C, which was assumed to affect aliphatic structures only, caused a greater weight loss of material extracted from the A_0 horizon than of that extracted from the B_h horizon. Thermogravimetric investigations by Schnitzer and Hoffman (1961) and Turner and Schnitzer (1962) revealed that the material from the A_o horizon was decomposed in two separate steps, which the authors assumed to be due to aliphatic and aromatic structures respectively, while the decomposition pattern of the material extracted from the B_h horizon was more irregular with the major decomposition taking place at a temperature intermediate between those of the two decomposition steps found for the A_o material.

In contrast Hansen and Schnitzer (1966) found that the organic matter from the B_h horizon of a Danish podzol was also subject to considerable decomposition at the temperature assigned to aliphatic compounds.

Shurygina et al. (1971) subjected humic and fulvic acids from a humus-illuvial horizon to thermogravimetric and differential thermal analyses. The shapes of the TG as well as the DTA curves were quite similar, the major difference being that the decomposition of the humic acids took place at a slightly higher temperature than that of fulvic acids. The largest weight loss occurred at a temperature slightly above 500 °C for humic acids and at approximately 450 °C for fulvic acids. The DTA diagrams showed a major exothermic reaction at the same temperatures. DTA investigations conducted by Schnitzer and Kodama (1972) also showed an exothermic reaction at 450 °C for fulvic acids from a podzol B horizon.

Schnitzer and Wright (1960a, 1960b) and Hansen and Schnitzer (1966, 1967) studied the products obtained by oxidation of the organic matter from podzol A and B horizons with alkaline potassium permanganate and with nitric acid. The organic matter of the A horizons was used directly after removal of plant residues, while that of the B horizons had been extracted with 0.5 n NaOH. In general, there was a tendency towards a higher relative yield of aromatic carboxylic acids among the oxidation products of the organic matter from the B horizons compared with that from the A horizons. However, there were some inconsistencies and the oxidation products accounted for only small fractions of the total organic matter content of the samples investigated. Nevertheless, it was concluded that the organic matter of the B horizons had a higher degree of aromaticity than that of the A horizons. Hansen and Schnitzer (1967) further suggested that the organic matter of the B horizon consists mainly of isolated aromatic rings which are heavily substituted. The aromatic rings were assumed to be linked to each other by aliphatic chains or saturated cyclic or hydroaromatic structures. The occurence of substantial amounts of condensed aromatic structures was considered unlikely.

Pollack, Lentz and Ziechman (1971) studied humic acids, extracted from podzol A and B horizons, by X-ray diffraction. They concluded that the diffractograms provided "good, but not positive, evidence that the humic acids contain aromatic structures". They estimated that aromatic compounds made up about 30 % of one of the humic acid preparations from a podzol A horizon.

Of great importance for the reactions of the organic matter in soils are the kinds and amounts of functional groups. This problem has also been investigated by Schnitzer and co-workers. NMR-studies by Barton and Schnitzer (1963) and Schnitzer and Skinner (1968b) produced no evidence for the presence of aromatic hydrogen in the organic matter from the B_h horizon. This was assumed to be due to complete substitution of the aromatic structures.

Wright and Schnitzer (1959) and Schnitzer and Desjardins (1962) reported contents of carboxyl, phenolic and alcoholic hydroxyl, carbonyl and methoxyl in organic matter preparations from the podzol A_o and B_h horizons. The results were obtained by chemical methods and confirmed by infrared spectrometry. The organic matter from the B_h horizon had a substantially higher content of functional groups (expressed as meq./g) than that from the A_o horizon. The largest difference was found in the carboxyl content which was 8-9 meq./g in the material from the B_h horizon compared with 1-2 meq./g in the material from the A_o horizon.

When comparing these results two facts should be considered. First, the material from the two horizons had been purified by two different methods: dialysis and treatment on an ion exchange resin. The material treated on the ion exchange resin will probably correspond to the fulvic acid fraction while that purified by dialysis is likely to be some mixture of humic and fulvic acids. This may not be too serious since there seems to be no major qualitative differences between the two fractions. More important is the fact that, as compared with dialysis, the ion exchanger treatment will be more efficient in removing metal ions from the organic compounds. Using methods similar to those of Wright and Schnitzer (1959), Gonzalez and Hubert (1972) have shown that a considerable number of carboxyl groups seem to be created by treatment of previously dialyzed humic and fulvic acids on an ion exchange resin. At the same time the content of iron and aluminium in the organic matter preparations was considerably reduced. This seems to imply that a part of the carboxyl groups of the material not treated on the ion exchanger were masked as strong iron and aluminium complexes.

The second fact to be considered is the specificity of the methods used in the determination of the functional groups. The most important methods used in the determination of carboxyl and total acidity, i.e. carboxyl + phenolic hydroxyl, are reactions with calcium acetate and barium hydroxide respectively. These reagents will distinguish between acidic groups having varying acid strength. However, the actual strength of a given functional group will depend to a large extent on the configuration of this group in the organic molecule, as is well-known from organic chemistry and as has been found for soil organic matter by Stevenson and Goh (1972). Schnitzer and Gupta (1965) found that the barium hydroxide and calcium acetate methods gave the theoretical values for some simple organic compounds but both methods failed in the case of polyhydroxy benzoic acids. For humic and fulvic acids they found a fair agreement between the two methods and some control methods. In the case of the barium hydroxide method the control method was the so-called discontinuous potentiometric titration (Schnitzer and Desjardins 1962). This seems to subject the organic compounds to a treatment almost identical to the barium hydroxide method and hence a good agreement is not surprising in this case. Wright and Schnitzer (1960) found a satisfactory agreement between the carboxyl content determined by various titration procedures and by a decarboxylation method. In this study similarly treated organic matter preparations from the A_o and B_h horizons of the soil used by Wright and Schnitzer (1959) and Schnitzer and Desjardins (1962) were employed, but the differences in the carboxyl content between the organic matter preparations from the two horizons were much smaller than those found in the study quoted above.

If only similarly treated organic matter preparations are compared the studies of Gonzalez and Hubert (1972) reveal no major differences between the organic matter from A and B horizons of the same soils.

The carbonyl content in the organic matter from the B_h horizon was further investigated by Schnitzer and Skinner (1965b), who prepared several derivatives and found 3.0-3.7 meq.per g organic matter. This is only about half the amount reported by Wright and Schnitzer (1959) for the same material. The quinone group is often assumed to be a major constituent of soil organic matter (Stevenson and Goh 1972), but Schnitzer and Skinner (1965b) were unable to demonstrate the presence of this functional group in the organic matter from the podzol B horizon.

The nature of the nitrogen compounds of the organic matter of a podzol B horizon was studied by Sowden and Schnitzer (1967). When untreated soil was subjected to hydrolysis for 20 hrs. with boiling 6 n HCl, 28 % of the nitrogen was found as amino acid-N, 22 % as NH_4-N and 2 % as amino sugar-N. Gonzalez and Hubert (1972) found considerable differences in the content of different nitrogen compounds of humic and fulvic acids from podzol A and B horizons. The amino sugar fraction was the dominant nitrogen fraction in the fulvic acids while so-called heterocyclic N was the most important N fraction of the humic acids. No major differences were found between soils or between horizons.

It has been mentioned already that a part of the organic matter may consist of polysaccharides. Gupta, Sowden and Stobbe (1963) found that monosaccharides liberated by hydrolysis accounted for less than 2 % of the total content of organic matter of a podzol 0 horizon and less than 1 % of that of the B_2 horizon of the same soil. In the hydrolyzed material galactose, glucose, mannose, arabinose, xylose, fucose-ribose and rhamnose were identified by means of paper chromatography.

Coffin and DeLong (1960) found that about 1.8 % of the organic matter extracted from a podzol B horizon by a water-benzene-8 hydroxychinoline mixture was carbohydrates.

Ogner and Schnitzer (1970) isolated various dialkyl phthalates from methylated fulvic acids extracted from a podzol B_h horizon. No dialkyl phthalates could be extracted with n-hexane or benzene prior to methylation of the fulvic acids. The dialkyl phthalates were identified in a benzene extract of the methylated fulvic acids by thin-layer chromatography, preparative gas chromatography, ultraviolet and infrared spectroscopy, and mass spectrometric analysis. These compounds accounted for only a very small fraction of the total amount of material soluble in benzene and for only 0.03 % (corrected for losses) of the initial amount of fulvic acids.

Similar compounds as well as alkanes and methoxybenzene carboxylic acids were identified from a methylated fraction of fulvic acids from the same soil by Khan and Schnitzer (1971). The fraction employed was that having the lowest molecular weight obtained by gel filtration (see section 5.4.1). The techniques used were rather similar to those used by Ogner and Schnitzer (1970) and the compounds isolated accounted for only a very small fraction, in this case too, of the initial amount of fulvic acids - approximately 0.25 %. The major compound isolated in both studies was bis (2 ethylhexyl) phthalate, which is a common constituent of industrial products, but the authors ruled out possibilities of admixture from the laboratory equipment by blank test. They believed the compounds isolated to be true constituents of the fulvic acids although all of them are hydrophobic compounds in contrast to the high solubility in water of the bulk fulvic acids. They suggested that these compounds are maintained in solution as 'complexes' with the hydrophilic constituents of the fulvic acids. Another, and more probable, possibility seems to be that the compounds are decomposition products formed by the strong chemical treatments involved in their isolation. Cifrulac (1969) found spectroscopic evidence for similar compounds in extracted soil organic matter, but in this case an organic extractant was employed.

However inaccurate and insufficient the knowledge of the properties of the soil organic matter may be, it follows from the results quoted in this chapter that the organic matter has a considerable content of acidic groups and a structural arrangement of these that enables it to f~~ro~~orm complex and chelate compounds with metal ions. As these properties are of utmost importance for podzolization they will be discussed thoroughly in subsequent chapters.

CHAPTER 6

IRON AND ALUMINIUM COMPOUNDS IN PODZOLS

6.1 General Considerations

Since podzolization as defined here involves a translocation of iron and aluminium compounds within the profile, podzols will have a characteristic distribution of these metals between the individual horizons. It is, therefore, possible to obtain valuable information on the extent of podzolization of a given soil by determining the iron and aluminium contents of the individual horizons. A determination of the total content of these elements does not involve any major difficulties but the results of such investigations are usually not sufficient to give a correct assesment of the podzolization. This is because most of the iron and aluminium of the majority of soils will be present as integral parts of the silicate minerals. This fraction of the metals has very little importance as far as an assessment of podzolization is concerned. If podzolization is evaluated on the basis of total iron and aluminium contents it may lead to erroneous conclusions since an enrichment or impoverishment of a given horizon might be due to a translocation of silicate clay.

It is, therefore, necessary to focus the interest on the fraction of the elements which is connected with podzolization as described in chapter 1. This fraction is, however, difficult to define clearly since it is rather heterogenous and contains the elements as part of various compounds. In chapter 1 this fraction is mostly referred to as 'free' sesquioxides, but this term is neither clear nor entirely correct. As will appear from the following sections and chapters, and as has been mentioned in chapter 4, these iron and aluminium compounds must be assumed to include crystalline and amorphous iron and aluminium oxides and hydroxides with varying water content, organic iron and aluminium compounds, possibly inorganic iron and aluminium compounds such as phosphates, and compounds transitional between these. The only common criteria of these compounds is that the iron and aluminium are not constituents of silicate compounds. The most appropriate term to apply to this group appears, therefore, to be 'non-silicate iron and aluminium'. It is not to be assumed that differences in the size of this fraction between different horizons will give an exact measure of the iron and aluminium translocated during podzolization. A part of the metals removed from the upper horizons may have escaped precipitation in the B horizon and become washed entirely out of the profile. On the other hand some of the metals precipitated in the B horizon may have reacted with silica to become a part of silicate compounds such as amorphous aluminium silicates, commonly known as allophanes, or, perhaps in some soils, true clay minerals. This fraction of the metals would formally be excluded from the non-silicate fraction. However, it seems impossible to suggest a more appropriate term to describe the fraction in question.

As it is difficult to define the metal fraction in question it is still more difficult to suggest methods for its chemical determination. Attempts to solve this problem or even to device methods capable of distinguishing between some of the fractions of the non-silicate iron and aluminium have not been lacking, however. All the methods proposed are based on assumed differences in solubility and/or dissolution rate of the different compounds. In general it must be presumed that the non-silicate fraction is more easily and rapidly soluble than the silicate fraction, although exceptions to this rule are easy to find. The methods, therefore, usually employ rather mild extractants such as slightly acid, reducing or complexing agents. In the following some of these methods will be discussed.

6.2 Methods for Determination of Non-Silicate Iron and Aluminium

It follows from the chemical properties of iron and aluminium that some extractants will affect compounds of both metals similarly while others will affect mainly or only one of these. Acids and complexing agents will have a similar, although usually quantitatively different, effect on both metals. On the other hand reducing agents will affect only iron compounds and alkaline solutions will affect only aluminium compounds.

Selective extraction of non-silicate iron compounds has received considerably more attention than the corresponding extraction of aluminium compounds. For practical reasons extraction of both metals will be treated simultaneously in the following, although some methods will be effective or have been used for one of the metals only.

Solutions of strong acids, especially hydrochloric acid, have been used frequently in such extractions. It seems unlikely that it is possible to obtain a good separation of the non-silicate and the silicate fraction by employing such reagents. The amount of metals extracted from both fractions must be assumed to increase with increasing concentration and increasing temperature and time of reaction. It will also depend on some properties of the soils. If the soil contains only small amounts of the silicate minerals which are fairly easily decomposed, e.g. certain clay minerals, the contribution from the silicate fraction to the amount of iron and aluminium extracted will, of course, be small, but this will apply to any extractant.

Tamm (1922) proposed a method for determination of the so-called colloidal fraction of iron, aluminium and silicon. The extractant is an oxalate buffer with pH 3.2-3.3. The action of this solution is due to the acidity as well as the complexing properties of the oxalate. Tamm (1932) found that the extractant had some destroying effect towards silicate minerals. Drosdoff (1935) used a modification of this method for investigations of clays.

Drosdoff and Truog (1935) used an ammonia solution saturated with gaseous H_2S as extractant for free iron oxides from soil colloids and found that limonite and goethite were dissolved completely and haematite almost completely, while silicate minerals remained unaffected. This method was modified by Truog et al. (1936) who used nascent H2S obtained from Na_2S and oxalic acid. This modification was found more effective and in addition to the iron small amounts of aluminium were extracted. Another modification employing gaseous H_2S was made by Drosdoff (1941) who found it to give results similar to the method of Truog et al. (1936).

Dion (1944) used nascent hydrogen produced by reaction between metallic aluminium and ammonium tartrate as reducing agent for extraction of iron oxides. The minerals montmorillonite, kaolinite and muscovite were only slightly affected but the method caused a substantial dissolution of iron from the iron-containing clay mineral nontronite.

Jeffries (1946) used nascent hydrogen produced by the action of an oxalic acid-potassium oxalate buffer on metallic magnesium for removal of free iron oxides from soils. In the modification employed by Jeffries no determination of the extracted iron was made.

Schofield (1949) found that the amount of iron extracted by Tamm's method increased when the extraction was carried out in sunlight. This was confirmed by Deb (1950b) who compared Tamm's method with a method employing sodium dithionite as reducing agent. He found that montmorillonitic clay minerals were affected to a greater extent by Tamm's solution than by the dithionite reagent. However, both solutions caused a considerable breakdown of montmorillonitic clay minerals as compared to other clay minerals which were attacked to a small extent only.

Williams (1950) found that Jeffries' (1946) method caused an incomplete dissolution of limonite, goethite, haematite, magnetite and ilmenite. Small amounts of aluminium were dissolved from bauxite, diaspore, kaolinite, montmorillonite, illite, chlorite and vermiculite, while one third of the total iron content, and significant amounts of aluminium, were dissolved from biotite.

Mitchell and Mackenzie (1954) compared Tamm's, Dion's and Deb's methods for removal of free iron oxides from clays. They found Deb's method to be most satisfactory but noted a precipitation of ferrous sulphide during the extractions. To overcome this they suggested a technique involving alternating extractions with dithionite and 0.05 n HCl.

Mackenzie (1954) found that somewhat greater amounts of iron were extracted from most soils by this dithionite-hydrochloric acid method than by Tamm's and Dion's methods. On the other hand somewhat larger amounts of aluminium were extracted by Tamm's method but the actual amounts extracted by the dithionite-hydrochloric acid method were assumed to express the correct trend along a profile. No improvement was obtained from an adjustment of pH of the dithionite solution towards neutrality.

Haldane (1956) replaced the magnesium in Jeffries'(1946) method with zink and found that ilmenite, biotite and hydrobiotite were attacked only slightly while a considerable fraction of the iron was extracted from nontronite.

Aguilera and Jackson (1953) modified Deb's (1950b) method by addition of sodium citrate to the dithionite reagent. A further modification involving buffering of the reaction mixture to pH 7.3 with sodium bicarbonate was introduced by Mehra and Jackson (1958). One extraction with this reagent dissolved haematite completely while three successive extractions were required to obtain a complete dissolution of goethite. The method was compared with Truog's,Deb's and Haldane's methods on soil and clay samples. No major differences were found in the amounts of iron, aluminium and silicon dissolved except for a sample of nontronite, where less iron and more aluminium and silicon were dissolved by the modified dithionite method as compared to the other methods mentioned.

Schwertmann (1959) compared the effects of Tamm's method (extraction performed in darkness) and Mehra and Jackson's method on different natural iron oxide accumulations. Employing X-ray technique and DTA he found an inverse relationship between the degree of crystal ordering of the iron oxides (goethite) and the amount of iron dissolved by the oxalate reagent. The dithionite reagent caused an almost complete dissolution of amorphous as well as crystalline oxides.

Asami and Kumada (1959, 1960) used a mixture of EDTA and sodium dithionite and found this method to give a more reproducible extraction of iron than the methods involving sodium dithionite and hydrochloric acid, hydrogen sulphide, oxalate and metallic magnesium, or sodium dithionite and sodium citrate. The percentage of iron extracted by the EDTA-sodium dithionite reagent was less dependant on the amount of soil used than that extracted by the other methods. The results obtained by all the methods were of the same order of magnitude for the soils used.

Kilmer (1960) modified Deb's method so that the extraction could be made at room temperature. The method was reported to give consistent results.

Aleksandrova (1960) used 0.1 m sodium pyrophosphate as extractant for iron and aluminium from various soils. She assumed this reagent to extract only iron and aluminium present in the soil as part of organic complexes and gave some experimental evidence to support this assumption. She further assumed that the organic complexes were rendered soluble by removal of calcium from the complexes as insoluble calcium pyrophosphate. This may be the case for some of the soils studied by Aleksandrova, but it is hardly the case if the reagent is applied to podzol B horizons as done by McKeague (1968) who correctly assumed that the dissolving action was due to direct complexation of iron and aluminium. However, the amounts of the metals dissolved may be much larger than those actually complexed by the pyrophosphate. As shown in chapters 9-11, dissolved organic matter can maintain considerable amounts of these metals in solution, but if a certain ratio of metals to organic matter is exceeded, a precipitation will take place. If it is assumed that the organic matter is maintained in a precipitated state by sufficient amounts of iron and aluminium it follows that a removal of relatively small amounts of the metals may cause dissolution of much larger amounts as soluble iron- and aluminium-soil organic matter complexes. This effect is, of course, not specific for pyrophosphate, but its relative importance will be greater for mild than for strong extractants.

It does not follow from these considerations that sodium pyrophosphate will exclusively dissolve iron and aluminium from organic complex compounds. In as far as it is possible to distinguish between the different iron and aluminium fractions in the soil, each fraction will contribute to the amount dissolved according to its solubility and dissolution rate. Due to the mechanism discussed above it is likely that the organic complex fraction will give a relatively high contribution to the amount dissolved by relatively mild extractants such as pyrophosphate. As shown by Titova (1962), sodium pyrophosphate is capable of dissolving appreciable amounts of iron from iron hydroxides and iron containing silicate minerals.

Tsyurupa (1961) found that Tamm's method was more effective towards amorphous and poorly crystalline than towards highly crystalline iron oxides. It also caused a significant dissolution of aluminium from silicates. The dithionite method without a complexing agent did not distinguish between amorphous and crystalline iron oxides and no aluminium was dissolved.

Gorbunov, Dzyadevich and Tunik (1961) compared Tamm's, Deb's, Mehra and Jackson's methods as well as methods employing EDTA and 0.2 n hydrochloric acid, respectively. They found Deb's method to be most effective for dissolving iron oxides and Tamm's method for dissolving iron + aluminium oxides. All of the methods were more effective towards amorphous than towards crystalline sesquioxides and the authors were unable to confirm the results of Mehra and Jackson (1958), which showed that crystalline iron oxides were dissolved completely by the dithionite-citrate-bicarbonate reagent.

Coffin (1963) replaced the bicarbonate buffer of Mehra and Jackson's method with a citrate buffer having pH 4.75. A single extraction of various soils with this reagent gave results identical to those obtained by Aguilera and Jackson's and by Mehra and Jackson's methods which require three successive extractions. A number of minerals such as lepidochrocite, goethite, haematite, siderite and ilmenite were only partly dissolved. Most clay minerals remained almost unaffected during the extraction; however, nontronite was attacked considerably.

Schwertmann (1964) confirmed the influence of light, first observed by Schofield (1949), on the amount of iron extracted by Tamm's method. Based on his earlier study (Schwertmann 1959) he assumed the amorphous fraction of the iron oxides to be represented by the amount of iron dissolved in darkness by Tamm's method, and the total amount of free iron oxides to be represented by the amount dissolved by Mehra and Jackson's method. The ratio between the two amounts was called the 'degree of activity' (Aktivitätsgrad) of the iron oxides. The iron compounds of some podzol B horizons were found to have a high degree of activity, i.e. there was no great difference between the amounts of iron extracted by dithionite and by oxalate. According to the assumption mentioned above this implies a low crystal ordering of the iron oxides.

Franzmeier, Hajek and Simonson (1965) replaced the citrate in Mehra and Jackson's method with sodium pyrophosphate to facilitate determination of organic carbon in the extract. The replacement reduced the efficiency of a single extraction but by repeated extractions no major differences were found between the two complexing agents when applied to podzol B horizons. The amounts of C, Fe and Al extracted by this method have been used in the definition of the spodic horizon, see chapter 1.

McKeague (1967) concluded that the sodium dithionite-sodium pyrophosphate mixture did not make any distinction between amorphous and crystalline iron and aluminium oxides. It was also found that there was a fairly constant relationship between the amounts of iron and aluminium extracted from various soils by oxalate and by 0.1 m sodium pyrophosphate, although the former reagent extracted somewhat larger amounts.

Holmgren (1967) used a solution containing dithionite and a large excess of sodium citrate as extractant for iron oxides. The extraction was carried out at room temperature. The reagent extracted more iron than that employed by Kilmer (1960). It was found that the reagent for all soil samples tested extracted about 90 % of the total iron content as determined by X-ray fluorescence spectroscopy. However, this fact seems to be of little relevance for evaluation of the method.

Using X-ray technique Douglas (1967) demonstrated that the citrate-dithionite reagent affected the crystal structure of biotite. At the same time some iron and potassium were extracted from the mineral. These effects were not found if either of the reagents were used alone.

Potassium pyrophosphate at pH 10 was suggested by Bascomb (1968) for extraction of iron and he prescribed a technique to remove so-called inorganic iron from the extract by addition of ammonium hydroxide. However, this operation does not seem to lead to the desired result.

Blume and Schwertmann (1969) stated that crystalline and amorphous aluminium oxides cannot be separated by application of Tamm's as well as Mehra and Jackson's methods, as is the case for the corresponding iron compounds. By contrast a good correlation was obtained between the amounts of aluminium extracted by the two methods and also with the amount extracted by sodium hydroxide.

Baril and Bitton (1969) found magnetite to be partly dissolved by Tamm's method. McKeague and Day (1969) concluded from analyses of a large number of soil samples from podzols that the absolute amount of oxalate-extractable aluminium was a suitable criterion for identifying podzol B horizons.

Jørgensen and Mitchell (1970) investigated the ability of 5 % sodium carbonate to dissolve aluminium from hydrous aluminas. They found that the amount of alumina dissolved was strongly dependent on the temperature of extraction, the particle size and the degree of crystal ordering.

Morgenstern (1970) found that Mehra and Jackson's method extracted more iron than Tamm's method from the entire fine earth fraction and from the > 60 μ-fraction of various hydromorphic and non-hydromorphic soil horizons.

The studies of Hubert and Gonzalez (1970) revealed no consistent differences between the amounts of iron and aluminium extracted from the horizons of four silty and sandy podzols by Mehra and Jackson's and by Tamm's methods. Somewhat smaller amounts of both elements were extracted by Franzmeier, Hajek and Simonson's (1965) method.

Zonn and Vin-Khitin (1971) compared the ability of the methods of Tamm (1922), Mackenzie (1954), Mehra and Jackson (1958), Coffin (1963) and Franzmeier, Hajek and Simonson (1965) to extract iron from tropical soils. The largest amounts of iron were extracted by the method of Mehra and Jackson (3 successive extractions) and by Coffin's method (1 extraction). The amounts of iron dissolved by these methods were almost identical and were assumed to represent the sum of amorphous and crystalline non-silicate iron compounds. Intermediate amounts of iron were extracted by the methods of Mackenzie (2 successive extractions) and Franzmeier, Hajek and Simonson (1 extraction) while substantially smaller amounts were extracted by Tamm's method.

McKeague, Brydon and Miles (1971) found that 0.1 m sodium pyrophosphate dissolved significant amounts of iron and aluminium from co-precipitates of fulvic acids and iron and aluminium hydroxide sols as compared to small amounts from amorphous hydroxides without fulvic acids. They compared the efficiency of Tamm's, Mehra and Jackson's, and the pyrophosphate methods. Mehra and Jackson's method extracted the greatest amounts of iron from podzol B horizons while Tamm's method was most effective for extraction of aluminium from these horizons. Much smaller amounts of the metals were extracted by sodium pyrophosphate, but, as compared to the other soil samples tested, larger amounts of iron and aluminium were extracted from podzol B horizons. This was concluded to be due to the presence of complex organic iron and aluminium compounds in these horizons.

In a comparative study Arshad, Arnaud and Huang (1972) found that ammonium oxalate extracted more iron and aluminium from biotite, chlorite and muscovite than sodium dithionite-citrate-carbonate and potassium pyrophosphate. No important differences were found between the two former extractants in the amounts of iron and aluminium extracted from illite. The amount extracted depended in all cases strongly on the particle size and was negligible for particles coarser than those belonging to the clay fraction.

Pawluk (1972) concluded from studies of the ability of ammonium oxalate and sodium dithionite-citrate-carbonate to extract iron from samples of an 'eluviated gleysol' that the amounts dissolved by the two extractants probably could serve as relative measures of the content of 'amorphous' iron oxide and total 'free' iron oxide respectively, but it was doubtful as to what extent an absolute measure of the two fractions was obtained. Schwertmann (1973) warned against a too rigorous interpretation of the results of the two extraction procedures.

Various other techniques have been employed in the determination of certain fractions of iron and aluminium in soils. Ignatieff (1941) recommended aluminium chloride as a suitable extractant for ferrous iron, but Pruden and Bloomfield (1969) showed that this method was likely to produce incorrect results in the presence of soil organic matter.

A biological reduction method for iron estimation was used by Allison and Scarseth (1942) but Bromfield and Williams (1963) found this method less satisfactory than chemical extractions. Van Diepen (1956) suggested a simple semiquantitative method by which the iron content of the soil was evaluated from the colour of ignited soil samples. Barnhisel, Phillippe and Blevions (1969) used an X-ray fluorescence technique for direct determination of the total iron content of soil samples without subjecting these to any chemical treatment.

An indirect approach towards the characterization of aluminium compounds in soils has been used by Fieldes and Perrott (1966). The method is based on an estimation of the hydroxyl ions released by reaction of aluminium hydroxides with fluoride. Brydon and Day (1970) used a modification of this method and found that the amount of hydroxyl ions released was greater in podzol B horizons than in any other soil or horizon tested.

6.3 Procedures for Iron and Aluminium Determinations Used in the Present Study

From the discussion above it is obvious that the relative amounts of iron and aluminium extracted by the different methods depend on a number of factors influencing the state of the iron and aluminium compounds in the soil. Although it is claimed that some of the methods are capable of extracting a specific fraction of the sesquioxides, the overall impression of the testing work made on the methods does not confirm this. The possibility of obtaining an accurate separation of the different sesquioxide fractions by selective extraction seems rather small. It does, however, seem justifiable to assume that the problem of avoiding extraction of iron and aluminium from the silicate fraction is rather small for the soils studied in the present investigation due to their low clay content.

There was, therefore, no attempt made to compare the different methods or to improve upon them. Instead it was decided to determine the iron and aluminium by two extractions employing a strong and a fairly mild extractant. The amounts of iron and aluminium extracted by these methods are not assumed to represent accurately any specific sesquioxide fraction in the soil, but they will still be useful in considerations concerning translocation of the sesquioxides in the soil.

The strong extractant selected was hot 20 % HCl. 5 g of soil was transferred to a 600 ml beaker; 200 ml 20 % HCl was added; and the beaker was covered with a watch glass and placed on a boiling water bath under frequent stirring for 8 hours. After cooling, the supernatant was filtered into a 500 ml volumetric flask, the soil was washed with water until free of chloride, and the flask made to volume. Iron and aluminium were determined in aliquots of the content of the volumetric flask by atomic absorption spectrophotometry. Repeated extraction removed only small amounts of iron and aluminium from the soil samples.

As the mild extractant, the reagent used by Asami and Kumada (1959) was found suitable. In the modification used by Asami and Kumada, the method was used for determination of iron only; however, it was found in the present study that a good reproducibility was obtained also for aluminium. The method is probably not superior to some of the other methods described above, but it was found rapid and convenient. Some objections may be made against this method. The system contains no buffer other than EDTA,2Na which is used primarily for the purpose of complexing the metals. However, it was found that the pH remained fairly constant around 5 during the extractions. Many of the authors quoted above have stated that ferrous sulphide may be precipitated at this pH. To what extent this may affect the results is not known, but results quoted above show that the method of Coffin (1963) employing sodium dithionite and a citrate buffer with pH 4.75 is just as effective as the method of Mehra and Jackson (1958) employing sodium bicarbonate with pH 7.3. In this study no precipitation of ferrous sulphide was noticed, but it would have been difficult to observe due to the black colour of most of the extraction mixtures. The concentration of EDTA is fairly low and will represent a limited excess as compared to the total extracted amount of iron and aluminium in some of the horizons most rich in those elements. However, as mentioned already, the extracting power of the reagent towards iron was found by Asami and Kumada (1959) to be relatively independent of the amount of soil used, and it was decided to maintain the low concentration of EDTA although it is realized that a greater concentration of EDTA might have increased the amount of sesquioxides, particularly of aluminium oxides, extracted from the samples high in these compounds. The method must be assumed to be more effective towards iron than towards aluminium as far as it is possible to make a comparison, since the reducing agent will affect iron compounds only.

The actual modification of the method used was as follows: 1.5 g of soil was transferred to a 100 ml PVC centrifuge tube, 2.25 g sodium dithionite and 75 ml 0.02 m EDTA,2Na were added. The centrifuge tube was placed in a water bath at 80 °C for 30 min. under frequent stirring. After cooling the mixture was centrifuged, and iron and aluminium were determined in the supernatant by atomic absorption spectrophotometry using a Perkin-Elmer model 303 atomic absorption spectrophotometer. The results were read out on a recorder.

Asami and Kumada (1959) prescribed that the extraction be carried out during 15 min. at 70 °C. By the procedure employed here the extraction mixture had an average temperature of 70 °C during the final 15 min. of the extraction. Asami and Kumada (1959) transferred the supernatant to a volumetric flask, washed the soil and filled the flask to volume. In preliminary trials it was found possible to avoid this manipulation if the standard solutions were treated similarly to the extraction mixtures, i.e. if the same amounts of reagents were added and they were subjected to the same heating procedure.

Due to the rather high concentrations needed in the atomic absorption spectrophotometric determination of aluminium, determinations of this metal always had to be made on undiluted extracts. Accordingly, all aluminium standard solutions were treated exactly as the soil extracts and contained the same concentration of reagents. The standard solutions were prepared from a stock solution of previously analyzed potassium aluminium sulphate.

In the case of iron it was usually necessary to dilute the soil extracts to obtain optimum concentrations for atomic absorption spectrophotometry. To avoid any errors due to different concentrations of reagents the standard solutions were always subjected to the same degree of dilution, e.g. if a soil extract was diluted 10 times, its iron content was calculated from a calibration curve made from solutions originally heated on the water bath with the specified amounts of reagents and 10 times the needed concentration of iron. After 10 times dilution these solutions contained the proper amount of iron and the same amounts of reagents as the soil extracts. The standard solutions were prepared from a stock solution of previously analyzed ferrum reductum dissolved in the minimum amount of sulphuric acid.

Similarly, care was taken that the standard solutions used in the determination of iron and aluminium in the hydrochloric acid extracts in each case had a concentration of hydrochloric acid equal to that of the soil extracts. With the procedure used for these extractions it was considered unnecessary to treat the standard solutions on the water bath. The stock solutions used for preparation of standard solutions were those mentioned above.

The determination of iron and aluminium by atomic absorption spectrophotometry is not without problems. A number of organic and inorganic compounds originating from the extractants or from the soil have been found to interfere during the determination. Raad, Protz and Thomas (1969) compared the absorbance of iron and aluminium in solutions containing Al, Fe, Si and Mn with the absorbance of iron and aluminium in solutions containing only the metal in question. The presence of the elements mentioned reduced the absorbance of both iron and aluminium. Addition of dithionite or oxalate to the solutions containing all four elements increased the absorbance of both iron and aluminium.

Yuan and Breland (1969) compared colorimetric and atomic absorption spectrophotometric determinations of iron and aluminium in extracts from soil and clay samples prepared with a number of extractants including oxalate and dithionite. In general, a good agreement was found for Al determined by the two methods, and Al added to the extracts were recovered satisfactorily by both methods. In soil extracts prepared with dithionite and oxalate, the atomic absorption spectrophotometric determination of iron gave too high results as compared to the colorimetric determination. When iron was added to the soil extracts, the increased content found by the atomic absorption spectrophotometric determination was higher than the amount added. Addition of an artificial humus preparation (Leonardite) did not affect the aluminium determination but caused an apparent increase in the iron content.

Ferris, Jepson and Shapland (1970) found that aluminium and silicon reduced the absorbance of iron and that the absorbance of aluminium was reduced by silicon but unaffected by iron. All the measurements were made in 7.5×10^{-3} m sodium pyrophosphate solutions.

To evaluate the possible effect of iron and silicon on the determination of aluminium, and of aluminium and silicon on the determination of iron, under the conditions employed in the present investigation a number of solutions containing varying amounts of iron, aluminium and silicon were prepared. All the solutions had EDTA and sodium dithionite concentrations similar to the soil extracts and all solutions were subjected to similar treatments on the water bath. The sources of iron and aluminium were the stock solutions used in preparation of the standard solutions described above. Silicon was added from a solution prepared by fusion of ground and ignited silica glass with sodium hydroxide followed by dissolution of the fusion mixture in water and partly neutralization of the sodium hydroxide with sulphuric acid. The absorbance values for aluminium were measured on undiluted solutions while those for iron were measured on ten-fold diluted solutions. As the atomic absorption measurements took some time, and as it was found impossible to avoid time fluctuations in the actual absorbance values measured with the atomic absorption spectrophotometer, the values recorded had to be corrected for these time fluctuations. This was accomplished by repeated measurements of the absorbance of some selected solutions with small time intervals and calibrating the absorbance of the remaining solutions against these. Similar precautions were taken to eliminate time fluctuations throughout the measurements on the soil extracts. The time fluctuations were larger for aluminium than for iron.

The results of the trial appear in Tables 4 and 5. It should be noted that absorbance values reported for solutions without silicon are averages of more single measurements than those for solutions containing silicon. Hence, the former must be considered more reliable than the latter. The values in Table 4 reveal no significant effect on the aluminium determination of either iron or silicon under the conditions employed here. Similarly, it appears from Table 5 that aluminium is without significant effect on the iron determination, but silicon gives a small reduction in the absorbance values for iron. However, the effect of silicon seems to be quantitatively important only at the higher $\frac{Si}{Fe}$-ratios. To estimate the quantitative effect on the soil extracts, some of these were analyzed for silicon by atomic absorption spectrophotometry. Expressed in mg element per l extract the content of silicon was usually only a small fraction of the iron content, and in no extract did the silicon content exceed the iron content. Hence, the effect of silicon on the results of the iron determinations was considered negligible under the conditions employed and no precautions were taken to eliminate it.

In another trial the effect of the organic matter dissolved by the extraction with dithionite and EDTA on the determination of iron was studied. Varying amounts of iron were added during the dilution (1:10) of a standard solution, containing 100 mg Fe per l before the dilution (prepared as described above), and of a soil extract from a B_1 horizon. The soil extract appeared completely black. Two sources of iron were

Table 4. Effect of Iron and Silicon on the Absorbance of Aluminium by Atomic Absorption Spectrophotometry

Al, mg per l	Fe, mg per l												
	0	50			100			150			200		
	Si, mg per l												
	0	0	100	200	0	100	200	0	100	200	0	100	200
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
40	0.161	0.160	0.159	0.158	0.157	0.160	0.161	0.159	0.156	0.155	0.158	0.142	0.142
80	0.303	0.305	0.313	0.309	0.311	0.299	0.305	0.304	-	-	0.303	0.306	0.313
120	0.437	0.434	0.418	0.439	0.434	0.443	0.443	0.429	-	-	0.427	0.440	-
160	0.542	0.541	0.530	0.560	0.538	0.533	0.527	0.550	-	-	0.538	0.538	0.547

Table 5. Effect of Aluminium and Silicon on the Absorbance of Iron by Atomic Absorption Spectrophotometry

Fe, mg per l	Al, mg per l												
	0	4			8			12			16		
	Si, mg per l												
	0	0	10	20	0	10	20	0	10	20	0	10	20
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5	0.144	0.146	0.138	0.132	0.146	0.134	0.126	0.146	0.140	0.135	0.145	0.134	0.130
10	0.272	0.272	0.273	0.262	0.277	0.277	0.258	0.275	0.272	0.262	0.272	0.266	0.259
15	0.389	0.390	0.376	0.376	0.391	0.390	0.379	0.390	0.384	0.365	0.390	0.385	0.369
20	0.482	0.489	0.470	0.478	0.484	0.475	0.471	0.485	0.479	-	0.473	0.483	0.471

used: the stock solution of ferrous sulphate described above, and an analyzed solution of ferric chloride containing a small excess of hydrochloric acid. The recovery of the iron added appears in Table 6. For most samples the amounts recovered are slightly higher than those added. This is probably due to the fact that the iron content is calculated from a calibration graph prepared from measurements on solutions not made to volume as described above. Addition of sodium dithionite will cause a small increase in volume which remains uncorrected, but which does not affect similarly treated soil extracts. However, in the trial described here it will give apparently too high an iron content.

There is a tendency towards a slightly smaller recovery of the iron added as ferric chloride to the soil extract as compared to that added to the standard solution. However, the difference is not much greater than the accuracy of the method and greater errors could easily be introduced if a removal of the organic matter was attempted. The trials described seem, therefore, to justify the determination of iron as well as aluminium in the untreated soil extracts by the technique outlined above.

Table 6. Atomic Absorption Spectrophotometric Recovery of Added Iron

Solution	Source of iron added	Iron, mg per l	
		Added	Found
Standard (10 mg Fe per l)	$FeSO_4$	2.50	2.55
		5.00	5.10
		7.50	7.65
	$FeCl_3$	2.80	2.90
		5.60	5.80
		8.40	8.55
Soil extract (8.9 mg Fe per l after dilution)	$FeSO_4$	2.50	2.55
		5.00	5.15
		7.50	7.75
	$FeCl_3$	2.80	2.85
		5.60	5.60
		8.40	8.40

6.4 Iron and Aluminium Contents of Podzols

A vast amount of data on the iron and aluminium content of podzols is available in literature. The actual amounts vary, of course, from soil to soil and according to the methods used in the determination. The results of the iron and aluminium determinations by the procedures described in the preceding section for the soils studied here are reported in Table 7, and in Fig. 2-11 the contents of iron, aluminium and organic carbon are plotted versus depth for each profile.

Table 7. Iron, Aluminium and Organic Carbon-Metal Ratios[*] in the Soils Investigated

Profile	Horizon	Extractant									
		Hydrochloric acid					Sodium dithionite+EDTA				
		Fe,%	Al,%	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al+\frac{Fe}{2}}$	Fe,%	Al,%	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al+\frac{Fe}{2}}$
Gørding Hede	A_o	0.38	0.20	130	120	61	0.26	0.09	180	260	110
	A_1	0.23	0.07	33	54	20	0.05	0.02	150	190	84
	A_2	0.22	0.09	12	15	6.6	0.05	0.02	53	66	29
	B_{1a}	1.99	0.76	5.7	7.5	3.2	1.79	0.46	6.4	12	4.2
	B_{1b}	2.04	0.83	4.5	5.5	2.5	1.84	0.56	5.0	8.2	3.1
	B_{2a}	0.97	0.60	2.5	2.0	1.1	0.54	0.24	4.4	5.0	2.3
	B_{2b}	0.68	0.65	2.9	1.5	1.0	0.25	0.23	7.9	4.3	2.8
	B_{2c}	0.50	0.40	1.2	0.73	0.45	0.17	0.11	3.4	2.6	1.5
	B_{2d}	0.28	0.17	0.57	0.47	0.26	0.13	0.05	1.2	1.6	0.70
	C	0.35	0.19	0.29	0.26	0.14	0.12	0.04	0.83	1.3	0.50
Skarrild	A_o	0.25	0.15	180	150	82	0.23	0.11	200	210	100
	A_1	0.10	-	180	-	-	0.07	0.05	260	180	110
	A_2	0.07	0.03	14	16	7.4	0.01	0.004	96	120	53
	B_1	0.22	-	71	-	-	0.18	0.38	86	20	17
	B_2	0.40	0.34	3.1	1.8	1.1	0.25	0.21	4.9	2.9	1.8
	C	0.51	0.30	0.90	0.77	0.41	0.32	0.11	1.4	2.1	0.85

[*] For definition and explanation of these ratios, see sections 9.4.1 and 9.6

Table 7. Continued

Profile	Horizon	Extractant									
		Hydrochloric acid					Sodium dithionite+EDTA				
		Fe,%	Al,%	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al+\frac{Fe}{2}}$	Fe,%	Al,%	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al+\frac{Fe}{2}}$
Stavshede	A_{oa}	0.31	0.23	260	180	100	0.13	0.10	620	400	240
	A_{ob}	0.30	0.25	270	160	100	0.13	0.12	630	340	220
	A_1/A_2	0.76	0.18	9.4	20	6.4	0.31	0.07	23	51	16
	B_{2a}	0.83	0.57	3.8	2.7	1.6	0.26	0.25	12	6.2	4.1
	B_{2b}	0.61	0.46	1.8	1.2	0.71	0.30	0.14	3.6	3.9	1.9
	B_{2c}	0.58	0.27	0.62	0.67	0.32	0.11	0.06	3.3	3.0	1.6
	C	0.70	0.33	0.29	0.30	0.15	0.09	0.04	2.2	2.5	1.2
Klelund	A_{oa}	0.48	0.29	180	150	81	0.12	0.11	710	390	250
	A_{ob}	0.51	0.20	120	160	69	0.11	0.11	570	290	190
	A_2	0.51	0.15	5.5	9.3	3.5	0.05	0.02	56	70	31
	B_1	1.42	0.64	13	14	6.7	0.10	0.54	180	17	15
	B_{2a}	1.42	1.10	0.34	0.22	0.13	0.09	0.06	5.3	4.0	2.3
	B_{2b}	0.53	0.34	0.53	0.41	0.23	0.08	0.05	3.5	2.8	1.6
	C	0.53	0.36	0.15	0.11	0.064	0.01	0.02	8.0	2.0	1.6
Tingheden	A_o	0.19	0.13	470	340	200	0.09	0.08	980	550	350
	A_1	0.12	0.04	76	110	46	0.01	0.01	910	460	300
	A_2	0.07	0.003	13	150	12	0.004	0.002	230	230	120
	B_1	1.38	0.76	6.9	6.3	3.3	0.47	0.48	20	9.9	6.7
	B_2	1.68	1.19	1.9	1.3	0.78	0.41	0.34	7.8	4.7	2.9
	C	3.66	1.26	0.11	0.17	0.068	0.75	0.12	0.56	1.8	0.42
Trehøje	A_o	0.44	0.24	140	130	67	0.31	0.03	200	1000	170
	A_1	0.34	0.06	53	150	39	0.07	0.01	260	900	200
	A_2	0.24	0.04	13	38	9.5	0.08	0.01	38	150	30
	B_1	1.32	0.84	11	9.0	5.1	0.94	0.11	16	69	13
	B_1/B_2	0.70	0.82	2.6	1.1	0.77	0.37	0.07	4.9	13	3.5
	B_{2a}	0.38	0.38	1.3	0.63	0.42	0.13	0.02	3.7	12	2.8
	B_{2b}	0.37	0.24	0.70	0.54	0.31	0.18	0.01	1.4	13	1.3
	C	0.40	0.23	0.15	0.13	0.070	0.13	0.01	0.46	3.0	0.40

Table 7. Continued

Profile	Horizon	Extractant									
		Hydrochloric acid					Sodium dithionite+EDTA				
		Fe,%	Al,%	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al+\frac{Fe}{2}}$	Fe,%	Al,%	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al+\frac{Fe}{2}}$
Løwenholm	A_{oa}	0.17	0.13	450	290	180	0.14	0.006	550	640	290
	A_{ob}	0.27	0.25	190	100	68	0.23	0.15	230	170	99
	A_2	0.08	0.10	37	15	11	0.01	0.03	300	49	42
	B_1	0.15	0.36	28	5.9	4.9	0.03	0.17	140	12	11
	B_{2a}	0.27	0.35	11	4.4	3.2	0.17	0.24	18	6.4	4.7
	B_{2b}	0.62	0.66	2.5	1.2	0.79	0.36	0.22	4.3	3.5	1.9
	C	0.35	0.42	0.91	0.38	0.27	0.08	0.06	4.0	2.7	1.6
Trinderup	A_o	0.56	0.38	93	68	39	0.37	0.17	140	150	73
	A_1/A_2	0.42	0.21	32	32	16	0.27	0.11	51	62	28
	B_1	0.67	0.55	11	6.9	4.3	0.43	0.38	18	9.9	6.3
	B_1/B_2	0.59	0.58	6.0	3.1	2.0	0.28	0.31	13	5.7	3.9
	B_2	0.47	0.45	1.4	0.76	0.50	0.16	0.12	4.3	2.8	1.7
	C	0.37	0.28	0.97	0.64	0.39	0.08	0.07	4.5	2.6	1.6
Støttrup Hede	A_o/A_1	0.12	0.09	250	170	100	0.12	0.06	250	250	130
	A_2	0.12	0.08	16	12	6.9	0.07	0.04	27	24	13
	B_1	0.39	0.49	7.4	2.9	2.1	0.25	0.23	12	6.3	4.1
	B_2	0.28	0.55	5.7	1.5	1.2	0.18	0.16	8.9	5.0	3.2
	C	0.41	0.47	0.78	0.34	0.24	0.09	0.09	3.6	1.8	1.2
Skarpholt	A_o	0.43	0.23	150	140	74	0.29	0.12	230	280	120
	A_1	0.52	0.16	16	26	10	0.12	0.06	71	71	35
	A_2	0.45	0.12	6.8	13	4.4	0.20	0.04	15	38	11
	B_1	1.30	0.52	2.5	3.2	1.4	0.99	0.29	3.3	5.7	2.1
	B_{2a}	1.08	0.76	3.3	2.4	1.4	0.59	0.37	6.1	4.8	2.7
	B_{2b}	0.45	0.32	1.9	1.3	0.79	0.12	0.11	7.2	3.9	2.5
	C	0.50	0.31	1.3	1.1	0.59	0.13	0.09	5.1	3.7	2.1

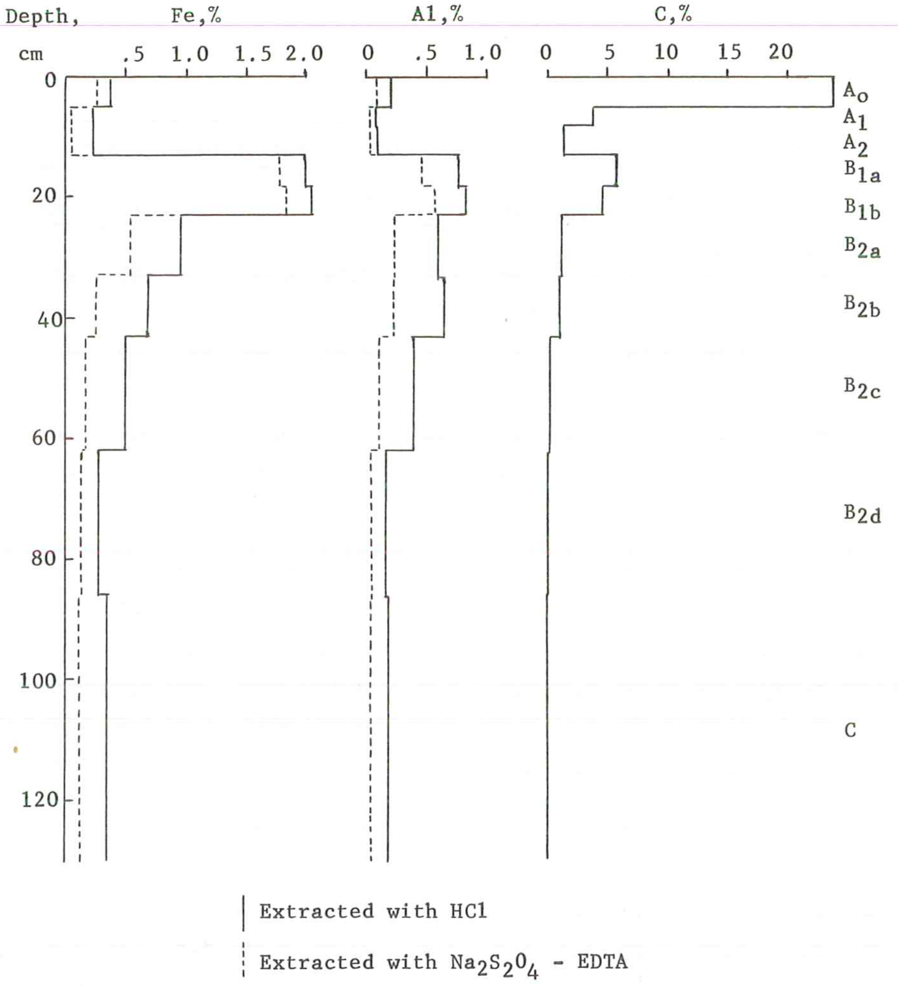

Fig. 2. Iron, aluminium and organic carbon contents in the Gørding Hede profile.

