SOME ASPECTS OF AMMONIA FIXATION

BY PEAT

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By

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SCOPE AND CONTENTS:　Examination of peat samples collected from hummocks
and hollows within a confined bog reveals that peat collected from
different locations, designated by surface topography, vary in ash content,
ash alkalinity, initial Kjeldahl nitrogen content, and fixed and total
nitrogen after ammoniation with an ammonia-air mixture.　The values
of these properties have shown hummocks and hollows to be true entities
having characteristic ranges of certain properties.

　　The results have shown that, although peat is heterogenous with
respect to certain properties, use can still be made of determined values
if ranges of these values are recognized and utilized.　Misinterpretations
and meaninglessness of results are possible if this is not done.

PREFACE

The motivation behind this investigation was primarily a desire to find some direction to the solution of how surface topography of a bog develops. It was hoped that the discoveries arising out of this study would contribute to an understanding of certain differentials noted when peat changes in relation to topographic dynamics, especially with respect to the hummock-hollow association.

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INTRODUCTION

Much work has been done to elucidate the complex pathways of the biogeochemical nitrogen cycle in soils. Now, a general workable understanding of this cycle exists, although mechanisms and controlling factors of few of the associated steps are completely understood. Of the investigations that have been done on this topic, most have been directed towards organic matter in mineral soils and not in peat. In mineral soils the role of microorganisms, water movements, leaching, and other features of the microenvironment, as they tend to affect organic matter, have been studied. These processes vary with geographical location, soil classes, climatic conditions, and time. It is very difficult therefore to make generalizations on the effects and application of these processes, particularly when dealing with peat.

Bremner (1952, page 500) has stated:

"The present information regarding the nature of soil nitrogen complexes is very unsatisfactory. The chemical nature of a considerable fraction of the soil nitrogen is unknown and information regarding the nitrogen complexes that have been identified is inadequate. It is equally clear that until more extensive information regarding nitrogen complexes is obtained we cannot hope to achieve a proper understanding of their roles in the nitrogen cycle or of the factors affecting their availability to plants."

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In peat too, information on the forms and chemical behaviour of the nitrogen complexes is nebulous or lacking. Essentially, this is for two major reasons. Firstly, fewer workers have directed their attention to peat than to mineral soils. Secondly, work done on mineral soils in many cases cannot be applied directly to peat because of the differences in structure and chemical behaviour of the components.

There is also a lack of knowledge of the chemistry of peat components (particularly colloids and lignin), plant deposition, and breakdown processes (Sjörs, 1950; Bremner, 1952). Even now, although the trend is to oppose this, many compounds in humus and peat are defined by the techniques used to extract them (Bremner, 1952; Ponomareva and Nikolayeva, 1961). Not only is the chemistry of the constituents vague, but also the forces influencing the physical and chemical transformations of these substances and their importance relative to one another are still uncertain. Yefimov (1962, page 643) has stated recently that there is "almost a complete lack of unified analysis of the system: peat producers-peat soils – soil water whereas there is a huge amount of unrelated analytical data on peat."

A large portion of research on origin, form, and behavior of peat pertains to areas drained for forestry, agriculture, or the peat processing industry (Sjörs, 1961). Prior to analysis, the natural condition of the bog has been modified, usually by drainage and removal of the surface vegetation (Sjörs, 1961). This generally brings about a subsequent lowering of the water level, accompanied by increased aeration and oxidation (Gorham, 1961; Heinselman, 1963; Vidal, 1963). These changes may enhance aerobic microbial activity (Paarlahti and Vartiovaara,

1958; Paarlahti, 1959) and accelerate changes in properties of the peat
(Waksman and Stevens, 1929; Nikonov and Minkina, 1962). If this occurs,
peat texture, the colloid state (Nikonova and Minkina, 1962), peat
chemistry, and peat permeability (Paarlahti and Vartiovaara, 1958) may
be altered. The conditions, as indicated by the results of these
investigations, may not be equivalent to the conditions existing in
undisturbed bogs and therefore, explanations of phenomena present in
drained bogs may require significant qualification if they are to be
regarded as meaningful for unaltered bogs (Sjörs, 1961).

In their natural condition bogs differ from one another in
water content (Vidal, 1963). Whatever the difference, the content
varies because of evapotranspiration and run-off from the bog and
sources of replenishment to the bog. The water entering the bog comes
either from the atmosphere as direct precipitation or from mineral
terrain as run-off and ground water. If most of the water comes directly
from the atmosphere, the bog is termed "ombrogenous", if most of the
water has come by way of mineral terrain the bog is termed "geogenous".
(Heinselman, 1963).

Use of this terminology may lead to difficulty. Previously
these terms applied to the different kinds of "wet of soil" (Swedish
markblöta, German bodennässe) and were used to describe the water in the
bog and not the bog itself (Sjörs, 1948, page 279). Presence of
substances in the water (for example, solid particles and dissolved
salts) may be implied without qualitative and quantitative restrictions,
when these terms are used. Short-comings of this system of classification

arise because of lack of sufficient quantitative information on other sources of water present and imperfect assessment of the influence of nutrients transported by these other forms of water and of the nutrients from all other sources as well.

Bogs receiving most of their water directly from the atmosphere (ombrogenous) have surface vegetation dependent on the atmosphere for nutriment (Mattson and Koutler-Andersson, 1954). Precipitation may remove "dust" from the air and may contain dissolved gases and various chemical compounds. Solid matter may settle out of the air onto the bog directly. Gases in the atmosphere may become dissolved in surface water of the bog depending on the ratio of concentration of gas in the solution to the concentration of gas above the solution at a given temperature (Handbook of Chemistry and Physics, 1963, page 3258). Chemical reactions of these gases with peat components may lower the partial pressure of the gas in the peat water.

Of the many substances that arrive at the bog surface from the atmosphere, some can be utilized immediately by plants for growth. Others may become available for plant uptake after further chemical changes and some may not be absorbed at all. If only small amounts of some elements are needed, these are called trace elements or micronutrients (Thomas, 1958). Other elements, however, are termed "essential" or macronutrients (Thomas, 1958) and are required in larger amounts (for example, nitrogen). Various forms of nitrogen present in the atmosphere are absorbed directly by growing plants and other forms are made available by microbial action. If only part of the entire

surface of a bog is dependent primarily upon the atmosphere for the element, the availability and usefulness of chemical forms of it should be examined. Some nitrogen-fixing organisms are now known to exist in peat (Paarlahti and Vartiovaara, 1958) and in plants growing on bogs (Bond, 1951, 1963), but generally nitrogen gas does not play an important role as a source of nitrogen for bogs. Ammonia, or ammonium ions, and oxides of nitrogen may arrive at the surface of a bog as gases or trapped by precipitation.

Mattson and Koutler-Andersson (1954, page 324) have stated: "among the gaseous constituents of the atmosphere ammonia and nitrogen oxides occupy an important position in the development of the raised bog inasmuch as these gases must be assumed to supply most of the nitrogen required by plants. The bog must be assumed to get more than its share of the nitrogen because no matter how low the gaseous pressure of the ammonia in the air, it must be lower in the highly base unsaturated peat. There must be a constant flux of ammonia from the air into the bog, apart from that which is brought down by the rain."

Once in contact with the peat, the ammonia is held securely or "fixed". Peat and mineral soils are known to retain atmospheric ammonia, in contrast to other forms of nitrogen, by physico-chemical fixation (Mattson and Koutler-Andersson, 1954; Sohn and Peech, 1958). Many aspects of this phenomenon have not yet been investigated in peats.

This project was undertaken to examine the phenomenon of ammonia fixation by peat. The proportion of this form of nitrogen to the total

nitrogen content of the peat, before and after ammoniation, is evaluated in relation to other selected properties of the peat and to the surface topography, especially that of the hummock-hollow association, of a bog.

CHAPTER I

A REVIEW OF THE LITERATURE ON AMMONIA FIXATION

Ammonia fixation has been known to take place in mineral soils

over a century ago (Malo and Purvis, 1964) and in peat more recently

(Mattson and Koutler-Andersson, 1943, 1954, 1955; Koutler-Andersson,

1960; Maksimow and Grudzinski, 1950; Bremner, 1952; Maksimow et al,

1963). Although the result, the fixation of ammonia or ammonium, is

similar the substances and mechanisms involved are not necessarily the

same. Possibly an approach to the study of ammonium fixation in peat

may have developed from that dealing with this reaction in mineral soils.

A brief examination of ammonia fixation by mineral soils will be

considered first and aspects of it will be compared and contrasted with

that occurring in the review of the literature on ammonia fixation by peat.