The general trend in the distribution of the sesquioxides is, as would be expected, a maximum content in the B horizon and a minimum in the A horizon. As would also be expected, the amounts of sesquioxides extracted by hydrochloric acid is always larger than the amounts extracted by $Na_2S_2O_4$ - EDTA. However, in the majority of the profiles the general trend in the distribution of the sesquioxides is similar for both extractants. The

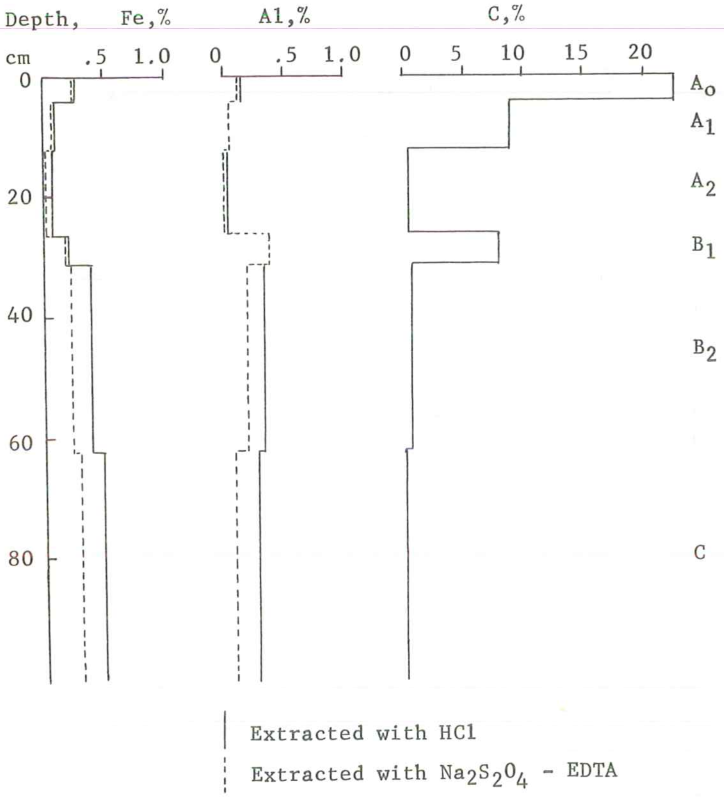

Fig. 3. Iron, aluminium and organic carbon contents in the Skarrild profile.

actual ratio between the amounts of sesquioxides extracted with the two reagents is subject to great variation. The ratios between the amounts of sesquioxides extracted with $Na_2S_2O_4$ - EDTA and with HCl are usually considerably smaller in C horizons than in A and, particularly, in B horizons of the same profiles.

The sesquioxide content is always low in both A_1 and A_2 horizons, and usually also in A_o horizons, but these should not be compared directly with the other horizons, since they consist primarily of organic matter. However, as far as the sesquioxide contents in the B horizons are concerned there are marked differences between subhorizons. The subhorizons having maximum content of iron, aluminium and organic matter within each profile are listed in Table 8. It is clear from this table that there is a high

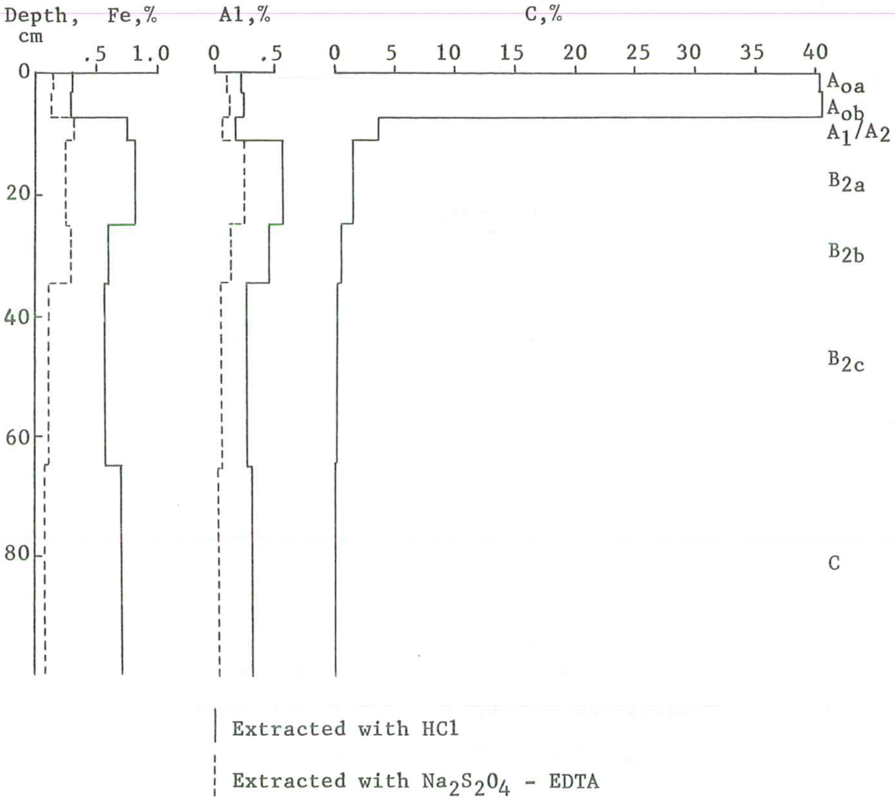

Fig. 4. Iron, aluminium and organic carbon contents in the Stavshede profile.

degree of coincidence between subhorizons containing maximum amounts of organic matter (exclusive of A horizons) and maximum amounts of sesquioxides. This is further clarified in Table 9 for both iron and aluminium and for both extractants. When studying the values in these tables it should be kept in mind that the division of the soil layers into subhorizons is done visually in the field and must necessarily be arbitrary to some extent.

From Table 9 it is obvious that the largest content of extractable iron and aluminium most often is found in the subhorizon having the largest amount of organic matter or in the subhorizon immediately below this one. Most of the exceptions to this rule may be explained as being due to special conditions. The only profile having the maximum content of $Na_2S_2O_4$ - EDTA- as well as HCl-extractable iron in the subhorizon above that having maximum organic

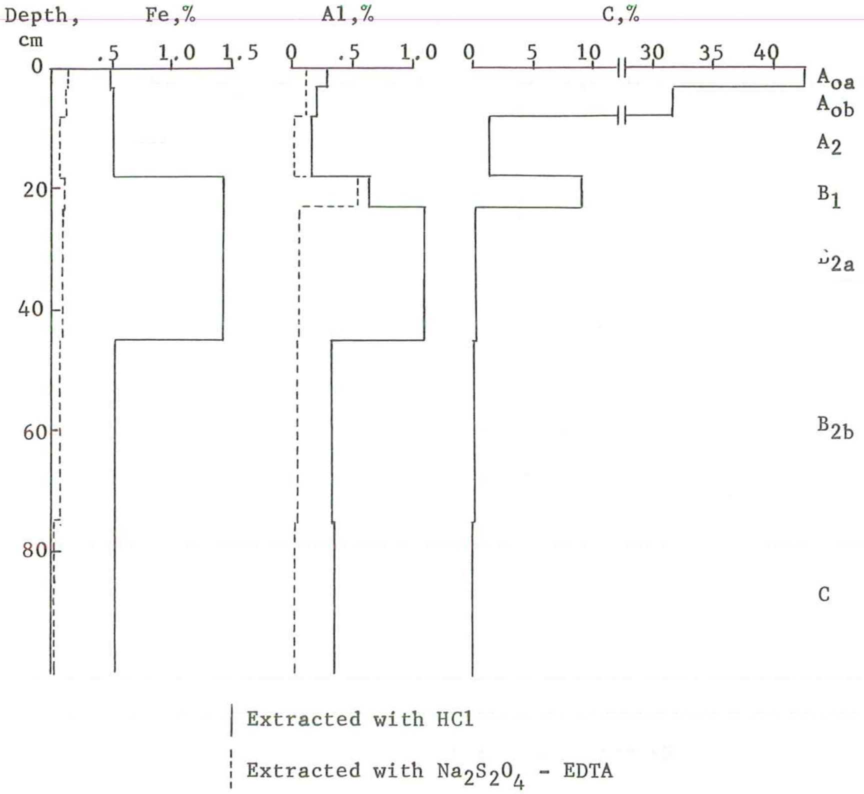

Fig. 5. Iron, aluminium and organic carbon contents in the Klelund profile.

matter content is the Skarpholt profile. However, this profile is different from all the other profiles, in which a B_1 horizon has been designated, in that it has the maximum content of organic matter in the upper part of the B_2 horizon. In fact there is only a very small difference in the organic matter content of the B_1 and the B_{2a} horizons. The Løwenholm profile has the highest content of HCl-extractable iron and aluminium and of $Na_2S_2O_4$ - EDTA-extractable iron in the lower part of the B horizon. As may be seen from the profile description in chapter 3, this horizon has been subject to partly reducing conditions and contains mottles which may have affected the distribution of the sesquioxides. Even though aluminium is not subject to reduction, Bloomfield (1952a) found that mottles contained more oxalate-extractable aluminium than the surrounding matrix.

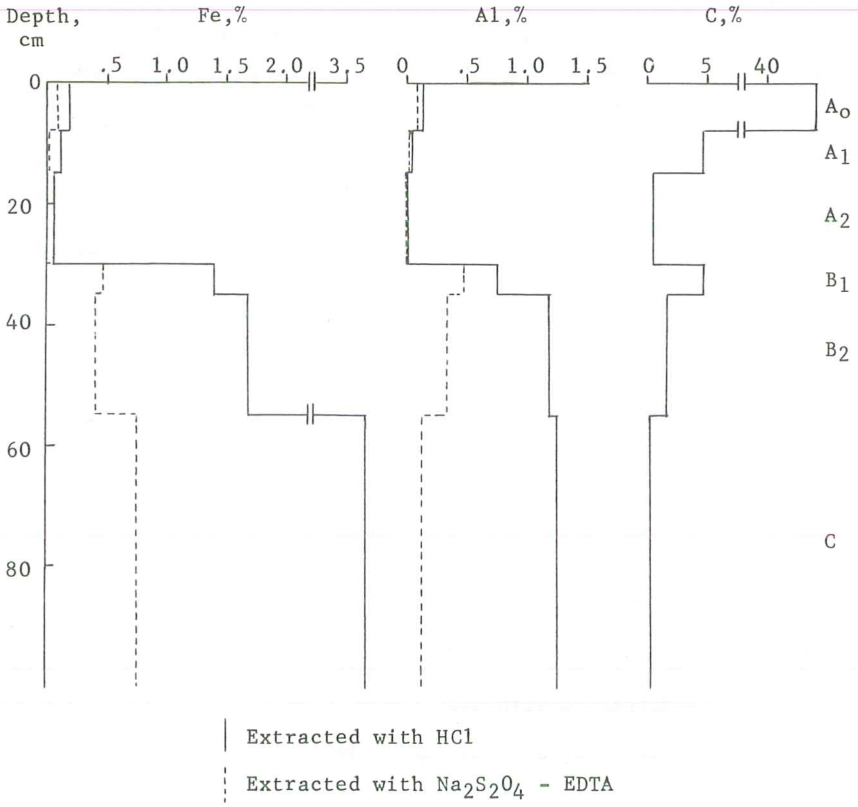

Fig. 6. Iron, aluminium and organic carbon contents in the Tingheden profile.

Reducing conditions may also partly or completely explain the fact that the maximum iron content in the Skarrild and Tingheden profiles, as well as the maximum content of HCl-extractable aluminium in the latter, are found in the C horizon. From the profile descriptions in chapter 3 it is seen that both of these C horizons are mottled. The only exception to the general trend that remains unexplained is the presence of the maximum amount of HCl-extractable iron in the C horizon of the Støttrup Hede profile which showed no signs of mottling.

It should be mentioned, however, that textural differences may have affected the distribution of the sesquioxides in some of the profiles. In the discussion above it has implicitly been assumed that the texture was without effect. This seems to be justified for most of the soils since all

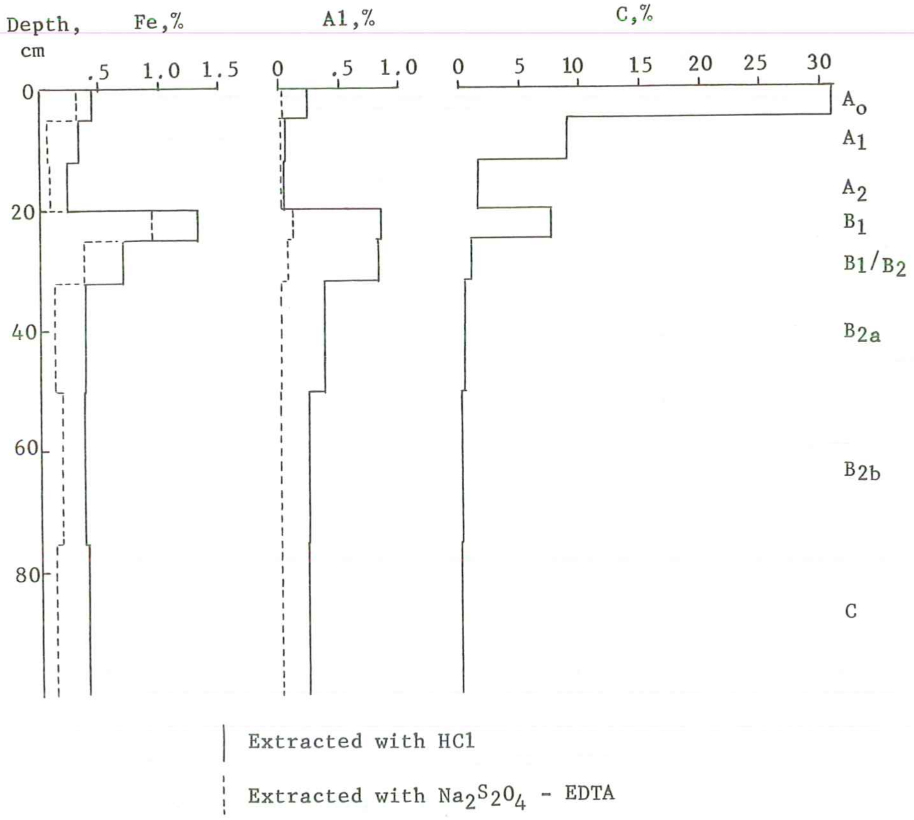

Fig. 7. Iron, aluminium and organic carbon contents in the Trehøje profile.

the profiles investigated were made up of sand with negligible silt and clay contents. To obtain some information on the effect of textural changes with depth, mechanical analyses using the pipette method described by Kjær (1968) were made on some horizons of the Tingheden and Løwenholm profiles. Besides the above mentioned irregularities in sesquioxide distribution, these profiles had, as judged in the field, the finest texture of all the profiles investigated. While the B_1 and B_2 horizons of the Tingheden profile contained approx. 5.5 % clay and 10 % silt, the C horizon contained approx. 11 % and 17 % of the two textural fractions, respectively. This suggests that the high iron and aluminium contents of this horizon may, at least partly, be due to the higher clay and silt content. The B_{2b}

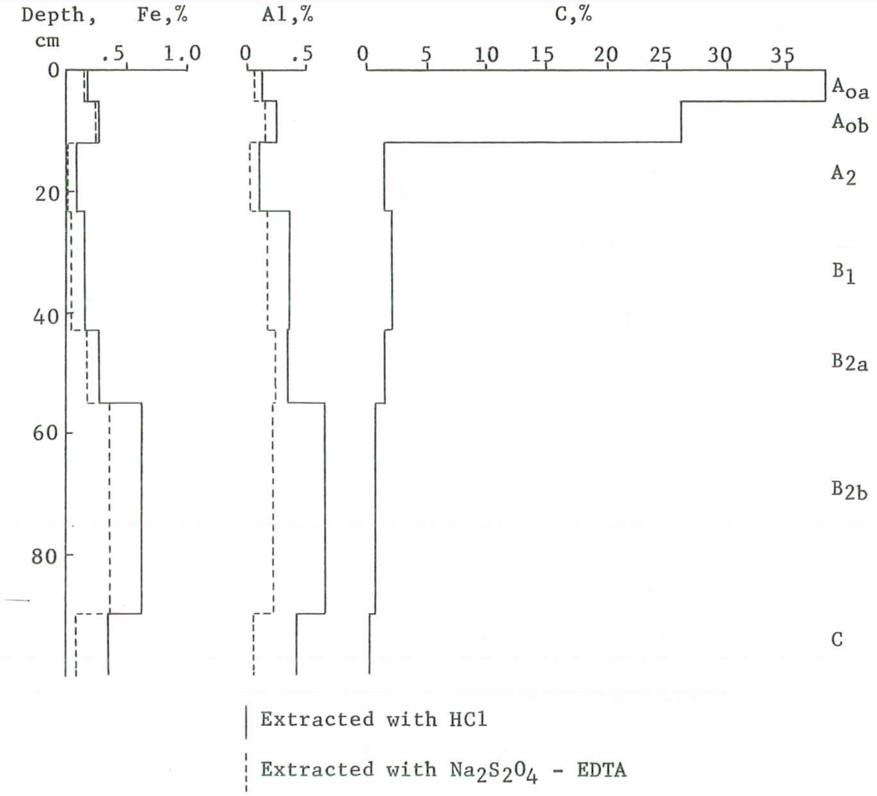

Fig. 8. Iron, aluminium and organic carbon contents in the Løwenholm profile.

horizon of the Løwenholm profile was found to contain 3.4 % clay and 6.4 % silt as compared to 4.2 % clay and 3.5 % silt in the overlying B$_{2a}$ horizon and 2.5 % clay and 3.3 % silt in the underlying C horizon. Hence, there seems to be little basis of explaining a high sesquioxide content in the B$_{2b}$ horizon in terms of a different texture.

The greatest amount of sesquioxides within a given profile is most frequently found in the B$_1$ horizon. This is clear from Table 8. There is a tendency that the maximum content of Na$_2$S$_2$O$_4$ - EDTA-extractable sesquioxides occurs above the maximum content of HCl-extractable sesquioxides. This tendency is more expressed for aluminium than for iron. This may be due to some separation of the sesquioxides during podzolization, but it cannot be excluded that it is also due to the fact that Na$_2$S$_2$O$_4$ - EDTA is a more

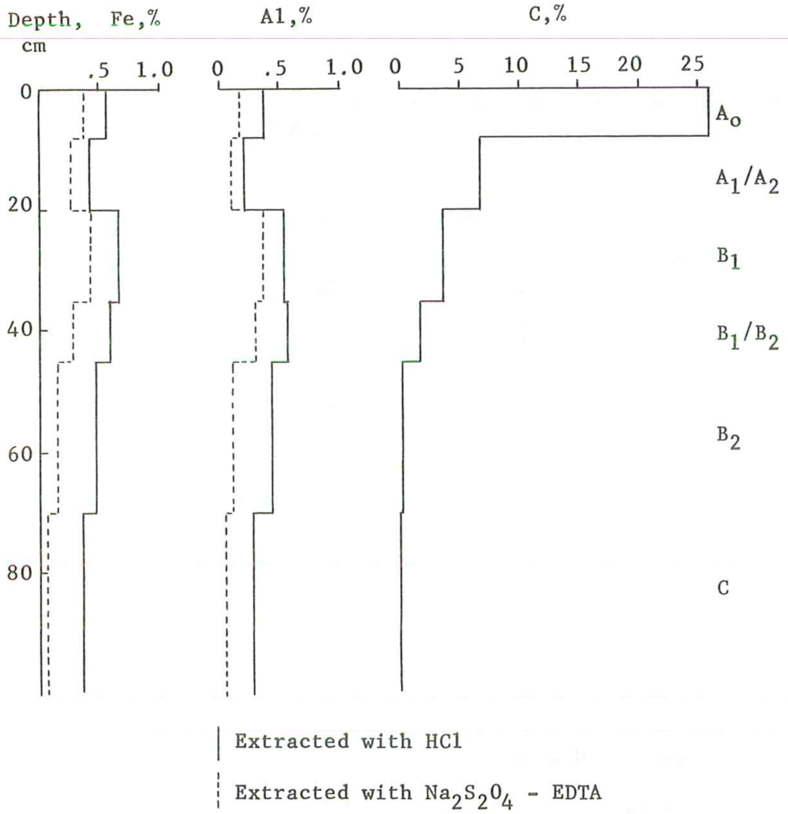

Fig. 9. Iron, aluminium and organic carbon contents in the Trinderup profile.

efficient extractant for iron compounds than for aluminium compounds as discussed previously. As appears from Table 9 the maximum amounts of aluminium extractable with $Na_2S_2O_4$ - EDTA coincides with the maximum organic matter content much more frequently than any other sesquioxide fraction.

The fact that the largest amounts of sesquioxides within a given profile most often occur in the B_1 horizon is quite interesting. Müller (1924) regarded this horizon as part of the eluvial horizon and Weis (1929, 1932) used the symbol A_3 for this horizon but his results, which for many soils were quite similar to those presented here, made him conclude that it was an illuvial horizon. As has been discussed in chapter 2 and as appears from the profile descriptions in chapter 3, the B_2 horizon, even in those profiles

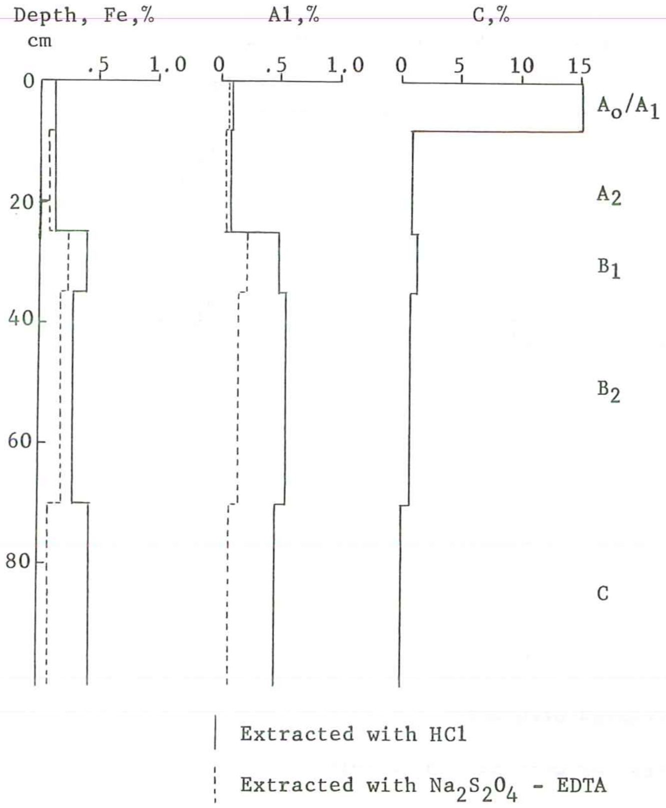

Fig. 10. Iron, aluminium and organic carbon contents in the Støttrup Hede profile.

having more iron in the B_1 horizon, is the horizon with the colour most influenced by iron oxides and hydroxides. The most obvious explanation for this is, of course, that the colour of the iron compounds in the B_1 horizon is covered by the intensive black colour of the organic matter. However, another fact suggests that there may be other reasons as well. It appears from most of the profile descriptions in chapter 3 that the sand grains of the B_1 horizons are bleached and hence lacking the iron coatings found on sand grains deeper in the profile. This fact was also noted by Müller (1924) and Weis (1929, 1932) and caused these authors to draw the conclusions mentioned above. The presence of the bleached sand grains and at the same time a high iron and aluminium content strongly suggest that the iron and the aluminium are present in some forms different

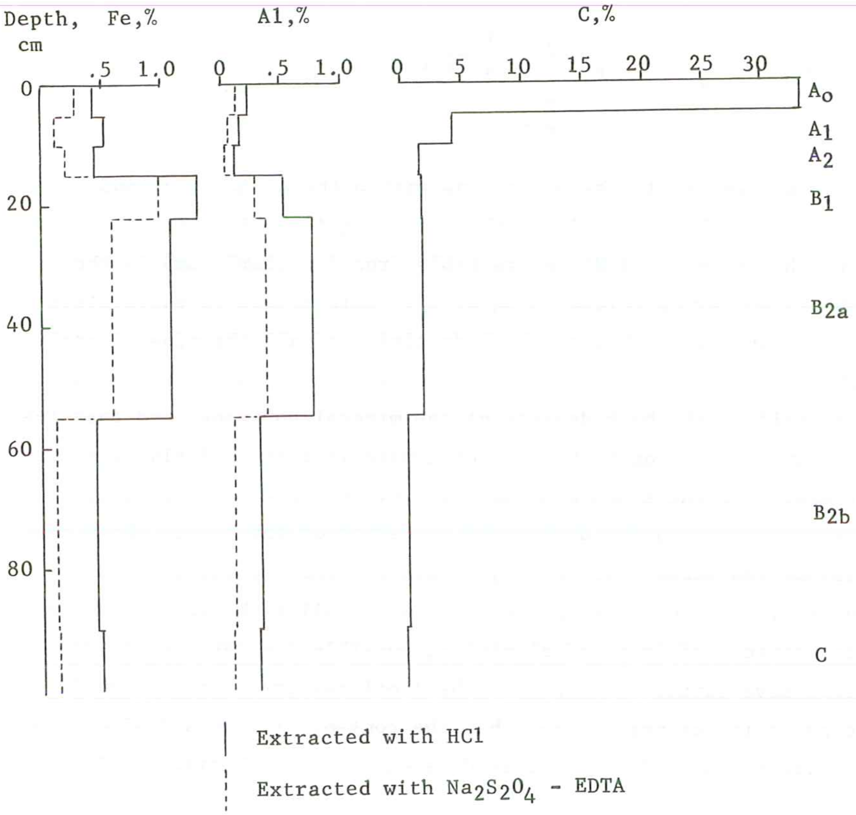

Fig. 11. Iron, aluminium and organic carbon contents in the Skarpholt profile.

from those found deeper in the profile, especially in the C horizon. The most reasonable assumption seems to be that the metals to a large extent are present in some combination with the organic matter. These problems will be discussed more thoroughly in the following chapter.

In an attempt to obtain some information on the iron and aluminium balance of the whole solum (A + B horizon) of the soils investigated, the values reported in Table 10 were calculated. These values are based on the amount of iron and aluminium extracted with hydrochloric acid except for the aluminium of the A_1 and B_1 horizons of the Skarrild profile, where the values obtained by extraction with $Na_2S_2O_4$ - EDTA were used due to lack of data on the HCl-extractable fraction. The weighted average R of the iron and aluminium contents of the A + B horizons is calculated from the equation

$$R = \frac{\frac{1}{2}\sum_{1}^{n} a_n d_n + \sum_{1}^{p} a_p d_p}{\sum_{1}^{p} d_p}$$

where n is the number of sub-subhorizons within the A_o horizon, and p the number of (sub-)subhorizons within the remaining A and B horizons: a_n and a_p are the contents of HCl-extractable iron (or aluminium) in the (sub-)subhorizon having thickness d_n or d_p. This method of calculation implies the assumptions that the bulk densities of all the mineral horizons within a given profile are equal, that the bulk density of the A_o horizon is half of the bulk density of the mineral horizons, and that the iron and aluminium in the A_o horizon originate from the underlying mineral material making up the A and B horizons, i.e. the A_o horizon is a layer of purely organic matter added during the formation of the soil. While the former assumption seems reasonably justifiable, the two latter ones are more doubtful. However, due to the thinness of all A_o horizons, and their rather low content of iron and aluminium, possible inaccuracies in these assumptions have little influence on the final results. In the considerations below it is further assumed that the content of iron and aluminium not dissolved by the hydrochloric acid is equal in all horizons. This

Table 8. Horizons with Maximum Content of Iron, Aluminium and Organic Carbon (For Organic Carbon Exclusive of A Horizons)

Profile	Iron		Aluminium		Organic Carbon
	HCl	$Na_2S_2O_4$+EDTA	HCl	$Na_2S_2O_4$+EDTA	
Gørding Hede	B_{1b}	B_{1b}	B_{1b}	B_{1b}	B_{1a}
Skarrild	C	C	B_1	B_1	B_1
Stavshede	B_{2a}	$A_1/A_2(B_{2b})$	B_{2a}	B_{2a}	B_{2a}
Klelund	B_1&B_{2a}	$A_{oa}(B_1)$	B_{2a}	B_1	B_1
Tingheden	C	C	C	B_1	B_1
Trehøje	B_1	B_1	B_1	B_1	B_1
Løwenholm	B_{2b}	B_{2b}	B_{2b}	B_{2a}	B_1
Trinderup	B_1	B_1	B_1/B_2	B_1	B_1
Støttrup Hede	C	B_1	B_2	B_1	B_1
Skarpholt	B_1	B_1	B_{2a}	B_{2a}	B_{2a}

Table 9. Combination between Horizons with Maximum Organic Carbon Content (Exclusive of A Horizons) and Horizons with Maximum Iron and Aluminium Content (Number of Profiles)

	Iron		Aluminium	
	HCl	$Na_2S_2O_4$ +EDTA	HCl	$Na_2S_2O_4$ +EDTA
Horizon with max. sesquioxide content identical to that with max. organic carbon content	4	4	4	8
Horizon with max. sesquioxide content immediately overlying that with max. organic carbon content	1	1	0	0
Horizon with max. sesquioxide content immediately underlying that with max. organic carbon content	1	2	4	2
Other combination	4	3	2	0

assumption seems reasonable for soils, as those investigated here, where the inorganic fraction consists mainly of rather coarse quartz sand and, therefore, presumingly has a comparatively small content of iron- and aluminium-containing silicate minerals. The amount of iron and aluminium not soluble in hot hydrochloric acid is probably small in such soils.

The two last columns in Table 10 show the net differences between the iron and aluminium contents of the A + B horizons and the C horizon. With one exception, where the differences are rather small and hardly significant, the differences have the same sign. Based on the sign of the differences, the profiles may be divided into three groups having positive, negative and no differences respectively.

Three profiles (Skarrild, Tingheden and Støttrup Hede) have negative differences indicating a net loss of iron and aluminium from the A + B horizons, or (and) an enrichment of the C horizon with these compounds. In these three profiles the differences in iron content are substantially larger (numerically) than the differences in aluminium content. The differences in aluminium content are hardly significant in the Skarrild and Støttrup Hede profiles. In the former profile the numerical difference would have been still smaller if data had been available for the HCl-extractable aluminium fraction in all subhorizons. The greater part of the large negative difference in the aluminium content of the Tingheden profile is probably most readily explained by the finer texture of the C horizon

Table 10. Iron and Aluminium Balance of the Profiles Investigated

Profile	A + B horizons, weighted average (R)		C horizon		A + B horizons − C horizon	
	Fe,%	Al,%	Fe,%	Al,%	Fe,%	Al,%
Gørding Hede	0.69	0.41	0.35	0.19	0.34	0.22
Skarrild	0.27	0.23	0.51	0.30	-0.24	-0.07
Stavshede	0.68	0.38	0.70	0.33	-0.02	0.05
Klelund	0.92	0.60	0.53	0.36	0.39	0.24
Tingheden	0.92	0.61	3.66	1.26	-2.74	-0.65
Trehøje	0.47	0.34	0.40	0.23	0.07	0.11
Løwenholm	0.39	0.47	0.35	0.42	0.04	0.05
Trinderup	0.56	0.47	0.37	0.28	0.19	0.19
Støttrup Hede	0.25	0.39	0.41	0.47	-0.16	-0.08
Skarpholt	0.78	0.49	0.50	0.31	0.28	0.18

of this profile (see remarks above). This may also account for a part of the large negative difference in the iron content of this profile, but an additional cause may be the mottling of the C horizon. The latter explanation is also offered for the negative difference in the iron content of the Skarrild profile while no immediate explanation is available for the Støttrup Hede profile, but the numerical differences in this profile are rather small and perhaps insignificant.

If the differences in the Støttrup Hede profile are considered insignificant it would in this respect be similar to three of the remaining profiles (Stavshede, Trehøje and Løwenholm) that show small, and presumingly insignificant, differences. This means that in these profiles all the iron and aluminium removed from the A horizon has been deposited in the B horizon, or that a net loss from these horizons is accompanied by a similar net loss from the C horizon.

The four remaining profiles (Gørding Hede, Klelund, Trinderup and Skarpholt) all have positive differences. This may be explained either by a net gain in the A + B horizons or a loss from the C horizon. A net gain in the A + B horizons arising from transport processes seems improbable. It could be explained in terms of a more intense weathering of the upper soil layers or by a removal of some superficial soil layers, e.g. by erosion. As the four profiles are all developed on coarse quartz sand, low in iron-and aluminium-containing, easily weatherable, minerals, the weathering hypothesis seems improbable, and no observations have been made to support an explanation in terms of erosion.

It would be possible to offer a number of other explanations for the phenomenon, but the most probable explanation seems to be that the C horizon has suffered a loss of iron and aluminium. It is remarkable that taking into account analytical errors and errors arising from the assumptions applied in the calculations of the weighted average contents of iron and aluminium in the A + B horizons, the ratio between the contents of these two metals in the A + B horizons is practically equal to the corresponding ratio in the C horizon. If the assumption that the positive differences are due to a loss of sesquioxides from the C horizon is correct, this would indicate that equal proportions of iron and aluminium have been lost. In chapter 9 more evidence is produced to support the hypothesis of a loss of iron and aluminium from the C horizon.

CHAPTER 7

METAL-ORGANIC MATTER COMPLEXES IN PODZOLS

7.1 General Remarks

The term 'complex' is used in various connections with more or less precise definitions. It will be used here in the definition given by Hägg (1963), according to which it is a molecule or ion formed directly from independently existing atoms, molecules or ions. To qualify for the designation 'complex' the bonds will usually be strong enough to prevent, or at least modify, the normal reactions of the molecular or ionic species making up the complex.

An important group of complexes consists of a metal ion, often called the central atom, and one or more organic molecules or ions called the ligands. Each metal ion will usually have a tendency to form a definite number of complex bonds irrespective of the nature of the ligands. This number, which is known as the coordination number of the metal, is normally greater than one. Similarly, some organic molecules have more than one complexing site and, depending on the actual number, they are called monodentate, bidentate, tridentate etc. If a metal ion forms a complex with one or more polydentate ligands the complex attains a ring structure and this type of complex is known as a 'chelate' (Martell and Calvin 1952). It is probably the most common type of metal-organic matter complexes.

As pointed out by Martell and Calvin (1952) and Mortensen (1963), the number of different organic functional groups capable of forming complex bonds is rather limited, but it includes such groups as the amino, carboxyl and hydroxyl groups which are abundant in organic compounds, including soil organic matter as described in chapter 5. The study of metal-soil organic matter complexes is subject to the same limitations as described in chapter 5 for the study of soil organic matter in general. Most of the techniques used in such studies require extraction, separation and/or purification of the organic matter and these operations may seriously affect the complexing properties of the organic matter. Himes and Barber (1957) found that extracted organic matter, although only accounting for approx. 15 % of the total organic matter content of the soil, had about 70 % of the capacity for complexing zinc. They suggested that this could be due to formation of new complexing sites during the extraction, but it may of course also be due, at least partly, to a selective extraction of the most active fraction of the organic matter.

Despite these limitations much circumstantial evidence has been produced to demonstrate the presence of such complexes in soils, as reviewed by Deuel (1960), Antipov-Karataev and Tsyurupa (1961), and Mortensen (1963). In the following some of the important investigations on the presence, formation and properties of metal-soil organic matter complexes will be discussed, with special attention paid to those relating to podzols.

7.2 Evidence for the Presence of Metal-Organic Matter Complexes in Soils

Some results quoted in the preceding chapters on the extraction from soils of organic matter, iron and aluminium indicate that a fraction of the iron and aluminium in some soil horizons, especially podzol B horizons, is combined in some way with the organic matter. In fact some of the earliest assumptions on the presence of metal complexes in soils, made by Bremner et al. (1946), were based on such extractions. These authors found that neutral solutions of complex-forming inorganic and organic compounds could bring about a simultaneous extraction of a number of metals and organic matter from soils. Fulvic acids extracted with sodium pyrophosphate from a podzol B horizon by Duchaufour (1963) had a large content of iron.

Although such results seem to provide good evidence for the presence of metal-organic matter complexes in the soil, extractions do not appear to be very suitable for quantitative consideration of the composition of the complexes. As already discussed, there is no reason to assume that the amount of organic matter, and particularly the amount of sesquioxides, extracted by certain reagents represents exactly the amount present as metal-organic matter complexes. It seems, therefore, of rather doubtful value to attempt a calculation of the molar ratio between iron and aluminium on the one hand and organic matter on the other from the amounts extracted with sodium pyrophosphate, as was done by McKeague (1968). The value of these calculations is further reduced by the fact that the molecular weight of the organic matter used in the calculations was that determined by Schnitzer and Desjardins (1962) for a different soil. This molecular weight is furthermore probably subject to considerable error, as discussed in chapter 5 and as shown by Hansen and Schnitzer (1969b). McKeague arrived at metal-organic matter ratios higher than those found for complexes prepared in the laboratory by Schnitzer and Skinner (1964). He suggested this could be due to a breakdown of the organic matter by microorganisms. Although there is no doubt that such a breakdown does take place, the most obvious explanation is that the pyrophosphate extracts iron and aluminium compounds other than those fixed by organic matter. Titova (1962) has shown that 0.1 m sodium pyrosphosphate is capable of extracting some iron from hydroxides and biotite.

Kononova and Belchikova (1970) carried out still more extensive calculations based on the amounts of iron, aluminium and organic matter extracted with pyrophosphate. They not only based their calculations on the above findings of Schnitzer and Skinner concerning the molar ratio between the organic matter and the metals, but also employed the conclusions drawn by Schnitzer and Skinner (1964) concerning a relationship between this molar ratio and the number of hydroxyl ions bound per metal ion in the complexes (see section 7.3). Using these relationships Kononova and Belchikova calculated the number of hydroxyl ions per metal ion in the organic matter complexes. This was done in spite of the fact that some of the soils were entirely different from those studied by Schnitzer and Skinner. Kononova and Belchikova mentioned that pyrophosphate may extract iron and aluminium from free oxides and clay minerals, and they used this fact to explain some results which, obviously, could not be explained in any other way. However, they paid no attention to this at all when doing the calculations mentioned above. These calculations therefore seem to involve so many inaccurate, and sometimes clearly erroneous, assumptions that they have little or no reliability. Any relation they may have to the actual conditions in the soils seems merely incidental.

Several authors have shown that various metals are adsorbed with different strengths in soils. Himes and Barber (1957) found that potassium chloride caused only partial removal of zinc, previously adsorbed by the soil, while cupric acetate caused its total removal. Broadbent and Ott (1957) saturated previously extracted and purified soil organic matter with Ba, Ca, Mg and Cu and determined the fraction of these metals that could be removed from the soil by an amount of hydrochloric acid equivalent to the amount of metal adsorbed by the soil. From the results the metals were arranged as follows according to their strength of adsorption: Cu $>$ Ba $>$ Ca $\geqq$ Mg. Broadbent (1957) found that a more concentrated solution of HCl was required for a total removal of Cu from previously Cu-saturated extracted organic matter than that required for total removal of Ca from Ca-saturated organic matter.

Since complexation of metals by most organic compounds involves dissociated acidic groups, it will cause an increase in the degree of dissociation and hence a reduced pH of a solution or suspension of the organic matter, and a corresponding shift of the titration curve towards lower pH values. These effects have been demonstrated for various soils and humus preparations and for various cations by Beckwith (1955), Beckwith (1959), Kawaguchi and Kyuma (1959), Khanna and Stevenson (1962), Schnitzer and Skinner (1963a), Khan (1969) and van Dijk (1971). In most cases it has been found that the effects of the trivalent cations iron and aluminium were greater than those of divalent cations, and that the extent of the latter's effects differed according to the sequence found by Mellor and Maley (1947) and Irving and Williams (1948). Some of the results obtained are deficient, however, since due attention has not been paid to the inherent acidity of certain metal solutions and the effects of this on the base consumption during the titrations. Martin and Reeve (1958) concluded that their titrations of soil organic matter with or without the presence of ferric iron and aluminium gave no evidence for the formation of complex compounds. However, there were some unexplained differences between the titrations carried out in the presence and in the absence of the metals. The organic matter used in these experiments was extracted with acetyl-acetone from a podzol B horizon.

Experiments made by Kononova and Titova (1961), Dyakonova (1962), Titova (1962) and Juste and Delas (1967) by means of electrophoresis have shown the existence of negatively charged soil organic matter compounds containing iron, aluminium and various other metals. Some of these compounds were extracted directly from soils, while others were prepared by addition of the metal to previously extracted organic matter.

It has been shown by several authors, e.g. Martin and Reeve (1958), Kaurichev and Nozdrunova (1961), Schnitzer and Skinner (1963b), and Ponomareva (1964), that dispersed soil organic matter may dissolve iron and aluminium compounds and maintain these in solution under conditions where the presence of free ionic species would lead to precipitation of the hydroxides. This has also been found in experiments carried out in this study and discussed in chapter 10. Similar results have been found for water extracts of leaves and other plant constituents by DeLong and Schnitzer (1955), Schnitzer and DeLong (1955), Schnitzer (1959), Bloomfield (1952b, 1953a, 1953b, 1954a, 1954b, 1954c, 1958, 1965, 1966, 1970), Himes, Tejeira and Hayes (1963), Muir et al. (1964), Muir, Logan and Bown (1964), King and Bloomfield (1968) and Ellis (1971). Most of these experiments were concerned with a study of the dissolution of iron compounds and as suggested by some of the authors it is likely that the dissolution of iron involves a reduction, even if the studies are made under aerobic conditions. Some of th experiments also showed evidence of the dissolution of aluminium compounds. Labroue (1971) attributed a high content of so-called free aluminium in surface horizons of neutral alpine soils to accelerated mineral weathering caused by complexation of aluminium by organic compounds.

Although the organic compounds are capable of dissolving iron and aluminium it has also been found in many experiments (Ashan 1907, Martin and Reeve 1960, Martin 1960, Stumm and Morgan 1962 , Wright and Schnitzer 1963, Ponomareva 1964, Schnitzer and Skinner 1964, Schnitzer 1969) that ferric ions and particularly aluminium ions have a flocculating effect on dispersed humus compounds. The studies quoted indicate that a certain minimum amount of metal is required to cause flocculation. This agrees well with the ability of certain complexing agents to extract soil organic matter, as described above. It must also be assumed to be of major importance for an understanding of the podzolization process and will, therefore, be discussed in greater detail in chapter 8. It has also been shown that freshly precipitated hydroxides of iron and aluminium may have a flocculating effect on dispersed humus compounds and that mixing of metal hydroxide sols with solutions of soil organic matter may cause mutual flocculation (Deb 1950a, Bloomfield 1955, Ponomareva 1964, Levashkevich 1966). The amount of metal hydroxide required to cause flocculation of a given amount of organic matter varies highly according to the conditions of the experiments and the nature of the metal hydroxide and the organic matter. However, the general impression of the experimental results is that the ratio of metal to organic matter exceeds that required, when an ionic form of the metal is used, by several orders of magnitude. Hence, the metals appear to be much less effective in the hydroxide than in the ionic state.

Additional evidence for the ability of soil organic matter to complex metals has been supplied by the experiments of Oades and Townsend (1963), who attributed an exothermic reaction at approx. 320 °C during DTA investigations of soil, previously treated with hydrogen peroxide, to stable iron-organic matter complexes. Schnitzer and Skinner (1964) and Schnitzer and Kodama (1972) found that various metals affected the temperature at which the major decomposition of extracted organic matter took place during thermogravimetric and differential thermal investigations. Increasing iron content in the organic matter preparations caused a shift in the temperature of the major decomposition towards lower values. The authors interpreted this as being due to strains in the complex molecules and ruled out the possibility of it being caused through catalytic effects of the iron by carrying out similar investigations on mixtures of organic matter and solid ferric oxides. Even though this physical admixture of iron failed to produce a decrease in the temperature of the major decomposition, the explanation given does not seem to be on secure ground. This view is further substantiated by the fact that an aluminium content in the organic matter failed to cause a reduction in the decomposition temperature, but only an irregular broadening of the temperature interval of the major decomposition. In most other respects the effects were similar whether the organic matter contained iron or aluminium.

Results of spectroscopic measurements in the ultraviolet, visible and infrared regions have also been interpreted by various authors (Broadbent and Ott 1957 , Schnitzer, Shearer and Wright 1959, Wright and Schnitzer 1963, Schnitzer and Skinner 1963a, Schnitzer and Hansen 1970) as evidence for the ability of soil organic matter to complex various metals, especially iron and aluminium.

7.3 Properties of the Metal-Organic Matter Complexes

Very little concrete evidence is available on the mechanism of complex formation between the metals and the soil organic matter and on the nature of the bonds formed.

By analogy with simple organic compounds and by comparison of titration curves for copper complexes of these and of soil organic matter, Beckwith (1959) concluded that hydroxyl groups took part in the bonding of the metals. Lewis and Broadbent (1961a, 1961b) and Randhawa and Broadbent (1965a, 1965b) studied the complexation of Cu, Ba, and Zn by soil organic matter. It was found that the complexation was strongly dependent on pH,and it was concluded that phenolic groups, carboxyl groups, and some groups more acid than usual carboxyl groups, took part in the complexation of the metals. Schnitzer and Skinner (1965a) studied the effect of blocking of various functional groups on the ability of the organic matter to take up ferric iron, aluminium and copper from an ion exchange resin saturated with these metals. The organic matter was extracted from a podzol B horizon. As the blocking caused the organic matter to become insoluble in water the experiments were carried out in a water-acetone mixture. It was concluded from the experiments that the major part of the complexing capacity was due to the joint action of strongly acid carboxyl groups and phenolic groups. This seems a plausible enough conclusion as judged from the molecular structure of many simple organic compounds known to form complex compounds with metals; provided, of course, that a sufficient number of these groups is available to satisfy the coordination number of the metals. However, the actual evidence produced by Schnitzer and Skinner seems too weak to permit acceptance of the conclusion without comment. The conclusion was mainly based on the fact that a blocking of either the acid carboxyl groups or the phenolic groups caused a substantial, and approximately identical, reduction in the capacity to complex metals. It is, however, questionable as to what extent the procedures employed will cause a specific blocking of one particular type of functional groups in a material like soil organic matter. It must be admitted that some calculations were presented to confirm the assumption of a selective blocking but they are not very convincing and based on earlier, none too reliable determinations of functional groups and molecular weights. In fact it has since been shown by Hansen and Schnitzer (1969b) that the molecular weight is incorrect. The investigation involved seven different derivatives, and all of these had a substantially smaller capacity (2-10 times) for complexing metals than the untreated organic matter. It is not surprising that any treatment of the kind employed will reduce the capacity to complex the metals when it is realized that the complexing of the metals requires a certain steric arrangement of a number of functional groups. Any treatment altering just one of these groups may cause the disappearance of the entire complexing site.

Schnitzer, Shearer and Wright (1959), Wright and Schnitzer (1963), and Schnitzer and Skinner (1963a) found that the addition of ferric iron to organic matter at low pH caused a change in the infrared spectrum of the organic matter similar to that caused by the addition of alkali to the organic matter. The change in the infrared spectrum was in both cases attributed to a change of undissociated carboxyl groups into carboxylate structures. This was taken as evidence for the participation of carboxyl groups in forming complex bonds with iron.

Schnitzer and Skinner (1963a) used a spectroscopic technique described by Vosburgh and Cooper (1941) in a study of the molar ratio of metal to organic matter in complexes prepared at pH 3 and 5. It was found that Cu^{++}, Fe^{+++} and Al^{+++} formed complexes having a molar ratio 1:1 at pH 3, while Cu^{++} and Fe^{+++} formed 1:2 (organic matter : metal) complexes at pH 5. The Al-complexes formed at pH 5 had a molar ratio 1:1. These results must be considered extraordinary since, as already mentioned, it was later proved by Hansen and Schnitzer (1969b) that the molecular weight of the organic matter was incorrect. Furthermore, it was pointed out by Vosburgh and Cooper (1941) that the method is applicable only if one complex is formed. If more than one complex is formed the method may still be used, but only if the complexes have clearly separated absorption maxima and if measurements are made at each of these. In light of this it is still more remarkable that Schnitzer and Hansen (1970), using the same method, but the corrected molecular weight for the organic matter, found that 1:1 complexes were formed at pH 3 and 5 of the organic matter and the metals Cu^{++}, Ni^{++}, Pb^{++}, Co^{++}, Mn^{++}, Zn^{++}, Ca^{++} and Mg^{++}. Fe^{+++}- and Al^{+++}-complexes having a molar ratio 1:1 were also formed at pH 1.70 and 2.35 respectively. It is difficult to be convinced by these results taking into account the limitations of the method and the heterogeneity of the organic matter.

It is not clear how some of these results are compatible with the report of Schnitzer and Skinner (1964) on the preparation of ferric iron and aluminium complexes containing 1, 3 and 6 moles of metal per mole of organic matter. In these studies an attempt was made to evaluate the actual metal ion species incorporated in the complexes. This was done by means of chemical analyses of the complexes, and the differences between 100 % and the accumulated weight percentage of the compounds determined were assumed to be due to hydroxyl ions bound to the metals. From this it was concluded that the 1:1 and 1:3 iron complexes contained the ion $Fe(OH)^{++}$, while 1:6 iron complexes contained $Fe(OH)_2^+$. The 1:1 aluminium complex contained $Al(OH)^{++}$ and the 1:3 and 1:6 complexes $Al(OH)_2^+$. Considering that the organic matter content of the complexes is calculated as twice the carbon content, that difficulties in determining the water contents are reported, and that small differences are important for the evaluation of the particular ionic species present, these conclusions are expressed in much too definite a fashion. Furthermore, the existence, at any rate as a free ion, of $Al(OH)_2^+$ is, according to Jackson (1963), doubtful. As found by Brosset, Biedermann and Sillén (1954) and Ruff and Tyree (1958) aluminium seems to form polymeric hydroxy-aluminium ionic species, and not simple ions of the type referred to above. Evidence for the presence of such polymeric ion species in soils and clays have also been obtained by Jackson (1963) and Schwertmann and Jackson (1964).

Stability constants for metal-soil organic matter complexes have been determined by Himes and Barber (1957), Randhawa and Broadbent (1965b), Schnitzer and Skinner (1966, 1967), and Ardakani and Stevenson (1972). The studies of Schnitzer and Skinner were made on the organic matter from a podzol B horizon referred to several times. These determinations were based on the distribution of the metal ions between an ion exchanger phase and an aqueous phase in equilibrium with this in the absence and presence of the soil organic matter. From this distribution measured over a range of concentrations the molar ratio of organic matter to metal and the stability constants of the complexes were calculated. In these calculations an expression given by Martell and Calvin (1952) was used. However, as pointed out by Clark and Turner (1969) the expression is a simplified form of a more complicated general equation. The simplified equation is applicable only to complexes having one metal ion per molecule, i.e. the molar ratio of organic matter to metal must be an integer. This was not the case for all the complexes studied by Schnitzer and Skinner (1966, 1967) and hence the results are probably of limited value. In reply to the criticisms of Clark and Turner (1969), Schnitzer and Hansen (1970) reconsidered the studies of Schnitzer and Skinner (1966, 1967) and concluded that the molar ratios calculated might be subject to extensive error, since the calculations involved were such that small analytical errors would cause considerable errors in the molar ratios. In an attempt to study the molar ratios by another method the authors found by spectroscopic measurements that 1:1 complexes were formed by all the metals. This results has already been commented on above. It was also found that the ionic strength affected the composition and stability of the complexes. Schnitzer and Skinner (1966, 1967) noted several deviations from the general rule concerning the relative stability of metal complexes given by Irving and Williams (1948). In general the stabilities of metal-soil organic matter complexes seem to be much lower than those of metal complexes of more simple organic complex-forming compounds such as EDTA.