A. Ammonia Fixation by Mineral Soils

In a brief survey of the literature, Malo and Purvis (1964)

reported that Liebig in 1847 suggested that soils may absorb atmospheric

ammonia. They also reported that Bretschneider, in 1872, and Schlossing

were among the first to make quantitative estimations regarding this

phenomenon. Since that time various aspects of absorption and fixation

of ammonia and ammonium ions by soils have been studied.

Although Ingham (vide Malo and Purvis, 1964) stressed the

importance of organic matter in soil, most of the attention,

with the exception of Mortland (1955) and Sohn and Peech (1958), has
been directed towards the inorganic fraction, particularly the clay
components, as they affect ammonia fixation. The clay minerals to
which fixation is mainly attributed are illite, vermiculite, and
montmorillonite (Nŏmmik, 1957; Stojanovic and Broadbent, 1960; Welch
and Scott, 1960). Nŏmmik (1957, page 395) reported that

"it has been suggested that fixation involves replacement

by NH_4^+ and K^+ of interlayer cations (Ca^{++}, Mg^{++}, Na^+) in

an expanded lattice of micaceous clay minerals. This

replacement results in contraction of the crystal lattice

and in an entrapment of the interlayer NH_4^+ and K^+.

Cations of the contracted lattice can be replaced slowly

by cations that expand the lattice."

Stanford and Pierre (1946) (reported by Nŏmmik, 1957, page 395) have
shown that

"ammonium and potassium, having almost the same ionic

radii, are fixed by the same mechanism. Thus, if

potassium salts were added to the soil prior to the

ammonium, the amount of ammonium fixed was reduced

in proportion to the amount of potassium previously

fixed."

Dhariwal and Stevenson (1958) report similar competition between NH_4^+
and K^+.

There exists no general agreement with reference to the
best method for the determination of ammonia (Harper, 1924) or of

exchangeable ammonia in the soils (Allison and Roller, 1955; Hanway and
Scott, 1956; Nõmmik, 1957; Statzy and Motensen, 1957; Dhariwal and
Stevenson, 1958; Stevenson, 1959; Dashevskiy, 1960). Nõmmik (1957, page
395) reported

> "Barshad (1951) proposed to define the 'fixed' NH_4^+ as the
>
> NH_4^+ which is not replaceable by prolonged extracting and
>
> leaching the soil with K^+ salt solutions".

More recently Allison and Roller (1955, page 361) stated: "Fixed or
difficulty exchangable NH_4^+ can best be defined as that NH_4^+ which is
not removed by extraction with 1 N KCl". Methods used for quantitative
determination of fixed ammonia are: KCl leaching (Harper, 1924; Allison
and Roller, 1955; Nõmmik, 1957; Stevenson, 1959; Dashevskiy, 1960;
Stojanovic and Broadbent, 1960), KOH/ NaOH distillation (Allison and
Roller, 1955; Hanway and Scott, 1956; Nõmmik, 1957; Leggett and Moodie,
1962), dilute acid leaching (Mayboroda, 1961), dilute acidified salt
solution leaching (Sohn and Peech, 1958) mild alkali distillation
(Harper, 1924), and K_2CO_3 or Na_2CO_3 aeration (Harper, 1924; Leggett and
Moodie, 1962). With most of these methods, a known amount of NH_4^+ is
added as a salt solution and the amount not extracted is considered
fixed. Dashevskiy (1960) has considered the adsorbed ammonium to be
present in three forms, according to the strength of combination with
the adsorption complex. These are: (1) readily exchangeable - that
NH_4^+ extracted by one treatment of 1% KCl, (2) exchangeable with
difficulty - that removed only with repeated KCl extractions,
(3) nonexchangable - that not extracted even with prolonged washing of

the soil with 1 N KCl. Mayboroda (1961, page 206) has stated:
"There is little dissolved ammonium in soils . It is mainly absorbed
by colloids from which it is practically impossible to extract with
water."

In addition to ionic competition, other variables have been
found to affect ammonia fixation of soils quantitatively. Several
workers (Nõmmik, 1957; Mayboroda, 1961) have shown that ammonium
fixation by mineral soils is strongly decreased quantitatively as the
pH of the soil decreases. Walsh and Murdock, (1960) showed that removal
of water from soil, after NH_4^+ addition increases fixation of NH_4^+.

The effects of the moisture content and pH on ammonia fixation
by soils have been presented as a comparison for the variables affecting
ammonia fixation by peat in which water and acidic conditions are
important.

B. Ammonia Fixation by Peat

Investigations of nitrogen in peat have been made for several
decades. In the early 1930's, Feustel and Byers (1933) reported that
"much work has been done in trying to make enriched [with nitrogen,
primarily] peat a fertilizer". This enrichment was brought about by
an addition of ammonia to peat at high temperatures and pressures
(Feustel and Byers, 1933). The major problem encountered was the
availability of this added (and firmly bound) nitrogen for plant
utilization. Work on this problem is being continued mostly in Europe
(Minnesota Peat Mission to Europe, 1958).

Attention has been directed also toward the natural nitrogen

content of peat. All the forms in which nitrogen exists in peat are still not known. Although quantitative analyses of some nitrogen compounds have been made, that remaining after subtraction of the amount of known forms from the total nitrogen content has been grouped into categories established by extraction techniques. Waksman and Stevens (1928a) divided the total nitrogen in peat into three fractions: " (1) Soluble in cold and in hot water; this includes ammonia, nitrates, amino acids, and soluble proteins and is the smallest fraction in peat. (2) Nitrogen hydrolyzed readily by dilute acids; this fraction can be considered as the true protein nitrogen. (3) Nitrogen not readily acted upon by the above acid treatment." They added that these three groups account for all of the nitrogen. They also state that "although the [water-insoluble] nitrogen is recorded as protein, it does not necessarily exist entirely in that form in peat." This general group has been used as a matter of convenience, (Waksman and Stevens, 1928b). "Peat contains a considerable amount of nitrogen in a very resistant form. This may be referred to as 'humin nitrogen' (Waksman and Stevens, 1928a). This fraction may account for one-third of the total nitrogen in lowmoor and one-half of the nitrogen in highmoor peat (Waksman and Stevens, 1928b).

Kupreenko and Logvinova, (in Waksman and Stevens, 1929, page 327) found that "sphagnum peat contains a large quantity of its nitrogen in the form of adsorbed ammonia." "This phenomenon was naturally explained by the high content of absorbed ammonia in the sphagnum peat, but no explanation was suggested for the origin of this ammonia". (Ibid)

Mattson and Koutler-Andersson (1943) reported that humus possesses the natural capacity to fix large amounts of ammonia. Extending their investigations to peat, they found that the ability to fix ammonia existed there too. This fixed ammonia was found to have come from microbial ammonification and the atmosphere (Mattson and Koutler-Andersson, 1943). These authors examined this phenomenon considering the prerequisites for and variables involved in ammonia fixation, the substances which can fix ammonia, the results of ammonia fixation on the organic matter, and suggested theoretical mechanisms involved in this investigation.

When investigating the variables involved in ammonia fixation, Mattson and Koutler-Andersson (1943) found that lignin played an important role and that previously unoxidized lignin fixed most of the ammonia in the presence of oxygen and that very small amounts of ammonia were fixed under anaerobic conditions. They (Ibid) also found some correlation between ammonia fixation and the alkalinity of the ash of the peat. It was determined that the lower the alkalinity of the humus and litter, the greater was the amount of ammonia fixed. "All peat formed under conditions of low base status undergo autoxidation [and ammonia fixation] in the presence of oxygen if even a moderate amount of alkali is added", (Ibid, page 344). Investigating the chemical composition of peat profiles, Mattson and Koutler-Andersson (1954) determined that a negative correlation exists between nitrogen content and "excess base". This excess base or ash alkalinity was determined by finding the equivalents of base present in the ashed peat sample

(Mattson and Koutler-Andersson, 1954; Koutler-Anderson, 1960). In connection with the base status, it was found by these workers, (1943), that there was a decrease in fixation of ammonia with an increase in acidity of the peat.

Organic substances capable of fixing ammonia were investigated. Mattson and Koutler-Andersson (1943, page 133) determined that "water soluble and lignin fractions fix more ammonia per unit weight of organic matter than the whole sample." Large amounts of water soluble materials which possess the power of ammonia fixation are also soluble in alcohol (Ibid).