Although some of the findings on metal-soil organic matter complexes are subject to serious criticism, as shown above, it seems well established that the organic matter is capable of forming complex compounds with metals including iron and aluminium, and that the complexation affects the solubility of the metals.

CHAPTER 8

MECHANISMS OF PODZOLIZATION

8.1 Problems of Podzolization

Many studies have been made to obtain information on the actual processes leading to the formation of podzols. No attempt will be made here to present a complete chronological review of these studies; a fairly thorough one has already been given by Ponomareva (1964). The approach used in what follows is a discussion and evaluation of various possible podzolization mechanisms.

The horizon sequence of podzols shows clearly that iron, aluminium and organic matter have been removed from the A horizon and, at least partly, deposited in the B horizon. The two important questions to answer in order to explain these translocations are therefore (1) How are the compounds mobilized in the A horizon? and (2) How are they immobilized in the B horizon? Any proposed mechanism of podzolization must include satisfactory and plausible answers to both questions for all the compounds involved. In the literature the former question seems to have received considerably more attention than the latter and, furthermore, many of the considerations pertain to iron only. This has led to suggestions of a number of mechanisms for iron mobilization, but the importance of many of these in natural podzol formation may be questioned on the grounds that they give no explanation of the mobilization of aluminium and organic matter and/or no explanation of the immobilization processes.

8.2 Soil Development Preceding Podzolization

As mentioned in chapter 2 all podzols are acid. Most authors (e.g. Iarkov 1954, Rode 1955, Stobbe and Wright 1959, Ponomareva 1964, Duchaufour 1967) therefore state that podzolization is preceded by a leaching of all basic compounds, such as carbonates, and practically all adsorbed mono- and divalent metal ions from the soil. Since the time required for complete leaching of the adsorbed mono- and divalent cations decreases with the buffer capacity of the soil, this is in agreement with the fact that podzols are found primarily on light textured parent materials. No findings reported in the literature show the existence of natural podzols with high pH values and there seems to be no reason to dispute the conclusion that acidification is a necessary prerequisite for podzolization. The mechanism through which acidification facilitates podzolization is not immediately clear, but in the following sections various possibilities will be discussed.

8.3 Translocation Processes

8.3.1 Translocation of the Metals as Simple Ions or their Hydroxide Complexes

The maximum amounts of iron and aluminium that can be present in the soil solution will be determined by the solubility of the least soluble compound that can be formed under the given conditions. Many inorganic and organic compounds may in this way limit the solubility of the metals. Due to a lack of information on the nature and the conditions of formation of many inorganic and practically all organic iron and aluminium compounds in the soil, it is not possible to calculate the actual solubility of the metals.

However, it is possible from energetic data to estimate an upper limit for the solubility of the metals because it can be assumed that in the absence of less soluble compounds, hydroxides and/or carbonates will eventually form, since hydroxide and carbonate ions will always be present in the soil solution. Due to the acidity of ferric and aluminium ions carbonates of these metals are not formed in aqueous systems. Hence, in the case of aluminium, the compound eventually limiting the solubility will be aluminium hydroxide. For iron the conditions are more complicated since oxidation and reduction may affect the reactions and in turn the solubility of this metal. Three slightly soluble compounds could, theoretically, limit the solubility of iron; these are ferric hydroxide, ferrous hydroxide and ferrous carbonate. Petersen (1965) calculated that ferrous hydroxide can be formed only if the partial pressure of carbon dioxide is lower than about 2×10^{-6} atm. A similar result was obtained by Ponnamperuma (1967). Carbon dioxide pressures below this limit are unlikely to occur in soils and hence the presence of ferrous hydroxide can be disregarded.

In the following calculations ion or molecular species in brackets denote molar concentrations and activity coefficients have been disregarded. If ferrous carbonate is formed in the soil the relation between the concentrations of ferrous and carbonate ions will be

$$[Fe^{++}] = \frac{K_{FeCO_3}}{[CO_3^{--}]} \qquad \text{..... (1)}$$

where K_{FeCO_3} is the solubility product of ferrous carbonate. Substitution of the expressions for the dissociation of carbonic acid

$$K_{H_2CO_3(1)} = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} \qquad \text{..... (2)}$$

and

$$K_{H_2CO_3(2)} = \frac{[H^+]\,[CO_3^{--}]}{[HCO_3^-]} \qquad \text{..... (3)}$$

into equation (1) yields

$$[Fe^{++}] = \frac{K_{FeCO_3}\,[H^+]^2}{K_{H_2CO_3(1)}\,K_{H_2CO_3(2)}\,[CO_2]}. \qquad \text{..... (4)}$$

According to Henry's law, $[CO_2]$ of a solution will be related to the partial pressure of carbon dioxide in atmospheres (P_{CO_2}) of a gaseous phase in equilibrium with the solution as

$$[CO_2] = K_{CO_2}\,P_{CO_2} \qquad \text{..... (5)}$$

where K_{CO_2} is a constant. Substitution into equation (4) yields

$$[Fe^{++}] = \frac{K_{FeCO_3}\,[H^+]^2}{K_{H_2CO_3(1)}\,K_{H_2CO_3(2)}\,K_{CO_2}\,P_{CO_2}} \qquad \text{..... (6)}$$

If ferric hydroxide is formed in the soil, then

$$[Fe^{+++}] = K_{Fe(OH)_3}\,[H^+]^3 \qquad \text{..... (7)}$$

where $K_{Fe(OH)_3}$ is the solubility product of ferric hydroxide divided by the dissociation constant of water raised to the third power.

At equilibrium the molar ratio of ferric to ferrous ions in the soil solution will be related to the redox potential **E** in volts as

$$\mathbf{E} = \mathbf{E}_o + 0.06 \log \frac{[Fe^{+++}]}{[Fe^{++}]} \qquad \text{..... (8)}$$

where $\mathbf{E}_o$ is the standard electrode potential in volts for the half-reaction

$$Fe^{+++} + e^- \rightleftharpoons Fe^{++}.$$

Hence, if the soil solution is in equilibrium with both ferrous carbonate and ferric hydroxide the conditions imposed by equations (6), (7) and (8) must be fulfilled. The combination of these leads to

$$E = E_o + 0.06 \log \frac{K_{Fe(OH)_3}\, K_{H_2CO_3(1)}\, K_{H_2CO_3(2)}\, K_{CO_2}\, P_{CO_2}\, [H^+]}{K_{FeCO_3}} \quad \ldots (9)$$

$$\text{or } E = E_o + 0.06 \log \frac{K_{Fe(OH)_3}\, K_{H_2CO_3(1)}\, K_{H_2CO_3(2)}\, K_{CO_2}}{K_{FeCO_3}}$$

$$+ 0.06 (\log P_{CO_2} - \mathrm{pH}) = K + 0.06 (\log P_{CO_2} - \mathrm{pH}) \quad \ldots (10)$$

$$\text{where } K = E_o + 0.06 \log \frac{K_{Fe(OH)_3}\, K_{H_2CO_3(1)}\, K_{H_2CO_3(2)}\, K_{CO_2}}{K_{FeCO_3}} . \quad \ldots (11)$$

At 25 °C E_o = 0.771 volt (Latimer 1950)

$K_{Fe(OH)_3}$ = 4×10^{4} (Latimer 1950)

$K_{H_2CO_3(1)}$ = 4.31×10^{-7} (Latimer 1950)

$K_{H_2CO_3(2)}$ = 4.70×10^{-11} (Latimer 1950)

K_{CO_2} = 3.26×10^{-2} (Landolt-Börnstein 1962)

K_{FeCO_3} = 2.11×10^{-11} (Latimer 1950)

and hence K = 0.60.

Substitution of this value of K into equation (10) yields

$$E = 0.60 + 0.06 (\log P_{CO_2} - \mathrm{pH}). \quad \ldots (12)$$

Only under conditions fulfilling equation (12) can ferrous carbonate and ferric hydroxide exist together in the soil. At redox potentials lower than those corresponding to given values of P_{CO_2} and pH, ferric hydroxide will be unstable and, conversely, ferrous carbonate will be unstable at higher redox potentials.

Assuming the maximum range of the partial pressure of carbon dioxide in the soil air to be from 0.0003 atm. to 1 atm. and the maximum pH range to be from 3 to 7, the quantity ($\log P_{CO_2}$ - pH) will have a maximum range from -10.5 to -3. Hence it can be concluded from equation (12) that equilibrium between ferric hydroxide and ferrous carbonate in the soil requires redox potentials between approximately 0 and 0.4 volts. The upper limit applies only at pH 3 and at a carbon dioxide partial pressure of 1 atm., and such a situation will hardly ever be realized in a soil. Hence, the presence of ferrous carbonate in the soil requires redox potentials somewhat below 0.4 volts.

Little is known about the compounds and reactions governing the redox potential of soils. Bohn (1971) points out redox couples involving unimolecular species of iron, manganese, sulphur, nitrogen, oxygen and hydrogen as the most important ones. If the soil is in equilibrium with the oxygen in the soil air the following relation exists between the redox potential E, pH and the partial pressure of oxygen in atm., P_{O_2}:

$$E \quad = \quad E_o + 0.015 \log P_{O_2} - 0.06 \text{ pH} \qquad \ldots\ldots (13)$$

where E_o is the standard electrode potential in volts for the half-reaction

$$\tfrac{1}{4} O_2 + H^+ + e^- \rightleftharpoons \tfrac{1}{2} H_2O.$$

The value of E_o at 25 °C is 1.23 V (Latimer 1950).
Hence (13) becomes

$$E \quad = \quad 1.23 + 0.015 \log P_{O_2} - 0.06 \text{ pH}. \qquad \ldots\ldots (14)$$

Combination with equation (12) yields

$$\log P_{O_2} \quad = \quad 4 \log P_{CO_2} - 42. \qquad \ldots\ldots (15)$$

At $P_{CO_2} = 1$ atm., P_{O_2} becomes 10^{-42} atm.

This extremely small value indicates that ferrous carbonate can be formed and can exist only in the complete absence of oxygen - provided, of course, that equilibrium is obtained. This limitation should be kept in mind when comparing the above calculations with redox potentials actually measured in soils. By conventional techniques redox potentials in soils are measured by so-called inert electrodes such as platinum electrodes, but according to Bohn (1971) any electrode, although considered inert, will discriminate between different redox couples. Hence, the values obtained will not represent true equilibrium values.

Redox potentials lower than the limiting value arrived at above have been measured in several soils including podzols (Quispel 1947, Marches et. al. 1952, McKenzie and Erickson 1954 , McKenzie, Whiteside and Erickson 1960). The very low redox potentials are usually found in poorly drained soils, and a deficiency in oxygen to the extent where ferrous carbonate becomes the stable iron compound appears improbable in most podzols.

Hence, in the following it will be assumed that the concentration of iron and aluminium in the soil solution is governed by the solubility of their respective hydroxides.

Due to the tendency of ferric and ferrous ions to form mono- and polynuclear hydroxide complexes the following iron-containing ion species may be found in solution in addition to simple ferric and ferrous ions: $Fe(OH)^{++}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{++++}$ (Sillén 1959) and $FeOH^+$ (Butler 1963). The actual concentrations of the ion species containing trivalent iron may be calculated from the following equations:

$$[Fe^{+++}] = K_{Fe(OH)_3}\,[H^+]^3 = 10^{3.40}[H^+]^3 \quad \text{.....} \; (16)$$

$$[Fe(OH)^{++}] = K_{Fe(OH)^{++}}\,\frac{[Fe^{+++}]}{[H^+]} = 10^{-2.46}\,\frac{[Fe^{+++}]}{[H^+]} \quad \text{.....} \; (17)$$

$$[Fe(OH)_2^+] = K_{Fe(OH)_2^+}\,\frac{[FeOH^{++}]}{[H^+]} = 10^{-4.70}\,\frac{[FeOH^{++}]}{[H^+]} \quad \text{.....} \; (18)$$

$$[Fe_2(OH)_2^{++++}] = K_{Fe_2(OH)_2^{++++}}\,\frac{[Fe^{+++}]^2}{[H^+]^2} = 10^{-2.85}\,\frac{[Fe^{+++}]^2}{[H^+]^2}. \quad \text{.....} \; (19)$$

The values of the constants used in equations (17), (18) and (19) are selected from Sillén and Martell (1964). Combination of (16) and (19) leads to

$$\frac{[Fe_2(OH)_2^{++++}]}{[Fe^{+++}]} = 10^{0.55}\,[H^+]. \quad \text{.....} \; (20)$$

From equation (20) it follows that the amount of iron found as $Fe_2(OH)_2^{++++}$ at pH 3 will be less than 1 % of that found as Fe^{+++}, and at higher pH values the percentage will be even smaller. Hence, the contribution from $Fe_2(OH)_2^{++++}$ to the amount of iron that can be present in the dissolved state may be disregarded and the total amount of dissolved ferric iron can be calculated as the sum of the amounts calculated from equations (16), (17) and (18).

Substitution of (16) into (17) leads to

$$[FeOH^{++}] = 10^{0.94}\,[H^+]^2 \quad \text{.....} \; (21)$$

and combinatiom of (18) and (21) yields

$$[Fe(OH)_2^+] = 10^{-3.76}\,[H^+]. \quad \text{.....} \; (22)$$

Addition of (16), (21) and (22) leads to an expression for the total concentration of ferric iron in moles per 1 as a function of the hydrogen ion concentration:

$$\text{Total ferric iron} = 10^{-3.76}[H^+] + 10^{0.94}[H^+]^2 + 10^{3.40}[H^+]^3. \quad \ldots\ldots (23)$$

In the pH-range 3 - 7 the two first terms in the right hand side of equation (23), i.e. $[Fe(OH)_2^+]$ and $[FeOH^{++}]$, are quantitatively predominant. The former is dominating at pH > 4.7 and the latter at lower pH-values. As compared with the amounts of iron that are present as $Fe(OH)_2^+$ and $FeOH^{++}$, the amount present as Fe^{+++} is negligible at pH > 4.

The maximum concentration of ferrous ions in the soil solution may be calculated from the concentration of ferric ions by means of equation (8). The concentration of the hydroxide complex of the ferrous ion, $FeOH^+$, is given by

$$[FeOH^+] = K_{FeOH^+} \frac{[Fe^{++}]}{[H^+]} = 10^{8.3} \frac{[Fe^{++}]}{[H^+]} . \quad \ldots\ldots (24)$$

The value of K_{FeOH^+} is from Sillén and Martell (1964). It follows from equation (24) that $[FeOH^+]$ is less than 5 % of $[Fe^{++}]$ at pH < 7. Hence, $[FeOH^+]$ may be neglected when the calculation relates to podzols.

The relative contribution of ferrous ions to the amount of dissolved iron may be evaluated by comparing $[Fe^{++}]$ with the concentrations of the predominant ferric ion species, i.e. $Fe(OH)_2^+$ at pH > 4.7 and $FeOH^{++}$ at pH < 4.7. Rearrangement of equation (8), substitution of the numerical value of $\mathbf{E}_0$, and combination with equations (17) and (18) leads to

$$\log \frac{[Fe(OH)_2^+]}{[Fe^{++}]} = \frac{\mathbf{E}}{0.06} + 2pH - 20.0 \quad \ldots\ldots (25)$$

and

$$\log \frac{[FeOH^{++}]}{[Fe^{++}]} = \frac{\mathbf{E}}{0.06} + pH - 15.3 . \quad \ldots\ldots (26)$$

It follows from equation (25) that $\frac{[Fe(OH)_2^+]}{[Fe^{++}]} > 100$ if $\mathbf{E} > 0.48$ volts at pH 7, and from equation (26) that $\frac{[FeOH^{++}]}{[Fe^{++}]} > 100$ if $\mathbf{E} >$ 0.86 volts at pH 3. It can also be calculated from equations (25) and (26) that $\frac{[Fe(OH)_2^+] + [FeOH^{++}]}{[Fe^{++}]} > 100$ if $\mathbf{E} > 0.74$ volts at pH 4.7. From equation (14) it follows that these **E**-values correspond to oxygen partial pressures of 10^{-22}, 10^{-12} and 10^{-14} atm. respectively. Hence, it

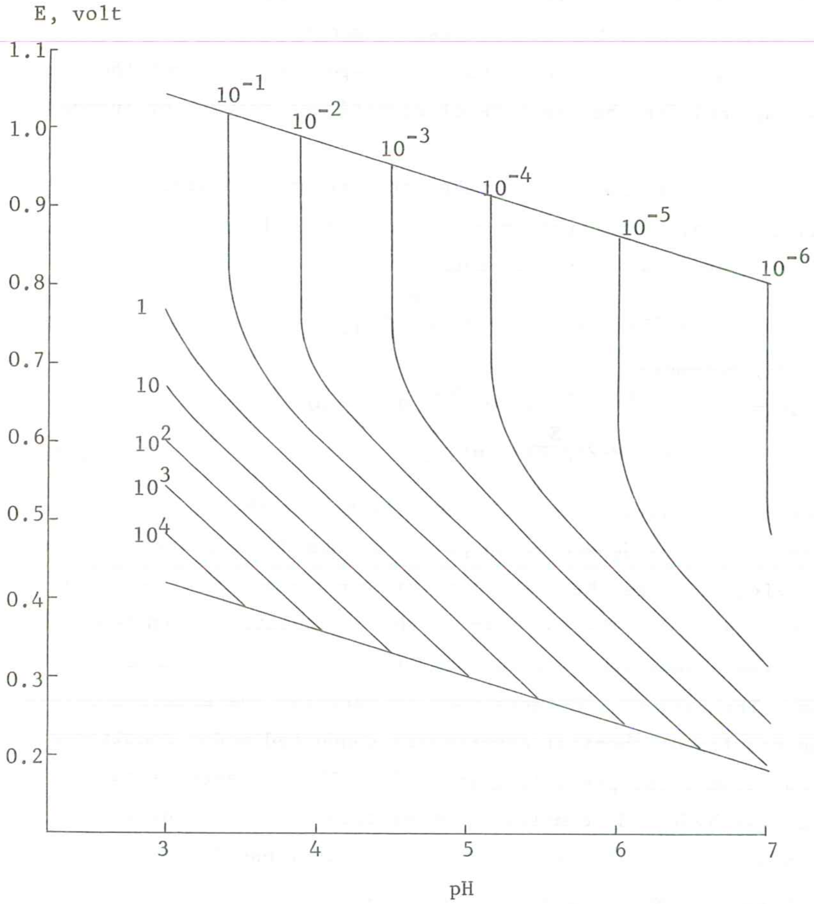

Fig. 12. Theoretical solubility of iron (mg per 1) as a function of redox potential (E) and pH.

may be concluded that ferrous ions can only contribute significantly to the amount of dissolved iron at extremely low oxygen partial pressures.

It cannot be excluded, however, that some horizons of podzols, at least temporarily, may have redox potentials lower than the limiting values arrived at above. When comparing these values with redox potentials measured in soils, allowance must be made for possible lack of equilibrium during the measurements. However, several investigators have found a fairly good agreement between the concentrations of the various ion species of iron and the redox potentials measured (Jeffery 1960, Mandal 1961, Collins and Buol 1970a, 1970b). This may be due to a good response to redox couples involving iron of the inert electrodes applied in the measurements, but it may also be due to the fact that the redox potential is most definitive in the oxygen-poor environment (Bohn 1971) that is required for the presence of significant amounts of ferrous ions.

Equation (23) may be expanded to take into account the amount of dissolved ferrous iron. Substitution of equation (16) into equation (8), rearrangement and antilogarithmation leads to

$$[\mathrm{Fe}^{++}] = 10^{(16.3-\frac{E}{0.06})}\,[\mathrm{H}^+]^3 \qquad \ldots\ldots (27)$$

and equation (23) becomes:

$$\text{Total iron} = 10^{-3.76}\,[\mathrm{H}^+] + 10^{0.94}\,[\mathrm{H}^+]^2 + 10^{3.40}\,[\mathrm{H}^+]^3 + 10^{(16.3-\frac{E}{0.06})}\,[\mathrm{H}^+]^3. \qquad \ldots\ldots (28)$$

This equation is valid at redox potentials higher than 0 - 0.4 volts, the actual limiting value depending on pH and carbon dioxide pressure, as shown above. Fig. 12 shows the solubility of iron in mg per 1 as calculated from equation (28). The validity of this calculation depends on the correctness of the assumptions and the numerical values on which equation (28) is based. The various constants used in deriving the equation originate from the results of chemical experiments conducted under conditions quite different from those prevailing in soils. The presence of mono- and/or polynuclear hydroxide complexes, other than those considered in the derivation above, may also affect the results. These limitations should be kept in mind when evaluating Fig. 12.

A study of Fig. 12 suggests that the acidity of podzols is normally insufficient for the dissolution of significant amounts of iron at high redox potentials. However, some allowance must be made for the fact that no activity coefficients have been employed in the calculations illustrated in Fig. 12 and that the calculations are based on experimental results obtained under conditions entirely different from those prevailing in soils. Acidity in combination with moderately reducing conditions could account for the amounts of dissolved iron actually found in most A horizons as reported in the following chapter. Assuming no gradient in redox potential with depth in podzols the pH gradient would facilitate precipitation of iron in the B horizon.

The hydrolysis of the aluminium ion seems in general to be more complicated than that of iron. Various authors have found evidence for the presence in aqueous solutions of a number of polynuclear aluminium hydroxide complexes. Most of them, e.g. Jackson (1963), Hunt (1965) and Scheffer and Schachtschabel (1970), seem to be of the opinion that the most important hydrolytic product, at least at relatively low pH values, is the monomeric $AlOH^{++}$ ion. On the other hand, Jackson (1963) states that at pH > 5 polynuclear complexes containing several Al-atoms predominate. Schwertmann and Jackson (1963, 1964) attributed a buffer capacity in the pH range 5.5 - 7.6 of partly neutralized and aged aluminium solutions, and of aged suspensions of montmorillonite clay originally saturated with hydrogen ions, to aluminium hydroxide complexes containing several Al-atoms per unit. Brosset, Biedermann and Sillén (1954) concluded that the most probable ion species in aluminium solutions at pH 3-5 was $Al_6(OH)_{15}^{+++}$. Their conclusion was partly based on the assumption that this ion would be particularly stable since it could attain a six-membered ring structure similar to the configuration of aluminium in many minerals. Ruff and Tyree (1958) studied the light scattering of partly neutralized aluminium nitrate solutions and found evidence for the existence of several different ion species in the solutions. The ion size increased with the degree of neutralization up to about 15 Al-atoms per ion. Hence, they rejected the assumption that $Al_6(OH)_{15}^{+++}$ should be considered particularly dominating.

Richburg and Adams (1970) studied the aluminium content of soil solutions and extracts from three originally acid soils that had been subject to various applications of lime and had pH-values ranging from 4.9 to 5.4. Basing their view on these studies and on extensive calculations, they favoured the assumption that the main hydrolytic product of aluminium in these soils was $Al_6(OH)_{15}^{+++}$. The authors seem, however, to have overlooked the fact that the ratio between $[Al^{+++}]$ and $[Al_6(OH)_{15}^{+++}]$ in any solution in equilibrium with solid aluminium hydroxide will be constant. This becomes obvious if the expression for the solubility of aluminium hydroxide

$$[Al^{+++}]\,[OH^-]^3 = K_{Al(OH)_3} \qquad \ldots\ldots (29)$$

is combined with the expression governing the formation of $Al_6(OH)_{15}^{+++}$

$$\frac{[Al_6(OH)_{15}^{+++}]}{[Al^{+++}]^6\,[OH^-]^{15}} = K_{Al_6(OH)_{15}^{+++}}. \qquad \ldots\ldots (30)$$

Raising equation (29) to its 5th power and substituting into (30) leads to

$$\frac{[Al_6(OH)_{15}^{+++}]}{[Al^{+++}]} = K^5_{Al(OH)_3}\,K_{Al_6(OH)_{15}^{+++}}. \qquad \ldots\ldots (31)$$

Hence, as long as the ion product $[Al^{+++}][OH^-]^3$ remains constant, it is impossible from a determination of the total aluminium content in solution to decide whether this is present as Al^{+++} or as $Al_6OH_{15}^{+++}$. This was also obvious from the results presented by Richburg and Adams (1970), which showed that $[Al^{+++}]\,[OH^-]^3$ was constant irrespective of the value assigned to the constant $K_{Al_6OH_{15}^{+++}}$. A range of variation of $K_{Al_6OH_{15}^{+++}}$ covering 10^{12} did not affect the constancy of $[Al^{+++}]\,[OH^-]^3$ although it of course had an effect on the numerical value - which, however, is comparatively small, since $[Al^{+++}]$ in equation (30) is raised to its 6th power.

The constant in equation (30) was evaluated on the form

$$K = \frac{[Al_6(OH)_{15}^{+++}]\,[H^+]^{15}}{[Al^{+++}]^6} \qquad \text{..... (32)}$$

by Brosset, Biedermann and Sillén (1954) from measurements in 2 M $NaClO_4$ at 40 °C, without application of activity coefficients, to be 1×10^{-47}. Applying the Debye-Hückel equation to the conditions employed by Brosset, Biedermann and Sillén, Richburg and Adams (1970) arrived at a K-value based on activities of 1×10^{-36}. If this value, together with the value 1.9×10^{-33} for the solubility product of aluminium hydroxide tabulated by Latimer (1950), is used for the calculation of the maximum soluble amounts of aluminium as a function of pH, values are obtained so high as to have no relation to practical experience at all. This indicates that the hydrolytic scheme, or at least its K-value, can hardly have been correctly assessed. It might, of course, be argued that the solubility product of aluminium hydroxide is incorrectly determined because attention has not been paid to the hydrolysis taking place. However, Jackson (1963) quotes an experiment revealing little hydrolysis below pH 5 and, furthermore, since the ratio between $[Al^{+++}]$ and $[Al_6OH_{15}^{+++}]$ is independent of pH it has no significance for the present purpose whether the aluminium is actually found as one ion or the other, as long as the solubility product is calculated from results including both ion apecies. It seems reasonable, however, when attempting a calculation of the maximum amount of aluminium that can be dissolved under given conditions in the soil, to take into account the above hydrolysis into $AlOH^{++}$ since most determinations of the solubility product have been made in acid solutions where the concentration of this ion is negligible compared with that of Al^{+++}. According to Jackson (1963) the hydrolysis to $Al(OH)_2^{++}$ is very limited and can be neglected. Since, as stated above, various polymeric ion species may be formed at pH > 5, the calculation should be applied cautiously to this pH range.

According to Sillén and Martell (1964)

$$\frac{[AlOH^{++}]\,[H^+]}{[Al^{+++}]} = 10^{-5.02}. \qquad \ldots\ldots (33)$$

Combination of (33) with (29), substitution of the ionization constant for water (10^{-14}) and the value 1.9×10^{-33} for the solubility product of aluminium hydroxide leads to

$$[Al^{+++}] + [AlOH^{++}] = 10^{9.28}\,[H^+]^3 + 10^{4.26}\,[H^+]^2 \quad \ldots (34)$$

Fig. 13 shows the solubility of aluminium in mg per l as calculated from equation (34). It is clear from Fig. 13 that many horizons of podzols, especially A horizons, are acid enough to facilitate the presence of substantial amounts of aluminium in the soil solution. As will be seen from the analytical results reported in the following chapter many solutions and extracts from A subhorizons of podzols are not saturated with aluminium hydroxide. The pH gradient with depth in most of the podzols investigated here is in the range where precipitation could occur in the B horizon solely as a result of a higher pH than in the A horizon.

From the discussion above it may be concluded that the general statement of many authors, e.g. Stobbe and Wright (1959), that the acidity of podzols is insufficient to account for the amounts of dissolved metals needs some modification, at least in the case of aluminium. This does not, of course, imply that the acidity, possibly combined with reduction, is actually the cause of the mobilization of the elements or that the precipitation in the B horizon is caused by its higher pH. Although such a mechanism cannot be ruled out, it is not the only one possible and evidence presented later points to various other mechanisms as being more probable.

Little evidence is available to substantiate considerations on the possible mobilization of organic matter due to acidity or reduction, and possible immobilization due to decreased acidity or oxidation. It is a

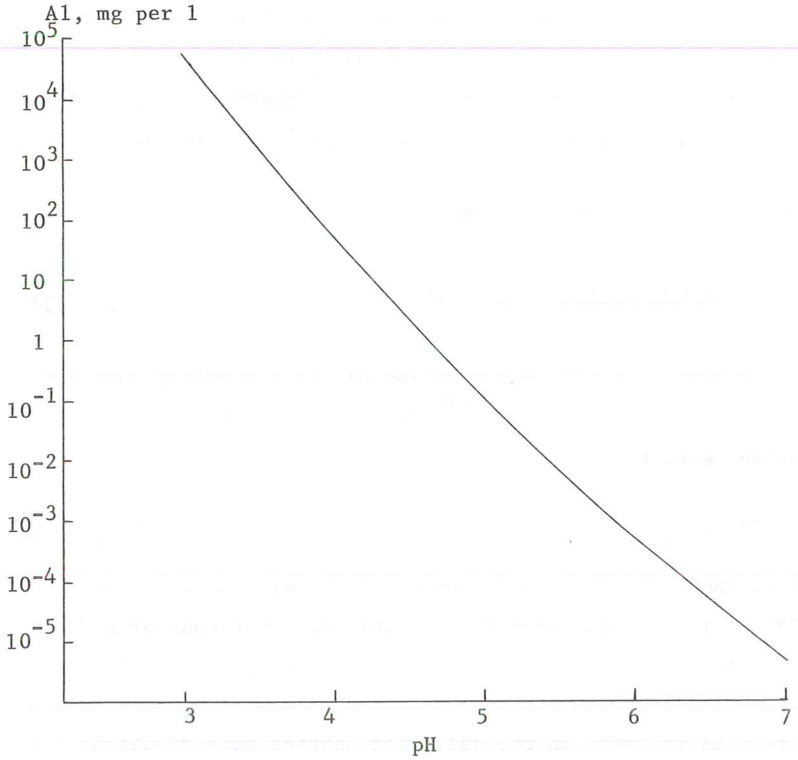

Fig. 13. Theoretical solubility of aluminium as a function of pH.

fact that some organic matter can be extracted, especially from B horizons of podzols, by means of acids. However, as discussed earlier, this seems to be due to a removal of metals from the organic compounds and not directly to an effect of the acid on the organic molecules. Some authors (Iarkov 1954, Kaurichev, Kulakov and Nozdrunova 1958, Kaurichev and Nozdrunova 1964) have shown that anaerobic conditions increase the amount of water-soluble organic matter in various soils. Similar results have been obtained in this investigation (Table 12). If reduction plays a role in translocation of organic matter during podzolization some mechanism must be responsible for the precipitation in the B horizon. Most of the authors quoted above seem to assume that precipitation can occur due to increased redox potential in the B horizon. However, it does not follow from the fact that more soluble organic compounds are formed under anaerobic conditions that these compounds will precipitate under more oxidizing conditions. The evidence available to substantiate considerations of such a mechanism is in fact contradictory. Ponomareva (1964) presented results showing that the solubility of soil organic matter increased with the degree of oxidation. This could be explained in terms of a higher content of oxygen-containing functional groups that will increase the hydrophilic properties of the organic molecules. On the other hand, certain organic compounds such as the so-called polyphenols discussed earlier (which according to many authors are closely related to soil organic matter and, as will be discussed in a following section, can play an important role in podzolization) may precipitate upon oxidation. The higher the pH of the medium, the more susceptible to oxidation these compounds are.

8.3.2 Translocation of the Matter in Colloidal State

Many authors have discussed podzolization mechanisms involving a translocation of the metals and the organic matter in a colloidal state. When considering such mechanisms it should be kept in mind that the difference between colloidal solutions of ferric and aluminium hydroxide and solutions containing the polynuclear hydroxide complexes discussed in the preceding section is one of degree rather than of nature. Colloids of ferric or aluminium hydroxide may remain dispersed due to a positive charge. If this charge is neutralized flocculation and precipation occur. Since the colloids, like the simple ions and their hydroxide complexes, have acid properties the positive charge may be neutralized by an uptake of hydroxyl ions and the colloids will therefore precipitate if the pH of the medium is increased to a value where the electrical charge of the colloids is completely neutralized or reduced to a small value. The pH where this occurs is usually known as the isoelectric point of the colloid.

Mattson and co-workers (Mattson 1933; Mattson and Gustafsson 1934, 1935, 1937a, 1937b; Mattson and Nilsson 1935) would explain podzolization entirely in terms of translocation of such positively charged ferric and aluminium hydroxide sols. According to these authors colloidal solutions of the hydroxides are formed in the A horizon and translocated downwards with the descending water. Due to the higher pH of the B horizon the colloidal hydroxides turn isoelectric and precipitate in this horizon. By a detailed consideration of this mechanism, Mattson and Gustafsson (1937a) described how the precipitation of sesquioxides starts from the bottom of the B horizon and causes it to expand upwards. In the initial stages only sesquioxides would be deposited in the B horizon; later negatively charged humus colloids would be precipitated in the upper part of the B horizon because of the sesquioxides already deposited here, and the precipitation of humic material would then proceed from the upper to the lower parts of the B horizon. Hence, a so-called iron podzol would be formed initially, and this would later turn into a humus podzol.

Mattson and co-workers considered the effect of uptake or release of hydrogen ions on the charge carried by the colloids to be the sole cause of the dissolution and precipitation reactions. A corollary of this theory was that negatively charged humus sols, assumed to be formed in the A horizon, could not be precipitated in the B horizon since the higher pH of this horizon would increase the negative charge of the colloids. As mentioned above this did not entirely exclude the deposition of humus in the B horizon since some deposition could take place because of reactions between the negatively charged humus colloids and the positively charged sesquioxide colloids.

The hypothesis that the B horizon grows upwards from the bottom was originally proposed by Aaltonen (1935), who based it on findings showing that the sesquioxides were deposited at greater depth in young than in old soils. It seems, however, that Aaltonen did not fully appreciate the importance of a number of other factors that may have contributed to the differences among the soils studied. Although Aaltonen (1939) interpreted a new series of findings to confirm his earlier hypothesis, he did not agree with the mechanism of formation outlined by Mattson and co-workers.

A detailed evaluation of Mattson's theories will not be given here, but it seems that the general characteristics of podzols cannot be properly explained by this relatively simple mechanism. The theory does not include a satisfactory answer to the question of how the sesquioxide sols are formed in the A horizon. Colloidal solutions of ferric and aluminium hydroxide can be prepared in the laboratory by partial neutralization of ionic solutions of the metals. However, such a mechanism can hardly be active in soils and it seems somewhat doubtful to assume that iron and aluminium liberated from minerals in the soil enter directly into a dispersed colloid state.

Mattson's theories do not account very well either for the quite definite distribution pattern in podzol profiles of sesquioxides in relation to organic matter (see chapters 9 - 11) and for the ratio of organic matter to sesquioxides in the soil solution (see chapter 9). Deb (1950a) found that ferric hydroxide could be precipitated from colloidal solutions by addition of small amounts of extracted soil organic matter, but precipitation took place only at certain, and rather high, iron-organic matter ratios. As these ratios were much higher than those normally found in the soil solution, Deb considered it more probable that the colloids actually translocated during podzolization were combined iron-organic matter colloids with a net negative charge. He regarded biological decomposition of these as responsible for their deposition in the B horizon.

Ponomareva (1964) also showed that a mutual precipitation could take place when solutions of colloidal ferric or aluminium hydroxide were mixed with solutions containing extracted soil organic matter (fulvic acids). In the case of ferric hydroxide, maximum precipitation took place at an Fe_2O_3:fulvic acid ratio of 16, largely irrespective of the initial concentration of the colloidal solution. A complete precipitation of colloidal aluminium hydroxide took place at a much lower Al_2O_3:fulvic acid ratio, whose actual value depended on the initial concentration of aluminium hydroxide. However, the ratios between the metal content and the organic matter content of the precipitates were of a higher order of magnitude than the ratio usually found in podzol B horizons, see chapter 9.

8.3.3 Translocation of the Matter as Metal-Organic Complexes

Organic compounds capable of forming soluble complexes with iron and aluminium will increase the mobility of these elements in the soil. This effect has been demonstrated for artificial chelating compounds by Lunt, Hemaidan and Wallace (1956), Moawad (1970a, 1970b) and O'Connor, Lindsay and Olsen (1971). Atkinson and Wright (1957) leached columns of a calcareous sand with a solution of EDTA, 2Na. The leaching caused a removal of the $CaCO_3$ and part of the iron from the sand in the upper part of the column. Thorp, Strong and Gamble (1957) found that leaching of columns of B_2 horizon soil from a Miami silt loam with 0.1 n oxalic acid, 2.5 % tannic acid, or water that had passed a 15 cm thick layer of beech leaves, caused the appeareance of so-called A_2 and B horizons in the columns. The Miami silt loam, according to Soil Survey Staff (1951), is a gray-brown podzolic soil. Small amounts of iron were found in the oxalic acid and water leachates, and substantially larger amounts in the tannic acid leachate. The aluminium content of all leachates was too small to be determined. The presence of crystalline clay minerals in the leachates was also demonstrated. Bétrémieux (1954) leached soil columns in the field with glucose solutions and found a considerable translocation of iron. A translocation to a smaller extent was found if the top soil was mixed with alfalfa and the columns leached with water. Experiments by Bloomfield (1952b, 1953a, 1953b, 1954a, 1954b, 1954c, 1956, 1966), DeLong and Schnitzer (1955), Schnitzer and DeLong (1955), Coulson, Davies and Lewis (1960a, 1960b), Kaurichev and Nozdrunova (1961), Himes, Tejeira and Hayes (1963), Muir et al. (1964), Muir, Logan and Bown (1964), King and Bloomfield (1968), Bruckert (1970a, 1970b), Ellis (1971), Dormaar (1971) and Saas and Matteoli (1971) have shown that aqueous extracts of various plant and soil materials contain organic compounds capable of dissolving iron and aluminium and maintaining these elements in solution under conditions where they would otherwise be precipitated as hydroxides. Costa et al. (1968) found that the addition of peat, horse or sheep manure, or fish meal waste to columns of a calcareous brown soil increased the mobility of iron during subsequent leaching of the columns. A similar effect was noted if soil columns without added organic matter were leached with aqueous extracts of the same organic materials.

Even though the dissolving action of various natural organic materials seems well-established little information is available on the actual compounds responsible for the dissolution of the metals and on the actual reactions taking place during the dissolution. Many investigations have been made in order to clear up some of these problems. Bloomfield (1953b) found that extracts of the leaves of Agathis australis had a greater capacity for dissolving iron than extracts of the bark of the same tree. Since the leaves contain more resins and fewer tannins than the bark Bloomfield suggested that the former group of compounds was the more active. This suggestion was also supported by the fact that access of air to the extracts had no reducing effect on its capacity for dissolving iron. If tannins were responsible the capacity would be expected to decline since the tannins would become oxidized. Bloomfield (1956) found that the capacity of various aqueous extracts for dissolving iron was increased by the addition of kaolinite and by passing the extracts through a column consisting of an anion exchange resin, while it was lowered by dialysis and by passage through a cation exchange column. It was concluded from these experiments that the ability to dissolve iron was mainly due to relatively small, negatively charged, molecules.

Coulson, Davies and Lewis (1960a) identified a number of so-called polyphenols in beech litter and soil extracts. It was found that fresh beech leaves from trees growing on soils with a low degree of base saturation had a higher content of polyphenols than leaves originating from trees on soils with a high degree of base saturation. Among the polyphenols identified were epicatechin and D-catechin. Coulson, Davies and Lewis (1960b) found that these compounds could reduce and mobilize substantial amounts of iron from precipitated ferric hydroxide and from diatomaceous earth, aluminium oxide and sand columns previously impregnated with ferric chloride. The reduction of iron took place even under aerobic conditions. In the sand columns some mobilization of aluminium was noted but blank tests revealed that this was due to the acetate buffer employed in the experiments.

Himes, Tejeira and Hayes (1963) found that aqueous extracts of oak leaves contained compounds capable of forming negatively charged compounds with ferric iron. Addition of ferric chloride to the extract produced a blue colour which was attributed to phenolic compounds in the extract. Bloomfield (1965, 1970) argued strongly that polyphenols originating from undecomposed plant materials were the active agents in the dissolution of iron compounds. In earlier experiments Bloomfield (1952, 1953a, 1953b, 1954a, 1954b, 1954c, 1956, 1966) showed that the dissolved iron was present partly as ferrous iron, even if the experiments were made under aerobic conditions. Some of these experiments also showed that the plant extracts could dissolve considerable amounts of aluminium. King and Bloomfield (1968) found no expressed correlation between the polyphenol content and the capacity for dissolving the ferric hydroxide of aqueous extracts of differently treated oak, beech and larch leaves.

Dormaar (1971) leached columns of soil from an Ah horizon of a chernozem with distilled water and with aqueous extracts of fresh leaves of two poplar species. The two extracts had approximately the same content of polyphenols but differed with respect to total acidity. An evaluation of Dormaar's results shows that this difference was due to a difference in calcium and magnesium content, i.e. to a difference in the degree of neutralization rather than in the total content of organic acids. As would be expected both extracts were more effective in leaching iron and aluminium from the soil than distilled water, but only small differences were found between the two extracts. Davies (1971) was also of the opinion that polyphenols play a major role in processes involving mobilization of iron, but attention has also been paid to many other compounds. Schnitzer and DeLong (1955) concluded that the principal component of various leaf extracts investigated by these authors was an acid polysaccharide or a mixture of such compounds. Experiments involving ultraviolet spectroscopy, electrodialysis, and liquid-liquid extraction failed to reveal evidence of complex formation. Hence, the authors were inclined to regard the dissolving action on iron as being due to a peptization effect.

Kaurichev and Nozdrunova (1960, 1961) and Kaurichev, Ivanova and Nozdrunova (1963) attributed the major iron-dissolving effect of aqueous soil extracts to simple organic acids, such as formic, oxalic, citric, succinic, malic, lactic and various amino acids. Muir et al. (1964) fractionated an aqueous extract of pine needles on cation and anion exchange resins. The fraction retained on the cation exchange resin consisted mainly of amino acids while that retained on the anion exchange resin contained mainly simple organic acids, such as malic and citric acid, and some organic acids with higher molecular weight. Muir, Logan and Bown (1964) found that the fraction consisting of simple organic acids, as well as a synthetic mixture of similar acids, was superior to the amino acid fraction in dissolving iron.

Jacquin and Bruckert (1965) identified a number of simple aliphatic and phenolic acids from oak and pine litter. The oak litter was from a locality with a brown lessivé-soil and mull humus while the pine litter originated from a podzol with mor humus. The oak litter contained larger amounts of acids than the pine litter but at the same time the acids from the oak litter were decomposed more rapidly, and the acid content found in the soils under the litter was larger on the pine locality. Bruckert (1966) found comparable amounts of simple organic acids in the litter on top of a lessivé profile and two podzol profiles. However, the acid content decreased more rapidly with depth in the lessivé profile than in the podzol profiles. This was taken to indicate that a rapid decomposition of the acids in the lessivé profile prevented movement of organic iron and aluminium complexes in this profile, while such a movement would be possible in the podzols.

Bruckert (1970a) found that an aqueous extract of a mor-layer contained simple aliphatic acids as well as polymeric unidentified compounds. Among the simple aliphatic acids, citric, malic, oxalic,malonic, succinic and lactic acids were identified and determined quantitatively. Although these acids apparently made up only a relatively small fraction of the organic matter of the extract, they were reported to account for about 75 % of the capacity of the extract for complexing iron. Unfortunately, the description given by Bruckert contains very limited information on the experimental technique employed and on the actual results of the measurements. It is not therefore possible to evaluate the justification of this conclusion. The complexation was investigated in strongly acid solution by means of Vosburgh and Cooper's (1941) technique described in chapter 7. It was also found that the simple acids, as compared with the polymeric compounds, could extract three times as much iron from a sample of a podzol B horizon. This was taken to confirm that about 75 % of the complexing power of the extract was due to the simple acids. However, although it is not quite clear from the description, it seems that the amount of iron complexed in the first experiment was about 5 times larger than that extracted from the B horizon sample, and under these circumstances there seems to be no obvious reason why the ratios should be similar in the two experiments. No attention was paid to the aluminium which must undoubtedly have been extracted from the B horizon sample together with the iron. Furthermore, while the optical density measured at 325 mμ of the solution containing the simple acids increased upon contact with the B horizon sample, that of the solution containing the polymeric compounds decreased to about one third of its original value. This was explained as being due to precipitation or adsorption of part of the organic matter caused by the sesquioxides in the B horizon sample. While this explanation seems probable in the light of various experiments described later, it is hard to understand why the complexing capacity of this fraction of the organic matter is disregarded.

Unfortunately these conclusions, which were based on only a few introductory experiments of a comprehensive investigation, led Bruckert to disregard the effect of polymeric compounds and concentrate the remaining investigation on the simple organic acids. These studies revealed results similar to those noted in many of the investigations above, namely that the amounts of simple aliphatic acids that could be extracted with water were higher in materials originating from trees and grasses normally not found on podzols than in materials originating from plants such as pine and heather typically inhabiting podzols. The author tried to explain this paradox as being due to a rapid breakdown, a smaller content of total organic matter in and on the soil, and a different seasonal pattern in the non-podzolized soils as compared with the podzols.

The evidence produced is not convincing, however. Calculations relating the amount of acid to the area show acid contents so small that they can hardly be solely responsible for the podzolization. As shown by Nykvist (1963, 1964) significant amounts of most of the acids (particularly citric) discussed by Bruckert (1970a) may be extracted from the litter of oak, beech, ash, alder, birch, spruce and pine. However, these acids are highly unstable in the presence of oxygen and organisms originating from the litter. In Nykvist's experiments virtually all of the acids disappeared completely from all extracts during 4 days' aerobic incubation. Under anaerobic conditions citric acid proved to be relatively stable while the content of lactic and succinic acid increased substantially. These acids were present in trace amounts only in the fresh extracts. Relying on these results Nykvist (1964) concluded that if the litter was moist, but not submerged, the water-soluble simple acids would decompose inside the litter and therefore be of minor importance for the mobilization of iron and other elements in the soil.

Ellis (1971) studied the effect of pH on the capability of various Eucalyptus litter extracts for dissolving iron form a soil sample containing goethite and little organic matter, and from hydrous and anhydrous ferric oxide. An increase in pH from 4 to 8 caused a very large increase in the amount of iron dissolved from the soil sample, a much smaller increase in the amount dissolved from the anhydrous ferric oxide, and a large decrease in the amount dissolved from the hydrous ferric oxide. He suggested that this could be due to polyphenols being more active in the dissolution of hydrous ferric oxide, and simple organic acids more active in the dissolution of iron from soil and anhydrous oxides. Since the polyphenols are unstable at higher pH values a smaller amount of hydrous iron oxides would be dissolved. Such a statement hardly concurs with the fundamental laws governing chemical processes. The reason for Ellis's results could be that the freshly prepared ferric hydroxide has become dispersed to form a colloidal solution at the lower pH values. The amounts reported to be dissolved were so large that they can hardly be complexed by the organic compounds in the extracts. In an experiment carried out in connection with the present study (see chapter 9) it was found that freshly prepared ferric hydroxide, upon mixing with water and soil samples from a podzol profile, remained partly dispersed for several months. The dispersion occurred irrepective of the horizon from which the soil sample originated. The suspension had a marked red colour and this could not be removed by centrifugation. It is remarkable that this effect has never been noted in any of the experiments discussed above, although many of them have employed freshly prepared ferric hydroxide and have been carried out at pH values similar to those of the soil samples.

Most of the studies quoted above have been concerned with the dissolving action of various organic substances on iron compounds. The conclusion most often drawn, explicitly or implicitly, from the experimental results is that the compounds having the largest complexing capacity are also those most important for podzolization. There is little justification for drawing such a conclusion, however. As mentioned at the beginning of this chapter, any proposed podzolization mechanism must account for the mobilization and immobilization of all the compounds translocated during podzolization, i.e. iron, aluminium and organic matter. In many of the studies quoted it has been shown that the dissolution and complexation is connected with a reduction of iron, and major significance is often attributed to this reduction. If reduction played a universal role in podzolization it would be expected that the pattern of iron translocation would be clearly different from that of aluminium translocation and it is difficult to find evidence of such different patterns in an overall evaluation of podzols. A study of the analytical results given in Table 7 gives no evidence for such different translocation patterns. This does not mean that soils cannot be found where the pattern of the iron distribution is different from that of the aluminium distribution. Several factors may cause such differences, but a universal effect that can be attributed to reduction of iron is not apparent. In some experiments it has been shown that the organic compounds can dissolve aluminium but this problem has received far less attention than the dissolution of iron.

The deposition and precipitation reactions have also received much less attention than the dissolution reactions. If the most important group of organic compounds is simple aliphatic acids, as suggested by some authors, it is indeed difficult to imagine a mechanism by which these should be accumulated in a specific soil horizon. The reaction most often proposed to explain this precipitation is a biological decomposition of the organic molecules. It is well known that certain bacteria can precipitate ferric hydroxide from ferric citrate solutions (Harder 1919, Mudge 1927, Alexander 1961). Crawford (1956) found that the B horizons of some podzols contained a large number of such bacteria. On the other hand McKenzie, Whiteside and Erickson (1960) were unable to confirm this; in fact, they found that the number of citrate oxidizing bacteria was substantially lower in B horizons than in A horizons of the same podzols. They therefore concluded that citrate complexes of iron would be decomposed before reaching the B horizon.

The statement that a high concentration of citrate oxidizing bacteria, or bacteria capable of decomposing other organic complexes, should be the cause of the deposition in the B horizon seems to be in contradiction to the general rules governing the distribution of organisms in soils and in other media as well. As stated by Alexander (1961) the capacity to grow in a given habitat is determined by an organism's ability to utilize the nutrients in its surroundings. Hence, the presence of an organism in a given locality depends upon the availability of the nutrients required by the organism. Consideration of a mechanism involving a downward movement of organic metal complexes does not immediately lead to the conclusion that this should favour an abundance of microorganisms capable of utilizing such compounds in the B horizon. Most authors are of the opinion that the acids responsible for complexing iron originate from the litter, i.e. from the topmost part of the A horizon. According to this assumption the concentration of such acids cannot be higher in the B horizon than in the upper part of the soil profile, and even if it is assumed that some acids may originate from the entire layer containing organic matter little increase would be expected with depth from the boundary between the A_1 and A_2 horizons. In fact Bruckert (1970a) showed that the concentration of acids was at a maximum in the litter and decreased rapidly with depth. Any organism preferring such compounds would therefore find more favourable conditions in the upper part of the profile than in the B horizon. If the organisms, nevertheless, are particularly abundant in the B horizon it must be because some other conditions favour their existence there. Since the growth of organisms depends on a number of parameters besides the availability of suitable organic nutrients, such as mineral nutrients, reaction, temperature and humidity, it might be possible to explain an abundance of certain bacteria in the B horizon in terms of one or more of these parameters, but in this case the ultimate cause would be the parameter in question, and not the presence of the bacteria per se. Until such a causal relationship has been established it seems difficult to accept that the ultimate cause of the deposition in the B horizon should be the presence of a particular bacteria flora.

Bruckert (1970b) studied the behaviour of four simple acids (citric, oxalic, vanillic and p-hydroxy benzoic) in contact with soil from the A_1 and B_h horizon of a podzol and from the A_1 horizon of a 'sol brun lessivé'. In some of the studies the acids contained carboxyl groups tagged with ^{14}C. By measuring the amount of carbon dioxide evolved in these experiments it was possible to obtain a measure of the decomposition of the compounds and, furthermore, the tagging of the carboxyl groups facilitated considerations concerning the decomposition pattern of the acids and the fractions of the acids incorporated into various humus separates.