Attempting to obtain more information on ammonia fixation by lignin Mattson and Koutler-Andersson, (1943) extracted lignin from different sources. They found that two general forms of lignin exist, as determined by ammonia fixation capabilities. Lignin from green leaves is about as active in ammonia fixation as that from ripe litter, but wood and straw lignin is less active. They (Ibid, page 130) referred to the "active" type as "functional lignin" and the less active (woody) type as "structural lignin". In addition to this it was determined that "lignin from a base-unsaturated area is much more active than the lignin from base-saturated soil. The latter has been autoxidized and has fixed ammonia in nature to a much greater degree than the former" (Ibid, page 115). By doing ammoniation of peat samples in the laboratory these two workers, (1954), showed that the sum of the fixed nitrogen and the initial nitrogen is closely correlated with the lignin content in a peat profile.

Organic compounds of known structure were examined by Mattson and Koutler-Andersson (1943) for ability to fix ammonia. This investigation revealed that "glucose, fructose, di- and triatomic phenols, gallic and tannic acids fix large amounts of ammonia, the aromatic compounds as much as 14%" (Ibid, page 134).

The ammonia which is fixed by peat is in a nonexchangeable form and the ligno-nitrogenous complex is chemically very stable (Ibid). The ammoniated complex is very stable toward acids and even the strongest acid dissolved less than ten percent of it. Much fixed ammonia is removed even by magnesium hydroxide and 2N sodium hydroxide removes almost one half of it (Ibid).

These authors (1954) determined the amount of fixed ammonia as follows. They found the initial Kjeldahl nitrogen content, and then took a similar sample and shook it with 12% ammonia solution in the presence of oxygen. The sample was then acidified with HCl and washed free from salt with dilute acid and then with water. A Kjeldahl nitrogen determination was made of the peat residue. This value then presented the sum of the initial nitrogen and the ammonia fixed. By subtracting the original from the final nitrogen content the amount of nitrogen fixed was determined.

Organic compounds which have fixed ammonia are chemically altered in the process. Coloured water—soluble compounds of litter and humus become water insoluble and soluble organic matter becomes acid-insoluble after ammoniacal autoxidation. Substances having fixed ammonia take on a deeper colour. The autoxidized and ammoniated solvates

assume a distinctly amphoteric character. The fixed ammonia lowers the capacity of humus and peat to bind base and raises the base status and therefore raises the pH (Ibid).

The mechanism involved in the fixation of ammonia by peat components is not fully known. Mattson and Koutler-Andersson (1943) showed ammonia fixation to be an oxidation reaction. Although there appears to be no strict parallelism between autoxidation and ammonia fixation, if one is small the other is small. Mattson and Koutler-Andersson (1943) considered that the strong reducing power developed in the lignin, resulting in rapid autoxidation and ammonia fixation, occurred because the presence of the ammonia catalyses the fixation of ammonia by raising the base status of the lignin. At low pH, the base binding capacity of peat is higher the lower the nitrogen content. This particularly affects mono- and divalent cations which are too mobile to be cumulative in bogs except where there is a high base-binding capacity (Mattson and Koutler-Andersson, 1954). These authors (1943, page 120) also proposed that "the basic nitrogen in the humus functions as electropositive groups, each of which compensates an electronegative group, either by direct linkage or by virtue of their electric fields. This reduces the polar attraction on the solvent dipoles and reduces the solvation." Because the fixed ammonia lowers the capacity of humus to bind base, Mattson and Koutler-Andersson (1943), thought this indicated that the basic nitrogen formed an inner salt with the carboxy group, thus compensating for the acidity and at the same time suppressing the properties due to this acidity.

CHAPTER II

ATMOSPHERIC NITROGEN

If bogs, particularly those which are predominantly ombrogenous,
receive most of their nitrogen supply directly from the atmosphere, a
brief qualitative and quantitative assessment of sources and forms of
this element present in the atmosphere would be helpful for assessing
the importance of fixation. This chapter is concerned with informing
the reader of the concentrations of various forms of nitrogen in the
atmosphere, sources of these compounds, conditions under which they vary,
and supplying a detailed analysis of atmospheric ammonia.

Nitrogen occurs in the atmosphere as nitrogen gas (N_2), oxides
of nitrogen, ammonium ions (NH_4^+), and ammonia (NH_3). Nitrogen gas is
the most abundant form representing $78.084^{\pm} 0.004\%$ of atmospheric air,
excluding water vapour. Although much less than nitrogen gas, nitrous
oxide (N_2O) is the next most abundant form, being present in the
concentration of 0.5 ± 0.1 ppm. (parts per million) of dry atmospheric
air (Handbook of Chemistry and Physics, 1963). The other forms of
nitrogen are usually less abundant. Eriksson (1952) reported ammonium
concentrations in the atmosphere to be about 0.007 to 0.87 mg./m^3
(milligrams per cubic meter). Malo and Purvis (1964) in 1961 found
atmospheric ammonia concentrations to be from a trace to 0.22 mg/m^3
for the period July through October for New Brunswick, New Jersey, with
a daily average of 0.06 to 0.15 mg./m^3 for individual four day periods.

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Oxides of nitrogen come predominantly from the oxidation of
nitrogen gas, mostly by electrical discharge during electrical storms,
but also by photochemical reactions and from meteorite trails
(Angström and Högberg, 1952). Angström and Högberg (1952) proposed
the following reaction brought about by energy supplied by the sun:

$$6 \ N_2 + 18 \ H_2O \longrightarrow 4 \ NH_4NO_3 + 4 \ NH_4OH + O_2$$

With this reaction the ammonium produced is twice as much as
the nitrate produced. These workers thought that on a world-wide scale
there is an almost constant ratio of 2:1 in which ammonium nitrogen and
nitrate nitrogen respectively appear in precipitation and they believe
accordingly that this reaction would account for this. They (Angström
and Högberg, 1952) hypothesized that this reaction would transform about
three percent of the nitrogen present to give present concentrations
of ammonium and nitrate in precipitation. Some oxides of nitrogen
sometimes are released in considerable amounts by certain industries.
Nitrous oxides and nitrogen gas are also produced in the denitrification
of nitrate and nitrite by microorganisms and concentrations of these forms
vary with the degree of anaerobiosis of the soil or organic matter
(McElroy and Glass, ed., 1956).

Ammonia and ammonium ions are derived primarily from the
combustion of organic matter (Mattson and Koutler-Andersson, 1954).
This may occur in nature as a result of fires and slow decay of organic
matter. However a source of ammonia in some industrialized areas is the
combustion of organic fuels and the ammonia is present in the air as a
contaminant (Eriksson, 1952). Malo and Purvis (1964, page 244).

attributed the unusually high NH_3 content of the air they sampled in
New Brunswick to "NH_3 residues from coal, oil, and gasoline consumption".
Another very important source is the ammonia released to the atmosphere
with the use of ammonium fertilizers, particularly on basic soils, and
on the addition of lime to fertilized soils (Eriksson, 1952). These
sources may be of considerable magnitude in agricultural areas. Ammonium
nitrogen may also arise from the Angström and Högberg photochemical
reaction.

Although it is not a source for areas as far inland as the bog
examined by the author, sea water may contribute ammonium nitrogen to
bogs along the sea coast. The influence of the sea as a source of ions
has been intensively investigated particularly in the United Kingdom
and Europe. The influence of the sea is greatly controlled by the
distance from the sea and prevailing winds for the carrying of the spray.

Another source of nitrogen that Eriksson (1952) thought should
be included as a source of nitrogen to the atmosphere is the nitrogen,
mostly in the form of ammonia, present in rocks. He reported that
Hutchington had found that igneous rocks contain about 0.005% nitrogen
(by weight) and sedimentary rocks about 0.051% nitrogen (0.046% being
biochemically fixed). This form of nitrogen is very likely to be
released very slowly but may be more important during volcanic activity
(Mason, 1960), being found in limited quantities in lava, volcanic
effusions and crater gases (Encyclopaedia Britannica, Vol. 1, 1957).
Ammonia released by volcanic activity would be of significance in very
limited areas of the world.

Concentrations of nitrate nitrogen and ammonium nitrogen vary
with location and time. Ammonium nitrogen concentration in the
atmosphere is highest at the equator and decreases with latitude until
it is least at the polar regions where the concentration may be only
50% that at the equator (Angström and Högberg, 1951). Nitrate is
also highest in the tropics (Angström and Högberg, 1951). Eriksson
(1952) reported that the ammonium content of the atmosphere has two
maxima, one in the spring and one in the late summer, but Malo and
Purvis (1964) discovered that NH_3 concentrations were highest in April
and May and lowest in the period July through October. The minimum
occurs during winter. The nitrate nitrogen maxima vary less with the
season and more with the rainfall but usually occur about one and one-
half months after the ammonium nitrogen maxima (Eriksson, 1952).