The results led Bruckert to conclude that the acids in the B horizons of podzols were made insoluble by a chemical process and further incorporated into humus compounds by biological reactions. Although it is not quite clear from the author's description it seems that the chemical reaction proposed is a decarboxylation of the acids. This proposal was based mainly on the fact that the concentration of radioactive carbon was higher in the carbon dioxide evolved than in the acids originally applied. The process was assumed to be mainly chemical because additional experiments, not involving measurement of the carbon dioxide evolved, showed that the amounts of acids retained by the soil were only negligibly larger at 20 °C than at 0 °C. The decarboxylation of an organic acid, originally being part of an organic iron complex, would lead to the precipitation of ferric hydroxide. Relying on the results of Bloomfield and others (see below), it was further suggested that this ferric hydroxide would adsorb other organic compounds, mainly compounds with a high molecular weight, and thereby cause their precipitation. As a third step in the reaction sequence it was proposed that these organic compounds could adsorb simple acids such as vanillic and citric acids, causing precipitation of these compounds in addition to that occurring by decarboxylation.

Without commenting in detail on the justification for this rather sophisticated precipitation mechanism it can be added that no information is given on the cause of the proposed decarboxylation. There also remains the question of why it only takes place in the B horizon, and the experimental results are far from being adequate evidence for all the hypothetical steps involved in the precipitation sequence.

As discussed in chapter 5, the polyphenols constitute a rather complex group of compounds and it is, therefore, difficult to consider in general their chemical behaviour in soils. Although Bloomfield (1965, 1970) stated that he had been unable to detect any mobilizing action on iron by humified material it seems questionable to what extent it is possible on a chemical basis to make a distinction between polyphenols and the so-called humus compounds. The chemical composition of the humus compounds is, to the extent it is known, in many respects similar to that of polyphenols, see chapter 5. Bruckert (1970a) also indicated the similarity between polyphenols and certain humus constituents. Davies (1971) outlined two theories for translocation of iron during podzolization, one involving fulvic acids and the other polyphenols. The two theories were,in fact, very similar in principle, and it was made clear that they should be considered complementary rather than alternative. Furthermore, the actual constituents of many soil and plant extracts which have been shown to react with iron and aluminium are often unknown and, in some respects, the reactions are similar irrespective of the compounds assumed to be present in the extract. There seems, therefore, to be little reason for separating the reactions of the two types of compounds, and in the following they will be treated together.

According to Davies (1971) it has been observed that if plant extracts are percolated slowly through a soil column the organic compounds are removed from the extract, which does not happen if the percolation takes place rapidly. This indicates that the deposition of the organic matter requires a certain time. Stobbe and Wright (1959) mentioned that it has been observed under field conditions that true or colloidal humus solutions filter rapidly through the A_2 horizon and slowly through the B horizon where an adsorption of the humus compounds takes place. However, no information is given on the adsorption mechanism.

Aristovskaya (1963) assigned major importance to microorganisms capable of decomposing humus-iron complexes for the accumulation of iron in podzol B horizons and in other natural deposits enriched in iron. She considered two groups of microorganisms to be active in the decomposition: the first group consisted of heterotrophic organisms utilizing the organic part of the complexes in their nutrition, while the second consisted of autotrophic and mixotrophic iron oxidizing species. The latter was considered more important but the mechanism by which these organisms cause the iron accumulation is not clear from Aristovskaya's description, and the evidence presented in favour of such a mechanism is not conclusive.

Bloomfield (1953a) showed that neither the organic matter of an extract of Scots pine needles nor the iron previously dissolved by the extract could be precipitated by a small change in pH or redox potential. Bloomfield (1955) found that addition of ferric hydroxide to plant extracts caused a decline in the content of dissolved organic matter and iron in the extract. Bloomfield explained this as being due to adsorption of the organic matter complexes on the surface of ferric hydroxide, and suggested that a similar adsorption could cause precipitation in the B horizon of podzols. As mentioned in chapter 7, Ashan (1907), Martin and Reeve (1960), Martin (1960), Wright and Schnitzer (1963), Ponomareva (1964) and Schnitzer and Skinner (1964) have shown that the addition of ferric or aluminium salts to solutions containing dispersed organic matter may cause a mutual precipitation of the metals and the organic matter. It seems likely that Bloomfield's results metioned above may be explained by an analogous mechanism. If this is the case the cause of precipitation of the organic compounds would not be a direct adsorption by the ferric hydroxide, but an initial dissolution of ferric iron followed by a precipitation of iron-organic compounds. With the exception of Ashan's studies, all the investigations above employed organic matter extracted from podzol B horizons. A complete precipitation of metal and organic matter was obtained only at a certain ratio between these compounds and within a certain pH range. It was further found that more iron than aluminium, when the comparison was made on a molar scale, was required to cause a complete precipitation of a fixed amount of organic matter.

A mechanism involving a precipitation of the organic matter in the B horizon caused by iron and aluminium initially taken up by the organic compounds would indeed tie in very well with a number of known properties of podzols. The availability of iron and aluminium increases with depth in podzols and a downward movement of some organic compounds capable of complexing these elements would necessarily lead to the uptake of larger and larger amounts of the metals. As discussed in chapter 5, results of experiments on the extraction of organic matter from podzol B horizons would be consistent with the assumption that the organic matter is maintained insoluble in these horizons by iron and aluminium compounds. Nevertheless, such a mechanism seems to have received only limited support in the literature. Ponomareva (1964) and Schnitzer (1969) seem to be those who assign most significance to it. Duchaufour (1964, 1965, 1967) also seems to advocate such a mechanism and he assumes aluminium to be more important than iron. This looks reasonable in the light of the experiments quoted above. On the other hand it is not quite clear from Duchaufour's work whether he regards the uptake of aluminium (and/or iron) as the initial cause of the precipitation or assumes some polymerization of the organic compounds to be a necessary prerequisite for precipitation. Davies (1971) mentions vaguely that one cause of precipitation of organic compounds in the B horizon may be uptake of iron.

To what extent such a mechanism should be considered a true chemical precipitation or a flocculation of organic colloids will depend on the nature of the organic compounds. It is therefore impossible to give a complete description of the process without a thorough knowledge of the organic compounds. However, the experiments quoted above reveal no major differences in this respect between organic compounds originating from fresh or partly decomposed plant material and organic compounds originating from so-called true humus material. In any case it seems reasonable to assume that the dispersed compounds consist of rather large molecules. Their solubility in water is probably due, at least partly, to a net negative charge. With the uptake of positive ions, especially small ones with a large positive charge such as aluminium ions, they change into neutral compounds with a decreased solubility in water.

Without at this stage attempting to rule out any of the possible podzolization mechanisms discussed in this chapter, it seems that the one involving dissolution of iron and aluminium by organic complexing molecules and their subsequent precipitation due to overloading of the complexes with the metals, expecially aluminium, would be in accordance with many of the known properties of podzols and give the most satisfactory answers to the questions asked at the beginning of this chapter.

CHAPTER 9

WATER-SOLUBLE COMPOUNDS IN PODZOLS

9.1 Introductory Remarks

The substances dissolved in water leaching through podzols have been studied in lysimeter experiments by Ponomareva, Rozhnova and Sotnikova (1968) and Sotnikova (1970) who found that the content of dissolved organic matter decreased with depth in the profile while the content of iron and aluminium increased in the B horizon. Schnitzer and Desjardins (1969) studied the components dissolved by water leaching through the A horizon of a humus podzol. The water contained approx. 60 mg organic matter and 17 mg ash constituents per l. The latter were mainly CaO, SiO_2 and Al_2O_3 while only minute amounts of iron were found. In the lysimetric liquids studied by Dyakonova (1971) most of the constituents were found as precipitates containing organic matter, iron, aluminium and silicon but little exact data on the composition of solutions and precipitates is given. Crawford (1956, 1965) incubated samples from podzol A and B horizons with water under aerobic and anaerobic conditions. In all cases he found a considerable dissolution of organic matter, iron and aluminium. Anaerobic conditions caused a moderate increase in the amount of all three constituents dissolved from the A horizon. In the B horizon a 2-5 fold increase was noted for organic matter and aluminium, but for iron there was a 10-30 fold increase. Crawford (1956) found an increase with time in the amounts of all constituents dissolved except for the anaerobic incubation of B horizon material, where a decrease with time was noted.

In this investigation the actual amounts of iron, aluminium and organic matter that can be dissolved in water have been studied in laboratory experiments where initially air-dried soil samples from various horizons of podzols were subjected to prolonged treatment with water. In another approach small samples of natural soil solution, collected by a special technique at frequent intervals from each horizon of two podzol profiles, were analyzed. Since in both cases, the concentrations of all three components were rather low special analytical techniques had to be employed. In order not to affect the contents of any of the compounds to be determined, it was considered mandatory not to attempt any means of increasing the concentration of the solutions. Apart from these considerations most samples available, especially those of the natural soil solutions, were too small to allow any such operation. In the following sections the analytical methods, the technique employed in the two kinds of experiments, and their results will be described. To distinguish the extracts prepared in the laboratory from the samples of the natural soil solutions the former are called 'soil extracts' and the latter 'soil solutions'.

9.2 Analytical Methods

pH-values of the soil extracts were measured with a Radiometer pH-meter equipped with glass and calomel electrodes. For the soil solutions a portable battery operated Radiometer pH-meter with combined glass and calomel electrodes was used.

Organic matter determinations on soil extracts were initially carried out by means of a method based on the amount of oxygen consumed by treatment of the extracts with a sulphuric acid-potassium dichromate mixture. Later an apparatus became available which facilitated a determination of the amount of carbon dioxide produced during combustion of the organic matter. The latter method was used for all soil solutions.

The sulphuric acid-potassium dichromate method was a modification of the method used for determination of glycerol by Reese and Williams (1954). The procedure adopted after initial trials was as follows: 5 ml of standard solution or soil extract (in case of a too high organic matter content in the latter, 5 ml of an appropriate dilution of this) was mixed with 5 ml of a solution containing 800 mg $K_2Cr_2O_7$ per 1 in a 100 ml volumetric flask. 11 ml conc. H_2SO_4 (analytical grade) was added and the flask was placed on a boiling water bath for 5 min. After cooling by means of externally applied water the content of the flask was made to volume with water; 5 ml of the solution was transferred to another 100 ml volumetric flask; approx. 90 ml of water was added; after mixing, 1 ml of a saturated alcoholic (96 % alcohol) solution of 1-5 diphenylcarbazide was added; the content of the flask was made to volume with water, mixed; and finally the absorbance was measured at 540 mμ on a Beckman model B spectrophotometer. When reacting with dichromate, 1-5 diphenylcarbazide gives a purple colour. The colour developed fairly rapidly, although not immediately, but it was not stable for longer periods and all measurements were made within 10 min. after the addition of 1-5 diphenylcarbazide.

It is, of course, problematic to use a method as the one described since it is impossible to prepare standard solutions from compounds identical to those in the soil extracts. The standards employed here were solutions containing 0-100 mg sucrose per l. There were two main reasons for selecting sucrose as a standard compound: 1. It was found that the amount of dichromate consumed by sucrose solutions was close to the amount calculated theoretically assuming a complete oxidation of the sucrose to carbon dioxide. Hence, a complete oxidation of the sucrose seems to be obtained. 2. The formal oxidation number of the carbon in sucrose is zero. Although the oxidation number of carbon in soil organic matter is not known exactly, and although it is probably subject to variations as described in chapter 4 and 5, it is generally assumed to be close to zero.

If this assumption is accepted and if it is further assumed that the dichromate treatment causes a complete oxidation of the organic matter of the soil extracts, it follows that the carbon contents of these may be read directly from a plot of absorbance value versus carbon content of the sucrose solutions. As shown below these assumptions are hardly justified, but it was found that the results were largely independant of the amounts of soil extract used, within the limits set by the amount of potassium dichromate present, and of the time of heating the solutions on the water bath. This, at least, suggests that there is some fairly constant relation between the total carbon content of the soil extracts and their reducing power as measured by the procedure described above. It was also found that the calibration curve based on the sucrose solutions was essentially a straight line. The slope was negative, of course, since the absorbance values are proportional to the excess dichromate.

It would have been possible to select numerous other organic compounds fulfilling the requirements described above. However, they will not be fulfilled by all organic compounds. This is obvious as far as the oxidation number of the carbon is concerned. Organic compounds also differ in their ability to become oxidized by potassium dichromate. Some compounds may remain unaffected or be subject only to incomplete oxidation. Williams and Reese (1950) used virtually the same method for determination of ethyl alcohol but this compound was oxidized only to acetaldehyde. Methods for determination of total soil organic matter based on similar principles usually require some correction to compensate for incomplete oxidation and/or an oxidation number of the carbon greater than zero (Bondorff 1946, Allison 1965).

Inorganic reducing compounds also present a potential source of error in this type of organic matter determination. The most probable compound under the conditions of the experiments described here would be ferrous iron. However, the results of iron determinations in the soil extracts given in Tables 12-18 indicate that even if the total iron content was present as ferrous iron this could cause only an insignificant error in the organic matter determinations. In this connection it could be mentioned that it is important that the sulphuric acid used in the procedure is free or almost free of reducing impurities. This is not the case of the 'pure' grade sulphuric acid commonly used as laboratory reagent. In preliminary trials it was found that the amounts of this sulphuric acid used in the analyses had a reducing power exceeding that of the soil extracts and standards several times. In the procedure outlined above errors due to reducing power of the sulphuric acid is eliminated since all standards, including a blind, and soil extracts are treated with equal amounts of sulphuric acid. However, this will be true only as long as the reducing power of the sulphuric acid is much smaller than the reducing power of the soil extracts and standards.

The method used for organic matter determinations in the later stages of the experiments involved an apparatus described by Cropper, Heinekey and Westwell (1967a, 1967b). The principle of this method is a combustion of the organic matter to carbon dioxide followed by a reduction of this compound to methane which finally is registered by means of a flame-ionization detector. The components in which these reactions take place are all connected in series. The first component is a combustion unit consisting of a silica tube filled with cupric oxide and placed vertically in an electrical tube furnace maintained at 850-900 °C. The solution with the organic matter is injected through a silicone rubber plug into the cupric oxide while a flow of nitrogen is maintained throughout the apparatus. The carbon dioxide produced when the cupric oxide oxidizes the organic matter is carried by the nitrogen stream through a heater, consisting of a glass tube filled with glass beads and maintained at 150 °C, to a reduction unit. The reduction unit is a glass tube filled with, a firebrick powder impregnated with a nickel catalyst prepared by reduction of nickel nitrate. The reduction unit is maintained at 300-350 °C during the anlytical runs. Prior to the reduction unit a stream of hydrogen is lead into the apparatus to facilitate the reduction of the carbon dioxide to methane. The methane produced is carried by the nitrogen-hydrogen stream through a long column of silicagel for removal of water, formed by evaporation of the sample and by the reduction of carbon dioxide to methane, to a flame-ionization detector. In the set-up used in the present investigation the silicagel column was connected to the inlet of the flame-ionization detector of a Perkin-Elmer model F 11 gas chromatograph equipped with a recorder. In this way the methane gives rise to a peak whose area is proportional to the amount of methane and, provided that complete combustion and reduction take place, to the amount of carbon in the sample injected. The injections and the reactions taking place in the apparatus cause some pressure changes which affect the flame-ionization detector. However, the long silicagel column serves the additional purpose of delaying the methane peak so that this can be separated from the small peaks resulting from the pressure changes.

The method has some inherent limitations. In order to secure a practically instantaneous combustion, which is a prerequisite for a well-defined, measurable peak, the amount of sample injected has to be kept small. The amount actually injected in all analyses was 10 µl. Free carbon dioxide, or carbonates destroyed by the temperature of the combustion unit, will be registered as organic matter. This can partly be corrected for by injection of a similar sample into the heater in which case no combustion takes place and volatile organic compounds other than methane are absorbed by the silicagel. All samples were checked for carbon dioxide by this operation but in all cases the amount of carbon dioxide registered was smaller than the experimental error on the organic matter determinations and no correction was attempted.

The apparatus required very careful adjustment of the gas flows and of the temperature of the various units heated. The gas flows were adjusted by means of flow controllers and continously read on flow meters. All the units heated were connected to low voltage variable electrical power sources. The temperature of the combustion unit was checked continously during the operation of the equipment by means of a thermoelement incorporated in the furnace. The heater and the reduction unit were prepared from constantan wire wound on the glass tubes and held in place by a hardened cement prepared by the mixing of a solution of sodium silicate with talcum. The temperature of these units could not be checked during the analytical runs but the voltage needed in order to maintain the required temperature was determined prior to the apparatus being assembled. Although utmost care was taken in the adjustments of the apparatus some variation could not be avoided. The effect of this variation was reduced as much as possible by many replications and by standards run intermittently. It was found that sucrose also was a suitable standard for this analysis. The shape of the peaks, which probably mainly depends on the rate of combustion, was similar for sucrose, soil extracts and soil solutions. Some other compounds tested gave higher and narrower, or lower and wider, peaks than the soil extracts and solutions. Although the area under the peak should be independent of the shape it was considered of some importance, also for the measurements of this area, to maintain the same ratio between height and width. The area was measured by means of a planimeter.

In order to compare the results of the two methods the organic matter content of five soil extracts was determined by both methods. The results appear in Table 11. Except for soil extract No. 1 all of the extracts are prepared similarly from the same A_0-A_1 horizon. It will be seen that the dry combustion method gives somewhat higher values. This may be due to an incomplete oxidation of the organic matter by the wet combustion or to an oxidation number of the carbon higher than zero. It seems reasonable to assign the major importance to the latter since it is demonstrated in chapter 4 and 5 that the organic matter of the B horizon is in a relatively high state of oxidation. The extracts originated admittedly from the A horizon but since the analyses were made on the water soluble fraction it does not seem unreasonable to assume that this is similar to the organic matter of the B horizon.

The wet combustion method shows, as would be expected, a greater degree of reproducibility than the dry combustion method. Nevertheless, the latter was preferred and used exclusively from the time the apparatus became available since its theoretical foundation seems superior to that of the other method. The relative experimental error for samples with a large or medium carbon content may probably amount to 10-15 % by the dry combustion method as compared with about 5 % for the wet combustion method.

Table 11. Comparison of C Determinations by Wet and Dry Combustion

Soil extract No.	Wet combustion C, mg per l(C_W)	Dry combustion C, mg per l(C_D)	$\frac{C_D}{C_W}$
1	101	136	1.35
2	105	154	1.47
3	107	149	1.39
4	107	161	1.50
5	112	152	1.36
Mean			1.41

All the conclusions drawn from the results are based on large differences exceeding by far the experimental error. Usually no conclusions have been drawn from differences between samples whose carbon content have been determined by the two different methods. Nevertheless, it was found appropriate to use the same scale for all determinations. This was done by multiplying all carbon contents determined by wet combustion with the factor 1.41 calculated from the values in Table 11.

Iron determinations in the soil extracts and soil solutions were made by atomic absorption specrophotometry. In practically all samples the iron content was well below the optimum range for determination by this method. However, by applying the electronic scale-expansion device of the Perkin-Elmer model 303 atomic absorption spectrophotometer used, it was possible to detect iron contents as small as 0.01 mg per l and obtain fairly reliable estimates of the actual iron contents of the soil extracts and solutions. The results were read out on a recorder connected to the atomic absorption spectrophotometer. The results obtained by this procedure are considered more accurate than the results obtained by the organic matter determinations described above and the aluminium determinations described below. Some results may have been affected by the organic matter in the soil extracts and solutions, but it was not found feasible to attempt any correction for this interference, and it is assumed that the effects are rather small. The standard solutions were prepared as described in chapter 6 and their iron content was in the same range as that of the soil extracts and solutions.

Aluminium determinations caused great problems due to the small content of this metal in the soil extracts and solutions, the limited amount of extracts and especially of solutions available, and the presence of interfering inorganic and organic compounds. The method finally adopted was a modification of the method described by Øien and Khera (1968) for determination of aluminium in potassium chloride extracts of soils. Prior to the analysis it was necessary to remove organic matter. The analytical procedure was as follows: The amount of soil extract or solution to be used in the analysis was transferred to a small beaker, 3 ml 30 % hydrogen peroxide was added and the beaker was placed on a boiling water bath. After evaporation to dryness to ensure complete removal of excess hydrogen peroxide 15 ml 0.04 n HCl was added and the evaporation was continued until the volume of the liquid was about 5 ml. Trials indicated that this treatment caused a complete dissolution of the aluminium in the evaporation residue. The solution was transferred to a separating funnel, the beaker rinsed with a total of approx. 13 ml of water which was also transferred to the separating funnel. Then 5 ml acetate buffer (pH 6.3), 2 ml 1 % sodium diethyldithiocarbamate and 10 ml trichloroethylene were added, and the mixture shaken for 2 min. By this treatment metals such as Fe, Co, Cu, Mn and Zn will be transferred to the trichloroethylene phase as diethyldithiocarbamate complexes. After shaking the funnel was left for 2 min. for the phases to separate and the trichloroethylene phase was discarded. 10 ml 2 % 8-hydroxyquinoline in toluene was added and the mixture shaken for 3 min. By this treatment aluminium is transferred to the toluene phase as the yellow 8-hydroxyquinoline complex. After the phases had separated the aqueous phase was discarded and the toluene phase was transferred to a 15 ml centrifuge tube, the tube was covered with a plastic lid and centrifuged for 2 min. to remove traces of water. The absorbance of the toluene extract was then measured at 385 mμ on a Beckman model B spectrophotometer. Aliquots of a previously analyzed stock solution of aluminium chloride were used as standards. The standards, including blinds, were subjected to exactly the same procedure, including the hydrogen peroxide treatment on the water bath and the two extractions, as the soil extracts and solutions. It was found essential to carry out the shaking at a temperature not exceeding that at which the centrifugation and the spectrophotometric measurement were made. If a temperature drop took place between these operations the toluene extract became turbid, probably due to separation of water dissolved in the toluene phase.

The amount of aluminium in each sample was 0-30 μg. It is of course rather hazardeous to subject a sample of this size to the treatment described since minute impurities may upset the results entirely. Especially the treatment on the water bath seems critical, but it was found that this treatment had no appreciable effect on the absorbance of the standards except for a small reproducible blank value, possibly caused by aluminium impurities in the reagents used. However, it should be noted that some analyses may have been affected by impurities. This may especially have been the case for soil solutions since these could normally not be repeated due to the available amounts of solution being insufficient. For the same reason these analyses often had to be made on very small amounts of solution causing a correspondingly small amount of aluminium in the sample and risk of large analytical errors. However, there seemed to be no alternative if the determinations were to be made, and although some of the results may be seriously affected by analytical errors useful information may be derived from these.

9.3 Experimental Technique

Soil extracts were obtained from 1:10 soil-water mixtures. 15 (25) g soil was transferred to a 300 ml erlenmeyer flask and 150 (250) ml water was added. The flask was closed with a rubber stopper in which two glass tubes were inserted. One of these was dipping into the water and through this atmospheric air was continously bubbled through the liquid to ensure aerobic conditions and to cause stirring of the mixture. In the actual set-up a number of erlenmeyer flasks containing different soil samples were connected in series to the same air pump. To avoid evaporation during the extractions which lasted 30-70 days the air was saturated with water vapor by passing two gas washing bottles, containing distilled water, prior to the erlenmeyer flasks. No significant evaporation loss was noted in any experiment. All extractions were made at room temperature.

In an initial experiment samples from all horizons of a podzol profile (Skarrild) were subjected to the extraction, and at various time intervals the pH of the suspensions was measured and samples of the supernatant was withdrawn, centrifuged and analyzed for organic matter, iron and aluminium. At the end of the experiment the soil was removed from the liquid by centrifugation, and the liquid was used for various experiments described in the following chapters.

Later samples from the A_0 and A_1 horizons of all the profiles described in chapter 3 were subjected to a simplified extraction procedure involving determination of pH before and after the extraction, and determination of dissolved organic matter, iron and aluminium at the end of the extraction only.

The effects of a number of factors on the amount of dissolved organic matter, iron and aluminium were studied in variants of the experiment. For all these variants, soil samples from the Skarrild profile were used.

The effect of anaerobic conditions was studied in an experiment where nitrogen was bubbled through the suspensions instead of atmospheric air. The nitrogen used was from a commercially available pressure tank. To remove possible traces of oxygen the nitrogen was passed through a gas washing flask containing a pyrogallol-potassium hydroxide-water mixture (Ostwald-Luther 1925) prior to its introduction into the gas washing bottle containing distilled water.

In a second variant the soil was treated in a ball mill until all of it passed a 0.385 mm sieve and 1 ml of a Dowex 50 W x 8, 20-50 mesh, ion exchange resin, previously saturated with ferric ions, was added to the soil-water suspensions. Only that fraction of the ion exchange resin not passing a 0.750 mm sieve was used. Since the soil was ground to a particle size smaller than 0.385 mm it was possible after the experiment to separate the ion exchange resin from the soil by wet sieving. The resin, originally on hydrogen form, was saturated with ferric ions by 3 consequtive additions of 3 ml 0.2214 M $FeCl_3$ to the resin in 10 ml water. After each addition the resin was left overnight and the following day the surplus of iron and the liberated hydrogen ions were removed by several washings with water. From the iron content of the combined washings, determined by atomic absorption spectrophotometry, the amount of iron taken up by the resin was calculated. After the conclusion of the experiment, and separation of the resin from the soil, the resin was treated 5 times with 5 ml 20 % HCl; after each treatment the resin was washed with water. The combined washings were transferred to a 200 ml volumetric flask for determination of total iron, aluminium and ferrous iron. The two former were determined by atomic absorption spectrophotometry and the ferrous iron was determined colorimetrically with 1-10-phenanthroline in a solution buffered with potassium hydrogen phthalate. This method, which is suitable also for determination of total iron if a reducing agent such as hydroxylamine is added (Fortune and Mellon 1938), was tested on solutions of pure ferrous and ferric compounds, as well as on mixtures of these, and found to give reliable results for the content of ferrous iron, even in the presence of a large excess of ferric iron.

In a third variant of the experiment samples from two horizons were mixed and extracted together. The amount of soil from each horizon and the amount of water were the same as in the basic form of the experiment giving on overall soil-water ratio of 1:5. In the last variant of the experiment soil extracts obtained from the A_0-A_1 and the B_1 horizons were used instead of water for extraction of underlying soil horizons. A soil:liquid ratio of 1:10 was maintained. This variant was also combined with the variants employing nitrogen and ion exchange resin. No resin was present during the second extraction.

Soil solutions were obtained from wet soil samples collected in the field at intervals of approx. two months during one year. A modification of the technique described by Davies and Davies (1963) was used for separation of the soil solution from the solid soil constituents. In the field the moist soil was filled directly into a 100 ml polythene centrifuge tube having a small hole in the bottom. Prior to filling the tube with soil this hole was covered with a layer of glass wool. Two or more tubes of soil were collected from each horizon. The tubes were brought to the laboratory and centrifuged as soon as possible. The tubes were kept closed with a plastic lid and the hole in the bottom with adhesive tape from the time the soil samples were taken until they were centrifuged. During the centrifugation the tubes were placed on top of a rigid container made from a solid polythene rod. This container was strong enough to support the centrifuge tube with the soil and the centrifugation caused some soil solution to pass through the hole in the bottom of the centrifuge tube into the container. Generally 10-15 ml soil solution was obtained from each horizon by each sampling, but variations due to the moisture content and the kind of horizon were, of course, noted. In order to obtain wet soil samples in the summer it was necessary to collect these within a short period after rain.

9.4 Organic Carbon, Iron and Aluminium Contents of Aqueous Soil Extracts

9.4.1 Simple Water Extracts

Results of pH, organic carbon, iron and aluminium determinations in simple aqueous extracts from each horizon of the Skarrild profile are reported in Table 12 (gas: air), Table 13 (iron saturated ion exchange resin: absent) and Table 14 (line 1-5). The experimental technique was identical in these experiments, and they are comparable except for smaller differences in the duration of the experiments. Although some differences are noted between the results of the three experiments the overall impression remains fairly consistent. The amount of organic matter dissolved is highest in the A_o-A_1 horizon (these two subhorizons were not separated during the sampling). Considerable amounts of organic matter are also dissolved from the B_1 horizon, which is similar to the A_o-A_1 horizon in that it has a high content of organic matter. As compared to these two horizons the amounts of organic matter dissolved from the remaining horizons are rather small, but they are still significant in the A_2 and B_2 horizons.

Table 13 shows an interesting time variation in the amount of organic matter dissolved from the A_o-A_1 horizon and from some other horizons as well. It is higher after ten days than at any later stage in the experiment. This trend is also noted in the presence of iron saturated ion exchange resin. From ten days to one month there is a decrease in the organic matter content of the extract followed by a smaller increase during the second month. This increase is also noted in the results reported in Table 12, but here no determination was made after ten days. The high content of organic matter in the initial phase of the extraction shows that the dissolution of the organic matter takes place rather rapidly.

The decrease in the organic matter content is not followed by a decrease in the iron content. On the contrary a substantial increase in the iron content is observed during the period from ten days to one month in the horizons showing decreasing organic matter content, and a furhter increase takes place during the second month. A similar trend is noted for both iron and aluminium dissolved from the A_o-A_1 and B_1 horizons in the experiment reported in Table 12. The results given in Table 13 include the aluminium content at the end of the experiment only.

In the organic carbon-metal ratios given in Tables 12-14, and in many subsequent tables, C is the content of organic carbon (mg per 1), Fe the iron content (mg per 1) and Al the aluminium content (mg per 1). In order

Table 12. pH, Organic Carbon, Iron and Aluminium in Aqueous Soil Extracts (Atmospheric Air or Nitrogen Passed through during Extraction from 21.1. to 27.3. 1969)

Soil hori-zon	Gas	Date														
		21.1.	27.2.	27.3.	27.2.	27.3.	27.2.	27.3.	27.2.	27.3.	27.2.	27.3.	27.2.	27.3.	27.2.	27.3.
		pH			mg per l						$2\frac{C}{Fe}$		$\frac{C}{Al}$		$\frac{C}{Al+\frac{1}{2}Fe}$	
					C		Fe		Al							
A_0-A_1	Air	4.90	4.88	4.84	134	142	1.46	1.80	0.57	0.82	184	158	235	173	103	83
	Nitrogen	5.05	5.35	5.17	246	323	1.88	2.66	0.81	1.79	251	243	304	181	141	103
A_2	Air	5.17	5.08	5.28	12	12	0.06	0.00	0.02	0.02	400	∞	600	600	240	600
	Nitrogen	5.29	5.20	5.33	20	20	0.00	0.08	0.13	0.02	∞	500	154	1000	154	333
B_1	Air	4.60	4.77	4.84	90	88	1.23	1.36	2.60	3.02	146	129	35	29	28	24
	Nitrogen	4.72	4.47	4.55	78	92	5.95	9.63	2.62	3.40	26	19	30	27	14	11
B_2	Air	4.98	5.23	5.26	8	7	0.11	0.08	0.39	0.53	146	175	20	13	18	12
	Nitrogen	5.02	5.22	5.25	14	14	0.77	1.37	0.43	0.63	36	20	33	22	17	11
C	Air	6.22	6.35	6.49	2	2	0.06	0.13	0.09	0.06	67	31	22	33	17	15
	Nitrogen	6.24	6.18	6.32	8	4	0.27	0.33	0.11	0.19	59	24	73	21	32	11

Table 13. pH, Organic Carbon, Iron and Aluminium in Aqueous Soil Extracts (Atmospheric Air Passed through during Extraction from 26.8. to 4.11. 1968)

Soil horizon	Iron saturated ion exchange resin	Date															
		26.8.	5.9.	28.9.	4.11.	5.9.	28.9.	4.11.	5.9.	28.9.	4.11.	4.11.	5.9.	28.9.	4.11.	4.11.	4.11.
		pH				mg per l							$2\frac{C}{Fe}$			$\frac{C}{Al}$	$\frac{C}{Al+\frac{1}{2}Fe}$
						C			Fe			Al					
A_o-A_1	Absent	4.05	4.35	4.41	4.40	196	145	163	1.07	2.15	3.47	1.30	366	135	94	125	54
	Present	4.02	4.05	4.11	4.18	168	95	107	1.24	1.22	2.16	0.67	271	156	99	172	61
A_2	Absent	4.81	5.01	4.97	5.07	23	16	15	0.02	0.05	0.00	0.10	2300	640	∞	150	150
	Present	4.45	4.27	4.25	4.12	18	30	11	0.16	0.10	0.14	0.03	225	600	157	367	110
B_1	Absent	4.80	4.78	4.73	4.77	62	71	81	0.60	1.08	1.47	3.07	207	131	110	26	21
	Present	4.32	4.32	4.38	4.38	55	43	44	0.62	0.77	0.79	1.48	177	112	111	30	23
B_2	Absent	5.30	5.30	5.18	5.11	8	9	10	0.09	0.23	0.12	0.45	178	78	167	22	20
	Present	4.45	4.27	4.16	4.04	12	12	18	0.27	0.48	0.67	0.75	89	50	54	24	17
C	Absent	6.70	6.77	6.84	6.81	2	6	5	0.09	0.08	0.11	0.16	44	150	91	31	23
	Present	6.21	4.70	4.57	4.32	3	5	6	0.09	0.08	0.21	0.15	67	125	57	40	23
No soil	Present	4.86	4.82	4.60	4.20	1	1	3	0.00	0.01	0.01	0.01	-	-	-	-	-

Table 14. pH, Organic Carbon, Iron and Aluminium in Aqueous Soil Extracts (Atmospheric Air Passed through during Extraction which Lasted 72 Days)

Soil horizon	pH		mg per l					
	before extraction	after extraction	C	Fe	Al	$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al + \frac{Fe}{2}}$
A_o-A_1	5.06	4.71	148	1.52	0.73	195	203	99
A_2	5.19	5.33	11	0.03	0.09	733	122	100
B_1	4.54	4.80	85	1.80	3.34	94	25	20
B_2	5.05	5.25	7	0.11	0.40	127	18	15
C	5.90	6.08	1	0.08	0.06	25	17	10
$(A_o$-$A_1)+B_2$	5.07	4.86	115	2.57	4.17	89	28	21
$(A_o$-$A_1)+C$	5.08	5.00	101	1.50	1.96	135	52	37
B_1+B_2	4.85	4.82	66	1.64	3.10	81	21	17
B_1+C	5.02	4.90	66	1.78	2.98	74	22	17

to make the ratios involving iron numerically comparable on a molar basis to those involving aluminium the iron content have been divided by 2, since the atom weight of iron is approximately twice that of aluminium.

All the organic carbon-metal ratios shown in Tables 12 and 13 for A_o-A_1 and B_1 horizons decrease with time. In the remaining horizons some deviations from this trend are noted but at least a part of these may be due to analytical errors since the contents of the elements in question are very small, and hence inaccurately determined, in these extracts. This decrease shows that the dissolution of the metals lacks behind the dissolution of the organic matter. This would in turn suggest, although not definitely prove, that the dissolved organic matter promotes or causes the dissolution of the metals.

Another fact which is clear from Tables 12-14 is that all organic carbon-metal ratios are substantially higher in the A horizon than in the lowerlying horizons. There is invariably a sharp drop from the A_2 to the B_1 horizon. The variation in the $\frac{C}{Al}$-ratio with depth seems to be more regular than the variation in the $2\frac{C}{Fe}$- and $\frac{C}{Al+\frac{1}{2}Fe}$-ratios. The lowest final $\frac{C}{Al}$-ratio shown for an A subhorizon in Tables 12-14 is 122 while the highest $\frac{C}{Al}$-ratio found in any lowerlying subhorizon is 33. The average drop in the $\frac{C}{Al}$-ratio from the A to the B horizon is, however, much larger and it seems from Tables 12-14 to be about one order of magnitude. It should be emphasized that not one single exception to this trend is found, even though particularly the aluminium determination involved large analytical difficulties.

The pH values of the soil extracts are subject to some variations between replications and also to time variation within the same replication. Both increasing and decreasing pH with time is noted. The largest differences are found within and between extracts from the A_o-A_1 horizon. No explanation for this variation will be attempted except for pointing out that there may be a connection between the lower final pH and the higher content of iron and aluminium in the A_o-A_1 extract in the experiment reported in Table 13 as compared with those reported in Tables 12 and 14.

In Table 15 values for dissolved organic carbon, iron and aluminium are given for the A_o and A_1 horizons of all the soils included in this study. Large variations are found from soil to soil but generally the amounts of organic matter and metals dissolved from the A_o horizons greatly

Table 15. pH, Organic Carbon, Iron and Aluminium in Aqueous Soil Extracts (Atmospheric Air Passed through during Extraction which Lasted 30-40 Days)

Profile	Horizon	pH		mg per l			$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al + \frac{Fe}{2}}$
		before extraction	after extraction	C	Fe	Al			
Gørding Hede	A_o	3.65	3.80	180	3.50	0.77	103	234	71
	A_1	3.98	4.20	35	0.50	0.02	140	1750	130
Skarrild	A_o	3.82	4.28	116	2.50	1.59	93	73	42
	A_1	3.85	4.22	66	1.05	0.60	126	110	58
Stavshede	A_{oa}	3.45	3.99	125	1.48	0.65	169	192	90
	A_{ob}	3.32	3.65	115	1.15	0.54	200	213	105
Klelund	A_{oa}	3.75	4.08	180	1.12	0.63	321	286	151
	A_{ob}	3.68	3.82	170	1.42	1.25	239	136	87
Tingheden	A_o	3.50	3.72	150	1.00	0.30	300	500	187
	A_1	4.21	3.90	30	0.31	0.33	194	91	61
Trehøje	A_o	3.80	3.72	161	3.10	1.71	104	94	49
	A_1	4.08	4.20	41	0.35	0.05	234	820	178
Løwenholm	A_{oa}	4.12	4.68	800	3.40	1.07	470	748	289
	A_{ob}	3.61	3.82	250	3.00	1.00	167	250	100
Trinderup	A_o	3.91	4.30	290	7.00	4.32	83	67	37
Støttrup Hede	A_o/A_1	4.00	4.50	n.d.	1.10	0.52	-	-	-
Skarpholt	A_o	4.42	4.88	465	6.40	2.32	145	200	84
	A_1	4.08	4.38	60	2.30	1.47	52	41	23

exceeds the amounts dissolved from the A_1 horizons of the same soils. There is in most soils a decreasing trend in the carbon-metal ratios from the A_0 to the A_1 horizon but several exceptions to this rule are noted. Although large variations are found in the organic carbon-metal ratios they are all comparable to those discussed earlier for the A horizon of the Skarrild profile and substantially higher than in the B (and C) horizon of this profile. The lowest $\frac{C}{Al}$-ratio in Table 15 is 41 while the highest in the B (and C) horizon of the Skarrild profile is 33. As compared with the general variation in these ratios the difference is not large, but the average difference is several times larger. When comparing the results in Table 15 with those in Tables 12-14 it should be borne in mind that the carbon contents reported in Table 15 are determined by the dry combustion method while those reported in Tables 12-14 are determined by the wet combustion method. The samples from the Skarrild profile used in the experiment reported in Table 15 originated from a sampling different from that of the samples used in the experiments discussed above.

The most important findings of the study of simple water extracts seem to be that the dissolution of the metals iron and aluminium lacks behind the dissolution of the organic matter, that the organic carbon-metal ratios, particularly the organic carbon-aluminium ratios, decrease markedly from the A to the B horizon, and that the dissolution of the organic matter is subject to a peculiar time variation giving rise to an initial rapid increase in organic matter content followed by a decrease and a renewed increase. These facts will be compared with other findings presented in subsequent sections and chapters and discussed further in the light of these.

9.4.2 Water Extracts Prepared in Absence of Oxygen

The effect of passing nitrogen through the suspensions during the water extraction will largely be to remove oxygen from the mixtures. This must in turn be assumed to produce reducing conditions in the mixtures due to reducing substances in the soil, presumedly mainly organic compounds. It seems reasonable not to attribute any reducing power to the nitrogen itself since it is relatively inert.

The effect of replacing atmospheric air with nitrogen on the amounts of dissolved organic matter, iron and aluminium from each horizon of the Skarrild profile is shown in Table 12. The amount of dissolved organic matter is approximately twice as high in the extracts prepared in the presence of nitrogen as in those made in the presence of air with the exception of the B_1 horizon where no significant difference is noted. When comparing the results it should be taken into account that the organic carbon content is determined by a method based on oxygen consumption, and it seems likely that the organic carbon dissolved in the presence of nitrogen is more reduced than that dissolved in the presence of air. Hence, the values recorded in the presence of nitrogen may be too high relatively to those recorded in the presence of air. There is no way to estimate to what extent this has affected the analyses but it could not account for a doubling of the carbon content, since this would imply an oxidation number of -4 of the carbon in the organic matter dissolved in the presence of nitrogen, if the organic matter dissolved in the presence of air is assumed to have oxidation number 0, and further assuming complete oxidation to carbon dioxide. It seems reasonable to assume that even though the values recorded in the nitrogen extracts may be too high there is still an important difference in the amounts of carbon dissolved by the two treatments from all horizons except the B_1 horizon. Assuming that a difference in oxidation number does exist the results indicate that nitrogen has a negative effect of the amount of organic matter dissolved from the B_1 horizon.

Anaerobic conditions would be expected to have a large effect on the dissolution of iron. This effect is noted in the B and C horizons where the amount of iron dissolved in the presence of nitrogen is several times larger than that dissolved in the presence of air. This effect is entirely absent in the A_0-A_1 horizon, however. The $2\frac{C}{Fe}$-ratios clearly show that the relative increase in the amount of dissolved organic matter is larger than the relative increase in dissolved iron, even allowing for some systematic errors in the carbon determinations.

The amount of aluminium dissolved increases also in the presence of nitrogen. A comparison of the $\frac{C}{Al}$-ratios within each horizon shows that the relative increase in the amount of dissolved aluminium is close to the relative increase in amount of dissolved organic matter, when allowance is made for analytical errors in the extracts having very small contents of organic matter and/or aluminium.

In most extractions the decreasing trend in the organic carbon-metal ratio with time noted in the presence of air is found also in the presence of nitrogen. The variation in the $\frac{C}{Al}$-ratio with depth is identical to the variation in the air extracts. Due to the increased dissolution of iron from the B and C horizons the decline in the $2\frac{C}{Fe}$- and the $\frac{C}{Al+\frac{1}{2}Fe}$-ratio with depth is more pronounced in the nitrogen extracts.

The replacement of air by nitrogen seems to have very little effect on the pH of the extracts. The findings of the nitrogen experiment confirm the earlier findings of the air experiments. They further suggest that reducing conditions have no or little direct effect on the dissolution of iron from the A horizon. The increased dissolution of both iron and aluminium seems to be connected to, and possibly a result of, the increased dissolution of organic matter. This does not necessarily mean that the dissolved iron is not wholly or partly found as ferrous iron. This problem will be discussed further in the following section.

9.4.3 Water Extracts Prepared in Presence of an Iron Saturated Ion Exchange Resin

The purpose of this variant of the experiment was to study the influence on the results of a source of readily available iron. In initial trials it was attempted to use freshly precipitated ferric hydroxide but this was brought into a highly dispersed state on contact with the soil of all horizons and could not be removed from the extract by centrifugation. The ferric hydroxide was therefore replaced by an ion exchange resin saturated with ferric ions. The results of this experiment are reported in Table 13.

In the horizons yielding large amounts of dissolved organic matter, particularly the A_0-A_1 and B_1 horizons, the presence of the ion exchange resin causes a reduced amount of dissolved organic matter as compared with that of the simple water extracts. While the difference is fairly small in the beginning of the experiment it increases to more than a third of the organic carbon content of the simple water extracts at the end of the experiment for the two horizons mentioned. This increased difference is mainly due to an absolute decrease in the amount of dissolved organic matter in the extracts prepared in the presence of the ion exchange resin.

It was anticipated that the iron from the ion exchange resin would increase the amount dissolved, but in the two horizons mentioned only a slight increase is noted in the initial phase of the extraction. By contrast a substantial decrease is noted in the later stages. There are no great differences in the $2\frac{C}{Fe}$-ratios in the absence and presence of the ion exchange resin in either horizon. The amount of dissolved aluminium at the end of the experiment is reduced to about half in both horizons causing some increase in the $\frac{C}{Al}$-ratios. The $\frac{C}{Al+\frac{1}{2}Fe}$-ratios seem to be rather independent of the presence or absence of the ion exchange resin. While the irregular pattern in the amount of organic matter, iron and aluminium dissolved from the A_2 horizon may in part be due to analytical errors, this does not seem to be the case for the considerable increase in the amount of organic matter, iron and aluminium dissolved from the B_2 horizon. The resin generally has a decreasing effect on the pH of the extracts. This is probably due to hydrolysis of the ferric ions. This will also explain the decrease in pH with time noted in the experiment where no soil was present.

Before attempting an explanation of the observed phenomena the effects on the ions adsorbed by the ion exchange resin should be considered. The kinds and amounts of ions adsorbed on the resin before and after the extraction are reported in Table 16. It is seen that it was not possible to recover all the iron added to the resin which had not been in contact with the soil. This is probably due to so strong an adsorption of some ferric ions to the ion exchange resin that these cannot be removed by hydrochloric acid. This effect has been noted earlier (Petersen 1965). If a similar effect is attributed to the resins that have been in contact with the soil, this would almost account for the deficiency in the ferric ions recovered from the resin in contact with the A_2 horizon soil, indicating little interchange of ions between the resin and the soil from this horizon. It would, however, make the excess of ions recovered from the resins that have been in contact with the B and C horizon soil still larger. This fact may be explained by assuming that some of the ferric and aluminium ions are found as hydroxide complexes on the resin after the extraction. Samuelson (1952) quotes an experiment where an ion exchange resin adsorbed ferric ions in amounts exceeding the exchange capacity of the resin and explained this by such a mechanism. It would also comply with the fact that the pH of the ferric chloride solution used for saturation of the ion exchanger was lower than that of the soil extracts, and with the lower pH of the suspensions in contact with the resin than in those without resin. In addition to the hydroxyl ions, some organic compounds originating from the soil might neutralize some of the metal valencies. The hydrochloric acid extract from the ion exchange resin that had been in contact with the B_1 horizon had in fact a brown colour showing the presence of organic matter. The

Table 16. Ions Adsorbed on Ion Exchange Resin Before and After Contact with Soil (meq.)

Soil horizon	Before contact	After contact			
	Fe^{+++}	Fe^{+++}	Fe^{++}	Al^{+++}	Total
A_0-A_1	2.65	0.58	0.63	0.14	1.35
A_2	2.75	2.24	0.01	0.03	2.28
B_1	2.75	1.58	0.08	0.87	2.53
B_2	2.75	2.01	0.01	0.93	2.95
C	2.83	2.35	0.04	0.49	2.88
No soil	2.79	2.35	0.02	0.00	2.35

only plausible explanation for the large deficit in the amount of metals recovered from the resin that had been in contact with the A_0-A_1 horizon is that this resin has given off iron to the soil and adsorbed hydrogen ions in return. Although not proved by analysis it seems unlikely that any other ion would be present in this horizon in amounts sufficient to satisfy the deficit. It should be noted that the amount of iron given off to the soil is smaller than that calculated by simple subtraction of the values in Table 6, since the ferrous iron recovered would account for 50 % more if calculated as ferric iron. The amount of hydrogen ion taken up by the resin remains, of course, unaffected of this, since the entire negative charge of the ion exchange resin must be balanced by positive ions, and the ferrous iron will only neutralize the number of meq. given in Table 16.

The results in Table 16 show two features of considerable interest: 1. An appreciable reduction of the iron on the resin that has been in contact with the A_0-A_1 horizon. 2. A considerable replacement of iron with aluminium on the resins that have been in contact with the B and C horizons. The latter fact seems fairly reasonable in view of equilibrium considerations. When an iron saturated ion exchange resin is brought into contact with the soil containing both iron and aluminium in various combination the net result must necessarily be a transfer of aluminium from the soil to the resin and a transfer of iron in the opposite direction. The total amount of aluminium transferred to the resin is about 1 meq. from the B_1 and B_2 horizons and about ½ meq. from the C horizon. Since 15 g soil was employed in each extraction this corresponds to about 0.06 % of the total amounts of soil in the B_1 and B_2 horizons and 0.03 % in the C horizon. By comparison with Table 7 it is seen that these amounts corresponds to about $\frac{1}{6}$ of the amount of aluminium extractable with $Na_2S_2O_4$-EDTA from the B_1 horizon. For the B_2 and C horizons the fractions are between $\frac{1}{4}$ and $\frac{1}{3}$.

Whatever mechanism is responsible for the transfer of aluminium from the solid soil phase to the solid ion exchanger phase, and the transfer of iron in the opposite direction, it seems necessary to assume that these transfers have taken place through the dissolved state. Since each extraction was made with 150 ml water it follows from the values in Table 13 that the total amounts of dissolved aluminium at the end of the extraction were about 0.2, 0.1 and 0.02 mg from the B_1, B_2 and C horizons respectively. The total amounts of aluminium transferred correspond, therefore, to about 50, 100 and 250 times the amounts dissolved at the end of the experiment from the three horizons. In other words, the amount of dissolved aluminium has been replaced the stated number of times during the extraction. Actually, these estimates are low since the amounts of dissolved aluminium probably have been lower at earlier stages of the extractions, and since some of the water was removed during the extractions for determination of iron and organic carbon, so that the average amount of water present in each mixture during the extraction was below 150 ml. Similar calculations based on the net transfer of iron in the opposite direction reveal that the amount of dissolved iron has been replaced 200-300 times during the extractions.

The actual reactions taking place during the exchange of iron and aluminium between the soil and the resin remain somewhat obscure and therefore not subject to quantitative theoretical considerations. General equilibrium considerations suggest that aluminium initially dissolved from the soil is removed from the solution by the resin and iron is given off from the resin to the solution. This in turn increases the ability of the liquid phase to dissolve more aluminium from the soil while the excess iron is given off from the liquid phase to the soil. The large amounts of aluminium transferred from the soil to the resin suggest the presence of a rather labile aluminium-iron system in the B and C horizons and the presence in these horizons of significant amounts of aluminium that can be easily mobilized. The much smaller transfer in the A horizon points to much smaller contents of easily mobilized aluminium in this horizon. These conclusions are, of course, not very surprising in view of the general properties of podzols. However, the extent of aluminium and iron transfer noted in the B and C horizons seems high.

The other fact noted above, namely the iron reduction taking place on the resin that has been in contact with the A_0-A_1 horizon also needs some attention. It is remarkable that more than half of the iron removed from the ion exchange resin after the extraction is found as ferrous iron, even though atmospheric air was passed through the suspension during the entire experiment. It is difficult to suggest the presence of any reducing agent other than organic matter and this must therefore be held responsible for the iron reduction. This will also be in accordance with the results of many experiments, mentioned in chapter 7 and 8, that have shown that various plant extracts have large reducing capacities towards ferric iron, even in the presence of atmospheric air. Iarkov (1954) found evidence for the presence of soluble complex organic ferrous compounds in A horizons of podzols, but he attributed the reduction to overall anaerobic conditions caused by temporary water saturation of the soil.

The reduction by which the ferrous iron found on the ion exchange resin after contact with the A_0-A_1 horizon is formed requires about 0.3 meq. reducing agent. Whether this could be supplied by the 15 mg organic carbon present in the solution in contact with the resin is difficult to evaluate. This would imply an equivalent weight as reducing agent of the organic matter of less than 100, assuming the carbon content of the organic matter to be about 50 %. Taking into account the polymeric nature of the organic matter this value seems low. Szilagyi (1971) found that 1 g of humic acid preparation could reduce only 1.6 mg or 0.03 mmole ferric iron. Using this value the amount of iron reduced here would require 10 g of organic matter. Although the materials and conditions employed by Szilagyi (1971) are not comparable to those used here, it is reasonable to assume that a part of the reducing power has been supplied by the undissolved fraction of the organic matter. This assumption is also supported by the results given in Table 13 and 16, which show that a large fraction of the iron has been transferred to the solid soil phase, and this transfer has probably taken place through the dissolved state. Unfortunately, no evidence is available to facilitate considerations about the oxidation state of this iron. It seems also probable that the iron present in solution is found mainly as ferrous iron, but there is no proof that all of it is present in this condition.

The mechanism by which the iron is reduced remains obscure. According to energetic considerations a reduction should be impossible under the conditions of the experiment. If the system contains organic compounds capable of reducing ferric iron these should be oxidized themselves by the oxygen also present, if equilibrium were obtained. However, it is well known that many, or perhaps most, oxidation-reduction reactions are extremely slow or fail to proceed at all, due to high activation energies. It would in fact be easy to mention a number of chemical compounds capable of reducing iron in the presence of oxygen without reacting, or reacting very slowly, with the oxygen. Assuming the presence in the extraction mixture of compounds capable of reducing iron is, therefore, not in contradiction with general experience.

The most probable explanation of the iron reduction is that it takes place through specific reactions between dissolved and/or undissolved organic molecules and the ferric iron. The iron reduction may be promoted by microorganisms. Roberts (1947) and Bromfield (1954a) showed that certain bacteria species have a specific ability to reduce ferric iron. Bromfield (1954b) found that only dissolved ferric iron could be reduced by such bacteria, and he concluded that the ability of the bacteria to reduce ferric iron was due to a production of complexing compounds that could dissolve ferric hydroxide. Even if bacteria promote the reduction the reducing power must be supplied by some organic compounds in the soil. Whether the bacteria population of podzol A horizons is particularly rich in those, relatively few, species that can reduce iron is unknown.

Regardless of the mechanisms by which the iron is reduced the facts that a large part of ferrous iron is found on the ion exchange resin after the experiment and that the major part of the reducing power probably has been supplied by solid soil organic matter seem to imply that a large two-way transfer of iron has taken place between the two solid phases. This transfer must be assumed to have taken place through the dissolved state, and it may have been promoted by complexing compounds present in the solution.

From Table 16 it is seen that only a very small fraction of the iron on the resin that has been in contact with the B_1 horizon has been reduced, although this horizon is also rich in organic matter. The most simple explanation for this is that the organic matter of the B_1 horizon has less reducing power than that of the A_o-A_1 horizon. This would comply with the results of some investigations mentioned in chapter 5 according to which the organic matter of the B horizon is more oxidized than that of the A horizon.

The lower content of dissolved organic carbon, iron and aluminium in the presence of the iron saturated ion exchange resin could in part be due to adsorption by the resin of aluminium and perhaps organic compounds as mentioned earlier. It is difficult to evaluate the extent of this adsorption, but it is remarkable that no drastic changes are noted in the carbon-metal ratios. Since the resin contained iron only, a decrease in the $2\frac{C}{Fe}$-ratio and an increase in the $\frac{C}{Al}$-ratio would be expected. Such a trend is also noted in the A_o-A_1 and B_1 horizons but only to a small extent. This confirms that the amounts of the metals dissolved is strongly dependent on the amount of organic matter dissolved. Hence, an explanation for the decrease in the amount of organic matter dissolved will also explain the decrease in dissolved iron and aluminium. Although insufficient evidence is available at this stage for substantiating a mechanism by which the ion exchange resin causes a decrease in the amount of dissolved organic matter, it will be postulated that this is due to the increased supply of iron. It is seen from Table 13 that, at the beginning of the extraction when the $2\frac{C}{Fe}$-ratio is still comparatively high, the amount of dissolved iron is slightly higher in the presence than in the absence of the resin. This applies both to the A_o-A_1 and the B_1 horizon. Later, as the ratio decreases the amount of dissolved organic matter also decreases. It would, therefore, be reasonable to explain the decrease in dissolved organic matter content as being due to increased uptake of iron, or in other words, the iron taken up from the resin precipitates the organic matter. Such a mechanism would be in accordance with well known reactions for more simple systems and with many properties of podzols as discussed in chapter 8. Butler (1963) states that many chelate compounds are insoluble, and it is a general experience that trivalent ions such as ferric ions and especially aluminium ions have a pronounced coagulating effect on negatively charged colloids. Crawford (1965) found that more than 80 % of the organic matter dissolved in experiments rather similar to those described here did not pass a cellulose membrane and hence consisted of rather large molecules. Irrespective of the size of the molecules their water solubility is probably due to negatively charged hydrophilic groups such as dissociated carboxyl and perhaps phenolic groups. When this charge is completely or partly neutralized a decreased solubility would be expected. Hence, if more and more iron (and/or aluminium) is taken up by the organic matter a precipitation may be the result.

While such a mechanism would explain the general trend noted in the A_0-A_1 and B_1 horizons the higher organic carbon-metal ratios in the presence of the resin in the A_0-A_1 horizon in the later stages of the experiment seem to be inconsistent with this scheme. However, it should be taken into account that both the dissolved and undissolved organic matter consists of an extremely heterogenous mixture of different compounds that vary in their capacity for complexing the metals, in the stability of the complexes formed,and in the amount of metal required to cause precipitation. The system must also be considered to be extremely labile and continuously subject to a number of chemical and biological effects giving rise to a large number of reactions,probably most of them in a non-equilibrium state. Conclusions based on minor differences in the parameters measured might therefore prove invalid.

Before concluding the discussion of this experiment the increase in the amount of dissolved organic carbon, iron and aluminium caused by the ion exchange resin in the B_2 horizon should be commented. As has already been mentioned this increase is probably significant. To explain this increase it is necessary to make one more assumption; namely, that a smaller amount (on a molar basis) is required of aluminium than of ferric iron to precipitate the organic matter and to maintain this insoluble. Such an assumption is in agreement with general experience on the flocculating power of the two ions and may be justified theoretically by the smaller size of the aluminium ion. Experimental results, showing that such an effect is active also for the organic matter dealt with here, are presented in chapter 10 and 11. Since,as shown in Table 16,a considerable amount of aluminium is removed by the resin from the soil-water system this would increase the solubility of the soil organic matter, even if an equivalent amount of iron is returned to the system. This is not in conflict with the increased total content of dissolved aluminium which is due, in turn, to the increased amount of the dissolved organic matter. The $\frac{C}{Al}$-ratio is in fact slightly higher in the presence of the resin. The difference in behaviour between the B_1 and B_2 horizons is probably due to differences in the kind of organic matter. The organic matter of the B_2 horizon has escaped precipitation in the B_1 horizon and the reason could be that it requires a higher metal (especially aluminium) content for precipitation than can be supplied by the B_1 horizon.

It cannot be avoided that the considerations must be speculative at this stage. However, more evidence will be presented in the following sections and chapters to substantiate the speculations. It should be mentioned that the hypotheses presented here would also explain the reduction in the amount of dissolved organic matter with time in the simple water extracts shown in Table 13 and discussed in section 9.4.1, since the amount of metals dissolved increases with time, and hence causes precipitation of some organic matter.

9.4.4 Water Extracts Obtained from Mixed Soil Samples

The results of extraction of mixtures of soil from the A_0-A_1 and B_1 horizons on one hand, and the B_2 and C horizons on the other, are shown in Table 14. If the soil from one horizon did not interfere with the extraction of the soil from the other horizon the final carbon, iron and aluminium contents would equal the sum of the contents of these elements in the extracts obtained from each horizon alone. This is, however, not the case at all. The presence of soil from the B_2 or C horizon causes lower carbon content in extracts from the A_0-A_1 and B_1 horizons than those obtained by extraction of these horizons alone. On the other hand the B_2 and C horizon soil increases the iron and aluminium content of the extract from the A_0-A_1 horizon while the effect on the contents of these metals in the extract from the B_1 horizon appears to be small. The results of the extraction of the mixtures of A_0-A_1 horizon soil with B_2 and C horizon soil are particularly interesting. They show clearly that the organic matter dissolved from the A horizon is capable of dissolving appreciable amounts of iron and aluminium from the B_2 and C horizon. On the other hand the increased content of these metals causes a reduction in the amount of organic matter dissolved, presumedly by a precipitating effect of the metals in accordance with the mechanism discussed in the preceding section. The fact that the amount of carbon dissolved by extraction of the A_0-A_1 + B_2 mixture is larger than that dissolved from the A_0-A_1 + C mixture, despite a higher metal content of the former, might be accounted for by carbon dissolved from the B_2 horizon itself. In accordance with the proposed hypothesis a removal of iron and aluminium from the solid phase of the B_2 horizon would have a dispersing effect on the organic matter of this horizon, which presumedly requires large metal contents to be maintained insoluble.

Except for a slight reduction in the dissolved organic matter content the effect of B_2 and C horizon soil on the amounts of material dissolved from the B_1 horizon is very small. The small differences noted are, however, in accordance with the general hypothesis since the reduced carbon content is followed by reduced carbon-metal ratios.

The pH values of the mixtures seem largely to be determined by the pH values of the horizon having the largest organic matter content which is not surprising in view of the greater buffer capacity of the soil from these horizons.

9.4.5 Effect of Contact with Underlying Soil Horizons on the Composition of Water Extracts

Tables 17 and 18 show the change in the composition of the water extracts caused by contact with underlying soil horizons. The soil extracts used were those discussed in the preceding sections and by comparison of the values in Tables 12 and 13 with those given for the 'no soil' treatments in Tables 17 and 18 it is seen that in practically all cases the iron and aluminium contents remain unaffected of a second treatment with air or nitrogen. Most differences are within the analytical error. The only difference that seems to exceed the analytical error significantly is noted in the aluminium content of the extract obtained from the B_1 horizon under nitrogen and subsequently treated with air. The decrease in the aluminium content during the second air treatment amounts to about 20 %, but since no precipitate was observed no explanation is available for this decrease, and it cannot be excluded that a large experimental error has occured.

All extracts obtained from the A_o-A_1 horizon in the presence of air and subsequently treated with air in the absence of soil seem to have suffered a small loss of carbon, which may be due to a slight oxidation of the organic matter. Since the carbon contents were determined by the oxygen consumption method, this oxidation does not necessarily mean that carbon is lost from the system; it could be due to an increased oxidation state of the carbon. However, since the loss amounts to only a few percent, the dissolved organic matter must be considered relatively stable to oxida-

Table 17. pH, Organic Carbon, Iron and Aluminium in Aqueous Soil Extracts after Contact with Underlying Soil Horizon for 65 Days (Atmospheric Air or Nitrogen Passed through)

Origin of soil extract		Soil horizon in contact with extract	Gas used during contact period	pH	mg per 1			$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al + \frac{Fe}{2}}$
Soil horizon	Gas				C	Fe	Al			
A_o-A_1	Air	A_2	Air	4.87	113	1.04	1.09	221	104	70
	Nitrogen		Nitrogen	7.18	402	1.66	1.94	483	207	145
	Air	B_1	Air	4.75	133	2.90	6.20	92	21	17
	Nitrogen		Nitrogen	6.64	894	34.5	35.0	52	26	17
	Air	B_2	Air	5.20	107	2.10	7.60	102	14	12
	Nitrogen		Nitrogen	6.92	404	3.70	10.7	218	38	32
	Air	C	Air	6.19	99	3.00	6.30	66	16	13
	Nitrogen		Nitrogen	7.10	328	5.20	8.44	126	39	30
	Air	No soil	Air	4.18	120	1.64	0.87	146	140	71
	Nitrogen		Nitrogen	7.22	420	2.56	1.69	328	248	141
B_1	Nitrogen	B_2	Air	6.02	56	0.73	1.94	153	29	24
			Nitrogen	4.83	64	7.40	2.86	17	22	10
		C	Air	6.25	44	3.20	2.02	27	22	12
			Nitrogen	4.97	56	9.80	2.76	11	20	7
		No soil	Air	6.70	81	9.20	2.78	18	29	11
			Nitrogen	6.02	82	9.80	3.34	17	25	10

Table 18. pH, Organic Carbon, Iron and Aluminium in Soil Extracts after Contract with Underlying Soil Horizon for 33 Days (Atmospheric Air Passed through)

Origin of soil extract		Soil horizon in contract with extract	pH	mg per l			$2\frac{C}{Fe}$	$\frac{C}{Al}$	$\frac{C}{Al + \frac{Fe}{2}}$
Soil horizon	Iron saturated ion exchange resin			C	Fe	Al			
$A_o - A_1$	Absent	A_2	3.97	148	1.35	1.80	219	82	60
		B_1	4.45	124	1.63	4.07	152	30	25
		No soil	4.17	158	3.35	1.35	94	117	52
	Present	A_2	3.82	96	0.54	1.18	355	81	66
		B_1	4.47	88	0.99	2.94	178	30	26
		No soil	4.35	102	2.32	0.87	89	117	50
B_1	Absent	B_2	5.08	61	1.08	3.32	113	18	16
		C	5.98	68	2.11	4.20	64	16	13
		No soil	4.85	82	1.38	3.22	119	25	21
	Present	B_2	4.66	38	0.58	1.88	131	20	18
		C	5.76	33	0.98	1.30	67	25	18
		No soil	4.77	44	0.81	1.46	111	30	24

tion. The pH-values seem to be rather unaffected by the second air treatment taking into account the small buffer capacity of the extracts.

In the soil extracts obtained from the B_1 horizon in the presence of air a second air treatment has essentially no influence on the results of the carbon determination and the pH is also unaffected. This indicates a high stability of the organic matter in these extracts.

A quite different picture emerges for the extracts prepared in the presence of nitrogen and subsequently treated with nitrogen or air. In the extract obtained from the A_0-A_1 horizon in the presence of nitrogen a second nitrogen treatment causes a considerable increase in pH and in the carbon content. Since no gain of carbon has been possible during the treatment the apparent increase in the carbon content must be due to a reduction of the carbon. The increased pH, which is noted also in all treatments containing soil, may be connected to the reduction of the carbon, but this cannot be true for the increase in pH for the extract obtained in the presence of nitrogen from the B_1 horizon. Although a second treatment either with air or nitrogen causes an increase in pH of this extract, the carbon content decreases during both treatments.

When evaluating the changes in the concentrations of the soil extracts during the contact period the amounts that would dissolve from the soil itself should be taken into account. The basis of comparison would, therefore, be the combined contents of the extracts from the horizon of origin and the contact horizon given in Tables 12-14. Since the amounts dissolved from all contact horizons other than the B_1 horizon are rather small it will mainly be important for extracts in contact with this horizon.

Considering first the extracts subjected to two air treatments, it is seen that the treatments: A_0-A_1 horizon extract in contact with soil from the A_2 and B_1 horizons, appear in both Tables 17 and 18. The results should, therefore, be comparable and they will be considered together. In both experiments the A_2 horizon soil, as compared with the 'no soil' treatment, causes a small decrease in the carbon content, a substantial decrease in the iron content and an intermediate increase in the aluminium content. The organic carbon-metal ratios remain rather high. The effect of the B_1 horizon is more complicated and less consistent. Taking into account the amounts that could be dissolved from the B_1 horizon soil itself a significant decrease in the carbon content is noted in both experiments. However, as compared to the 'no soil' treatment Table 17 reveals an increase and Table 18 a decrease in the organic matter content. It is difficult to give a detailed account for the changes and differences in the amounts of dissolved iron and aluminium in the two extracts. However, in both cases the $\frac{C}{Al}$- and the $\frac{C}{Al+\frac{1}{2}Fe}$-ratios are typical for those found in B_1 horizons, i.e. they are significantly smaller than those of the original A_o-A_1 extract.

From Table 17 it is seen that the effect of the B_2 and C horizon soil on the soil extract from the A_o-A_1 horizon is similar to that of the B_1 horizon. In these horizons a decrease in the organic matter content, as compared with the 'no soil' treatment, is noted. This is accounted for by the smaller amount of organic matter dissolved from these horizons themselves. The increase in dissolved iron and aluminium is large and since only insignificant amounts of the metals dissolve in water from these two horizons, the increase must be attributed to the dissolving action of the organic matter of the A_o-A_1 extract. The pH values are practically identical to those found in the water suspension of the contact horizon, see Tables 12-14. This would be expected since the buffer capacity of the extract is small as compared with that of the soil.

The effect of the B_2 and C horizon soil on the concentration of the extract from the B_1 horizon is small. Soil from both horizons causes some decrease in the carbon content and some increase in the aluminium content while the two horizons have an opposite effect on the iron content.

The extracts prepared in the presence of the ion exchange resin behave in all cases almost identically to the corresponding simple extracts. It is also clear from Table 17 that, as compared with the 'no soil' treatment, the behavior of the A_o-A_1 extracts prepared in the presence of nitrogen and subjected to a second nitrogen treatment is similar to that of the corresponding air-treated extracts when contacted with the A_2, B_2 and C horizons. It is remarkable, however, that in these three horizons all organic carbon-metal ratios, also the $2\frac{C}{Fe}$-ratio, are larger in the presence of nitrogen than in the presence of air. In the first treatment (Table 12) the $\frac{C}{Al}$-ratio of the nitrogen extracts were similar to those of the air extracts while the first nitrogen treatment caused a decrease in the $2\frac{C}{Fe}$-ratio, as would be expected if the dissolution of iron is promoted by overall reducing conditions. Hence, the results in Table 17 indicate that the reducing conditions during the second nitrogen treatment have little direct influence on the dissolution of iron. The large increase in the organic carbon-metal ratios in the second nitrogen treatment is, of course, due to the reduction of the organic matter as noted also in the 'no soil' treatment and discussed above. However, even if the organic carbon-metal ratios found after the second nitrogen treatment are corrected for the apparent increase in carbon content noted in the 'no soil' treatment, all the ratios in the A_2, B_2 and C horizons remain higher than in the air treatment. This suggests that the reduction of the organic carbon has a negative, rather than a positive, effect on the ability of the organic matter to extract aluminium and even iron from the solid soil material.

The B_1 horizon behaves rather differently from the other horizons in its effect on the concentration of the A_o-A_1 extract. In this horizon a large increase is noted in all three constituents of the extract. The largest relative increase is noted in the iron content as would be expected. The reason for the large increase in dissolved organic matter is obscure, but it could be due to the organic matter of the B_1 horizon being a favorable substratum for a microflora carried over from the A_o-A_1 horizon. While the $2\frac{C}{Fe}$-ratio is somewhat lower in the presence of nitrogen than in the presence of air, the $\frac{C}{Al}$-ratios are almost identical if the ratio found in the presence of nitrogen is corrected for reduction as described above.

In the presence of nitrogen the B_2 and C horizons soil tends to lower the content of all three dissolved compounds of the extract from the B_1 horizon prepared in presence of nitrogen. An air treatment of this extract lowers the content still more, but it should be noted that this lowering takes place only in the presence of soil.

The results discussed in this section indicate that overall reducing conditions have little influence on the dissolution of iron, except possibly in the B_1 horizon. A reduction causes in most cases an increased dissolution of all three elements, but the increase in dissolved iron and aluminium is probably a consequence of the increase in dissolved organic matter. The results also confirm that the metals have a precipitating effect on the dissolved organic matter. Practically all the results found may be explained in terms of such a mechanism, even though the relationship necessarily is complicated since a precipitation of organic matter also leads to a precipitation of the metals. The definite relationship noted earlier between the organic carbon-metal ratios, especially the $\frac{C}{Al}$-ratios, and the kind of horizon have been found also in this experiment, and adds further evidence to substantiate the hypothesis.

9.5 Organic Carbon, Iron and Aluminium Contents of Soil Solutions

Results of the analyses of the soil solutions from the Gørding Hede and Skarrild profiles are presented in Tables 19-21. When evaluating these results the analytical problems discussed in section 9.2 should be taken into account. Especially the aluminium determinations for the B_2 and C horizons of the Gørding Hede profile may be subject to considerable errors since very little soil solution could be obtained from these horizons due to their coarse texture and small organic matter content. Hence, the zero aluminium contents listed for these horizons, as well as the large aluminium content found in the extract from the C horizon on April 13, should be regarded with caution.

Also the dynamics of the soil solution must be considered before comparing the differences between the individual horizons. The solutions extracted from different horizons will have been present in the soil for different periods of time. As described above the sampling was made shortly after rain in the summer while no attention was paid to the occurence of rain during that part of the year when the soil is permanently moist. This may cause some biasing of the results since the water extracted during the summer may have been present in the soil for a shorter time than that extracted during the remaining part of the year. As shown by the experiments discussed in section 9.4.1 the amount of organic matter and especially of metals dissolved will depend on the length of time of contact between soil and water. This seems of particular importance for the A horizon. By the time most of the samples were taken there was probably no or only very little downward movement of water. This means that the soil solutions extracted would not move further downwards until renewed rainfall. Under these conditions it would be expected that the solution moving downward would become gradually more and more dilute with time after the onset of rainfall. It will also mean that the average concentration, at least of the water leaving the upper A horizon, will be smaller than the values given in Table 19. This will also lead to fluctuations in the concentrations of the solutions from the lower horizons. Upward water movement may also occur from time to time. To evaluate the effects of these factors would require detailed studies on the particular localities of the water movement as influenced by evaporation and precipitation, and such studies have not been included in the present investigation.

Table 19. Organic Carbon, Iron and Aluminium in Soil Solutions(mg per 1)

Profile	Horizon	Date																	
		20.2.	13.4.	4.6.	3.8.	2.10.	18.12.	20.2.	13.4.	4.6.	3.8.	2.10.	18.12.	20.2.	13.4.	4.6.	3.8.	2.10.	18.12.
		C						Fe						Al					
Gøring Hede	A_o	102	117	134	-	293	420	0.53	0.99	2.38	-	0.93	2.30	0.40	0.26	0.61	-	0.90	1.44
	A_1	53	73	126	143	134	185	0.56	0.83	0.99	0.77	0.71	1.70	0.80	0.61	0.88	1.10	1.26	1.68
	A_2	84	77	76	118	118	60	1.18	0.45	0.61	1.23	0.47	0.45	1.47	0.37	0.93	1.00	1.10	1.04
	B_1	39	55	49	62	49	32	1.99	0.35	0.43	0.27	0.24	0.45	1.40	0.83	0.93	1.23	0.70	0.68
	B_{2a}	40	85	20	97	60	30	0.97	0.19	0.09	0.29	0.07	0.08	0.77	0.00	0.00	0.00	0.00	0.14
	B_{2b}	33						0.51						0.37					
	B_{2c}	51	10	38	82	83	51	0.33	0.04	0.07	0.33	0.09	0.00	0.23	0.00	0.00	0.23	n.d.	0.00
	B_{2d}	70						0.38						0.65					
	C	71	17	67	55	62	49	0.84	0.06	0.27	0.43	0.23	0.15	0.70	2.20	0.00	0.33	0.00	0.14
Skarrild	A_o		52	118	218	247	560		0.46	0.88	0.77	0.66	6.60		0.36	1.19	1.23	0.77	4.26
	A_1		66	59	101	66	88		0.54	0.33	0.86	0.15	1.90		0.20	0.40	0.62	0.08	1.68
	A_2		68	43	62	123	34		0.33	0.17	0.32	0.44	0.25		0.47	0.25	0.77	0.30	0.38
	B_1		55	69	42	66	51		0.23	0.13	0.98	0.12	0.15		0.86	1.53	0.76	1.68	0.88
	B_2		15	37	41	44	39		0.17	0.15	0.20	0.20	0.00		0.10	0.65	0.40	0.33	0.13
	C		8	17	25	26	37		0.06	0.08	0.40	0.26	0.05		1.00	0.33	0.33	0.18	0.30

Table 20. Carbon-Metal Ratios in Soil Solutions

Profile	Horizon	Date																	
		20.2.	13.4.	4.6.	3.8.	2.10.	18.12.	20.2.	13.4.	4.6.	3.8.	2.10.	18.12.	20.2.	13.4.	4.6.	3.8.	2.10.	18.12.
		$2\frac{C}{Fe}$						$\frac{C}{Al}$						$\frac{C}{Al+\frac{1}{2}Fe}$					
	A_o	385	236	113	-	631	365	255	450	220	-	326	292	152	154	75	-	214	162
	A_1	189	176	254	372	378	218	66	120	143	130	106	110	49	71	91	96	83	73
	A_2	142	342	249	192	502	267	57	208	82	118	107	58	41	140	61	73	88	49
Gørding Hede	B_1	39	314	228	459	409	142	28	66	53	50	70	47	16	54	43	45	60	35
	B_{2a}	83	895	445	669	1714	750	52	∞	∞	∞	∞	214	32	850	400	650	1500	167
	B_{2b}	129						89						52					
	B_{2c}	309	500	1085	497	1845	∞	222	∞	∞	356	-	∞	127	500	950	205	-	∞
	B_{2d}	368						108						85					
	C	169	567	496	256	539	654	101	8	∞	239	∞	350	63	8	478	100	516	223
	A_o		226	268	567	748	155		145	99	177	321	131		88	72	135	224	74
	A_1		244	358	235	880	93		330	148	163	825	52		140	103	96	440	33
Skarrild	A_2		412	505	387	559	272		145	248	81	410	90		106	126	67	246	67
	B_1		478	1061	86	1100	680		64	27	55	39	58		56	43	34	38	53
	B_2		177	493	410	440	∞		150	63	102	133	300		83	51	88	102	300
	C		265	425	125	200	1480		8	76	76	144	123		8	46	47	84	112

Table 21. pH and Colour of Soil Solutions

Profile	Horizon	Date											
		20.2.	13.4.	4.6.	3.8.	2.10.	18.12.	20.2.	13.4.	4.6.	3.8.	2.10.	18.12.
		pH						Colour*					
Gørding Hede	A_o	3.62	4.41	4.01	-	3.76	3.64	f.y.	yi.b.	yi.b.	-	f.y.	f.y.
	A_1	3.65	4.02	3.54	5.97	3.57	3.81	f.y.	yi.b.	y.	yi.b.	y.	bi.y.
	A_2	6.82	5.05	4.32	7.09	5.53	5.62	bi.y.	yi.b.	f.y.	bi.	bi.y.	f.y.
	B_1	6.48	5.83	6.19	5.56	5.86	6.03	f.y.	bi.y.	f.y.	f.y.	a.c.	a.c.
	B_{2a}	7.07	6.18	6.38	7.62	7.78	6.62	f.y.	c.	c.	a.c.	a.c.	c.
	B_{2b}	6.99						c.					
	B_{2c}	7.09	6.88	6.26	7.32	6.92	6.57	c.	c.	c.	c.	c.	c.
	B_{2d}	7.43						c.					
	C	7.24	5.89	6.44	6.97	7.39	6.65	c.	c.	c.	c.	c.	c.
Skarrild	A_o		3.89	3.85	3.49	4.25	4.14		yi.b.	yi.b.	f.y.	f.y.	d.b.
	A_1		4.08	4.50	4.08	5.36	4.10		yi.b.	y.	yi.b.	y.	d.b.
	A_2		5.07	5.40	5.44	6.19	5.24		yi.b.	y.	b.	bi.y.	yi.b.
	B_1		4.85	5.51	5.96	6.29	6.08		bi.y.	bi.y.	f.y.	bi.y.	f.y.
	B_2		5.75	5.83	7.06	6.87	6.53		c.	f.y.	a.c.	c.	c.
	C		5.33	5.43	6.96	6.81	6.19		c.	c.	c.	c.	c.

* a.: almost, b.: brown, bi.: brownish, c.: colourless, d.: dark, f.: faint, y.: yellow, yi.: yellowish

Nevertheless, the results in Table 19 give a rather clear picture of the leaching taking place in the profiles. The amounts of organic matter and metals dissolved in the A horizon are comparable to those found in the water extracts. The organic matter content declines with depth and although some exceptions are noted, especially in the Skarrild profile, the greatest decline is found between the A_2 and the B_1 horizons. However, as compared with the water leaving the A_o horizon there is a decrease in the organic matter content in the A_1 and A_2 horizons. Part of this decrease could result from decreasing concentration in the water leached out of the A_o horizon during a rainy period, but it seems problematic to attributed the entire decrease to this phenomenon. An alternative explanation is that a partial removal of organic carbon occurs during the passage of the water through the A_1 and A_2 horizons.

It should be noted that in no case the total content of organic matter is removed from the water in the B horizon. The soil solution in the B and C horizons still contains significant amounts of organic matter. The content of solid organic matter in the C horizon is small in both profiles, but it is not actually zero. This indicates that a small precipitation of organic matter does take place in this horizon, but the rather high contents of organic matter in the soil solution of the C horizon indicates that a considerable amount of organic matter is leached entirely out of the profile. This does not necessarily have to be organic matter transported through the whole profile. A part of the organic matter in the soil solutions of the lower horizons might have been dissolved in some subsurface horizons. In fact the hypothesis concerning a precipitation caused by metals would favour such a phenomenon but no information is available to provide evidence for it.

It is interesting to compare the colours of the soil solutions with their carbon contents. Although the colour evaluation is made visually and hence of a qualitative nature, the absence of any colour from all solutions obtained from C horizons, and from most of those obtained from B_2 horizons, does not seem to be in accordance with the rather considerable carbon content in some of these solutions. From Table 19 and 21 it is possible to select a number of examples of colourless soil solutions from C horizons having carbon contents exceeding those of coloured solutions from horizons above. This seems to indicate that the organic matter in the C horizon solutions is of a different kind, probably having a smaller molecular weight, than that of the solutions of the horizons above. This could, in agreement with the hypothesis proposed earlier, be explained by a separation of the organic matter during the passage through the soil profile, by a replacement of a part of the original organic matter with other compounds, or by a combination of both.

The metal contents of the solutions are subject to large variations. There seems to be a clear decline in both iron and aluminium content below the B_1 horizon. It is difficult to see any regularity in the variation of the iron and aluminium content above the B_1 horizon. As compared to the solutions from the B_2 horizons those from the C horizons seem to contain slightly more iron and aluminium. Since this iron and aluminium must be assumed to be leached entirely out of the profile this would in the long run lead to a loss of iron and aluminium from the C horizon. As mentioned in chapter 6 some of the profiles studied seem to have suffered a loss of sesquioxides from the C horizon.

The irregularity in the variation of the metal content of the solutions is followed by an irregular variation of the $2\frac{C}{Fe}$-ratios. However, the $\frac{C}{Al}$-ratios are subject to much less variation and the drop from the A_2 to the B_1 horizon noted in the soil extracts is also found in the soil solutions. The lowest $\frac{C}{Al}$-ratios in the profiles are always found in the B_1 horizon. The actual values are somewhat larger than those found in the soil extracts but this could be due to a smaller time of contact between solid and liquid phase. The more irregular trend in the variation of the $2\frac{C}{Fe}$-ratios could be due to reduction processes affecting the iron content, but it could also be taken to substantiate that aluminium is of greater importance for causing precipitation of organic matter than iron.

It is not possible from the data in Table 19 to evaluate the precipitation processes in detail. This would require a continuous measurement of the changes in concentration at small depth intervals. A precipitation caused by aluminium would mean that when the soil solution arrives at a given level some aluminium is initially dissolved and subsequently precipitated with the organic matter. Since the organic matter is heterogenous it seems reasonable to assume that different fractions of the organic matter are precipitated at different $\frac{C}{Al}$-ratios. This implies that the organic matter requiring only little aluminium would precipitate first and subsequently precipitated organic matter would contain more and more aluminium. Some fractions of the organic matter need not to be precipitated at all, even though they may still have a potential for dissolving aluminium. Such a mechanism would agree well with the results shown in Table 19. The high degree of coincidence between maximum organic matter content and maximum aluminium content in the profile discussed in chapter 6 need not to be in contradiction with this mechanism since each profile is separated into few rather thick horizons only. In section 9.6 it will be shown that the distribution of the organic matter and aluminium in the profiles agrees well with such a mechanism. It is not known if this mechanism can explain the reduction in carbon content in the A_1 and A_2 horizons. The $\frac{C}{Al}$-ratios are high in these horizons, and the results of the water extractions discussed in the previous sections suggest that a different mechanism should be proposed to explain this reduction.

The results in Table 19 indicate some seasonal fluctuations although these may be affected by the factors mentioned earlier. In the A horizon of both profiles the content of dissolved organic matter increases during the year, and this increase is to some extent accompanied by a, probably resulting, increase in the metal contents. A simple explanation for the increased content during the year would be that the higher biological activity during the warmer months gives rise to a high content of water soluble compounds in the A_o horizon, and that these compounds are leached out during the autumn and early winter. However, the actual reduction during the winter has not been confirmed since the results are from two different winters. If the values in Table 19 represent the true cyclus the greatest amounts of organic matter and metals are translocated in the autumn and the winter.

The results obtained by lysimetric studies over three years by Sotnikova (1970) show exactly similar seasonal fluctuations, but much less expressed. This may be due to differences both in natural and experimental conditions. While the iron and aluminium contents found in the lysimetric water from the various horizons of the Karelian sandy humus-iron-illuvial podzol studied by Sotnikova are comparable to those found here, the carbon content is much smaller. This makes the organic carbon-metal ratios calculated from Sotnikova's results and shown in Table 22 much smaller than those found here. However, comparison of the two sets of values is difficult due to insufficient information supplied by Sotnikova on the analytical procedures used when analyzing the lysimetric water.

Table 22. Organic Carbon-Metal Ratios in Lysimetric Water from a Sandy Humus-Iron-Illuvial Podzol (Calculated from the Data Published by Sotnikova 1970)

Hori-	$2\frac{C}{Fe}$				$\frac{C}{Al}$				$\frac{C}{Al+\frac{1}{2}Fe}$			
zon	Sp.	S.	A.	W.	Sp.	S.	A.	W.	Sp.	S.	A.	W.*
A_0	8.2	38	63	25	19	27	35	25	5.7	16	22	13
A_1A_2	4.6	23	25	∞	26	42	57	16	3.9	15	18	16
A_2	2.9	22	22	7.2	7.1	45	26	12	2.1	15	12	4.5
B	1.7	1.5	3.2	1.3	5.5	4.8	1.7	10	1.3	1.1	1.1	1.2

* Sp.: Spring, S.: Summer, A.: Autumn, W.: Winter

9.6 Organic Carbon-Metal Ratios in the Solid Soil Material

It seems reasonable at this stage to compare the organic carbon-metal ratios of the soil extracts and solutions with those of the solid soil phase given in Table 7. The $\frac{C}{Al}$- and the $\frac{C}{Al+\frac{1}{2}Fe}$-ratios of the solid phase of all profiles are plotted on a log scale versus depth in Fig. 14-23. The ratios used in the plots are those calculated from the iron and aluminium extracted with sodium dithionite-EDTA, since these must be assumed to give an expression for the most mobile fraction. The reason for using a log scale is merely to be able to show the entire variation within a profile in one plot. Only the curve showing the $\frac{C}{Al}$-ratio has been drawn.

The change in the $\frac{C}{Al}$-ratios with depth is identical for all profiles and only one insignificant exception to a monotonous decline in the ratio with depth is found in the ten profiles comprising a total of 68 horizons. It is, of course, not surprising that the A_0 horizon, consisting almost entirely of poorly decomposed plant material, has a high $\frac{C}{Al}$-ratio and that the C horizon, consisting of quartz sand with coatings of iron and aluminium oxides, has a low $\frac{C}{Al}$-ratio. However, the uniformity of the change with depth, especially from the lower part of the A horizon to the upper part of the B horizon seems remarkable. Furthermore, almost all the graphs show at this depth a bend of the curves which would have been much more pronounced if the plots were made on a linear scale. The absolute

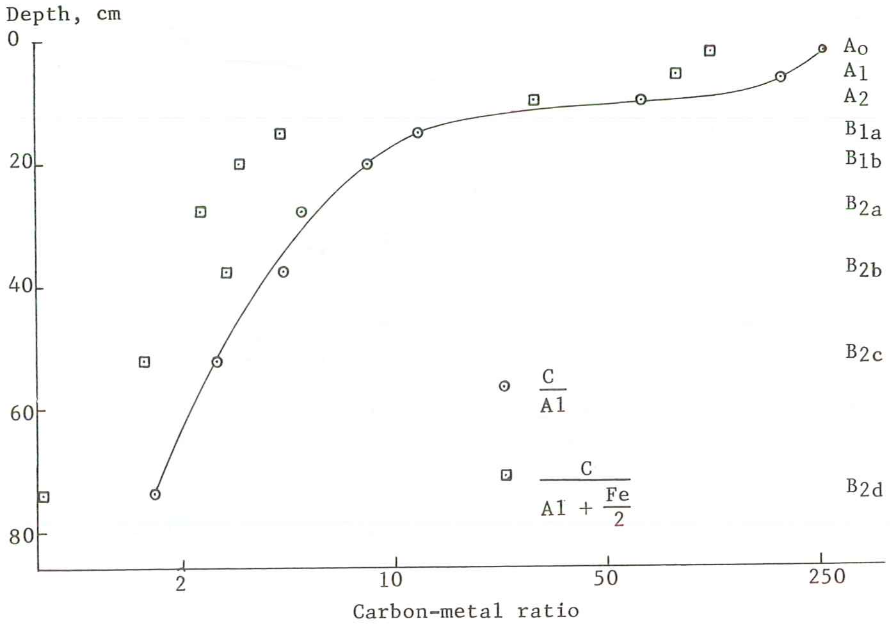

Fig. 14. Carbon-metal ratios in the Gørding Hede profile.

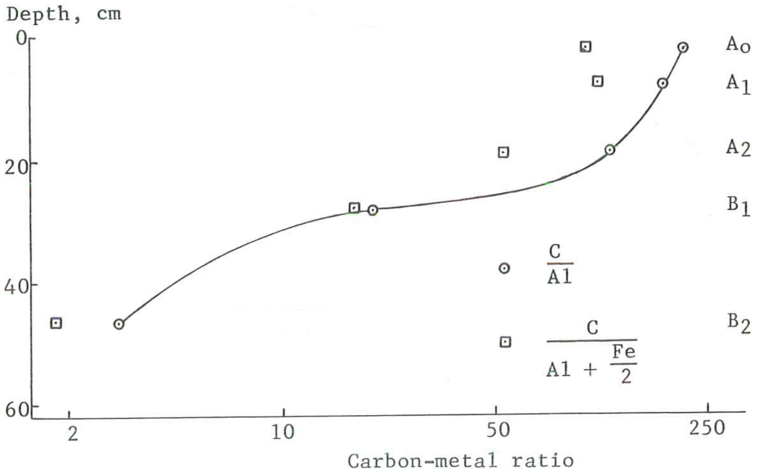

Fig. 15. Carbon-metal ratios in the Skarrild profile.

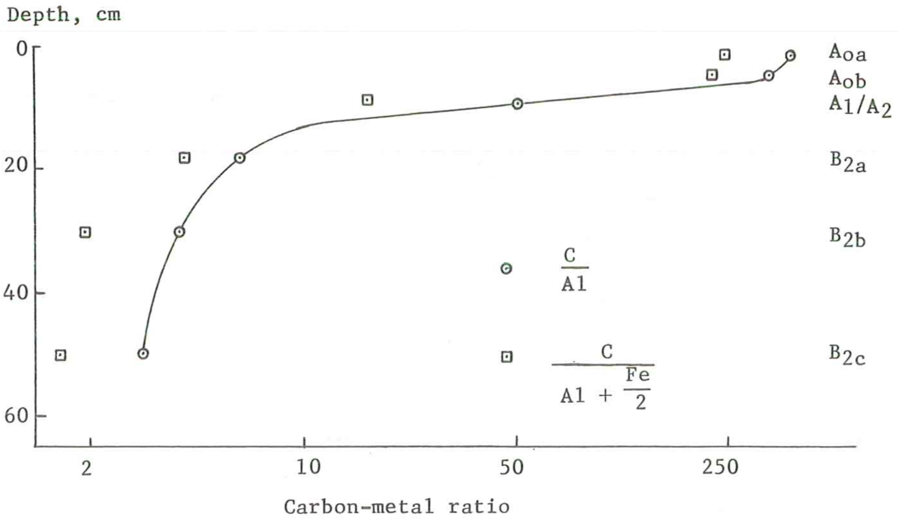

Fig. 16. Carbon-metal ratios in the Stavshede profile.

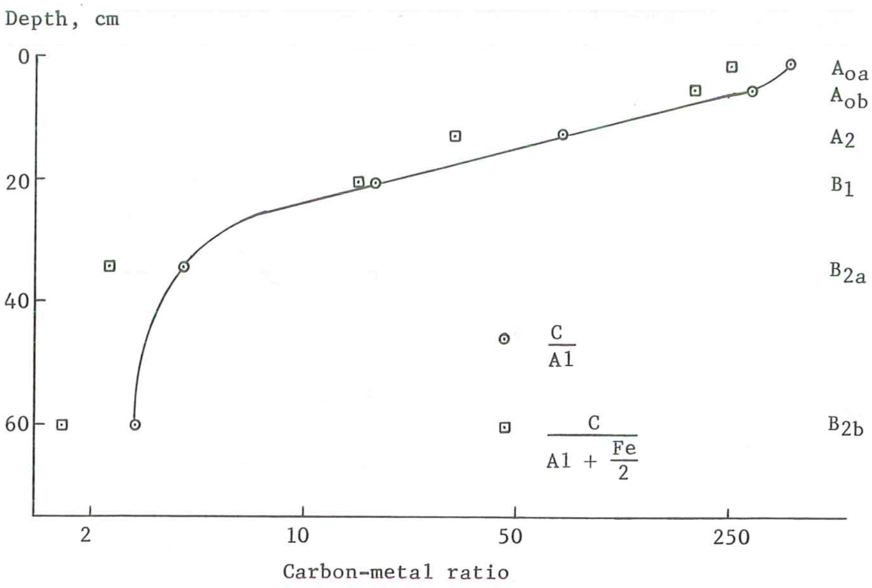

Fig. 17. Carbon-metal ratios in the Klelund profile.

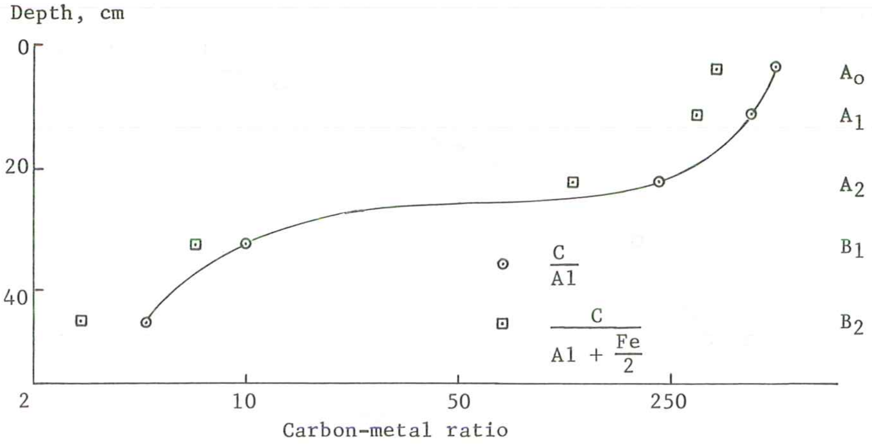

Fig. 18. Carbon-metal ratios in the Tingheden profile.

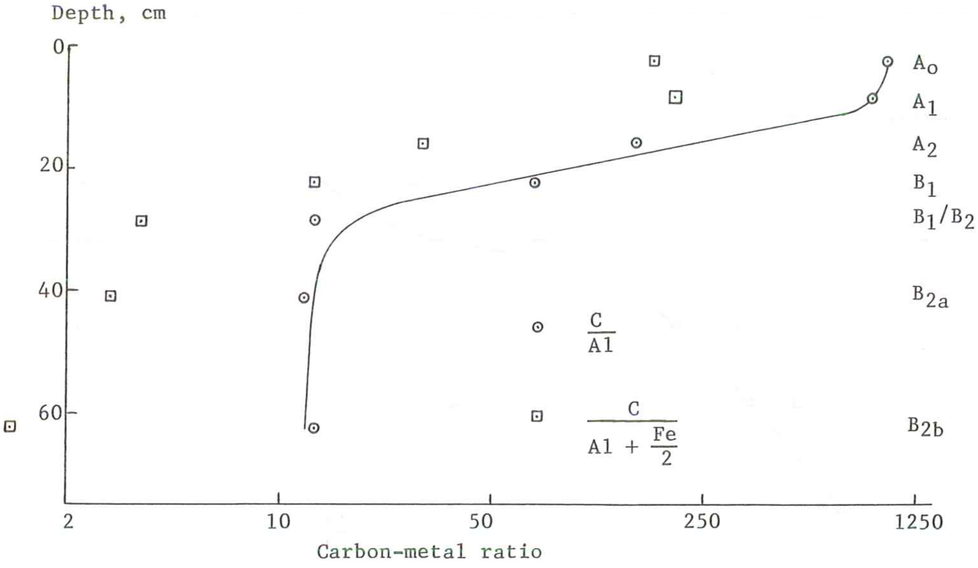

Fig. 19. Carbon-metal ratios in the Trehøje profile.

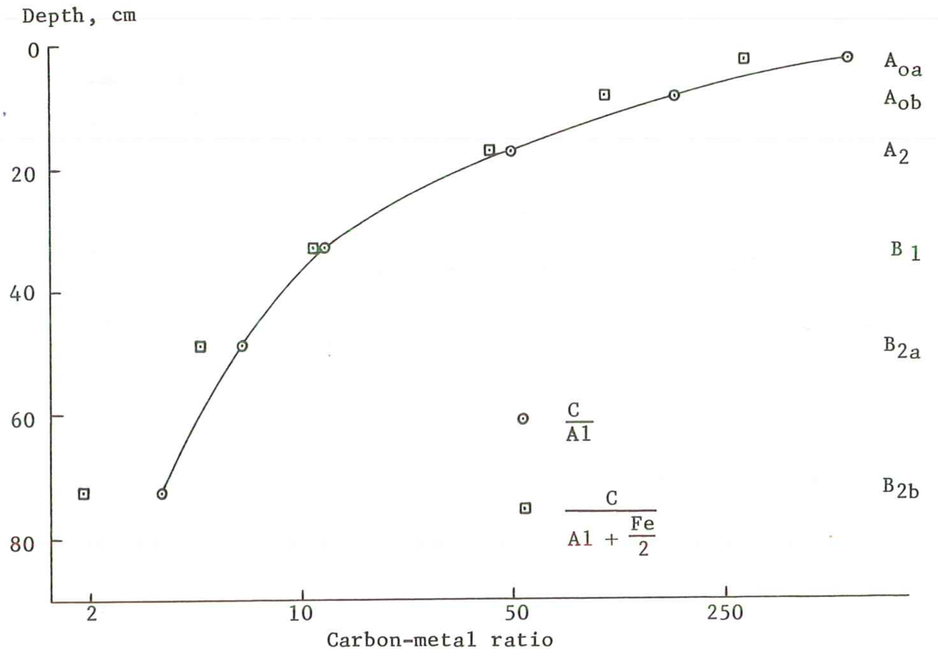

Fig. 20. Carbon-metal ratios in the Løwenholm profile.

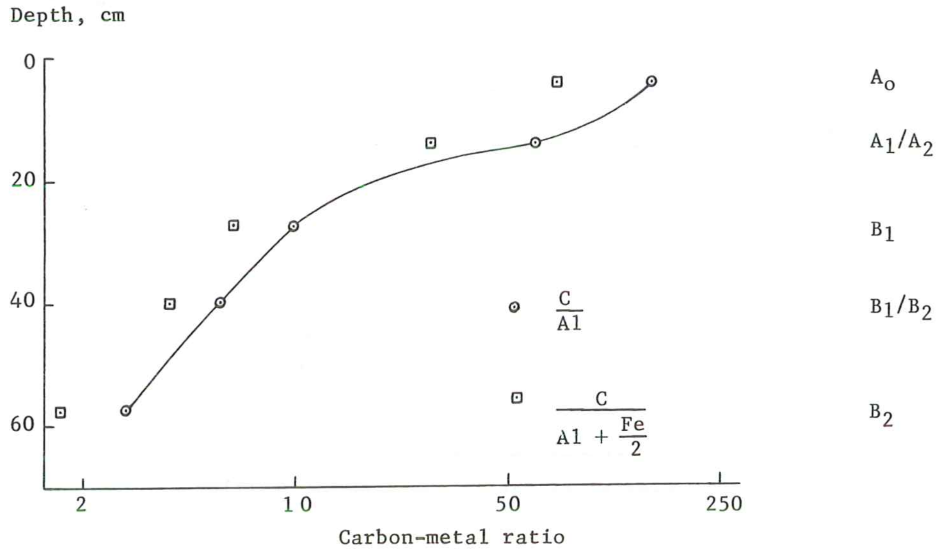

Fig. 21. Carbon-metal ratios in the Trinderup profile.

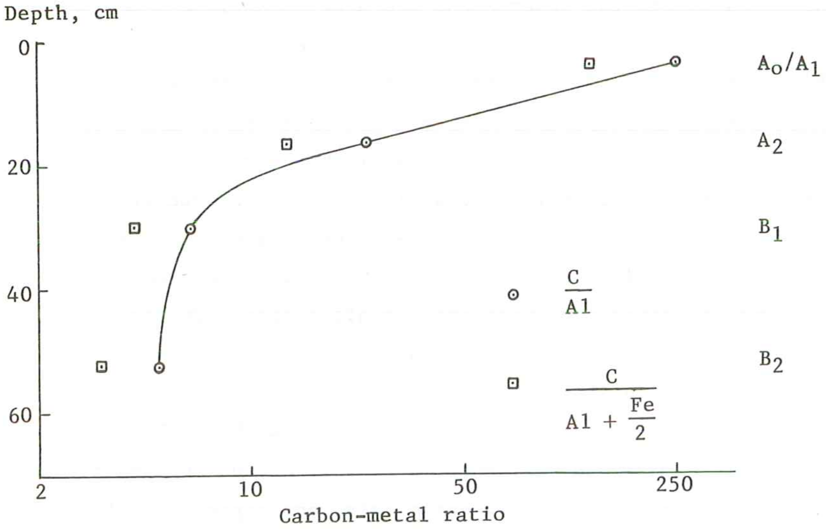

Fig. 22. Carbon-metal ratios in the Støttrup Hede profile.