The ammonium nitrogen content of the air varies with the amount
of precipitation having fallen previously (Angström and Högberg, 1951)
and with sources of replenishment. These variables bring minor minima and
maxima in concentrations of ammonium nitrogen within the larger trend
stated above. Very important factors with which the ammonium nitrogen
does not vary are the frequency of electrical storms (Angström and
Högberg, 1952) and the annual amount of rainfall (Eriksson, 1952).
Variations in atmospheric NH_3 content have been found to be as great
from day to day at one location as between different locations
(Malo and Purvis, 1964).

NH_3 content of rainwater was found to be significantly higher
in the relatively dry months. Malo and Purvis (1964) found that each

acre-inch of precipitation contained slightly more than 0.2 lb. NH$_3$-N
and that approximately 8.3 lb. N /acre was contained in the annual
precipitation. The concentration of ammonium nitrogen in precipitation
reaching the surface of a bog (or field) also varies with the form of
precipitation (Eriksson, 1952). Generally the ammonium concentration
increases as water droplet size decreases. Therefore fog and very fine
rains contain more of this form of nitrogen than rains made up primarily
of large droplets (Eriksson, 1952). The ammonium concentration also
tends to be higher in forms of precipitation derived closer to the
ground. Dew is generally very rich in ammonium particularly nitrogen
(Eriksson, 1952). This would be true particularly in regions of high
rates or organic decay and regions of intense nitrogen fertilization.
This source would be generally very low in arid regions where little
organic matter exists.

Extensive investigations of ammonium nitrogen in the atmosphere
have not been done because ammonia is not considered a common
atmospheric contaminent in cities[1]. In a review of the literature
Eriksson (1952) found a minimum in the amount of ammonium and nitrate
nitrogen brought to earth by precipitation of 1.9% kg./ha./yr. In this
review he reported an average ammonium nitrogen content reaching the
earth at Ottawa, Ontario, of 0.98 kg./ha./yr. between 1908 and 1924, but
there was an increase every year. The city of Hamilton, Ontario,
Municipal Laboratory on Smoke, reported ammonium nitrogen to be very

1. Personal communication with Hamilton Air Pollution
   Laboratory, June 9, 1964.

scarce in the atmosphere of that city, less than 0.01 ppm. (parts per million). A study was made of NH_3 in 1959 and 1960 in the area surrounding the American Cyanamid factory, a company producing urea at the time. Here the ammonia concentration in the air was 0.00-0.10 ppm. 84%, 0.11-0.20 ppm. 9.5%, 0.21-0.50 ppm. 6%, 0.51-1.0 ppm. 0.8%, and more than 1.1 ppm. 0.6% of the time, throughout these two years. This increase could be detected only in the immediate vicinity of the factory. The nitrogen trichloride method of analysis used was claimed to be accurate to 0.01 ppm.[2]

Information presented here has shown that the concentration of ammonia in the atmosphere is very low and variable with respect to some other forms of nitrogen and many other gases in the atmosphere. A mechanism by which this form of nitrogen, an essential element, can be used may be of signifcant ecological importance, if the utilization of more abundant forms of nitrogen is not possible.

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2.   Personal communication with Hamilton Air Pollution
       Laboratory, June 9, 1964.

CHAPTER III

COPETOWN BOG

The area from which samples were taken is a bog, referred to as
the Copetown Bog or Summit Bog (Spencer Creek Conservation Report, 1960),
situated along Highway 52, about two-thirds of a mile south of Copetown,
just within the northern border of Ancaster Township, Wentworth County,
Ontario (Atlas of the County of Wentworth, 1960). The location is
approximately $43^{\circ}14'$ N. and $80^{\circ}03'$ W. and is slightly less than 800
feet above mean sea level (Topographic Map, Brantford Sheet, 1934).

The bedrock underlying the bog is dolomite of the Guelph
Formation of the Silurian Period. This overlies dolomite of the
Lockport Formation which is the bedrock just to the north-east of the
bog. These formations overlie deposits of Rochester shale; Clinton
dolomite, limestone, and shale; Medina sandstone, shale; and limestone;
and shale of the Queenston Formation (Spencer Creek Conservation Report,
1960; Atlas of the County of Wentworth, 1960).