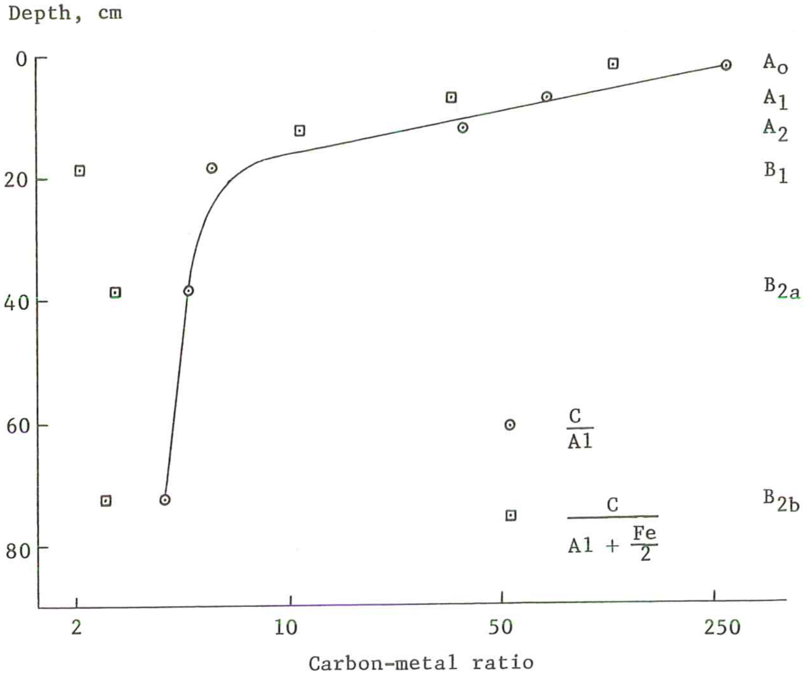

Fig. 23. Carbon-metal ratios in the Skarpholt profile.

values of the $\frac{C}{Al}$-ratios in the lower A and the upper B horizons are similar in all profiles, taking into account the inherent problems involved in the determination of the different fractions of the sesquioxides as discussed earlier. As compared to the $\frac{C}{Al}$-ratios of the soil extracts and solutions the values found in the solid soil phase are generally somewhat, but not considerably, lower. This would be in accordance with a higher aluminium content of the organic matter precipitated, but it is also partly due to the ability of the extractant to dissolve aluminium which is not found in combination with the organic matter. The trend in the $2\frac{C}{Fe}$-ratio with depth is generally similar to the trend observed in the $\frac{C}{Al}$-ratio, but less regular.

The variation in the organic carbon-metal ratios with depth in the solid soil material seems to add evidence in support of the mechanism of a precipitating action of the trivalent metals, and especially of aluminium, on the dispersed organic matter. The same variation with depth is found within each subhorizon as may be seen for the Gørding Hede profile, where some subhorizons have been divided into a number of sub-subhorizons not showing great morphological differences.

CHAPTER 10

SOLUBILITY INTERACTIONS BETWEEN IRON/ALUMINIUM AND SOIL ORGANIC COMPOUNDS

10.1 Methods

The studies reported in this chapter were made in an attempt to obtain more information on the reactions accompanying the dissolution and precipitation of iron, aluminium and organic matter. The experiments were made by means of a Radiometer automatic titrigraph. In the set-up used in these investigations the equipment included a pH-meter with glass and calomel electrodes, an automatic titrator, a recorder, a burette operated automatically by the titrator, and a titration vessel equipped with an automatic stirring device. This equipment can basically perform two functions: 1. Automatic recording of pH versus amount of titrant (acid or base) added. The speed of titration can be preset and varied within wide limits. The titration is made so as to maintain a constant rate of pH-change with time. 2. pH-stat function, where the pH of the solution in the titration vessel is maintained at a preset value by automatic addition of acid or base. The amount of acid or base added is recorded versus time. Both functions were utilized in the experiments reported here.

10.1.1 pH-Stat Experiments

The purpose of these experiments was to study the effects of iron and aluminium on the solubility of the organic matter of aqueous soil extracts under conditions of constant pH, and to obtain information on the amount of hydrogen ions liberated by possible reactions between the metals and the organic matter.

In the basic form of the experiment 5 ml soil extract was placed in the titration vessel and a solution of 5×10^{-3} M $FeCl_3$ or 5×10^{-3} M $AlCl_3$ was added slowly to the soil extract under vigorous stirring. Besides the stated concentration of ferric, or aluminium, chloride both solutions were 0.01 n with respect to HCl in order to reduce hydrolysis of the metal ions. The solution was added manually from a semimicroburette at a rate of 0.05-0.1 ml per minute. Since no precautions were taken to ensure a constant addition rate some variation occurred within each experiment and between different experiments. However, no observations indicated that smaller changes in the addition rate had any significant effect on the results. During the addition of the solutions the titrigraph maintained pH at the original value of the soil extract by addition of 0.02 n NaOH. The sodium hydroxide reservoir was equipped with a tube containing soda lime to keep the sodium hydroxide free from carbonate. The maximum amount of ferric or aluminium chloride solution added to any 5 ml sample of soil extract was 2.0 ml.

For comparison the basic experiments were supplemented by several modifications. In some of the modifications the soil extract was replaced by or diluted with water. In all experiments the volume of soil extract, diluted soil extract, or water, originally placed in the titration vessel, was 5 ml. In other modifications a mixed solution consisting of equal volumes of the iron and aluminium chloride solutions mentioned above was employed in place of the pure solutions. The effect of adding 7.5×10^{-3} M calcium chloride solution or 1.5×10^{-2} M sodium chloride solution, both 0.01 n with respect to HCl, to the soil extract in place of ferric or aluminium chloride was also studied.

After a predetermined amount of metal chloride solution had been added the reaction mixture was transferred to a centrifuge tube and left for 24 hours, the extent of precipitation of the organic matter and metals was judged visually, and the mixture was centrifuged. Iron or aluminium was then determined in the supernatant by atomic absorption spectrophotometry as described in chapter 9. The exact concentration of ferric iron and aluminium in the solutions added during the experiments was also determined by atomic absorption spectrophotometry. In one experiment involving addition of aluminium chloride to a diluted soil extract the visual evaluation of the extent of precipitation of the organic matter was supplemented by measurements of the optical density of the centrifuged reaction mixtures at 380 mμ. These measurements were made in 1 cm quartz cuvettes on a Beckman model DU spectrophotometer. The percentage of organic matter remaining in solution in each mixture was calculated from the ratio of the extinction measured for the mixture in question and that measured for an untreated soil extract subjected to an identical dilution.

10.1.2 Automatic Titrations

In these experiments 5 ml soil extract was mixed with 2.0 ml 5×10^{-3} M $FeCl_3$ or 5×10^{-3} M $AlCl_3$, both 0.01 n with respect to HCl, in the titration vessel. During approximately 6 hours the mixtures were titrated with

0.01 n NaOH to pH 10. Similar titrations were made of the same amounts of the ferric and aluminium chloride solutions in 5 ml water and of 2.0 ml 0.01 n HCl mixed with either 5 ml soil extract or 5 ml water. If 'a' is the amount of sodium hydroxide consumed at a given pH value by the ferric, or aluminium, chloride solution (and the hydrochloric acid contained in this) in water, 'b', the amount consumed at the same pH by 2.0 ml 0.01 n HCl in 5 ml soil extract and 'c', the amount consumed by 2.0 ml 0.01 n HCl in 5 ml water, then 'd' = a + b - c will be the amount of sodium hydroxide consumed at that pH by a solution that is 5 x 10^{-3} M with respect to $FeCl_3$ or $AlCl_3$ and 0.01 n with respect to HCl, and 5 ml soil extract. A comparison of a plot of pH versus d and a plot of pH versus amount of sodium hydroxide consumed by the ferric (aluminium) chloride, hydrochloric acid and soil extract, when these were titrated together, will, therefore, show the effects on the sodium hydroxide consumption of interactions between the metals and the organic matter.

10.2 Results and Discussion

The pH-stat experiments were made with several soil extracts from the A_o-A_1 and B_1 horizons of the Skarrild profile. The general trend was the same for all samples and since the results of the experiments made on samples from the A_o-A_1 horizon must be considered to be of most practical interest, only these are reported here. Furthermore, to ensure a maximum degree of comparability the results reported in Tables 23-25 are all from experiments made with the A_o- A_1 soil extract mentioned in Table 14. This extract contained 148 mg C per l.

Titrations were made of several soil extracts including those listed in Table 15. Also in this case the general trend was similar for all extracts and only the results of the experiments employing a mixture of the four A_o-A_1 soil extracts numbered 2-5 in Table 11 are shown in Fig. 37-38. This mixed soil extract contained 154 mg C per l.

10.2.1 Solubility Effects

When the results of the experiments are interpreted it should be kept in mind that it is unknown to what extent an equilibrium has been approached in the various experiments. In fact, it seems doubtful that a true equilibrium has been obtained in any pH-stat experiment. For example, it may be seen from Table 24 that no precipitation of aluminium hydroxide occurs when aluminium chloride is added to water at pH 4.8 although the amount added is large as compared to the solubility of

Table 23. Effects of Addition of Ferric Chloride to A_o-A_1 Soil Extract at pH 4.8

Soil extract, ml	Water, ml	Fe added, μeq.	Slope*			Precipitation	% Fe in solution
			changes at(μeq.)	before change	after change		
5	0	7.20	-	0.85	-	None	104
5	0	10.80	-	0.85	-	None	106
5	0	14.4	-	0.82	-	Little	81
5	0	18.0	14.2	0.89	1.07	Complete	5
5	0	28.8	15.0	0.85	1.01	Complete	1
5	0	28.8	15.6	0.85	0.99	Complete	1
0	5	7.2	-	1.00	-	Some	46
0	5	26.4	-	1.00	-	Complete	0

* see section 10.2.2

Table 24. Effects of Addition of Aluminium Chloride to A_o-A_1 Soil Extract at pH 4.8

Soil extract, ml	Water, ml	Al added, μeq.	Slope*	Precipitation	% Al or organic matter (O.M.) in solution
5	0	4.83	0.64	None	96 (Al)
5	0	8.06	0.67	Little	95 (Al)
5	0	12.08	0.66	Almost Complete	12 (Al)
5	0	16.1	0.68	Complete	0 (Al)
5	0	20.1	0.65	Complete	12 (Al)
5	0	32.2	0.66	Complete	19 (Al)
0	5	32.2	(0.32)	None	103 (Al)
2.5	2.5	3.22	0.71	None	92 (O.M.)
2.5	2.5	4.83	0.71	None	102 (O.M.)
2.5	2.5	4.83	0.72	None	104 (O.M.)
2.5	2.5	5.64	0.65	Little	81 (O.M.)
2.5	2.5	6.44	0.60	Complete	10 (O.M.)
2.5	2.5	8.06	0.72	Complete	4 (O.M.)
2.5	2.5	12.08	0.72	Complete	1 (O.M.)
1.25	3.75	1.61	-	None	104 (O.M.)
1.25	3.75	3.22	0.67	Almost Complete	28 (O.M.)
1.25	3.75	4.83	0.64	Complete	4 (O.M.)

* see section 10.2.2

Table 25. Effects of Addition of Ferric and Aluminium Chloride to A_0-A_1 Soil Extract at pH 4.8

Soil extract, ml	Water, ml	Fe added, μeq.	Al added, μeq.	Slope*			Precipitation	% Fe or Al in solution
				changes at(μeq.)	before change	after change		
5	0	3.60	4.04	-	0.67	-	None	101 (Fe)
5	0	5.40	6.05	-	0.73	-	Little	88 (Fe)
5	0	7.20	8.07	-	0.74	-	Complete	3 (Fe)
5	0	9.00	10.1	14.7	0.73	0.88	Complete	2 (Fe)
5	0	14.4	16.1	15.2	0.75	0.87	Complete	2 (Fe)
0	5	3.60	4.04	-	0.80	-	None	101 (Fe)
0	5	11.5	12.9	-	0.72	-	None	97 (Fe)
5	0	3.60	4.04	-	0.74	-	None	120 (Al)
5	0	5.40	6.05	-	0.77	-	Little	102 (Al)
5	0	7.20	8.07	-	0.85	-	Some	75 (Al)
5	0	9.00	10.1	15.0	0.79	0.94	Complete	0 (Al)
5	0	14.4	16.1	14.9	0.73	0.86	Complete	0 (Al)
0	5	12.9	14.6		0.86	-	None	103 (Al)

* see section 10.2.2

aluminium hydroxide shown in Fig. 13. Each pH-stat experiment included the determination of only one of the compounds remaining in solution, i.e. only iron, aluminium or organic matter, and in the case of organic matter only a relative determination based on the light absorption of the solutions at 380 mμ was made. Hence, there is no way to compare the effects on the different compounds within the same experiment, if the comparison is to be based on actual measurements. However, the visual evaluation of the extent of precipitation in each experiment is in all cases consistent with the amount remaining in solution of the compound measured, irrespective of whether this is iron, aluminium or organic carbon. Hence, it seems reasonable to assume that all the three compounds are precipitated together. In this connection it should be stressed that the results reported in Table 25 are from two different pH-stat experiments. The experimental procedure was identical in the two experiments and the reason for their deviation is not known, but the fact that one experiment involved iron determination, and the other aluminium determination, should not lead to the false conclusion that different percentages of the

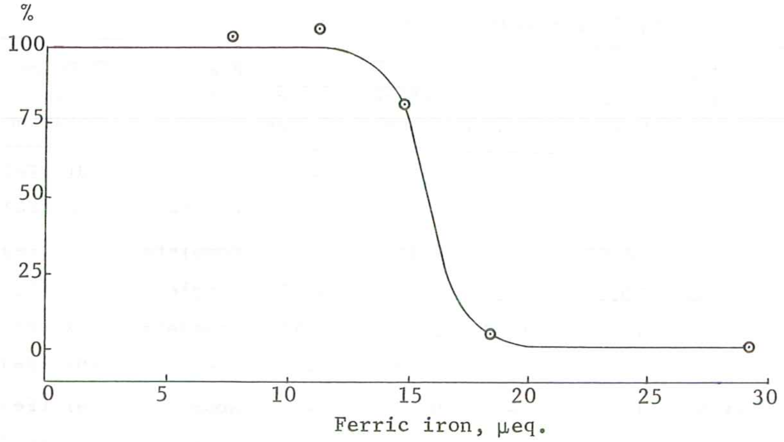

Fig. 24. Percentage of iron remaining in solution as a function of the amount of iron added to 5 ml soil extract at pH 4.8.

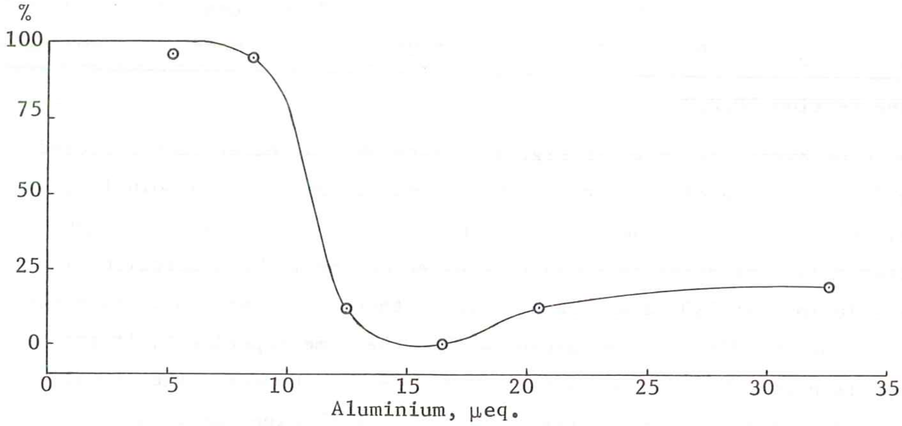

Fig. 25. Percentage of aluminium remaining in solution as a function of the amount of aluminium added to 5 ml soil extract at pH 4.8.

two metals are precipitated. If the results of the determination of either metal are compared with the results of the visual evaluation of the precipitation taking place in the same experiment there is no reason to assume any differences in the extent of precipitation of the two metals.

The visual evaluation of the precipitation taking place in each experiment as reported in Tables 23-25 indicates that no precipitation occurs until a certain amount of iron or aluminium has been added. When

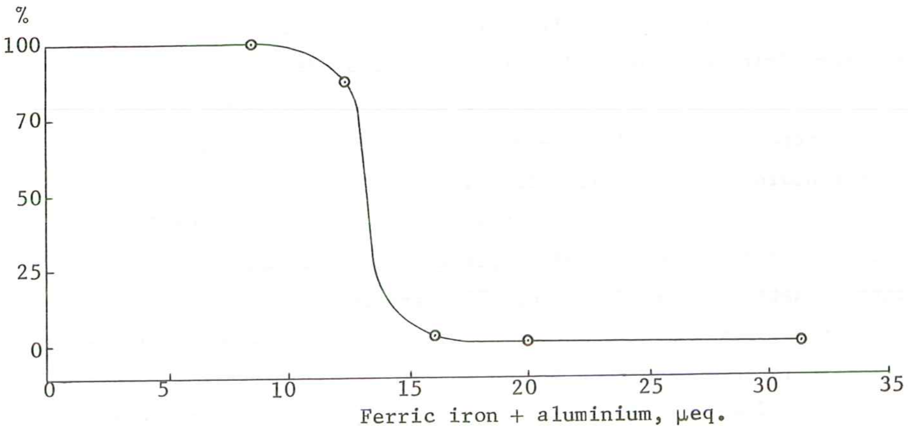

Fig. 26. Percentage of iron remaining in solution as a function of the amount of iron + aluminium added to 5 ml soil extract at pH 4.8.

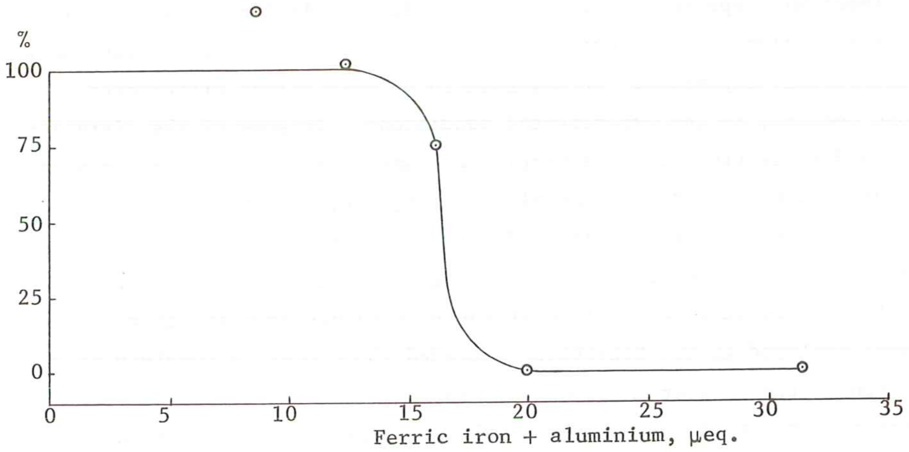

Fig. 27. Percentage of aluminium remaining in solution as a function of the amount of iron + aluminium added to 5 ml soil extract at pH 4.8.

this amount exceeds a certain critical value a practically complete precipitation of metals as well as of organic matter is observed. The percentage of iron or aluminium remaining in solution has been plotted as a function of the amount of these metals added in Fig. 24-27, and a smooth curve has been fitted through the points in the plots. Due to the low number of observations in each experiment, no great accuracy should be assigned to these curves. However, all the graphs bring out clearly the fact mentioned above; namely, that no precipitation takes place until a certain amount of metal has been added, after which a sudden and complete precipitation occurs. It should be noted that there is a small difference between the amounts of iron and aluminium shown in Fig. 24-27 and those reported in Tables 23-27 since the former includes the amounts already contained in the soil extract.

From the plots it is seen that a smaller amount of aluminium than of iron is required to cause complete precipitation at constant pH. The amounts of metals required to cause 50 % precipitation seem to provide some numerical means of comparison of the precipitating power of the two metals. It is seen from Fig. 24 and 25 that a precipitation to this extent occurred after addition of approximately 15.8 μeq. ferric iron but only 11.0 μeq. aluminium was required to cause a similar precipitation. Fig. 26 shows that in one case an intermediate amount was required when a mixture of aluminium and ferric iron was used. However, when this experiment was repeated (Fig. 27) the result was similar to that obtained for iron alone. This deviation which has already been mentioned above is not readily explained. It may have to do with slight differences, beyond control, in the experimental conditions. In some of the titrations described in section 10.1.2 a precipitate was formed immediately upon mixing the soil extract and the metal solution, i.e. at a rather low pH. In other experiments a precipitate did not occur until pH had been increased to a higher value, and in all cases it disappeared again at pH values 7-8. Also the metals were redissolved at these pH values even though the amounts employed in the titrations exceeded those causing complete precipitation in the pH-stat experiments. Furthermore, the solutions were remarkably stable at these high pH-values. Some mixtures of the A_0-A_1 soil extract and ferric chloride that had been titrated to pH 10 were subjected to determination of dissolved iron after having been kept in the laboratory in a stoppered test tube for several months. It was found that the entire amount of iron remained in solution. In all titrations it was noted that maximum precipitation took place at pH 4-6. This range corresponds largely to the normal pH-range of podzols and the pH-stat experiments were made in this range. No detailed study has been made on the effect of minor pH-changes but it is not to be excluded that such changes may have some influence on the precipitation.

Despite the deviations between the two experiments involving addition of a mixed solution of ferric and aluminium chloride, the results of the pH-stat experiments confirm that aluminium has a larger precipitating effect than ferric iron, but, on the other hand, there is only a quantitative difference between the two elements, since either metal (or both together) may cause a precipitation.

It is interesting to compare the carbon-metal ratios required for precipitation with those found in soil extracts and solutions and in the solid soil material of podzols. In the four experiments shown in Tables 23-25 the $\frac{C}{Al}$ -, $2\frac{C}{Fe}$ - and $\frac{C}{Al+\frac{1}{2}Fe}$-ratios at 50 % precipitation are 7.5, 5.0 and 6.1 (5.0) respectively. In the calculation of these ratios as well as in the calculation of the amount of metal required for 50 % precipitation the amount of the metal already contained in the soil extract has been included. Since this amount is small as compared with the amount added, it has only insignificant effects on the results. No $\frac{C}{Al+\frac{1}{2}Fe}$ - ratios have been calculated for the experiments where only iron or aluminium have been added since these ratios for identical reasons would be insignificantly different from the $\frac{C}{Al}$ - and $2\frac{C}{Fe}$-ratios. When comparing these ratios with those discussed in chapter 9 it seems to be most reasonable in all cases to make the comparison against the $\frac{C}{Al+\frac{1}{2}Fe}$-ratio since this ratio, like the ratios calculated for the precipitates in the pH-stat experiments, includes the total amount of trivalent metal that can have reacted with the organic matter. Although ferric iron and aluminium do not behave quantitatively identically in this respect, any discrepancies arising from this fact will be small compared with the general variation in the ratios.

The carbon-metal ratios found at 50 % precipitation in the pH-stat experiments are significantly lower than those found in any soil extract or solution from a B horizon. Since the soil extracts and solutions represent the soluble fraction of the organic carbon and the metals, a lower ratio could be expected in the fraction precipitated. It might, therefore, appear to be more appropriate to compare the ratios with those of the solid soil material. It is seen from Table 7 and from Fig. 14-23 that the ratios found at 50 % precipitation in the pH-stat experiments are of a magnitude similar to those found in many B horizons. A rigorous conclusion should not be drawn from this fact, however, since the carbon-metal ratios of the solid soil material are likely to be underestimated as compared with the ratio of the material actually precipitating in these horizons. The two major reasons for this are that the organic matter in the B horizon has been subject to biological decomposition after the precipitation took place, and that the extractant employed in the iron and aluminium analyses must be assumed to extract considerable amounts of iron and aluminium from inorganic compounds in addition to that being extracted from organic compounds. It seems reasonable, therefore, to conclude that the amount of metal required to precipitate a fixed amount of organic matter in the pH-stat experiments is somewhat higher than the amount required to cause precipitation in the soil as inferred from the results of the investigation of the solid soil material, soil extracts and solutions.

To study whether the total concentration of organic matter had any influence on the amount of metal required to cause precipitation, two experiments involving addition of aluminium chloride to a diluted soil extract were made. It is seen from Table 24 that the total concentration, and therefore also the total amount of organic matter,used in these experiments were $\frac{1}{2}$ and $\frac{1}{4}$ of that used in the basic experiment. Since the amounts of aluminium, present in the solutions from where no precipitation had taken place, were insufficient to allow a reasonable accuracy if aluminium was to be determined by atomic absorption spectrophotometry the precipitation taking place was evaluated from measurements of the optical density as described previously. The results of these experiments are plotted in the usual way in Fig. 28. It is seen that there is a small tendency towards an increasing amount of aluminium being required with the increasing degree of dilution. The $\frac{C}{Al}$-ratios at 50 % precipitation are 7.0 and 6.2 for the 1:1 and 1:3 diluted soil extracts respectively as compared to 7.5 for the undiluted extract.

The precipitation pattern noted in the pH-stat experiments appear to be somewhat different from that taking place in the soil. Although no determination of the percentage of carbon precipitated has been made in any pH-stat experiment it appears that a complete precipitation takes place abruptly as soon as the critical amount of metal has been added, while only little precipitation takes place as long as the amount of metal added is below the critical value. The results of the investigations of the soil extracts and solutions reported in chapter 9 indicate that the precipitation in the soil occurs more gradually, and in no case a complete precipitation has been found. As discussed in chapter 9 the

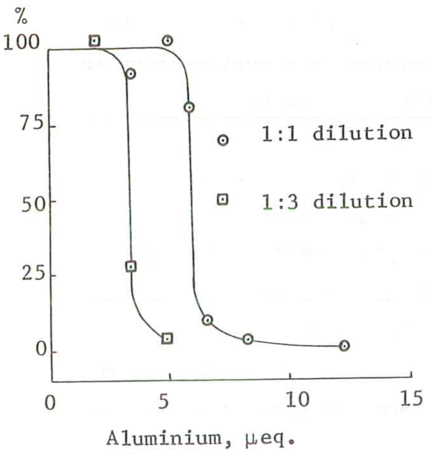

Fig. 28. Percentage of organic matter remaining in solution as a function of the amount of aluminium added to 5 ml diluted soil extract at pH 4.8.

actual precipitation occurring when an A_0-A_1 extract comes into contact with a B horizon may be larger than that measured from the decline in the total carbon content of the extract. The hypothesis that precipitation of the organic matter is caused by metals would imply that the uptake of metals by precipitating organic matter originating from the A horizon would tend to make some of the organic matter, previously precipitated in the B horizon, more soluble. Hence, a part of the organic matter precipitated could be replaced by newly dissolved organic matter from the B horizon and, accordingly, the actual precipitation taking place would be larger than that measured from the decline in organic carbon concentration of the extracts. It is not suggested that this should explain the entire discrepancy between the precipitation pattern noted in the pH-stat experiments and that inferred from the investigations described in chapter 9. A part of the discrepancy observed is undoubtedly due to the different conditions in the various kinds of experiments. An uptake of metals from the soil must necessarily occur more gradually than the rapid uptake from the chloride solution used in the pH-stat experiments.

Despite these inconsistencies it seems justified to take the results of the pH-stat experiments to confirm that precipitation of organic matter is caused by trivalent metals. The possible mechanisms of reaction will be discussed in the following section. It was found that addition of sodium or calcium chloride in amounts corresponding to twice the amount of iron, and three times the amount of aluminium, (compared on the basis of number of equivalents added) required to cause 50 % precipitation, had no effect on the solubility of the organic matter. Hence, the precipitating effect seems to be solely a property of the trivalent metals iron and aluminium.

The well-defined mutual precipitation taking place upon addition of the critical amount of ferric iron or aluminium to a soil extract is in contrast to the results of the blank experiments where the soil extract was replaced by water. When aluminium chloride or a mixture of ferric and aluminium chloride were added to water no precipitation occurred in any experiment. When ferric chloride was added alone in large amounts, a complete precipitation took place while a fraction remained dispersed if a small amount was added. If a surplus, as compared to the critical value, of ferric chloride or of a mixture of ferric and aluminium chloride was added to a soil extract, the entire amount of metal was precipitated. This was not the case if aluminium chloride was added alone (see Fig. 25). In this case a part of the surplus remained dispersed. Some of the possible reactions connected with these observations will be discussed in the following section.

10.2.2 Nature of the Reactions between the Metals and the Organic Matter

Fig. 29-35 show the amount of sodium hydroxide consumed as a function of the amount of ferric and/or aluminium chloride added in some of the pH-stat experiments. The amounts of iron and aluminium contained in the untreated soil extract are not included in the abscissa values. The sodium hydroxide values have been corrected for the amount required to neutralize the hydrochloric acid contained in the ferric and aluminium chloride solutions. Since the units of both axes are μeq. a total transformation of the metals into hydroxides would give rise to a straight line having a unit slope and intercepting both axes in the point (0.0). This is, however, not the case in all the experiments.

Since the experiments involving iron present the most clear picture these will be considered first. Fig. 29 shows that the plot obtained for iron added to water is essentially a straight line with the characteristics mentioned above indicating that the iron is completely transferred into ferric hydroxide. As seen from Table 23 this does not necessarily lead to a complete precipitation since only about half of the iron was precipitated when the total amount added was 7.2 μeq. Hence, the ferric hydroxide seems to form a fairly stable colloidal solution under these conditions.

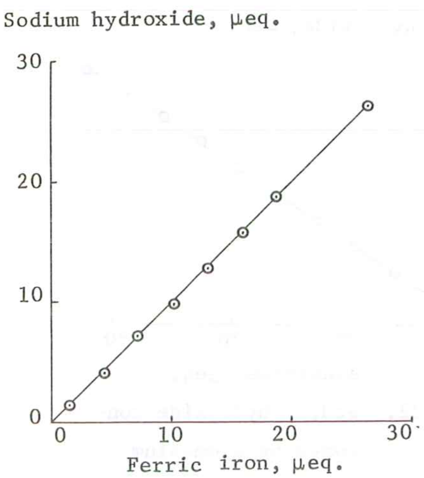

Fig. 29. Sodium hydroxide consumed by ferric chloride added to 5 ml water at pH 4.8.

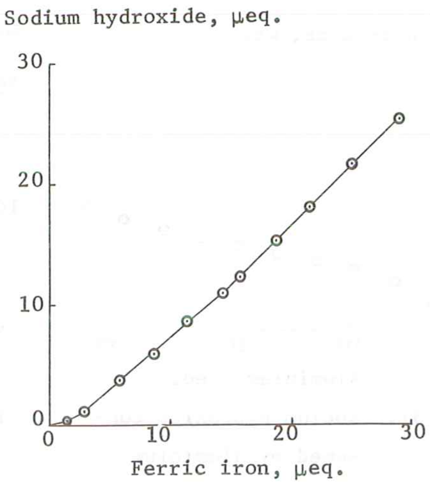

Fig. 30. Sodium hydroxide consumed by ferric chloride added to 5 ml soil extract at pH 4.8.

A different plot is obtained when ferric chloride is added to a soil extract. Fig. 30 shows that the amount of sodium hydroxide consumed by the iron added first is much smaller than that required to change the iron into ferric hydroxide. After addition of about 3 µeq. iron the amount of sodium hydroxide consumed becomes proportional to the amount added but the slope of the line remains below unity indicating that less than three hydroxyls are taken up per ferric ion. After addition of 15 µeq. Fe a change of the slope into unity occurs. The slope of the line below 15 µeq. is 0.85 indicating that slightly more than 2.5 hydroxyl ions are consumed by each ferric ion. Although only one plot is shown here, Table 23 shows that practically identical slopes were obtained in all the experiments involving iron and that the change in slope occurred at a fairly constant value of added iron.

The deficit in base consumption up to the point where the slope changes into unity is larger than that calculated from the slope of the line below this value since a still smaller base consumption is caused by the first 3 µeq. of iron added. The total deficit as calculated from Fig. 30 is 3.5 µeq. Deficits close to this were found

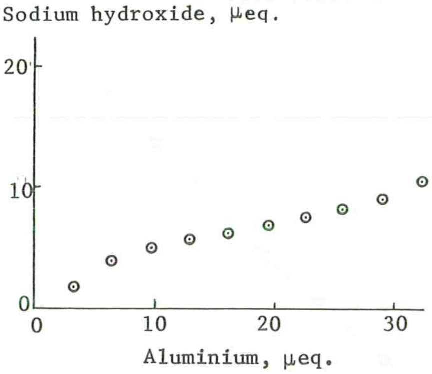

Fig. 31. Sodium hydroxide consumed by aluminium chloride added to 5 ml water at pH 4.8.

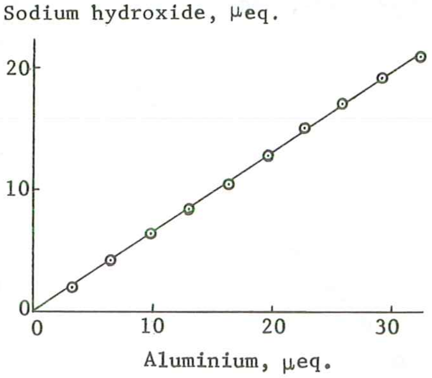

Fig. 32. Sodium hydroxide consumed by aluminium chloride added to 5 ml soil extract at pH 4.8.

for the two other experiments involving addition of a surplus of iron and shown in Table 23. The point where the slope changes corresponds closely to that of 50 % precipitation (Fig. 24).

Fig. 31 shows the base consumption caused by addition of aluminium chloride to water. The result is entirely different from that obtained for ferric chloride. No uniform slope is obtained and the total amount of sodium hydroxide consumed by 32 µeq. aluminium chloride corresponds to only about one hydroxyl ion per aluminium ion. Hence, some soluble aluminium hydroxide complexes seem to form under these conditions although, as discussed above, this does not correspond to an equilibrium condition.

When aluminium chloride is added to a soil extract a line with a uniform slope is obtained (Fig. 32). The graph differs from that showing the effect of addition of ferric chloride in that no reduced base consumption is noted for the first few µeq. added and that no change in slope occurs. The slope is 0.66 corresponding to the uptake of two hydroxyl ions per aluminium ion and, as appears from Table 24, a similar slope was obtained for all experiments. Since no change in slope occurs, it is not possible to calculate a total deficit as in the case of iron, but the deficit at 50 % precipitation, i.e. the deficit after about 10.6 µeq. aluminium chloride has been added, is very close to that obtained for iron at the point where the slope changes and precipitation occurs.

The base consumption caused by addition of a mixture of ferric and aluminium chloride to water is shown in Fig. 33. A straight line with slope 0.86 is obtained. It is seen from Table 25 that this slope varies somewhat from one experiment to another but all values are above the mean value of the two experiments involving addition of either ferric chloride or aluminium chloride to water. Hence the uptake of hydroxyl ions by aluminium in the presence of iron is increased and, furthermore, controlled to an extent where a

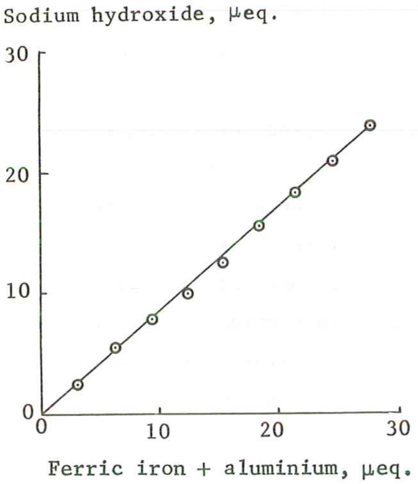

Fig. 33. Sodium hydroxide consumed by ferric and aluminium chloride added to 5 ml water at pH 4.8.

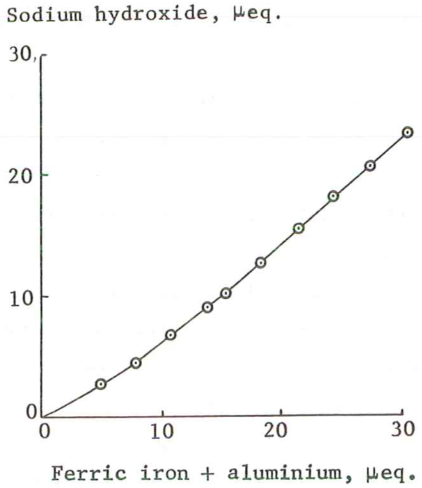

Fig. 34. Sodium hydroxide consumed by ferric and aluminium chloride added to 5 ml soil extract at pH 4.8.

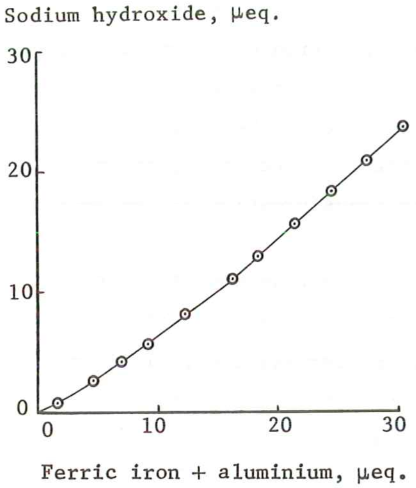

Fig. 35. Sodium hydroxide consumed by ferric and aluminium chloride added to 5 ml soil extract at pH 4.8.

straight line is obtained in place of the irregular plot obtained for aluminium alone. If it is assumed that iron is fully neutralized each aluminium takes up somewhat less than 2 hydroxyl ions. However, no precipitation occurs in any experiment.

Two plots showing the results of addition of mixed ferric and aluminium chloride to soil extract are shown in Fig. 34-35. It should be noted that although the plots represent two experimental series giving somewhat different results with respect to precipitation as mentioned above the plots are identical within the experimental error. Most of the parameters that can be derived from the plots are intermediate between those derived from the corresponding plots for addition of iron or aluminium alone. However, the change in slope occurs at the same value as in the experiment with iron alone, and hence in one of the experiments there is a deviation between change in slope and precipitation. The deficit in base consumption at the point where precipitation occurs is somewhat larger in both cases than that obtained for iron alone.

It is clear from the results presented above that addition of ferric and/or aluminium chloride to a soil extract in all cases gives rise to a base consumption different from that obtained by addition of the same solutions to water. This difference must be due to some interactions between the metals and the organic matter. Since the precipitation of the organic matter always coincides with the precipitation of the metals it is reasonable to assume that the metals and the organic matter form some compounds not dissociating in water. In all experiments the amount of sodium hydroxide consumed by the metals in the presence of organic matter is smaller than that required for a complete transformation of the metals into hydroxides.

This must mean that the metals contribute a net amount of positive electrical charge to the organic compounds provided that this is not counteracted by uptake of negative ions other than hydroxyl ions. It is not possible to estimate to what extent such an uptake of negative ions may have occurred in the experiments. Considerable amounts of chloride were present and ferric as well as aluminium ions are known to form chloride complexes, but it is unknown to what extent such complexes could be incorporated into the proposed metal-organic matter compounds.

In connection with the present experiments it has been demonstrated that a part of the organic compounds when subjected to electrophoresis moved towards the anode, even if the electrophoresis was made in a rather acid buffer solution. This shows that the compounds are negatively charged and similar results have been obtained in many other investigations (see chapter 7). The electric charge would be expected to affect the solubility of the compounds in such a way that decreasing charge will decrease the solubility. If it is assumed that the uptake of iron and/or aluminium by the organic compounds is not accompanied by an uptake of negative ions other than hydroxyl ions, or that the uptake of such ions is negligible, it follows that the combined metal-organic matter compounds formed have a negative charge that is smaller than that of the original metal-free organic compounds. This will in turn reduce their solubility.

Such a mechanism would tie in very well with the results of the pH-stat experiments since, as shown above, the precipitation seems to occur at a certain deficit in base consumption. If the compounds precipitated are fully neutralized it can be calculated from the deficit in base consumption at precipitation (approximately 3.5 μeq.) and the amount of organic carbon per 5 ml soil extract (740 μg) that the organic matter originally contains approximately 1 equivalent of negative charge per 210 g carbon.

Although such a mechanism would explain why the precipitation takes place, it would not provide any information on the nature of the reactions between the organic matter and the metals, or on the maximum amount of metal that can react with a given amount of organic matter. There is no reason to assume that the organic matter should stop taking up metals once they are electrically neutral. Precipitation would probably slow down any reactions but not prevent these, and a precipitation is not likely to occur instantaneously as soon as the compounds are electrically neutral. When considering these aspects it should be taken into account that Fig. 29-35 each represent one single pH-stat experiment carried out within a few minutes while Fig. 24-28 are constructed from a number of different experiments, where the reaction mixture from each experiment had been allowed to stand overnight before the precipitation was estimated.

When the organic matter can be precipitated by a smaller amount of aluminium than of iron it is simply because a given amount of aluminium contributes a greater amount of positive charge to the metal-organic matter compounds, and it does not indicate any differences in the capacity of the organic matter to react with the two metals. No evidence is available to estimate the capacity of the organic matter for uptake of the metals. However, it is probably larger than that corresponding to precipitation. It has already been mentioned that at high pH values the organic matter contained in 5 ml soil extract may maintain about 30 μeq. of iron in solution. Fig. 32 also indicates that some reactions occur between the metals and the organic matter in the region where precipitation already has taken place, since the base consumption in this area is different from that found when aluminium chloride is added to water. On the other hand, Fig. 25 shows that a part of the aluminium remains in solution when the amount added exceeds about 15 μeq. and a change in slope is noted approximately at this value when the solution added contains iron, and this change in slope does not necessarily coincide with precipitation. It seems, therefore, that there could be some change in the nature of the reaction after addition of about 15 μeq. metal under the conditions of the pH-stat experiments.

The sodium hydroxide consumed by the addition of the metals to the soil extracts may have been used for two principally different processes. It may have been taken up by the metal ions in which case the compounds formed between the organic matter and the metals could be regarded as mixed hydroxide-organic matter complexes. It may also have been used for neutralization of hydrogen ions displaced from acidic functional groups in the organic compounds by the metals taken up. This reaction which is well-known from many simple metal-organic complexes would lead to the formation of true organic matter-metal complexes. The latter type of reaction can hardly be responsible for the entire base consumption. If the organic matter in 5 ml soil extract (740 μg) should react with 15 μeq. metal this would indicate dissociation of 1 equivalent hydrogen per 49 g carbon, i.e. one hydrogen ion for each 4 carbon atoms. Furthermore, if true metal-organic matter complexes are to be formed, a certain steric arrangement of a number of organic functional groups is needed to satisfy the co-ordination requirements of the metals. Since the organic compounds must be assumed to have a rather high molecular weight and, to a large extent, a random orientation of functional groups, it is unlikely that one metal ion can be complexed by a carbon structure involving, on an average, 12 carbon atoms.

On the other hand, if hydroxyl ions satisfied a part of the co-ordination requirements of the metals, a much lower number of acidic groups would be needed, and the requirements concerning the steric arrangement would be much less rigorous since the hydroxyl ions could orient themselves in relation to the structural arrangement of the organic molecules. It must, therefore, be assumed that the compounds formed in the experiments are mixed hydroxide-organic matter complexes. This is in accordance with the conclusions of several investigators who have studied complex formation between iron and/or aluminium and soil organic matter (see chapter 7).

However, such mixed hydroxide-organic matter complexes would be expected to be considerably less stable than true metal-organic matter complexes. This is also in accordance with experimental results quoted in chapter 7 showing that the stability constants of metal-soil organic matter complexes are several orders of magnitude lower than those of complexes between the same metals and simple organic molecules such as EDTA.

There is, of course, no reasons to assume that each metal ion involved in the mixed complexes has attached a definite number of hydroxyl ions. Considering the heterogenous nature of soil organic matter, any stage from true metal-organic matter complexes to compounds consisting mainly of metal hydroxides associated with minor amounts of organic matter could occur. As the organic matter starts taking up metals the organic structures satisfying the co-ordination requirements of the metals most closely must be filled first. As more and more metal is taken up the available sites have a successively less appropriate structure and more and more hydroxyl ions are required to satisfy the co-ordination requirements, and the complexes formed become less and less stable. Finally, it could be suggested that the divergencies between the carbon-metal ratios found when precipitation occurs in the pH-stat experiments and those found in soil extracts and solutions and in the solid soil material could be due to more hydroxyl ions attached to the metal ions taken up in the pH-stat experiments compared with those taken up under the conditions in the soil. If more highly charged ion species are taken up, without displacement of an equivalent amount of hydrogen ions, the electrically neutral point is reached at a lower metal content. It does not seem unlikely that the rapid addition of metal ions and the simultaneous addition of hydroxide in the pH-stat experiments would cause uptake of metal ions with a higher number of attached hydroxyl ions, than the slow metal uptake occurring in the soil. The metals taken up from the soil will have been present in an insoluble state and their dissolution probably requires that the complexes have a higher stability, and hence involve a lower

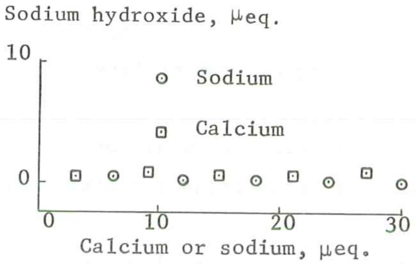

Fig. 36. Sodium hydroxide consumed by calcium or sodium chloride added to 5 ml soil extract at pH 4.8.

number of hydroxyl ions, than those formed in the pH-stat experiments.

It must be admitted that the possible reaction and precipitation mechanisms outlined above involve many assumptions and that the experimental evidence is inadequate for substantiating all details of the mechanisms. Although some modifications may prove necessary as more investigations are made, the mechanisms seem to be in agreement with the experimental data produced in this investigation and in many other investigations as well.

Fig. 36 shows the base consumption caused by addition of sodium and calcium chloride to the A_0-A_1 soil extract. Since neither sodium nor calcium takes up hydroxyl ions to any significant extent at pH 4.8 no base consumption could be caused by these ions alone, i.e. if they were added to water. It is seen from Fig. 36 that addition of sodium chloride to the soil extract does not cause any base consumption at all. In the case of calcium no base consumption is caused by addition of calcium in excess of approximately 5 μeq., and the base consumption noted for smaller amounts is so small (~ 0.5 μeq.) that it could be due to experimental error. If the base consumption is real it could be explained as being due to a small amount of hydrogen ion being displaced from the organic compounds by calcium ions forming some kind of complex compounds with these. Except for this, there is no evidence for complex formation between the two metals and the organic compounds. It is a well known fact that sodium has little tendency towards forming complex compounds with organic molecules and that calcium complexes of simple organic compounds usually are less stable than the corresponding ferric and aluminium complexes.

The results shown in Fig. 36 do not actually prove that a complexation does not occur but it would be difficult to imagine a complexation mechanism having no effect on the base consumption. If the organic compounds take up sodium or calcium ions without liberation of hydrogen ions the result would be that the assumed negative charge of the organic molecules would be neutralized and a precipitation would occur in accordance with the mechanism proposed above, but no precipitation was noted

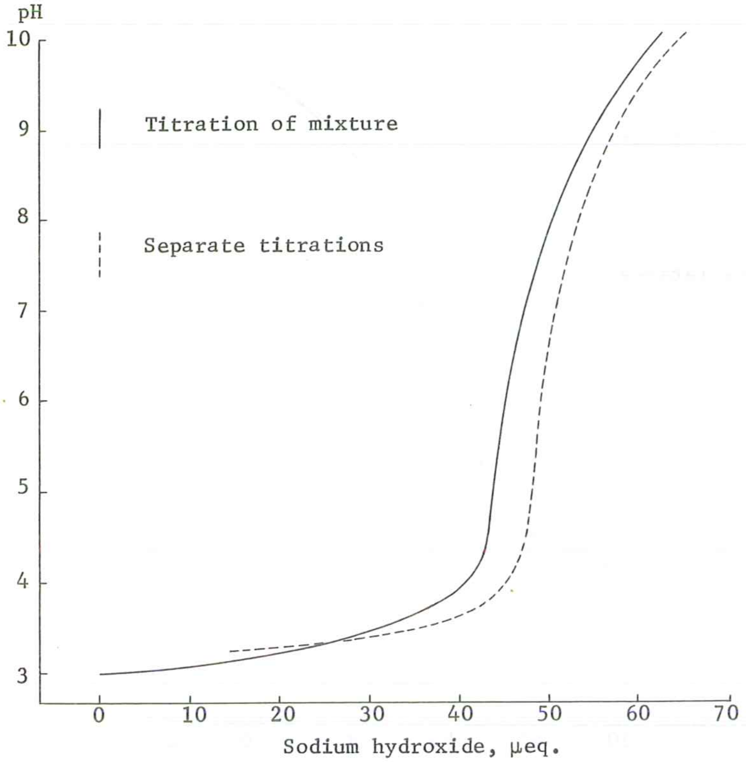

Fig. 37. Titration of a mixture of ferric chloride, hydrochloric acid and soil extract, and separate titrations of these compounds.

upon addition of sodium or calcium chloride. Although, this would be in agreement with the observations and with the mechanism outlined for the co-precipitation of the sesquioxides and the organic matter it must again be admitted that further investigations are required to provide a definite proof of the mechanism.

The results of the experiments involving sodium and calcium prove at least that the precipitation under these particular experimental conditions takes place only in the presence of ferric iron or aluminium, and that it is not due to other ions, e.g. chloride, since identical amounts of these ions were present in the sodium and calcium experiments.

The results of the titrations shown in Fig. 37 and Fig. 38 are in agreement with the results of the pH-stat experiments. At low pH values there is a tendency that the amount of sodium hydroxide consumed at a

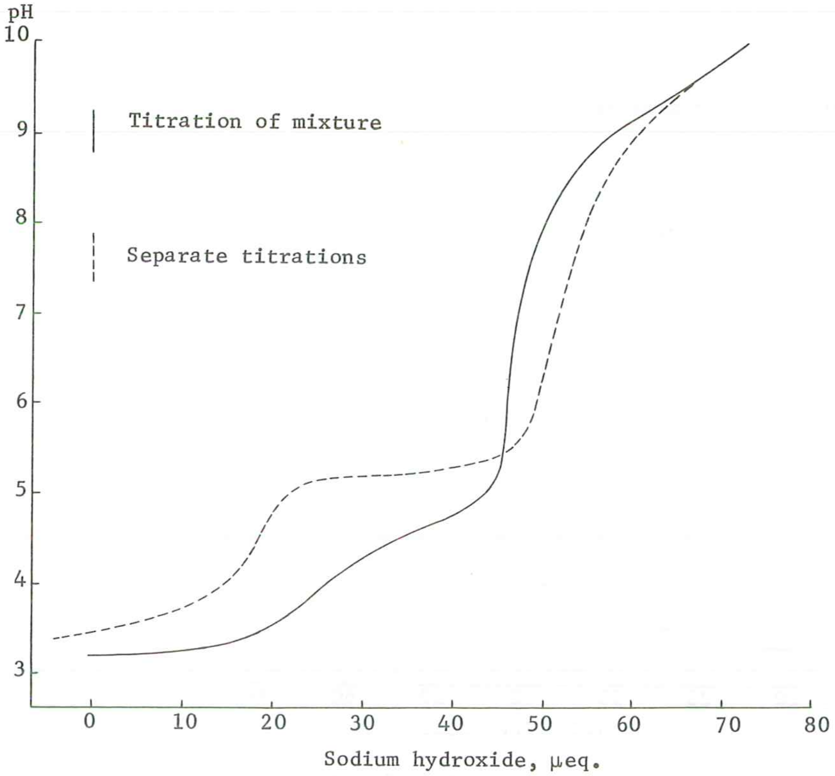

Fig. 38. Titration of a mixture of aluminium chloride, hydrochloric acid and soil extract, and separate titrations of these compounds.

given pH by a mixture of ferric or aluminium chloride and organic matter is larger than the sum of the amounts consumed when the components are titrated separately as described in section 10.1.2. This can be interpreted either as an increased displacement of hydrogen ions from the organic molecules by the metals or as an increased uptake of hydroxyl ions by the metals in the presence of organic matter. In the case of iron (Fig. 37) this effect is rather small and the curves intersect at pH about 3.4 so that the amount of sodium hydroxide consumed at any pH value higher than 3.4 by the ferric chloride-organic matter mixture is smaller than that consumed when the components are titrated separately. The difference in sodium hydroxide consumption at pH 4.8 is close to the deficit in base consumption calculated from the results of the pH-stat experiments and this difference is rather constant in the pH interval 4-7 but declines somewhat at higher pH values. The slope of both curves in the pH interval 5-9 indicates that the organic molecules have some buffer capacity in this interval. The fact that the metal-organic compounds, precipitated at lower pH-values, are redissolved at higher pH-values, as discussed in Section 10.2.1, could be explained by the negative charge of the molecules being restored through a dissociation of hydrogen ions. This would be in agreement with the precipitation mechanism postulated above.

It is seen from Fig. 38 that the base consumption calculated from separate titrations of aluminium chloride and organic matter at pH 4.8 largely corresponds to that consumed by the hydrochloric acid contained in the aluminium chloride solution. Hence, little hydroxyl has been taken up by the aluminium ions at this pH value. This is in agreement with the low uptake of hydroxyl noted when aluminium chloride was added to water in the pH-stat experiments. The large buffer capacity in the pH range 5 to 5.5 indicates that uptake of hydroxyl ions occurs mainly in this range. By contrast the major uptake of hydroxyl ions occurs at lower pH values when aluminium chloride and organic matter are titrated together. This is also in agreement with the results of the pH-stat experiments. At pH 5.4 the two curves intersect and the total amount of hydroxyl ions taken up by aluminium chloride and organic matter is higher at any pH value above 5.4 when the compounds are titrated separately than when they are titrated together. This shows that mixing of the aluminium chloride with the organic matter also causes a deficit in base consumption and, on the assumption that no negative ions other than hydroxyl ions are taken up, the negative charge of the aluminium-organic compounds at pH > 5.4 is smaller that that of the same organic compounds without aluminium. At higher pH-values the difference between the curves obtained by titrating the compounds together and separately is less regular than the corresponding difference for iron. This is probably due to a beginning formation of aluminate ions.

10.3 Effects of Organic Compounds on the Solubility of Iron and Aluminium

The experimental results reported in this chapter show that addition of ferric and/or aluminium chloride to organic matter extracted with water from the A_0-A_1 horizon of a podzol eventually leads to the mutual precipitation of the metals and the organic matter. It seems probable that the compounds precipitated are mixed hydroxide-organic matter complexes of the metals. The results indicate that precipitation occurs at a well-defined carbon-metal ratio and that the reason for precipitation is that the complexes at this ratio have no, or only a small, overall electrical charge.

It is worth noting that the results bring out more clearly the ability of the organic matter and the metals to precipitate each other than the ability of the organic compounds to maintain the metals in solution. Conclusions regarding the latter problem are difficult to draw because no or incomplete precipitation tended to occur when the metals were added to water in the absence of organic compounds. This is presumedly due to lack of equilibrium and/or stabilization of the metal hydroxides in a colloidal state. This seems in turn to be due to the fact that the metals were added as ionic solutions. The metals taken up by the organic matter in the soil will originate from some solid compounds and hence the equilibrium is approached from the opposite side, and in this case formation of a colloidal solution of the metals seems unlikely. Taking these aspects into consideration, the experimental results in combination with the results presented in chapter 9 may be taken to indicate that the organic compounds have a capacity to maintain the metals in solution as long as the amount of metal is so small that the negative charge of the organic compounds is not completely neutralized.

The mechanism outlined in this chapter implies that the organic compounds responsible for translocation of iron and aluminium during podzolization mainly have a rather high molecular weight. It cannot be rejected that simple organic compounds capable of forming more stable metal complexes may be formed in the soil, but most of these compounds would not precipitate by a mechanism as that proposed here, and these complexes would therefore tend to be leached entirely out of the profile or be deposited at random due to different mechanisms.

CHAPTER 11

LABORATORY SIMULATION OF PODZOLIZATION

11.1 Methods

The conditions under which the interactions between iron and/or aluminium and organic matter were studied in the experiments described in chapter 10 differ from the conditions prevailing in natural podzols in at least two respects. The source of the metals in the experiments was soluble salts as contrasted to some solid metal sources in the soil, and the content of salt (NaCl) was high in the experiments compared with the presumably negligible salt content in most natural podzols. With a view to eliminating these differences, a series of experiments was made in which cation exchanger columns saturated with various cations were leached with a soil extract from a podzol A horizon. The soil extract was the same as in the titrations described in chapter 10, i.e. a mixture of the four soil extracts numbered 2-5 in Table 11.

In preliminary experiments it was attempted to use a weakly acidic cation exchange resin containing carboxyl groups (Amberlite IRC-50) since this would have a controlling effect on the pH at which the reactions took place. However, it was found that this ion exchange resin on the H-form could take up only negligible amounts of aluminium (and presumably still smaller amounts of ferric iron), probably because the aluminium ions have a larger acid strength than the active groups of the ion exchange resin. Accordingly, the experiments made use of a strongly acidic cation exchange resin containing sulphonic acid groups (Dowex 50 W x 8, 50-100 mesh). It was found that this resin took up an amount of aluminium closely corresponding to its specified capacity.

The ion exchange resin was placed in glass tubes of 4.5 mm internal diameter to form a 10 cm high column supported by a plug of silica glass wool. The set-up is shown in Fig. 39. Solutions were applied through a funnel connected to the upper end of the glass tube containing the resin, and the outlet was raised to a point above the column to prevent the resin from running dry. The flow rate was controlled by means of a clamp attached to the plastic tube connecting the column to the outlet tube.

Five columns of this type were prepared from the resin originally on H-form. The columns were saturated with hydrogen, sodium, calcium, aluminium and ferric iron respectively by slowly passing two 5 ml portions of a 3 n solution of the metal (or hydrogen) chloride in question through the column. Subsequently, water was passed through the columns until chloride could not be detected with silver nitrate in the effluent.

The columns were then leached with ten 5 ml portions of distilled water, ten 5 ml portions of the A_0-A_1 soil extract, and ten 5 ml portions of distilled water, in that order. The flow rate was adjusted so that it took 6-8 hours for each 5 ml portion to pass through the column. Each 5 ml portion was collected separately and analysed for organic carbon by the dry combustion method (chapter 9) and for the metal present in the column leached. Iron and aluminium were determined by the methods described for soil extracts in chapter 9, calcium by atomic absorption spectrophotometry and sodium by flame emission spectrophotometry. The pH of all leachates was measured with a Radiometer portable pH meter equipped with a combined glass and calomel electrode.

The absorption spectrum of the untreated soil extract and of the soil extract that had passed through the columns (portion No. 5) was recorded in the wavelength region 400-1000 mμ. These measurements were made in 1 cm cuvettes against water on a Beckman model DU spectrophotometer.

11.2 Precipitation of Organic Matter in the Ion Exchanger Columns

Immediately upon application of the soil extract to the columns containing aluminium or ferric iron a deposition of organic matter could be seen near the top of the columns. As more soil extract was applied the deposition zones grew larger and after application of ten 5 ml portions of soil extract it covered nearly the entire column. This is clearly seen from Fig. 39, which shows the columns after the passage of ten portions of soil extract, and Fig. 40, which shows the columns at the conclusion of the experiment, i.e. after the columns had been leached with ten portions of water. This last water treatment caused no visible changes in the columns. When comparing the columns it should be taken into account that the ferric iron itself caused a dark colouring of the column saturated with this ion. Hence, the very dark colour of

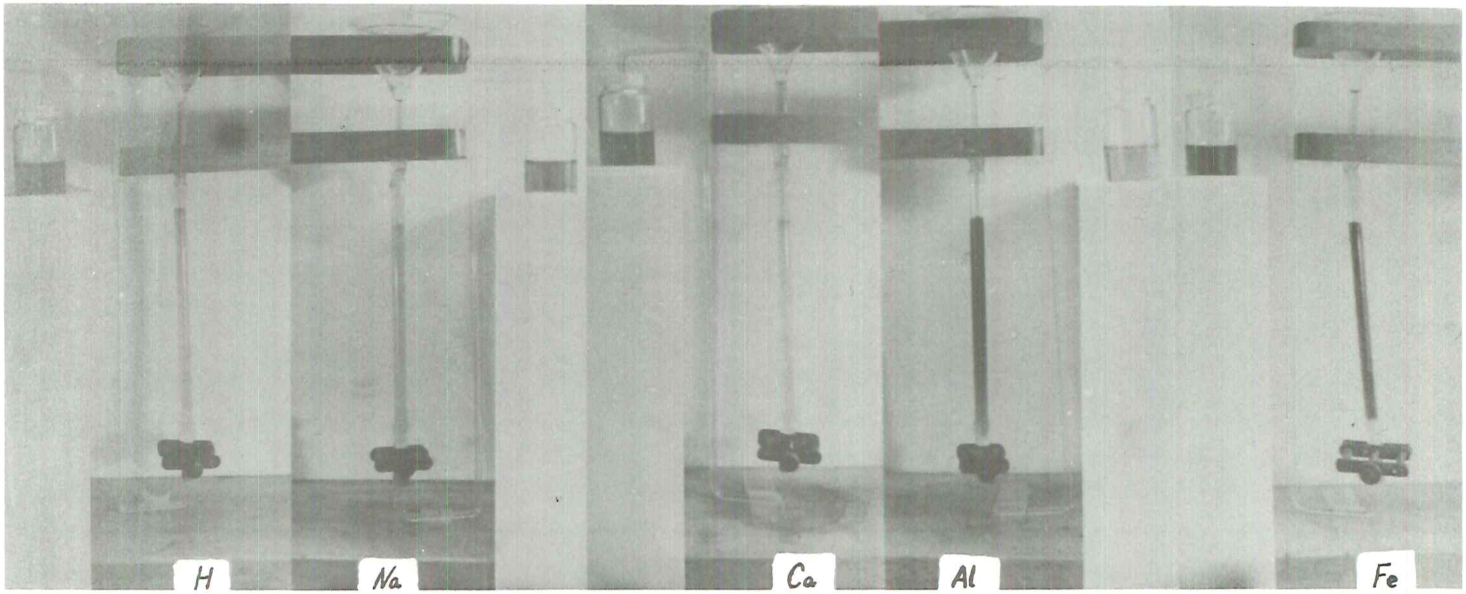

Fig. 39. Ion exchanger columns after leaching with soil extract.

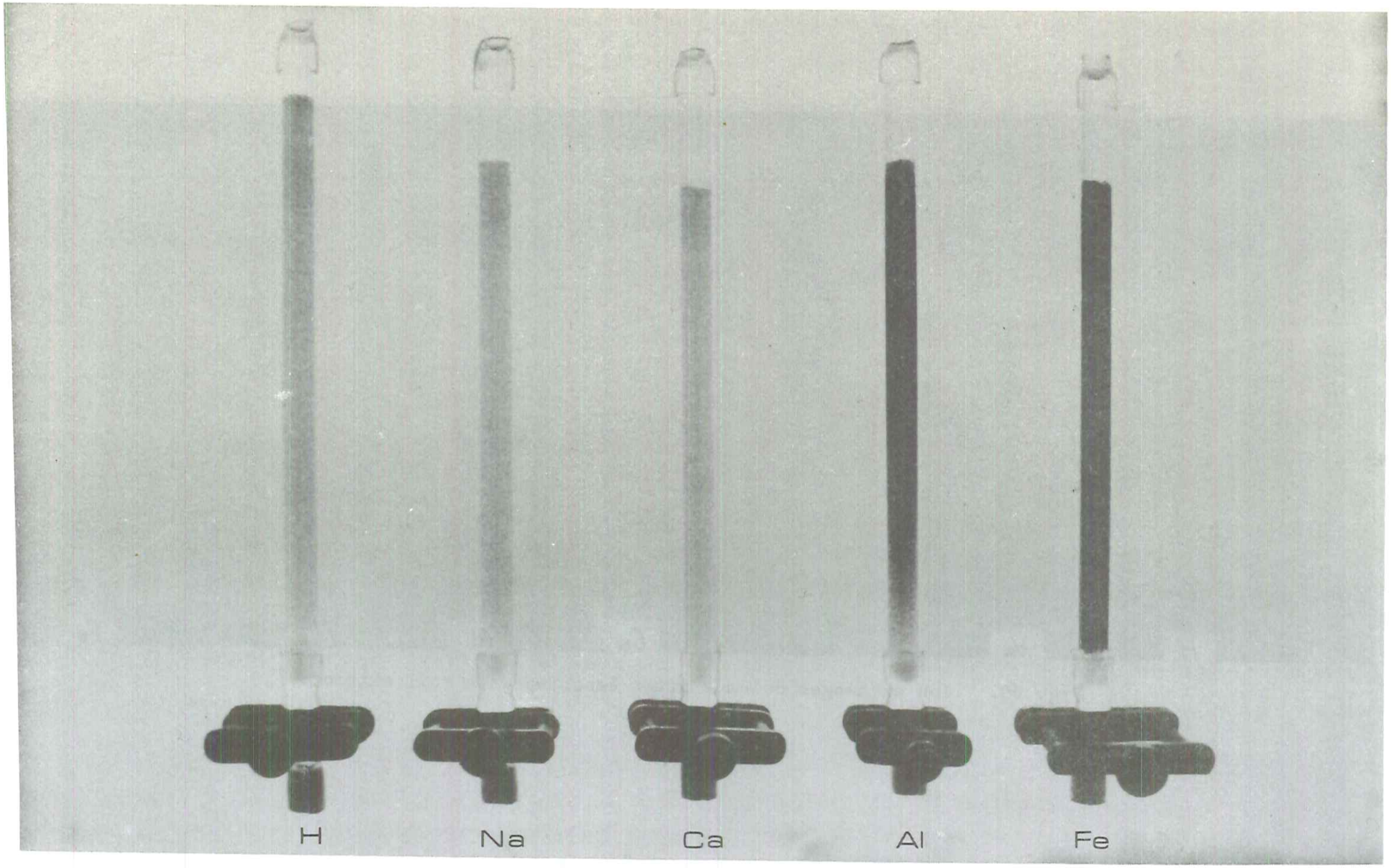

Fig. 40. Ion exchanger columns after final leaching with water.

the ferric iron column in Fig. 39 and 40 is not due to organic matter alone but mainly to the iron itself. Despite the original colour of this column it could be clearly seen during the experiment that organic matter was being deposited in the column.

The original colour of the column saturated with aluminium was, as far could be seen by the naked eye, identical to that of the columns saturated with hydrogen, sodium and calcium. All these columns had the faint yellow colour of the ion exchange resin itself. Hence, the difference in colour between the column saturated with aluminium on the one hand, and those saturated with hydrogen, sodium and calcium on the other, as shown in Fig. 39 and 40, is solely due to organic matter deposited in the column saturated with aluminium. It can be seen that a small zone at the bottom of this column has a lighter colour than the rest of the column and hence contains a smaller amount of deposited organic matter. Compared with the column saturated with aluminium, those saturated with hydrogen, sodium and calcium only contain very small amounts of deposited organic matter.

These observations are confirmed by the carbon analyses shown in Table 26. The small, but probably significant, carbon contents in the leachates from the initial treatment of the columns with water indicate that a small amount of organic matter is given off from the ion exchange resin to the water.

The carbon content of the untreated soil extract, as calculated from the average of several analyses made intermittently with the analyses of the leachates reported in Table 26, was 148 mg C per l. This is slightly different from the results shown in Table 11, but since it is based on a large number of analyses made simultaneously with the analyses of the leachates, it will be used for comparison with the results shown in Table 26. It can be seen that there is a considerable reduction in the carbon content of the soil extract that has passed the aluminium saturated resin and a smaller, but still marked, decrease in the carbon content of the extract that has passed the resin saturated with ferric iron. Compared with these differences the decreases in the carbon content caused by the hydrogen and calcium saturated resins, and the increase caused by the sodium saturated resin, are relatively small.

To evaluate the statistical significance of these decreases and increases the differences between the mean values of the carbon content

Table 26. Carbon Contents of Leachates from Ion Exchanger Columns (mg per 1)

Liquid applied	Portion No.	Column saturated with				
		H	Na	Ca	Al	Fe
Distilled water	1	3	3	4	3	1
	2	6	3	6	2	2
	3	5	6	10	6	2
	4	6	4	7	2	1
	5	2	3	7	2	2
	6	1	3	2	2	1
	7	2	6	0	0	1
	8	1	3	3	2	1
	9	2	5	3	1	1
	10	2	7	7	1	1
A_o-A_1 soil extract	1	84	111	88	54	49
	2	135	161	140	120	116
	3	148	155	132	109	123
	4	117	165	130	108	120
	5	137	154	141	98	128
	6	140	157	124	99	129
	7	129	157	131	113	116
	8	130	153	133	100	128
	9	146	156	140	111	126
	10	149	159	130	122	123
Distilled water	1	67	70	68	54	68
	2	4	8	9	33	17
	3	9	11	9	13	17
	4	7	2	3	10	5
	5	4	11	7	14	7
	6	5	5	6	4	6
	7	5	4	6	5	5
	8	1	3	6	8	4
	9	3	1	2	7	5
	10	3	5	3	5	4

of leachates No. 2-10 from each column, and the mean value obtained for the untreated soil extract as described above, were subjected to a t-test. Any possible blank value caused by the resins giving off organic carbon to the extracts was neglected. It was found that the decreases caused by the aluminium and iron saturated resins were highly significant ($P < 0.001$), and the decrease caused by the calcium saturated resin was significant to the five percent level, while the effects of the hydrogen and sodium saturated resins were not even significant to this level.

Table 26 shows that more organic matter is retained in the column saturated with aluminium than in that saturated with iron. It can further be seen that a small amount of organic carbon is leached from these columns by the water applied to the columns after the soil extracts; but after the passage of 3-5 portions of water the carbon content declines to values similar to those found before the application of the soil extract, and the total amount of organic matter removed from the columns accounts for only a small fraction of that retained during the leaching with soil extract. The low carbon content in portion No. 1 of the soil extract, and the high carbon content in portion No. 1 of the water applied after the soil extract, are of course due to mixing with water or soil extract left over in the columns.

11.3 Metal Content of Leachates

Fig. 41-44 show the metal content of each portion of leachate collected from the four columns saturated with metal ions. It can be seen that the columns saturated with aluminium or iron release no or insignificant amounts of these metals to distilled water. The first 3-5 water leachates collected after the leaching with soil extract contain some aluminium or iron. This is in agreement with the observation mentioned above, that these leachates contain some organic matter. The calcium content of the water leachates is also negligible, about 0.7 mg per l in the leachates collected before as well as after the treatment with soil extract. However, a considerable amount of sodium (7.1 mg per l) seems to be released to the water from the sodium saturated resin. Although it cannot be excluded that some of the sodium originates from the glassware with which the leachates have been in contact, the bulk has probably been supplied by the resin. The reason that more sodium, compared with calcium, aluminium and iron, is released is presumably that the monovalent sodium ion is adsorbed less

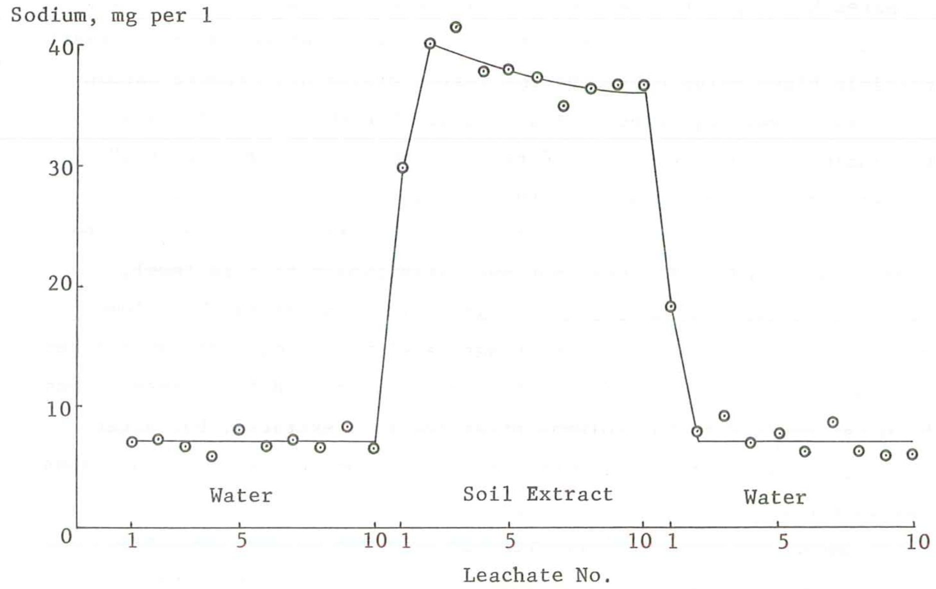

Fig. 41. Sodium contents of leachates from sodium saturated ion exchanger column.

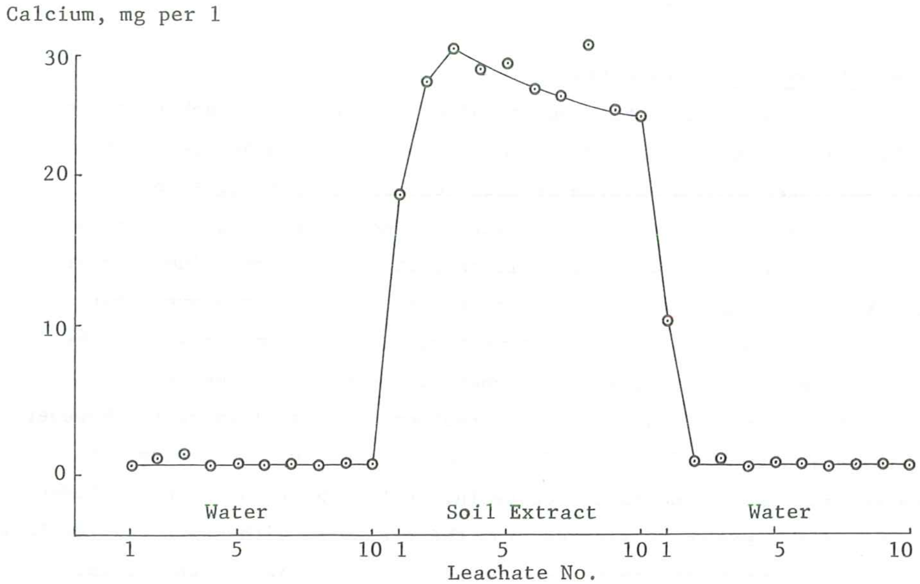

Fig. 42. Calcium contents of leachates from calcium saturated ion exchanger column.

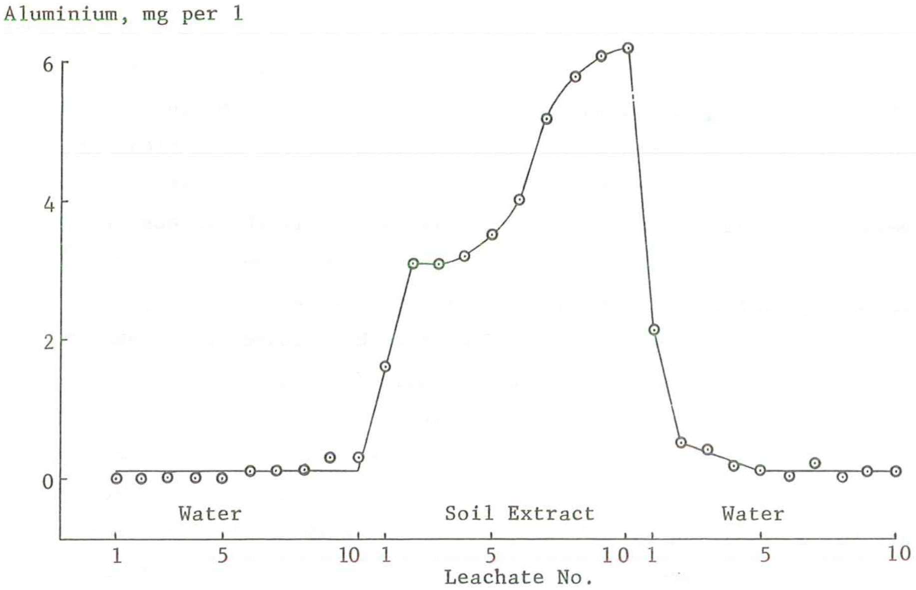

Fig. 43. Aluminium contents of leachates from aluminium saturated ion exchanger column.

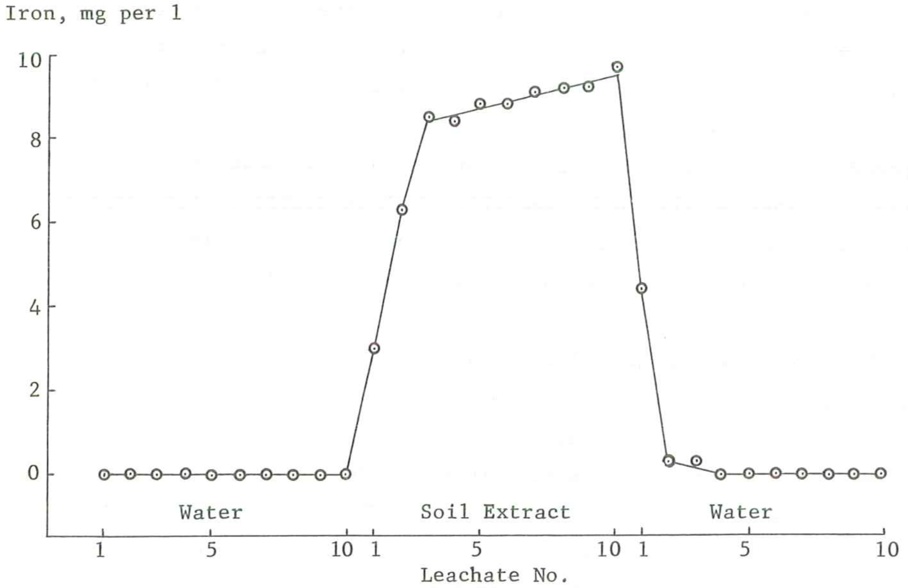

Fig. 44. Iron contents of leachates from ion exchanger column saturated with ferric iron.

strongly to the ion exchange resin than the di- and trivalent ions.

Fig. 41 and 42 show a small tendency towards a decline in the amount of sodium and calcium taken up by the soil extract with the increasing amount of soil extract applied. However, this decline is relatively small. The mean sodium and calcium content of soil extract leachates Nos. 2-10 are 37.7 and 26.2 mg. per 1 respectively. If these values are corrected for the metal contents of the water leachates given above, it appears that the compounds present in the soil extract have caused an uptake of approximately 1.3 meq. per 1 of either metal. The soil extract must have an identical concentration of negatively charged ion species. This condition must be fulfilled irrespective of the extent to which the compounds in the leachates are ionized. It cannot be excluded that the soil extract has a small content of inorganic anions such as chloride or sulphate. If it is assumed that the concentrations of such ions are negligible compared with the concentration of organic anions, it can be calculated from the carbon content of the extract that the organic compounds contain about 110 g of carbon, i.e. about 9 C-atoms, per equivalent of negative charge. Since the assumption concerning the absence of inorganic anions is probably not fully justified, this value may be regarded as a lower limit. In addition, the organic compounds may contain some weakly acidic groups which do not contribute to the uptake of sodium or calcium from the ion exchange resin and some groups engaged in strong complex compounds with metals other than sodium or calcium. However, the small content of other metals, and especially of those liable to form stable complex compounds, in the original soil extract (as shown in Table 27) indicates that the latter phenomenon has no appreciable effect on the result of the calculation.

Table 28 shows the pH values of all the water and soil extract leachates. No great accuracy should be assigned to the pH-values tabulated for the water leachates. The readings obtained during the measurements of these values were rather unstable, indicating that these leachates have a low buffer capacity. Taking into account this limitation, the kind of ion with which the column is saturated seems to have no effect on the pH of the water leachates. Similarly, there are no differences between the pH values of the water leachates collected before and after application of the soil extract. The only exception to this rule is noted for the three water leachates collected immediately

Table 27. Metal Content of the A_0-A_1 Soil Extract Used for the Leachings of the Ion Exchanger Columns (mg per 1)

Na	3.8
K	5.9
Ca	0.65
Mg	0.24
Fe	1.74
Al	0.83

after the soil extract leachates from the columns saturated with aluminium and iron. The pH values of these leachates are lower and better defined than those of the remaining water leachates. The reason for this is, of course, that these leachates contain some organic matter, as mentioned above.

There is a definite relationship between the ion with which the resin is saturated and the pH of the soil extract leachates. Furthermore, judging from the stability of the readings, these leachates have a considerably larger buffer capacity than the water leachates. As would be expected, the leachates having the lowest pH are obtained from the column saturated with hydrogen ions. A comparison of these pH values with the total content of negatively charged groups, as calculated above from the metal content of the leachates from the columns saturated with sodium or calcium, indicates a high degree of dissociation of these groups. If the entire amount of negative charge is due to organic anions these have an acid strength exceeding that of normal carboxyl groups. However, since it cannot be excluded that the soil extract contains some inorganic anions such as chloride and sulphate, the corresponding strong inorganic acids may contribute to the low pH of the soil extract leachates from the hydrogen saturated column. It can be seen that there is a difference of about 1 pH-unit between the leachates from the calcium and sodium saturated resins. This difference may be due to a number of factors such as differences in the degree of dissociation or slight differences in the amount of metal taken up from the resin. Although it has been shown above that approximately equivalent amounts of the two metals are taken up, it is also clear that there is a small but significant decrease in

Table 28. pH of Leachates from Ion Exchanger Columns

Liquid applied	Portion No.	Column saturated with				
		H	Na	Ca	Al	Fe
Distilled water	1	7.4	7.7	8.1	7.5	7.6
	2	7.6	7.6	7.7	7.7	7.3
	3	7.3	7.3	7.5	7.7	7.5
	4	7.4	7.6	7.7	7.8	7.6
	5	7.5	7.7	7.6	7.9	7.5
	6	7.6	7.7	7.8	7.7	7.8
	7	7.7	7.8	7.8	8.2	7.9
	8	7.6	7.7	7.9	7.7	7.5
	9	7.5	7.9	7.9	7.8	7.6
	10	7.8	7.6	7.6	7.8	7.6
A_o-A_1 soil extract	1	3.58	7.26	6.10	6.37	3.88
	2	3.31	6.78	5.78	5.58	3.54
	3	3.19	6.74	5.40	5.84	3.52
	4	3.27	6.68	5.48	5.84	3.53
	5	3.26	6.62	5.53	5.38	3.47
	6	3.28	6.57	5.33	5.31	3.52
	7	3.27	6.38	5.49	4.66	3.48
	8	3.28	6.42	5.55	4.53	3.47
	9	3.28	6.46	5.33	4.56	3.45
	10	3.26	6.48	5.47	4.55	3.46
Distilled water	1	3.76	6.66	6.49	5.73	3.87
	2	7.1	7.4	7.3	6.80	6.80
	3	6.7	7.8	7.2	6.88	6.83
	4	7.0	8.4	7.5	7.2	7.3
	5	7.6	8.4	7.4	7.1	7.3
	6	7.8	7.7	7.4	7.2	7.2
	7	7.8	7.7	7.5	7.0	7.3
	8	7.0	8.2	7.8	7.2	7.6
	9	7.6	7.7	7.9	7.0	7.3
	10	7.7	7.7	7.5	7.1	7.5

the carbon content of the extract that has passed the calcium saturated resin, and small differences in these parameters could cause the pH difference.

As would be expected from the acidity of ferric and aluminium ions the leachates obtained from the columns saturated with these ions have a lower pH than those obtained from the sodium and calcium saturated columns. Since the ferric ion is a stronger acid than the aluminium ion the lowest pH values are recorded in the leachates from the column saturated with ferric iron. Furthermore, the pH value of the leachates from this column remains fairly constant throughout, while the pH of the leachates from the aluminium saturated resin seems to decline with the increasing amount of soil extract applied to the resin. At the same time the aluminium content of the leachate increases, and there is a fairly close relationship between the concentrations of hydrogen and aluminium ions in the leachates. The amount of iron and aluminium, calculated on an equivalent basis, taken up by the soil extract is somewhat smaller than the corresponding amounts of sodium and calcium even if allowance is made for the amount of organic matter deposited in the columns. The $\frac{C}{Al}$-ratios range from 34 to 17 and the $2\frac{C}{Fe}$-ratios from 29 to 25. These values are of a magnitude similar to those found for soil extracts and solutions from B horizons.

No attempt will be made to give a detailed account of the, presumably rather complicated, interactions taking place between the ferric iron or aluminium on the ion exchange resin, the ion exchange resin itself, the soluble constituents of the soil extracts and the precipitates in the ion exchanger columns. The precipitation taking place in the columns is likely to be due to formation of electrically neutral compounds between ferric iron or aluminium and organic matter as suggested in the preceding chapter, but it could also be caused by the formation of positively charged compounds becoming adsorbed on the negatively charged resin. However, both mechanisms would require the formation of some compounds between the metals and the organic matter, and both mechanisms could operate in soils where the solid soil material has cation exchange properties.

11.4 Optical Density of Leachates

Fig. 45-50 show the absorption spectra of the untreated soil extract and of the leachates from the ion exchanger columns. The general pattern of the absorption spectra is similar for the untreated soil extract and all leachates. At wavelengths higher than 800 mμ the extinction is negligible, and from 800 mμ it increases strongly with the decreasing wavelength. Similar absorption spectra were found for organic matter extracted from various soils by Kononova (1966), who found that humic acids caused a higher extinction than fulvic acids at all wavelengths from 465 mμ to 726 mμ. She also found that humic acids from a chernozem caused a substantially higher extinction than humic acids from a so-called strongly podzolic soil in the wavelength region mentioned. She attributed a higher optical density to a higher degree of condensation of the aromatic rings in the organic structures.

Scheffer (1954) and Welte (1955) found a relationship between the steepness of the absorption curve and the kind of soil horizon from which the humic acids that were used in the studies had been extracted. They used the so-called $\frac{E_4}{E_6}$ -ratio, which is the ratio of the extinction measured at 465 mμ to that measured at 665 mμ, as an index of this steepness. According to Kononova (1966) the value of this ratio for humic acids from so-called podzolic soils is about 5.0, and between 6.8 and 8.5 for fulvic acids, irrespective of the kind of soil. Schnitzer (1970) found that this ratio varied from 8.6 to 13.2 for fulvic acids extracted with sodium hydroxide from 9 different podzols, and he attributed these high ratios to an open organic structure with a low degree of condensation. The $\frac{E_4}{E_6}$-ratio calculated from Fig. 45-50 are shown in Table 29. Since the extinction at 665 mμ is comparatively small for the untreated soil extract as well as for the leachates, a small difference in this extinction will have a large effect on the $\frac{E_4}{E_6}$-ratio. This should be taken into account when judging the values in Table 29 and no rigorous conclusions should be based on small differences between the ratios.

In addition to the extinction as measured against water the differences between the extinction caused by the leachate in question and that caused by the untreated soil extract are plotted in Fig. 46-50. It can be seen that these differences in the case of sodium and calcium are very small. Small positive differences are recorded for both metals at low wavelength, but compared with the absolute extinction occurring at these wavelength the differences are almost negligible. The $\frac{E_4}{E_6}$-ratios of these two leachates are also close to that of the untreated soil extract.

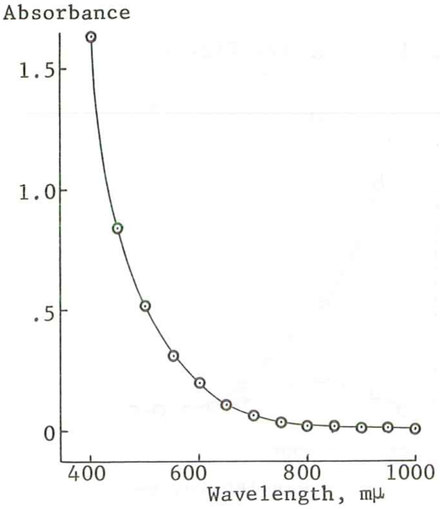

Fig. 45. Absorption spectrum of untreated soil extract.

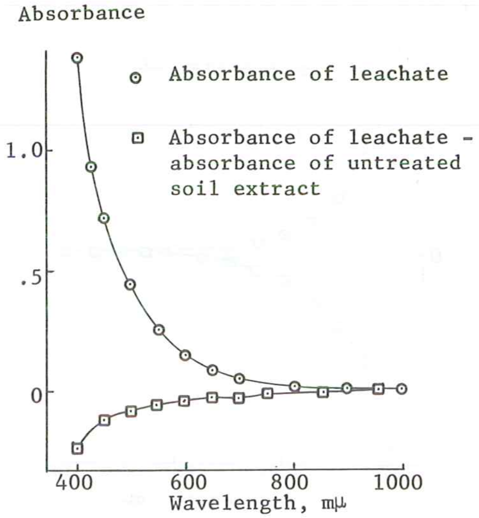

Fig. 46. Absorption spectrum of leachate from hydrogen saturated ion exchanger column.

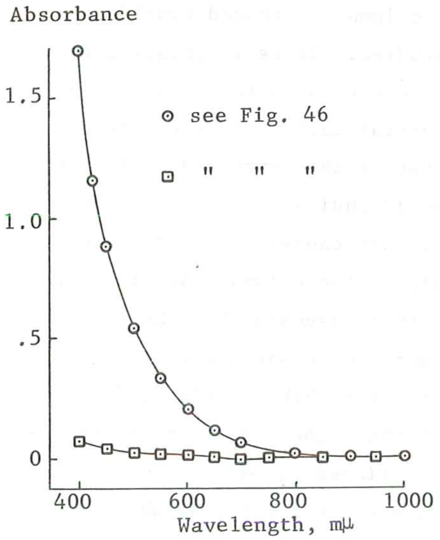

Fig. 47. Absorption spectrum of leachate from sodium saturated ion exchanger column.

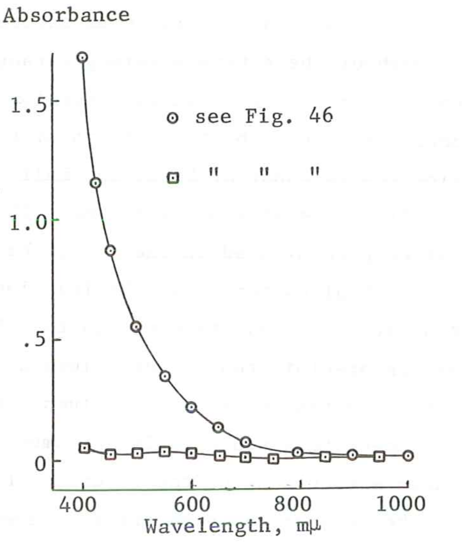

Fig. 48. Absorption spectrum of leachate from calcium saturated ion exchanger column.

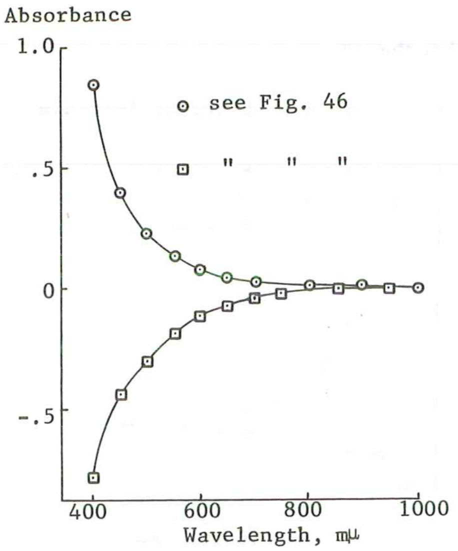

Fig. 49. Absorption spectrum of leachate from aluminium saturated ion exchanger column.

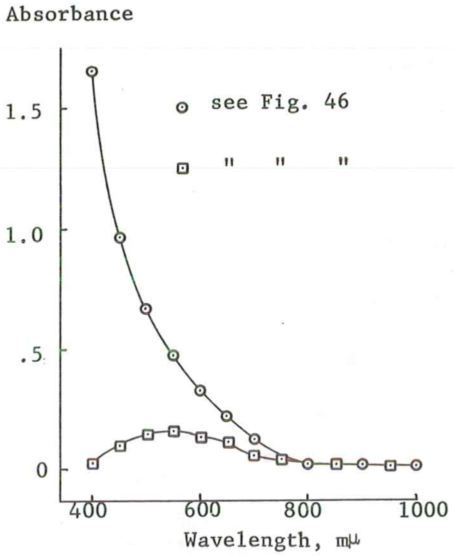

Fig. 50. Absorption spectrum of leachate from ion exchanger column saturated with ferric iron.

It is clear from Fig. 49 that the extinction of the soil extract which has passed the aluminium saturated column is reduced considerably throughout the entire wavelength range studied. It is interesting to note that, whereas the measured reduction in the carbon content (Table 26) does not exceed about one third of the initial carbon content, the extinction is about or below one half of that of the untreated soil extract at all wavelengths below 800 mμ. This would indicate that the organic matter precipitated in the ion exchange column causes a higher extinction, per unit of carbon, than the fraction passing the column. According to Kononova's (1966) statement quoted above this suggests that the organic matter precipitated in the column has a more condensated aromatic structure than that passing the column. According to Schnitzer's (1970) statement this would be in agreement with the higher $\frac{E_4}{E_6}$-ratio of the organic matter passing the column, but as mentioned already these ratios may be subject to large errors. However, since the water solubility of the organic matter must be expected to decrease with the increasing degree of condensation it seems reasonable to assume that the organic matter retained in the column has a higher degree of condensation than that passing the column.

Table 29. $\frac{E_4}{E_6}$-Ratios of Untreated Soil Extract and Leachates from Ion Exchanger Columns

Untreated soil extract	7.2
Leachate from hydrogen saturated column	9.6
Leachate from sodium saturated column	8.1
Leachate from calcium saturated column	7.0
Leachate from aluminium saturated column	9.3
Leachate from iron saturated column	4.4

Despite the fact that a reduction in the carbon content was also caused by the resin saturated with ferric iron, Fig. 50 shows that the leachate from this column has a higher optical density than the untreated soil extract in the wavelength range investigated. This must be due to extinction caused by the iron taken up from the resin. This iron, obviously, not only compensates for the extinction caused by the organic matter deposited in the column but causes additional extinction. It is impossible to decide whether the increased optical density is due to the ferric iron itself or to some complex organic iron compounds. The ferric ion is colourless (Bjerrum 1956) and, furthermore, the concentration of this ion is negligible at the pH of the leachate (conf. chapter 8), but hydroxide complexes or other inorganic ferric complexes might cause extinction in the wavelength range where the largest differences are found. However, the total iron concentration in the leachate is, after all, relatively small and it seems more likely that the extinction is caused by some iron complexes involving organic matter. The difference in colour between the leachate from the iron saturated column and the untreated soil extract could be seen with the naked eye. It should be noted that the difference is small at 400 mμ and that the trend of the plot suggests that negative differences would be found at smaller wavelengths. If this is the case it would be consistent with a decrease in organic matter content. The iron also causes a considerable reduction in the $\frac{E_4}{E_6}$-ratio. This is inconsistent with the effect of aluminium and shows that this index will not give a correct assessment of the structure of the organic compounds in the presence of iron.

Fig. 46 shows that the hydrogen saturated resin has caused a small decrease in the extinction at wavelengths from 400 to 800 mμ. Although the absolute difference is largest at 400 mμ, the relative difference is larger at higher wavelengths. This may be due to a small pH effect on the extinction caused by the organic compounds or to retention of a small amount of organic matter in the ion exchanger column. Kononova (1966) found only a slight pH effect on the extinction caused by humic acids, but she only investigated the pH range 7-13. As discussed in section 11.2 there seems to be a small decrease in the carbon content of the extract that has passed the hydrogen saturated column, although this decrease is not statistically significant. However, a small deposition would be expected to remove the organic matter having the most condensated aromatic structures from the extract and would most readily explain the reduced extinction. It would also be consistent with the increase in the $\frac{E_4}{E_6}$-ratio, although this index should be treated with some caution.

In general, it may be stated that the results of the experiments reported in this chapter confirm the explanations proposed in the preceding chapter for the translocation of organic matter, iron and aluminium during podzolization. The organic matter in the soil extract is capable of mobilizing iron and aluminium from an ion exchange resin saturated with one of these ions. However, a fraction of the organic matter is precipitated by the metals and this fraction is larger in the case of aluminium than in that of iron. Although alternative explanations could be proposed, the results of the leaching studies agree with a mechanism involving formation of mixed hydroxyl-organic matter complexes of ferric iron and aluminium, as suggested in the previous chapter.

CHAPTER 12

THE OVERALL PODZOLIZATION PROCESS

The findings reported in the previous chapters strongly suggest that podzolization is a result of interactions between iron and aluminium compounds on the one hand, and originally water-soluble organic compounds on the other. Hence, the formation of such water-soluble organic compounds is a necessary prerequisite for podzolization. Except for solubility in water these organic compounds seem to have many characteristics in common with the normal humus compounds. It therefore seems reasonable to assume that these compounds are produced during the decomposition of plant residues in the soil by biological reactions of a similar nature to those leading to the formation of normal, insoluble, humus compounds.

As discussed in chapter 4 it is well known that the organic matter of the A horizon of podzols is less decomposed than that of most other soils. This is due to the low and little diversified biological activity of these soils. In turn, this may be attributed to the acidity and the low content of mineral nutrients of podzols. The more specialized microflora might cause a production of less condensated and hence more soluble organic compounds than those formed by the more diversified microflora of other soils.

It also seems likely that the chemical properties of the soils may affect the reactions of the organic compounds directly. A higher soil pH may give rise to the formation of more highly condensated compounds. This effect may not be solely due to the hydrogen ion activity of the soil solution itself, but also to the presence of a larger amount of adsorbed divalent metal ions in soils at a higher pH. The pH of a soil is closely related to the base saturation percentage of the adsorption complex and in most non-acid soils the dominant adsorbed cation is calcium. Many authors (e.g. Kononova 1966) state that calcium plays role in maintaining the insolubility of humus compounds. This may be due to some insoluble complexes formed between the organic compounds and calcium. It is a general experience (Kononova 1966) that the amount of organic matter that can be extracted from a soil by some of the reagents discussed in chapter 5 may be increased if the soil is pre-treated with acid, and this effect is usually attributed to the removal of calcium from the organic compounds. Another fact that can be taken to confirm such an effect of calcium is that some of the most decomposed, and most highly condensated, humus found in any soil is present in chernozem soils that are rich in adsorbed calcium. This should not be taken to indicate that a high content of adsorbed calcium is the only factor necessary for the formation of highly condensated humus or that adsorbed calcium will always cause this result. The nature of the humus formed is probably the result of complicated interactions of many factors, one of which may be the calcium content of the soil.

Since many acid soils are not podzolized it is clear that a high calcium content is not the only factor that can hamper podzolization. It is clear from the experiments and investigations reported in the previous chapters, and from the podzolization mechanism proposed, that if the A horizon contains sufficient iron or aluminium the soluble organic compounds, or at least the fraction of these that can precipitate in the B horizon, would precipitate and hence be immobilized in the A horizon. Under such conditions no podzolization could take place. Since aluminium is more effective in immobilizing the organic compounds, the content of easily available aluminium is particularly crucial in this respect. It is well established that the dominant adsorbed cation of clayey acid mineral soils is aluminium that has been liberated from various minerals and amorphous aluminium compounds. Since the adsorbed aluminium must be assumed to react easily with the organic compounds, podzolization would not take place at all, or would be of a very limited extent, in such clayey soils. On the other hand the results reported in Table 7 show that the sandy podzols investigated here are low in easily soluble aluminium. Hence, a major reason that clayey soils are unlikely to become podzolized is their larger content of easily available aluminium.

This conclusion gives a very simple and, in the light of the experimental results reported in the previous chapters, obvious explanation of the fact that only sandy soils are susceptible to podzolization. On the other hand it may seem paradoxical that a low content of easily available aluminium and iron is one of the necessary conditions for podzolization. Nevertheless, this fact seems properly established and in agreement with the general properties of podzols. Furthermore, it also underlines the greater importance of aluminium, as compared with iron, in the process of podzolization. When podzolization has more often been associated with a translocation of iron than of aluminium, the main reason seems to be that the iron compounds because of their colour may be more easily recognized by a visual examination of the soil.

Relying on previous discussions and findings it is possible to give a fairly simple description of the conditions necessary for podzolization and of the overall process. As long as a soil has a fairly high pH value and a high content of adsorbed divalent cations, mainly calcium, podzolization will not take place, since water-soluble organic compounds will be present in insufficient amounts. If the soil has a high clay content it will, even in the absence of calcium, be rich in easily available aluminium capable of precipitating the water-soluble organic compounds as they are formed and podzolization is again unlikely to occur. The soils susceptible to podzolization are, therefore, sandy soils which contain little calcium, aluminium or iron, and become acid easily. In such soils the water-soluble organic compounds will take up only small amounts of aluminium and iron in the place where they are formed. In a humid climate these compounds will be leached downwards. During their downward movement they will take up more and more aluminium and iron. The organic compounds probably remain soluble only as long as they have a sufficient number of negatively charged functional groups. The uptake of aluminium and iron presumably causes a neutralization of this charge. After a certain amount of metal has been taken up precipitation occurs because of the reduced charge.

In the preliminary stages of the podzolization of a given soil sufficient available aluminium and iron will be present in a shallow soil layer and precipitation will occur at shallow depth. As podzolization proceeds the precipitation horizon will move towards greater depth. At the same time the A horizon becomes more and more deficient in available aluminium and iron, and the compounds arriving in the B horizon will have a lower and lower metal content. Since it has been shown that the organic compounds are relatively strong acids the upper soil layers will become very acid. These factors make podzolization a process that amplifies itself as long as the external conditions remain unchanged, and the B horizon will move to greater and greater depth. There will be a constant competition for aluminium and iron between the organic compounds in the leaching water and those in the solid soil material. At the upper boundary of the B horizon the soluble organic compounds will tend to remove metals from metal-organic matter compounds precipitated earlier.

This will in turn tend to disperse some of the organic matter originally precipitated. This organic matter will move further downwards and may be precipitated at greater depth where the availability of aluminium and iron is higher. This process may be repeated several times. Such a mechanism is in accordance with the field observations reported by Tonkonogov (1969, 1971). These observations showed that the thickness of the A_2 horizon of humus-illuvial podzols decreased, while the humus content of the B_1 horizon increased, with the increasing sesquioxide content in the C horizon.

The results obtained in this investigation indicate that the precipitation of the organic compounds in the B horizon is incomplete. A fraction of the organic material may be leached entirely out of the profile and remove some metals from the A + B and/or the C horizons.

The process will of course be modified by the biological decomposition of the organic compounds precipitated in the B horizon. Biological alterations may make these compounds less susceptible to redissolution on partial removal of the metals, but the biological decomposition may also cause production of new water-soluble compounds. The organic compounds dissolved in the leaching water must also be assumed to be subject to biological attack but (although this may alter their solubility characteristics) it can hardly be responsible for the regular precipitation pattern observed in podzols.

The results of the investigation reported in this text seem to provide a solid foundation for postulating the podzolization mechanism outlined above. However, a number of the problems need further study. The mechanism of the reactions between the metals and the organic compounds is incompletely understood. It has been proposed that the precipitation occurs because of neutralization of the negatively charged functional groups but this needs more experimental verification. It is important, however, that the studies be made as far as possible on natural organic compounds actually occurring in podzols. The use of simple model compounds having only some of the characteristics of the natural compounds may provide correct answers to some questions but are likely to cause erroneous conclusions in many other cases. Valuable information might be obtained from comparative studies involving experiments similar to those described in this text, but including soils other than podzols.

SUMMARY

Chapter 1. The Podzol Concept

The designation 'podzol' is of Russian origin. Its literal meaning is usually assumed to be 'under ashes', but it may also be interpreted as 'ashy soil'. It was introduced into Western soil nomenclature in the beginning of the twentieth century.

In Russian soil literature the presence of a bleached layer is considered the most important feature of a podzol and many so-called podzols or podzolic soils have an illuvial horizon with an elevated clay content as compared with the over- and underlying horizons. In Western Europe the podzol designation is normally limited to soils in which a translocation of humus, iron and/or aluminium compounds has taken place and to qualify as a podzol, a soil must contain a B horizon enriched with these compounds. This is clearly defined in the soil classification systems presently used in Britain, France and Germany.

Some Soviet soil scientists are inclined to follow the West European trend towards a distinction between soils that have been subject to clay translocation and those that have been subject to translocation of humus, iron and/or aluminium compounds. However, most present Soviet soil scientists seem to be reluctant to accept a difference in kind between the two translocation phenomena since they believe that an elevated clay content in a subsurface horizon is due to neosynthesis of clay within that horizon rather than to a translocation of unaltered clay particles from overlying horizons.

Until recently the podzol definition applied by the soil classification systems used in the USA and Canada was more similar to the Russian than to the West European concept and many soils characterized mainly by a textural B horizon were classified as podzolic soils. However, in recent American and Canadian soil classification systems, a clear distinction has been made between the two groups of soils and although the podzol designation is not used in the present American soil classification system, the soils classified as 'spodosols' are practically equivalent to those classified as podzols in Western Europe. Also the international soil classification system used by FAO/UNESCO for compilation of a soil map of the World makes a clear distinction between true podzols and soils that have been subject to clay translocation.

Hence, with the exception of the Soviet podzol concept, there is a high degree of agreement among the remaining soil classification systems that a true podzol must contain an eluvial horizon impoverished in sesquioxides and an illuvial horizon enriched in these compounds and/or humus. In the present study this definition has been adopted and the discussion relates throughout to this podzol concept.

Chapter 2. Environment and Some General Properties of Podzols

Well developed podzols have rather distinct horizons. The upper horizon (A_0) of a virgin podzol typically consists mainly of poorly decomposed organic matter (mor). This horizon may rest directly on a strongly bleached horizon (A_2) from which sesquioxides have been removed, but more often a mineral horizon (A_1) with a dark colour due to humus compounds are found between the A_0 and A_2 horizons.

The illuvial horizon (B) found below the A horizon is typically made up of an upper subhorizon (B_1) with a dark colour originating from humus compounds and a lower subhorizon (B_2) with a brown or reddish-brown colour due to iron compounds. Often tongues of the B horizon extend downward into the C horizon, which is usually considered to be fairly unchanged parent material. The colour and other properties of this horizon depend on the nature of the parent material. Often it is yellow sand.

Podzols are developed in a humid climate. Although often considered soils of cool regions podzols have been described in many climatic zones from boreal forests to the tropics.

Podzols, as defined in chapter 1, seem to occur only on coarse textured parent materials. Their typical natural vegetation in temperate regions is coniferous forest or heath vegetation, but they also may be found under various other types of vegetation. Tropical podzols are found mainly under savannahs or rain forests.

The drainage characteristics of podzols are subject to variations. Most soil classification systems make a distinction between well drained and poorly drained podzols. The latter usually contain mottles, at least in the lower part of the profile. The drainage characteristics also affect other properties of the soils.

Acidity is an inherent characteristic of podzols. The pH of the upper horizons will often be below 4 and a slight increase in pH is normally encountered with depth. The acidity is due to a base saturation percentage close to zero of the cation exchange complex, which, due to the sandy texture, consists mainly of organic compounds.

Chapter 3. Podzol Soils Investigated in the Present Study

This chapter contains descriptions of 10 Danish podzol profiles investigated in the present study. The profiles are all developed on coarse sandy parent materials including glacial outwash and moraine deposits from the Würm and Riss glaciations, late glacial marine deposits, and inland sand dunes. Most sites have a heath vegetation with Calluna vulgaris as the predominant plant species, but some are covered with Picea abies or Fagus sylvatica. As far as it could be ascertained the sites have not been disturbed by cultivation or any other activity of man on any recent occasion.

Almost all profiles contain all of the horizons mentioned in the type description given in chapter 2. The pH values measured in soil-water and soil-0.01 M $CaCl_2$ suspensions are reported together with the profile descriptions. Typically the pH values increase with depth from slightly below 4 in the upper horizons to approximately 5 in the C horizon.

Chapter 4. The Organic Matter Content of Podzols, and its Physical and Biological Properties

The definitions of podzols given by the soil classification systems mentioned in chapter 1 require that the B horizon of podzols has an accumulation of either sesquioxides or soil organic matter. Hence, an elevated content of sesquioxides in the B horizon could qualify a soil as a podzol even if it contained no organic matter in this horizon. However, all soils, otherwise fulfilling the requirements of the podzol definition, that have been described in the literature, seem to have an accumulation of humus at least in a subhorizon of the B horizon.

All the soils investigated in the present study have an A_0 horizon in which organic matter accounts for a considerable fraction, often more than half, of the total material. The underlying A_1 and A_2 horizons contain 3 - 9 % and 0.5 - 1.5 % organic carbon, respectively. With the exception of one profile that has no clear A_2 horizon, the organic matter content of the B_1 horizon is higher than that of the A_2 horizon. Although a considerable decrease in the organic matter content is noted from the B_1 to the B_2 horizon, the latter horizon of all profiles still contains significant amounts of humus.

The organic matter of the A_o horizon is poorly decomposed mor in which the plant structure may be recognized in a large fraction of the material. A higher degree of decomposition is noted in the organic matter of the A_1 and A_2 horizons. The organic matter of the B horizon is different in character, often being found as coating on mineral grains, as so-called pellets, or as intergranular bridges between sand particles. It is well decomposed.

As compared to mull layers, the biological activity of mor layers is small and the microflora is less diversified and contains a higher proportion of fungi. Earthworms are rarely found in mor soils. The biological activity declines with depth in podzols as in other soils; some authors have reported the presence of a great number of citrate oxidizing bacteria in the B horizon, but other authors have been unable to confirm this.

Chapter 5. Chemical Properties of the Organic Matter of Podzols

Soil organic matter consists of a variety of highly complex compounds and many methods used in the study of simple organic compounds are not suited for the study of soil organic compounds. Except for simple investigations, such as the determination of the total amounts of carbon and nitrogen, it is usually necessary to separate the organic matter from inorganic soil constituents in order to study the properties of the former. This separation is most often made by extracting the organic matter by means of some extractant. However, no extractant that will cause a complete extraction of soil organic matter is known and all extractants that have been employed must be assumed to change some of the properties of the organic matter.

It is characteristic that only strongly alkaline solutions can extract a considerable fraction of the organic matter of A horizons of podzols, while a variety of bases, acids, complexing agents, and ion exchange resins can extract almost completely the organic matter of B horizons.

All of these agents are capable of removing metals from the organic compounds, and this fact, therefore, suggests that metals are responsible for maintaining the organic matter in an insoluble state in podzol B horizons.

The organic matter of podzol B horizons seems to have lower contents of carbon and hydrogen and a higher oxygen content than that of A horizons. No consistent difference is found in the nitrogen content.

The average molecular weight reported for soil organic matter extracted from podzols and other soils vary within wide limits. The humus compounds are generally assumed to consist of a mainly aromatic core to which various, mainly aliphatic, side chains are attached. They are often thought to have some similarity to the polyphenols which is a poorly defined group of compounds apparently related to the tannins. The predominant functional groups of soil organic matter seem to be the carboxyl, phenol, alcohol and carbonyl groups, but the results reported in the literature differ widely with respect to the content of these groups. Some investigations have shown a higher content of functional groups in the organic matter of podzol B horizons than in that of A horizons, but other investigations have failed to reveal major differences.

Acid hydrolysis of the organic matter of a podzol B horizon has led to production of amino acid N, ammonium N and amino sugar N.

Chapter 6. Iron and Aluminium Compounds in Podzols

A determination of the content of non-silicate iron and aluminium in each horizon of a podzol will provide some information on the extent of podzolization. Several chemical methods have been suggested for carrying out such determinations. Most of these employ rather mild extractants that are assumed to dissolve the non-silicate iron and aluminium and to be without effect, or to have only a small dissolving effect, on iron and aluminium of silicate minerals. Although some extractants may fulfill this aim with a certain degree of approximation, a complete separation of the two sesquioxide fractions hardly seems possible by chemical extraction.

In the present study two extraction procedures have been used. In one of these, the soil was treated with hot 20 % HCl for 8 hours and in the other one the soil was treated with a solution of sodium dithionite and EDTA,2Na for 30 min. on a water bath at 80 °C. In both extracts, iron and aluminium were determined by atomic absorption spectrophotometry.

The variation pattern down the profile in the amounts of iron and aluminium extracted by the two procedures was similar for both extractants and all profiles. In 8 of the 10 profiles investigated, the B sub-horizon that had the highest content of organic matter also had the highest content of $Na_2S_2O_4$-EDTA extractable aluminium while the coincidence between the maximum organic matter content and the maximum content of $Na_2S_2O_4$-EDTA extractable iron, HCl-extractable iron or HCl-extractable aluminium was somewhat lower.

As compared with the C horizon, three profiles seemed to have suffered a net loss of iron and aluminium from the A+B horizons. In these profiles the loss of iron was greater than that of aluminium. Three profiles showed small and insignificant differences between the weighted average of iron and aluminium contents in the A+B horizons, and the contents of these metals in the C horizon. This would indicate a complete retention in the B horizon of the metals removed from the A horizon, or a net loss from the C horizon equal to that from the A+B horizons. In the four remaining profiles the weighted average iron and aluminium contents in the A+B horizons were higher than the contents in the C horizon. This seems to be most readily explained by a loss of iron and aluminium from the C horizon.

Chapter 7. Metal-Organic Matter Complexes in Podzols

The most common type of metal-organic matter complexes seems to be the 'chelates' which have a ring structure. Such compounds are assumed to be present in soils although it is difficult to provide evidence that actually proves their existence due to the complicated molecular structure of soil organic matter. The following facts have been taken to indicate that soil organic matter forms complex compounds with metals:

1) Extractants capable of extracting metals often have a dispersing effect on the organic matter.
2) Various metals are adsorbed with various strength in soils and a relation exists between the strength of adsorption and the tendency of the metal to form complex compounds with simple organic molecules.
3) The presence of metals capable of forming complexes affect the titration curves of soil organic matter.
4) Electrophoresis experiments have shown that soil organic matter may cause metals to move toward the positive electrode.

5) Dispersed soil organic matter may maintain metals in solution under conditions where they would be precipitated as hydroxides.
6) Metal ions such as ferric and aluminium ions may under certain conditions precipitate dispersed soil organic matter.

Results of spectroscopic investigations have also been interpreted as evidence for the ability of soil organic matter to complex metals.

Carboxyl and phenolic groups seem to be the functional groups most often involved in the formation of complex compounds between soil organic matter and metals. Some, although weak, evidence suggests that the metal ion species most often involved in complex compounds between ferric iron or aluminium and soil organic matter are hydroxyl complexes rather than the simple ions.

Chapter 8. Mechanisms of Podzolization

Since podzolization involves a translocation of humus, iron and aluminium, any proposed podzolization mechanism must include satisfactory explanations of the translocation of all three compounds.

Many authors have pointed out that the acidity of podzols is too low to allow translocation of ferric iron and aluminium as simple ions. However, thermodynamic calculations show that it is not possible to rule out that aluminium can be mobilized in the A horizon due to its acidity and that iron can be mobilized under moderately reducing conditions. A precipitation of the metals can occur in the B horizon due to the higher pH of this horizon. It seems more difficult to explain the translocation of organic matter in terms of acidity and/or reducing conditions.

A translocation mechanism involving colloidal solutions of the metal hydroxides and the organic matter could be possible. Laboratory experiments have indicated that mutual precipitation may occur on mixing colloidal solutions of metal hydroxides with colloidal solutions of soil organic matter. However, the precipitation seems to occur only at metal-organic matter ratios much higher than those found in podzol B horizons. It is rather difficult to visualize a mechanism by which colloidal solutions of ferric or aluminium hydroxide could form in soils.

Many experiments have shown that water-soluble organic compounds originating from soils or plant materials have a dissolving effect on iron and aluminium. Such compounds have often been assumed to play a role in podzolization. Some authors believe that the most active compounds in this respect are simple organic acids, while others attribute greater effect to polymeric compounds of the so-called polyphenol type. If the active compounds are simple organic acids it seems difficult to suggest a plausible explanation of the deposition of these compounds in the B horizon. Most often this deposition is thought to be due to decomposition of the complex compounds by bacteria or other microorganisms, but there seems to be no obvious reason why such organisms should be particularly abundant in the B horizon. It seems easier to explain a precipitation of polymeric compounds in the B horizon. Many experiments have shown that such polymeric compounds may precipitate if the amount of iron and aluminium taken up by the organic molecules exceeds a certain critical limit.

Chapter 9. Water-Soluble Compounds in Podzols

Soil extracts and soil solutions obtained from various horizons of podzols have been analyzed for iron, aluminium and organic carbon. Soil extracts were prepared by prolonged treatment of soil samples with water and soil solutions by centrifugation of moist soil samples without artificial addition of water. The following ratios were calculated for extracts and solutions: $\frac{\text{C (mg/l)}}{\text{Al (mg/l)}}$, $2\frac{\text{C (mg/l)}}{\text{Fe (mg/l)}}$, $\frac{\text{C (mg/l)}}{\text{Al(mg/l)} + \frac{1}{2}\text{Fe(mg/l)}}$. The iron content has been divided by 2 in order to make all ratios numerically comparable on a molar basis, since the atom weight of iron is approximately twice that of aluminium.

Soil extracts from horizons with a high organic matter content, i.e. A_o, A_1 and B_1 horizons, always had a high content of dissolved organic matter. The carbon-metal ratios defined above decreased markedly from A to B horizons. Soil extracts prepared in the absence of oxygen had a somewhat higher content of organic matter and metals than extracts prepared in the presence of oxygen. Anaerobic conditions decreased the ratios involving iron in extracts from the B and C horizons but had no effect on these ratios in extracts from A horizons or on the $\frac{C}{Al}$-ratio of any extract.

Soil extracts prepared in the presence of an ion exchange resin saturated with ferric iron in most cases had a lower content of dissolved organic matter than extracts prepared in the absence of the resin. The $2\frac{C}{Fe}$-ratios were hardly affected by the resin, but an increase was noted in the $\frac{C}{Al}$-ratios. A considerable fraction of the ferric iron on the resin that had been in contact with soil from the A_0-A_1 horizon was reduced to ferrous iron during the extraction even though this was made under aerobic conditions. Furthermore, a part of the iron was removed from the resin by the soil. A considerable fraction of the iron on the resins that had been in contact with B and C horizon soil was replaced by aluminium.

Extracts of mixtures of soil from A and B or C horizons had a smaller carbon content and a higher metal content than would be expected from the results obtained by separate extractions of soil from the same horizons. Addition of a soil extract obtained from the A_0-A_1 horizon to soil from B or C horizons led to a decrease in the carbon content and an increase in the metal content of the soil extract.

The content of organic matter in soil solutions decreased with depth, but although the soil solutions of C horizons often appeared colourless, they usually had an appreciable organic carbon content. The content of iron and aluminium in soil solutions declined below the B_1 horizon and was subject to irregular variation above this horizon. There was a clear drop in the $\frac{C}{Al}$-ratio from the A_2 to the B_1 horizon, while the variation of the ratios involving iron was less regular.

The results found by the investigations reported in this chapter strongly suggest that organic matter dispersed mainly from the A_0 horizon has a dissolving effect on iron and aluminium compounds in the soil. As the solution of the organic matter moves to deeper soil layers, where iron and aluminium become more and more abundant, larger and larger amounts are dissolved. However, at a certain metal content the organic compounds become insoluble and a mutual precipitation of the organic matter and the metals occurs. Such a mechanism is further substantiated by a study of the organic carbon-metal ratios of the solid soil material.

Chapter 10. Solubility Interactions between Iron/Aluminium and Soil Organic Compounds

Two types of experiments have been made in order to obtain more information on the reactions accompanying the dissolution and precipitation of iron, aluminium and organic matter. In the first type a solution of ferric and/or aluminium chloride was added slowly to a soil extract. This experiment made use of a pH-stat that maintained pH constant by addition of sodium hydroxide. In the second type of experiments a mixture of soil extract and of ferric or aluminium chloride was titrated automatically with sodium hydroxide from low pH values up to pH 10. A diagram of pH versus amount of sodium hydroxide consumed was obtained.

In the pH-stat experiments, carried out at pH 4.8, it was found that the organic matter of the soil extract, as well as the ferric iron or aluminium added, remained dissolved until a certain amount of the latter, had been added. At his stage a sudden and complete precipitation of organic matter and metals occured. Precipitation required larger amounts of ferric iron than of aluminium and the carbon-metal ratios at which precipitation took place were lower than those reported for soil extracts and solutions of B horizons in the preceeding chapter.

The amount of sodium hydroxide consumed by the ferric chloride added to the soil extract corresponded to somewhat less than 3 hydroxyl ions per ferric ion up to the point where precipitation occured. After this point exactly 3 hydroxyl ions were consumed by each ferric ion. The amount of sodium hydroxide consumed by the aluminium chloride was smaller than that consumed by the ferric chloride, and the change towards the theoretical value at precipitation noted for iron did not occur for aluminium. In blind experiments where no soil extract was present, ferric chloride caused a consumption of the theoretical amount of sodium hydroxide, while much smaller and varying amounts were consumed by aluminium chloride.

The results may be interpreted as a formation of mixed hydroxide-organic matter complexes of the metals. Calculations showed that precipitation occured at a rather constant deficit in base consumption. This would suggest that the precipitation occured after a definite amount of negative electrical charge of the organic compounds had been neutralized by the positive electrical charge contributed by the metals. The results of the automatic titrations largely confirmed the findings and the interpretation of the pH-stat experiments.

Chapter 11. Laboratory Simulation of Podzolization

Five ion exchanger columns (Dowex 50 W x 8) were saturated with hydrogen, sodium, calcium, aluminium and ferric iron, respectively, and leached with an aqueous soil extract from the A_0-A_1 horizon of a podzol. The leachings caused no visible changes in the columns saturated with hydrogen, sodium and calcium, but the column saturated with aluminium attained a dark, almost black, colour due to deposition of organic matter. A deposition of organic matter was also noted in the column saturated with ferric iron but the colour change was less marked due to the original dark colour of the ion exchange resin caused by the ferric ions.

Analyses showed a considerable and highly significant decrease in the organic carbon content of the effluents from the aluminium and iron saturated columns as compared with the untreated soil extract. A small decrease in the carbon content was noted in the extract that had passed the calcium saturated column. This decrease was significant to the five percent level whereas the changes in the carbon content caused by the hydrogen and sodium saturated columns were insignificant (to the five percent level).

The soil extract caused a removal of metal ions from the resins saturated with sodium, calcium, aluminium and ferric iron. While almost equivalent amounts of sodium and calcium were taken up by the soil extract, the amounts of aluminium and ferric iron taken up were somewhat smaller, even allowing for the fraction of organic matter deposited in these columns. The $\frac{C}{Al}$- and $2\frac{C}{Fe}$-ratios of the effluents from the columns saturated with aluminium and iron respectively were of a magnitude similar to those found in soil extracts and solutions from podzol B horizons.

The optical density of the leachates from the hydrogen, sodium and calcium saturated columns was practically identical to that of the untreated soil extract throughout the wavelength range investigated (400-1000 mμ). The relative difference between the optical density of the untreated soil extract and of the leachate from the aluminium saturated column was larger than the relative difference between the carbon contents of these liquids. Statements in the literature suggest that this could be taken to indicate that the organic matter fraction deposited in the column had a more condensed structure than the fraction passing the column.

Despite a lower carbon content, the leachate from the iron saturated column had a higher optical density than the untreated soil extract throughout the wavelength range investigated. This seems to be most readily explained as being due to coloured iron-organic matter complexes.

Chapter 12. The Overall Podzolization Process

Podzolization seems to be a result of interactions between iron and aluminium compounds on the one hand and soluble organic compounds of a nature similar to that of true humus compounds on the other. The formation of such compounds may be attributed to the low and little varied biological activity, the acidity and the practically complete absence of divalent metal ions in podzols. The fact that clayey soils, despite a high acidity, are little susceptible to podzolization may be explained by a high content of easily available ferric iron and, particularly, aluminium in such soils, since these trivalent metal ions will immobilize the organic compounds in the A horizon where they are produced.

When the water soluble organic compounds have been produced in the A_o and A_1 horizons of podzols, they will move downward with the leaching water. As the availability of ferric iron and aluminium increases with depth the organic compounds will take up more and more of these metals as they move downward. At a certain stage the amount of metals taken up will give rise to a mutual precipitation of the metals and the organic matter, probably due to a neutralization of the original negative charge of the organic compounds. In the initial stages of podzolization, sufficient iron and aluminium will be available in a shallow soil layer and precipitation will occur at shallow depth. As more and more iron and aluminium are removed from the upper layers, the precipitation will occur at greater depth and hence the horizon in which precipitation takes place moves gradually downward.

Some, possibly fairly simple, organic compounds may have an ability to take up iron and aluminium without becoming precipitated and those compounds may cause iron and aluminium to be leached entirely out of the soil profile.

Further research is needed to substantiate some parts of the podzolization mechanism outlined above.

DANSK RESUME

Kapitel 1. Podzolbegrebet

Betegnelsen "podzol" er af russisk oprindelse. Ordet tillægges normalt betydningen "under aske", men det kan også udlægges som "askeagtig jord". Det vandt indpas i vestlig jordbundsvidenskabelig nomenklatur i begyndelsen af det tyvende århundrede.

I russisk jordbundsvidenskabelig litteratur anses tilstedeværelsen af en afbleget horisont for det vigtigste kendetegn på en podzol, og mange såkaldte podzol- eller podzolagtige jorde har en udfældningshorisont, der er karakteriseret ved et højt lerindhold i forhold til de over- og underliggende horisonter. I Vesteuropa bruges podzolbetegnelsen normalt kun om jorde, hvori der er sket en flytning af humus-, jern- og/eller aluminiumforbindelser, og en jord kan kun klassificeres som en podzol, hvis den har en B-horisont, der er beriget med disse forbindelser. Dette er klart udtrykt i de jordbundsklassificeringssystemer, der benyttes i England, Frankrig og Tyskland.

Nogle sovjetiske jordbundsforskere er tilbøjelige til at følge den vesteuropæiske opfattelse og skelne mellem jorde, hvori der er sket en flytning af ler, og jorde, hvori der er sket en flytning af humus-, jern- og/eller aluminiumforbindelser. Imidlertid synes de fleste sovjetiske jordbundsforskere at være tilbageholdende med at acceptere, at der skulle bestå en principiel forskel mellem de to flytningsprocesser, idet de er af den opfattelse, at et højt lerindhold i en ikke-overfladehorisont skyldes nydannelse af ler i denne horisont snarere end en mekanisk nedslemning af lerpartikler fra overliggende horisonter.

I de jordbundsklassificeringssystemer, der benyttedes i USA og Canada indtil for få år siden, svarede definitionen af podzoljorde mere til den sovjetiske end til den vesteuropæiske opfattelse, og mange jorde, hvis vigtigste kendetegn var en B-horisont med et højt lerindhold, klassificeredes som podzolagtige jorde. Dette er imidlertid ændret i de senere år med indførelsen af nye jordbundsklassificeringssystemer i de to lande. I disse nye systemer skelnes der klart mellem de to jordtyper. Betegnelsen "podzol" bruges ganske vist ikke i det nye amerikanske system, men jorde, der klassificeres som "spodosols", svarer praktisk talt til dem, der i Vesteuropa klassificeres som podzoljorde. Også i det internationale jordbundsklassificeringssystem, der benyttes af FAO/UNESCO i forbindelse med udarbejdelsen af et Verdensjordbundskort, skelnes der skarpt mellem egentlige podzoljorde og jorde, hvori der er sket en nedslemning af ler.

Med undtagelse af den sovjetiske opfattelse af podzoljorde er der derfor en høj grad af overensstemmelse mellem de øvrige jordbundsklassificeringssystemer i, at en egentlig podzol skal have en eluvial horisont, der har været genstand for udludning af sesquioxider, og en illuvial horisont, i hvilken der er sket en udfældning af disse forbindelser og/eller humus. Denne definition er også benyttet i nærværende arbejde, der udelukkende beskæftiger sig med podzoljorde i denne betydning.

Kapitel 2. Podzoljordenes relation til klima og vegetation samt nogle af deres generelle egenskaber

I veludviklede podzoljorde findes et antal udtalte horisonter. Den øverste horisont af en udyrket podzol (A_o) består typisk overvejende af dårligt omsat organisk stof (mor). Direkte under denne kan man finde en stærkt afbleget horisont (A_2), fra hvilken der er sket en udludning af sesquioxider, men hyppigere findes mellem A_o- og A_2-horisonterne en horisont (A_1), der består overvejende af uorganisk materiale, men som har en mørk farve, der skyldes humusforbindelser.

Illuvialhorisonten (B), der findes under A-horisonten, kan typisk opdeles i en øvre B_1-horisont med en mørk farve, der skyldes humusforbindelser, og en nedre B_2-horisont, der har en brunlig eller rødbrun farve, som stammer fra jernforbindelser. Tunger fra B-horisonten strækker sig ofte ned i den underliggende C-horisont, der normalt antages at repræsentere forholdsvis uændret udgangsmateriale. Denne horisonts farve og andre egenskaber afhænger af udgangsmaterialets natur, ofte vil dette være gulligt sand.

Podzoljorde udvikles kun i et fugtigt klima. Skønt de ofte angives at forekomme typisk i et køligt klima, findes der beskrivelser af podzoljorde udviklet i mange klimabælter fra subarktiske egne til troperne.

Podzoljorde synes kun at udvikles på sandede udgangsmaterialer. Deres typiske vegetation i et tempereret klima er nåleskov eller hedevegetation, men de findes også udviklet under andre vegetationsformer. Tropiske podzoljorde findes normalt under savanne eller regnskov.

Podzoljordenes fugtighedsforhold varierer. I de fleste jordbundsklassificeringssystemer skelnes mellem veldrænede og vandlidende podzoljorde. I de sidstnævnte findes som regel karakteristiske rustfarvede pletter eller mønstre, oftest i den nederste del af profilen. En del andre egenskaber påvirkes også af dræningsforholdene.

Alle podzoljorde er sure. pH i de øverste horisonter er ofte under 4; med stigende dybde sker der normalt en lille stigning i pH. Det lave pH skyldes en basemætningsgrad nær 0. Adsorptionskomplekset består p.g.a. podzoljordenes sandede tekstur overvejende af organiske forbindelser.

Kapitel 3. Beskrivelser af undersøgte podzolprofiler

I dette kapitel er beskrevet 10 danske podzolprofiler, der er undersøgt i forbindelse med nærværende arbejde. Alle profilerne er udviklet på sandede udgangsmaterialer omfattende hedesletter og morænedannelser fra Würm- og Riss-istiderne, senglaciale marine dannelser og flyvesand. De fleste lokaliteter er dækket af hedevegetation med Calluna vulgaris som den dominerende planteart, men profiler bevokset med Picea abies og Fagus sylvatica forekommer også. Såvidt det har kunnet fastslås, er ingen af lokaliteterne forstyrret ved dyrkning eller andre kunstige indgreb indenfor et betydeligt åremål.

I næsten alle profilerne findes alle de horisonter, der er nævnt i typebeskrivelsen i kapitel 2. pH-værdier målt i jord-vand- og jord-0,01 M $CaCl_2$-opslemninger er anført sammen med profilbeskrivelserne. Typisk stiger pH med dybden fra lidt under 4 i de øverste horisonter til ca. 5 i C-horisonten.

Kapitel 4. Podzoljordenes indhold af organisk stof samt dets fysiske og biologiske egenskaber

Ifølge den definition af podzoljorde, der er indeholdt i de i kapitel 1 omtalte jordbundsklassificeringssystemer, skal B-horisonten være beriget med enten sesquioxider eller organisk stof. Et forhøjet indhold af sesquioxider i B-horisonten er derfor tilstrækkeligt til at tilfredsstille denne definition, også selv om der ikke findes organisk stof i B-horisonten. Imidlertid synes alle jorde, der iøvrigt opfylder definitionens betingelser, at have en ophobning af humus, i det mindste i en del af B-horisonten.

Alle de jordbundsprofiler, der er undersøgt i forbindelse med nærværende arbejde, har en A_o-horisont, hvis materiale overvejende består af organisk stof. I mange profiler er indholdet af organisk stof over 50 % i A_o-horisonten. I de underliggende A_1- og A_2-horisonter er indholdet af organisk kulstof henhv. 3-9 % og 0,5-1,5 %. Med undtagelse af en profil, i hvilken der ikke findes nogen udtalt A_2-horisont, er indholdet af organisk stof højere i B_1-horisonten end i A_2-horisonten. Skønt B_2-horisonten altid indeholder betydeligt mindre organisk stof end B_1-horisonten, har førstnævnte horisont et kendeligt indhold af organisk stof i alle profiler.

A_o-horisontens organiske stof er dårligt omsat mor, i hvilken den oprindelige plantestruktur kan erkendes i en stor del af materialet. I forhold hertil er det organiske stof i A_1- og A_2-horisonterne nedbrudt i højere grad. Det organiske stof i B-horisonten er af en anden karakter. Det findes ofte som belægninger på overfladen af mineralske partikler, som afrundede aggregater eller som ansamlinger mellem sandkorn. Det er vel omsat.

Morlag er i sammenligning med muldlag karakteriseret ved en lav biologisk aktivitet og en mindre alsidig mikroflora, der i høj grad består af svampe. Regnorme findes sjældent i mor-jorde. Den biologiske aktivitet aftager med dybden i podzoljorde såvel som i andre jorde. Nogle forskere har angivet, at podzoljordes B-horisonter indeholder et stort antal bakterier, der er i stand til at nedbryde citrat, men dette har ikke altid kunnet eftervises.

Kapitel 5. Kemiske egenskaber af det organiske stof i podzoljorde

Jordbundens organiske stof består af et stort antal meget komplicerede forbindelser, og mange af de metoder, der normalt anvendes ved studier af simple organiske forbindelser, er ikke egnede til et studium af jordbundens organiske stof. Med undtagelse af simple undersøgelser, som f. eks. bestemmelse af totalindhold af kulstof og kvælstof, er det normalt nødvendigt at adskille det organiske stof fra jordbundens uorganiske bestanddele for at kunne studere dets kemiske egenskaber. En sådan adskillelse foretages normalt ved en ekstraktion af det organiske stof. Imidlertid kendes intet ekstraktionsmiddel, der kan ekstrahere det organiske stof fuldstændigt, og alle ekstraktionsmidler, der er i stand til at ekstrahere en kendelig del af det organiske stof, må antages at ændre nogle af dets egenskaber.

Det er karakteristisk, at kun stærkt alkaliske opløsninger er i stand til at ekstrahere en betydelig del af det organiske stof fra podzoljordenes A-horisont, medens mange baser, syrer, kompleksdannende stoffer og ionbyttere kan ekstrahere det organiske stof fra B-horisonten næsten fuldstændigt. Alle de nævnte stoffer er i stand til at fjerne metaller fra de organiske forbindelser, og denne kendsgerning lader formode, at metalioner er årsag til, at de organiske forbindelser findes i uopløselig tilstand i podzoljordenes B-horisont.

Det organiske stof i B-horisonten synes at have et lavere indhold af kulstof og brint og et højere iltindhold end A-horisontens organiske stof. Der synes ikke at være nogen sikker forskel i kvælstofindholdet.

De gennemsnitlige molekulvægte, der angives for organisk stof ekstraheret fra podzoljorde og andre jorde, er genstand for stor variation. Humusforbindelserne antages i almindelighed at bestå af en aromatisk kærne og sidekæder, som overvejende er alifatiske. Ofte anses de for at have en vis lighed med såkaldte polyfenoler, som er en dårligt defineret og dårligt afgrænset gruppe garvesyrelignende stoffer. De dominerende funktionelle grupper i jordbundens organiske stof er formentlig carboxyl-, fenol-, alkohol- og carbonylgrupper, men de kvantitative angivelser, der findes i litteraturen angående indholdet af disse grupper, varierer indenfor vide grænser. Nogle undersøgelser har vist, at organisk stof fra B-horisonten har et højere indhold af funktionelle grupper end A-horisontens organiske stof, medens andre undersøgelser ikke har afsløret væsentlige forskelle. Syrehydrolyse af organisk stof fra en B-horisont førte til frigørelse af aminosyre-N, ammonium-N og aminosukker-N.

Kapitel 6. Jern- og aluminiumforbindelser i podzoljorde

En bestemmelse af ikke-silikatbundet jern og aluminium i de enkelte horisonter af en podzolprofil vil give nogen oplysning om podzoleringsgraden. Adskillige kemiske metoder er foreslået til brug ved sådanne bestemmelser. Ved de fleste af disse benyttes forholdsvis svage ekstraktionsmidler, der antages at opløse det ikke-silikatbundne jern og aluminium og at have ringe eller ingen opløsende effekt overfor det jern og aluminium, der findes som bestanddele af silikatmineraler. Selv om en vis adskillelse kan opnås med visse ekstraktionsmidler, synes en absolut adskillelse af de to sesquioxidfraktioner næppe at være mulig ved kemiske ekstraktioner.

I nærværende arbejde har to ekstraktionsmetoder været benyttet. Ved den ene behandledes jorden i 8 timer med varm

20 % saltsyre, og ved den anden behandledes jorden i 30 minutter med en opløsning af natriumdithionit og EDTA,2Na ved 80 °C. I begge ekstrakter bestemtes jern og aluminium ved atomabsorptionsspektrofotometri.

Variationen i jern- og aluminiumindholdet ned gennem profilen viste samme tendens for de to metoder i alle de undersøgte jorde. I 8 af de 10 profiler fandtes det højeste indhold af $Na_2S_2O_4$-EDTA-opløseligt aluminium i den del af B-horisonten, der havde det højeste indhold af organisk stof (normalt B_1). Der var en noget mindre hyppighed af sammentræf mellem det højeste indhold af organisk stof og det højeste indhold af $Na_2S_2O_4$-EDTA-opløseligt jern, HCl-opløseligt aluminium eller HCl-opløseligt jern.

I sammenligning med C-horisonten syntes tre profiler at have lidt et netto-tab af HCl-opløseligt jern og aluminium fra (A+B)-horisonterne. I disse profiler var tabet af jern større end tabet af aluminium. I tre andre profiler fandtes små og usikre forskelle mellem jern- og aluminiumindholdet i (A+B)-horisonterne (beregnet som et vejet gennemsnit) og indholdet af disse metaller i C-horisonten. Dette kan tydes som en fuldstændig udfældning i B-horisonten af det jern og aluminium, der er udludet fra A-horisonten. Det kan også skyldes, at C-horisonten har lidt et tab af jern og aluminium, der svarer til netto-tabet af disse metaller fra (A+B)-horisonterne. I de resterende fire profiler var jern- og aluminiumindholdet i (A+B)-horisonterne større end i C-horisonten. Den mest simple forklaring på dette synes at være, at C-horisonten har lidt et tab af jern og aluminium.

Kapitel 7. Organiske metalkomplekser i podzoljorde

Det antages, at jordbundens organiske stof kan danne såkaldte chelatforbindelser med metalioner. Chelatforbindelser er metalkomplekser med en ringstruktur. Det er imidlertid vanskeligt at føre et egentligt bevis for tilstedeværelsen af disse forbindelser i jordbunden p.g.a. humusstoffernes komplicerede natur, men følgende erfaringer er blevet udlagt som tegn på, at de organiske stoffer kan kompleksbinde metaller:

1) Ekstraktionsmidler, der kan ekstrahere metaller fra jord, har ofte en dispergerende virkning på de organiske stoffer.

2) Forskellige metaller bindes med forskellig styrke i jorden, og der består en sammenhæng mellem bindingsstyrken og metallernes evne til at danne kompleksforbindelser med simple organiske stoffer.

3) Titreringskurver for organisk stof ekstraheret fra jord påvirkes af metalioner.

4) Elektroforese-undersøgelser har vist, at metaller i nærvær af ekstraheret organisk stof kan bevæges mod den positive elektrode.

5) Opløst organisk stof kan holde metalioner i opløsning under betingelser, hvor de ellers ville udfældes som hydroxyder.

6) Ferri- og aluminiumioner kan under visse omstændigheder forårsage udfældning af opløst organisk stof.

Spektroskopiske undersøgelser har også sandsynliggjort, at det organiske stof kan kompleksbinde metalioner.

Det organiske stofs kompleksdannende evne synes overvejende at skyldes carboxyl- og fenolgrupper. En del erfaringer taler for, at kompleksforbindelser mellem organisk stof og ferrijern eller aluminium ikke indeholder de simple metalioner, men deres hydroxylkomplekser.

Kapitel 8. Podzoleringsmekanismer

Under podzoleringen sker der en flytning af humus-, jern- og aluminiumforbindelser, og en podzoleringshypotese må derfor give en tilfredsstillende forklaring på flytningen af alle tre stoffer.

Mange forskere har understreget, at podzoljorde ikke er sure nok til, at jern og aluminium kan opløses og transporteres som simple ioner. Imidlertid viser thermodynamiske beregninger, at man ikke umiddelbart kan afvise, at aluminium kan opløses ved de lave pH-værdier, der normalt træffes i podzoljordes A-horisonter, og jern vil kunne opløses, hvis der hersker moderat reducerende betingelser. En udfældning vil kunne ske i B-horisonten p.g.a. dennes højere pH. Det er vanskeligere at forklare flytningen af det organiske stof som en følge af forskelle i pH og/eller redoxpotentiale.

Det har ofte været foreslået, at metalhydroxyderne og det organiske stof transporteres i form af kolloide opløsninger. Laboratorieforsøg har vist, at der kan ske en gensidig udfældning, når kolloide opløsninger af ferri- eller aluminiumhydroxyd blandes med kolloide opløsninger af humusforbindelser. Imidlertid synes en sådan udfældning kun at ske ved et metal: humus-forhold, som er meget højere end det, man normalt finder i podzoljordes B-horisonter. Det synes vanskeligt at foreslå en mekanisme, ved hvilken kolloide opløsninger af ferri- og aluminiumhydroxyd kan dannes i jorden.

Mange forsøg har vist, at vandopløselige organiske forbindelser, som stammer fra jord eller plantematerialer, har en evne til at opløse jern- og aluminiumforbindelser. Sådanne organiske stoffer er ofte blevet tillagt betydning for podzoleringen. Nogle forskere anser simple organiske syrer for at være mest betydningsfulde i så henseende, medens andre tillægger polymere forbindelser, specielt såkaldte polyfenoler, større betydning. Hvis de mest aktive forbindelser er simple organiske syrer, er det vanskeligt at forklare deres udfældning i B-horisonten. Oftest antages denne udfældning at skyldes biologisk nedbrydning af de komplekse forbindelser, men der synes ikke at være nogen umiddelbar grund til, at organismer, som har speciel evne til at nedbryde disse, skulle være særligt dominerende i B-horisonten. Det er lettere at forklare en udfældning af polymere forbindelser i B-horisonten. Mange forsøg har vist, at sådanne polymere forbindelser kan udfældes, hvis de optager mere end en vis, kritisk, mængde ferrijern eller aluminium.

Kapitel 9. Vandopløselige forbindelser i podzoljorde

Jordekstrakter og -opløsninger fra forskellige horisonter af podzolprofiler er analyseret for jern, aluminium og organisk kulstof. Jordekstrakterne blev fremstillet ved langvarig behandling af jordprøver med vand, og jordopløsningerne blev udvundet ved centrifugering af fugtige jordprøver uden tilsætning af vand. Følgende brøker blev beregnet for jordekstrakter og -opløsninger: $\frac{C\ (mg/l)}{Al(mg/l)}$, $2\frac{C\ (mg/l)}{Fe(mg/l)}$ og $\frac{C\ (mg/l)}{Al(mg/l) + \frac{1}{2}Fe(mg/l)}$. Faktoren 2 i de to sidstnævnte brøker bevirker, at alle brøker giver sammenlignelige relative udtryk for indholdet af organisk kulstof pr mol metal, idet atomvægten af jern er tilnærmelsesvis to gange atomvægten af aluminium.

Jordekstrakter fra horisonter med et højt indhold af organisk stof, d.v.s. A_o-, A_1- og B_1-horisonter, havde i alle tilfælde et højt indhold af opløst organisk stof. Kulstof: metal-forholdene defineret ovenfor aftog i alle tilfælde kraftigt fra A- til B-horisonter. Jordekstrakter fremstillet i fravær af ilt havde et noget højere indhold af organisk stof og metaller end ekstrakter fremstillet i nærvær af ilt. Anaerobe forhold gav anledning til lavere $2\frac{C}{Fe}$- og $\frac{C}{Al+\frac{1}{2}Fe}$-forhold i ekstrakter fra B- og C-horisonter, men havde ingen indflydelse på disse forhold i ekstrakter fra A-horisonter eller på $\frac{C}{Al}$-forholdet i nogen jordekstrakt.

Jordekstrakter fremstillet i nærvær af en ionbytter mættet med ferrijern havde i de fleste tilfælde et lavere indhold af opløst organisk stof end ekstrakter fremstillet i fravær af ionbytteren. $2\frac{C}{Fe}$-forholdet påvirkedes praktisk talt ikke af ionbytteren, men der skete en stigning i $\frac{C}{Al}$-forholdet. En betydelig del af jernet på den ionbytter, der havde været i kontakt med jord fra A_o-A_1-horisonten, var blevet reduceret til ferrojern under ekstraktionen, selv om denne foregik under aerobe betingelser. Desuden blev en del af jernet fjernet fra ionbytteren af jorden. En betydelig del af jernet på de ionbyttere, der havde været i kontakt med jord fra B- og C-horisonterne, var blevet ombyttet med aluminium.

Ekstrakter fra blandinger af jord fra A- og B- eller C-horisonter havde et lavere kulstofindhold og et højere metalindhold i forhold til de indhold, der kunne forventes på grundlag af ekstraktioner udført hver for sig på de samme jordprøver. Når en jordekstrakt fra en A_o-A_1-horisont bragtes i kontakt med jord fra en B- eller C-horisont, skete der en nedgang i kulstofindholdet og en stigning i metalindholdet.

Indholdet af organisk stof i jordopløsningerne aftog med dybden, men selv om jordopløsningerne fra C-horisonten oftest var farveløse, havde de normalt et kendeligt kulstofindhold. Indholdet af jern og aluminium aftog under B_1-horisonten og var genstand for uregelmæssig variation over denne horisont. Der skete et udtalt fald i $\frac{C}{Al}$-forholdet fra A_2- til B_1-horisonten, medens variationerne i $2\frac{C}{Fe}$- og $\frac{C}{Al+\frac{1}{2}Fe}$-forholdene var mere uregelmæssige.

Resultaterne af de undersøgelser, der er beskrevet i dette kapitel, kan tydes derhen, at opløste organiske forbindelser, som overvejende stammer fra A_o-horisonten, er i stand til at opløse jern- og aluminiumforbindelser. Efterhånden som opløsningen af de organiske forbindelser bevæges mod dybere jordlag, hvor jern og aluminium er til stede i større og større mængder, opløses mere og mere af disse metaller. Imidlertid bevirker et vist metalindhold, at de organiske forbindelser bliver uopløselige, og når denne grænse er nået, sker der en samtidig udfældning af metallerne og det organiske stof. En sådan mekanisme underbygges yderligere af dybdevariationen i kulstof:metal-forholdet i de undersøgte podzolprofiler.

Kapitel 10. Jern- og aluminiumforbindelsers virkning på opløseligheden af organisk stof, samt det organiske stofs betydning for metallernes opløselighed

Der er udført to typer eksperimenter for at undersøge arten af de reaktioner, der ledsager opløsningen og udfældningen af jern, aluminium og organisk stof. Ved den ene type tilsattes en opløsning af ferri- og/eller aluminiumchlorid langsomt til en jordekstrakt fra en A_o-A_1-horisont. Ved disse eksperimenter benyttedes en pH-stat, der fastholdt pH på en konstant værdi ved tilsætning af natriumhydroxyd. Ved den anden type eksperimenter titreredes en blanding af jordekstrakt og ferri- eller aluminiumchlorid automatisk med natriumhydroxyd fra lave pH-værdier til pH 10. Et diagram, der viste pH som funktion af tilsat mængde natriumhydroxyd, blev optegnet under titreringen.

pH-stat-eksperimenterne, der udførtes ved pH 4,8, viste, at jordekstraktens organiske stof såvel som det tilsatte jern og aluminium forblev i opløsning indtil en vis metalmængde var tilsat. Når denne mængde blev overskredet, skete der en pludselig og fuldstændig udfældning af metaller og organisk stof. Udfældningen krævede større mængder jern end aluminium, og det kulstof:metal-forhold, ved hvilket udfældningen skete, var lavere end de kulstof:metal-forhold, der blev fundet for jordekstrakter og -opløsninger fra B-horisonter ved de i foregående kapitel beskrevne undersøgelser.

Den mængde natriumhydroxyd, som blev brugt af det tilsatte ferrichlorid, svarede til noget mindre end tre hydroxylioner indtil det punkt, hvor udfældningen skete. Efter dette punkt forbrugtes nøjagtigt tre hydroxylioner for hver ferriion. Aluminiumchlorid forbrugte mindre natriumhydroxyd end ferrichlorid, og den ændring til den teoretiske mængde, der fandtes for ferrijern, skete ikke for aluminium. Ved blindforsøg udført uden jordekstrakt forbrugte ferrichlorid den teoretiske mængde natriumhydroxyd, medens mindre og varierende mængder natriumhydroxyd forbrugtes af aluminiumchlorid.

Resultaterne kan tydes som en dannelse af metalkomplekser, i hvilke liganderne dels er hydroxylioner og dels organiske forbindelser. Beregninger viste, at udfældningen skete ved et forholdsvis konstant baseforbrugsdeficit. Dette tyder på, at udfældningen sker, når en vis mængde negativ ladning hos de organiske forbindelser er blevet neutraliseret af positiv elektrisk ladning fra de optagne metaller.

Resultaterne af de automatiske titreringer bekræftede stort set resultaterne og tolkningen af pH-stat-eksperimenterne.

Kapitel 11. Eksperimentel efterligning af podzolering

Fem ionbyttersøjler (Dowex 50 W x 8) blev mættet med henhv. brint-, natrium-, calcium-, aluminium- og ferriioner. Derefter udludedes søjlerne med en vandig jordekstrakt fra en podzoljords A_o-A_1-horisont. Udludningen gav ikke anledning til synlige ændringer i de søjler, der var mættet med brint, natrium eller calcium, men den aluminiummættede søjle antog en mørk, næsten sort, farve, som skyldtes udfældning af organisk stof i søjlen. En udfældning af organisk stof kunne også erkendes i den søjle, der var mættet med ferrijern, men farveændringen var mindre udtalt, fordi ferriionerne i sig selv bibragte ionbytteren en mørk farve.

Analyser viste en i forhold til den ubehandlede jordekstrakt betydelig nedgang i indholdet af organisk stof i de jordekstrakter, der havde passeret de aluminium- og jernmættede søjler. En lille nedgang fandtes i den ekstrakt, der havde passeret den calciummættede søjle. Denne nedgang var signifikant til 5 %-grænsen, hvorimod de ændringer i kulstofindholdet, der skete ved passage af de brint- og natriummættede søjler, ikke var signifikante til denne grænse.

Jordekstrakterne opløste metalioner fra de ionbyttere, der var mættet med natrium, calcium, aluminium og jern. Jordekstrakten optog praktisk talt ækvivalente mængder af natrium og calcium, men noget mindre mængder af aluminium og jern, også selv om der blev taget hensyn til den mængde organisk stof, der udfældedes i disse søjler. $\frac{C}{Al}$- og $2\frac{C}{Fe}$-forholdene i de udløbne væsker fra de aluminium- og jernmættede ionbyttere var af samme størrelsesorden som i jordekstrakter og -opløsninger fra podzoljordes B-horisonter.

I bølgelængdeområdet 400-1000 mμ forårsagede den udløbne væske fra de brint-, natrium- og calciummættede ionbyttere praktisk talt samme lysabsorption som den ubehandlede jordekstrakt. Den væske, der havde passeret den aluminiummættede ionbytter, forårsagede en mindre lysabsorption end den ubehandlede jordekstrakt, men forskellen var mindre, end der skulle forventes på grundlag af forskellen i kulstofindhold.

Støttet på angivelser i litteraturen kan dette udlægges som et tegn på, at det organiske stof, der er udfældet i søjlen, har en mere kondenseret struktur end den fraktion, der har passeret søjlen. Til trods for et lavere kulstofindhold forårsagede den udløbne væske fra den jernmættede ionbytter en større lysabsorption end den ubehandlede jordekstrakt i hele det undersøgte bølgelængdeområde. Dette skyldes formentligt farvede komplekser bestående af jern og organisk stof.

Kapitel 12. Podzoleringsprocessen i almindelighed

Podzolering synes at ske som følge af reaktioner mellem opløselige organiske stoffer på den ene side samt jern- og aluminiumforbindelser på den anden. De opløselige organiske forbindelser er formentligt af samme natur som de egentlige humusforbindelser. Deres dannelse kan tilskrives podzoljordenes ringe og ensidige biologiske aktivitet, deres lave pH og ringe indhold af adsorberede divalente metalioner. Når podzolering sjældent eller aldrig iagttages i jorde med et højt lerindhold, skyldes det antageligt, at sådanne jorde har et højt indhold af let tilgængeligt ferrijern og, især, aluminium. De trivalente metalioner vil udfælde de opløselige organiske stoffer, hvor de produceres, d.v.s. i A-horisonten.

Når de opløselige organiske forbindelser er blevet dannet i podzoljordenes A_o- og A_1-horisonter, vil de transporteres nedad med nedsivende vand. Da mængden af jern og aluminium stiger med dybden, vil de organiske stoffer optage mere og mere af disse metaller, efterhånden som de bevæges nedad. Når en vis mængde metal er optaget, vil der ske en samtidig udfældning af metallerne og det organiske stof. Hvis det antages, at de organiske stoffers opløselighed skyldes, at de er negativt ladede, kan udfældningen forklares ved, at metallerne neutraliserer denne ladning. I podzoleringens indledende stadier vil der være tilstrækkeligt jern og aluminium til stede i et tyndt overfladisk jordlag, og udfældningen vil ske i ringe dybde. Efterhånden som mere og mere jern og aluminium fjernes fra de øvre jordlag, vil udfældningen ske i større og større dybde, og udfældningshorisonten flyttes derfor gradvist nedad.

Nogle organiske forbindelser kan tænkes at kunne optage jern og aluminium uden at blive udfældet. Sådanne forbindelser, som sandsynligvis har en temmelig simpel molekulstruktur, kan give anledning til, at en del jern og aluminium fjernes helt fra jordprofilen.

Nogle af de ovenfor anførte betragtninger er baseret på et utilstrækkeligt grundlag, og yderligere undersøgelser er påkrævede for at gøre dette mere fuldstændigt.

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