Physiographically, the surrounding terrain is classed as kame
moraine and outwash (Spencer Creek Conservation Report, 1960). The
characteristic features are hummocky, sandy areas of water washed sands
and gravels, dissected by drainage patterns (Spencer Creek Conservation
Report, 1960). The soil is sandy loam, with varying amounts of clay,
tending to be stony and shallow (Spencer Creek Conservation Report, 1960).

The dominant Great Soil Groups are Grey-Brown Podzolic,and, in poorly
drained areas, Dark Grey Podzolic (Matthews and Baril, 1960). According
to land capability classification, the mineral terrain in the region of
the bog varies from being "suitable for cultivation with simple to
intensive practices", particularly concerning erosion control, to being
"suitable only for permanent vegetation with moderate to severe
restrictions" (Spencer Creek Conservation Report, 1960; "Recommended
Land Use" Map).

In the Atlas of the County of Wentworth (1960) the dividing
line between the Grand River and Spencer Creek Systems is indicated as
the eastern edge of the Copetown Bog, however, the bog is under the
jurisdiction of the Spencer Creek Conservation Authority (1960). The
salient feature is that this bog lies right on the watershed. Although
free water is present within this bog, no inflowing stream can be found.
A culvert which was constructed presumably to restore the natural
drainage system which may have existed before the road was constructed,
exists at the southern end of the bog but water flow is detectable
only during high water (Stewart, 1963). Undoubtedly the bog receives
some water as run-off from the road and railroad embankments and from
the mineral slopes to the north but this would seem to be a small amount
in comparison with the total water content of the bog. The presence of
occasional mineral laminae in the peat (Ibid) well within the periphery
of the bog indicates that silt-clay bearing waters have covered at least
parts of the bog briefly during its development. It is suspected that
much of the water content of the bog is derived from a water table or

spring(s) directly under the bog (Ibid). Evidence points to the
condition that the present bog area was once open water (Ibid). A
high water level exists in spring, after snow thaw and spring rains.
This is followed by a decrease in water content at the bog surface as
a result of evapotranspiration and some runoff.

Sulphur Creek, part of the Spencer Creek System, arises to the
east of the bog from mineral springs, many of which are saline or
sulphurous (Spencer Creek Conservation Report, 1960). The dolomitic
rocks of the Guelph and Lockport Formations supply water good in
quality and quantity, but waters from the Queenston, Median, and Clinton
Formations may contain much iron, sulphur, and sodium chloride (Ibid).
The qualitative and quantitative information on the water which feeds the
bog is not available. It is assumed that the source is water table or
springs. The water from the small pond within the bog has been used in
the past as a source of water from steam locomotives on the nearby
railroad and for watering of livestock (Stewart, 1963).

The climate is also an important variable which affects
development of vegetation on the bog. The Copetown Bog lies just south
of the 45°F. annual isotherm which marks the northern boundry of the
"Lake Erie Counties", a region having one of the most favourable climates
for agriculture in Ontario (Putman and Chapman, 1938). The length of the
growing season is 190-200 days and the frost-free season is 140-150 days
(Ibid). The average winter temperature is about 23°F. and the average
summer temperature is about 67°F (The Climate of Canada, 1962; Putman
and Chapman, 1938). The average precipitation is reported to be less

than 32 inches of which 6 inches represents about 60 inches snowfall
(The Climate of Canada, 1962; Spencer Creek Conservation Report, 1960).
The prevailing winds are from the south-west (Spencer Creek Conservation
Report, 1960).

The bog itself is approximately 2000 ft. by 850 ft. and has an
area of about 28 acres (Stewart, 1963). The pond, north-east of the
centre of the bog, is reported to be over 45 ft. (14m.) in depth. A
discontinuous lagg exists with a water content which varies with the
season. Stewart's records indicate a maximum peat depth of about 7.5m.
(Ibid). The mineral matter below the peat is silt with some clay and
sand (Ibid).

The living vegetation is very characteristic of many other bogs
which the author has seen near Parry Sound, Ontario, and many of
Radforth's coverage formulae (Radforth, 1952) are present. As far as
the author knows, the vegetation, especially that near the centre of
the bog, has been altered little except for the decapitation of a few
spruce trees for use as Christmas trees. Quite likely the water regime
has been altered considerably by the building of the road and railroad
embankments but now the effect of this on plant associations is difficult
to assess. It is apparent that garbage left along the edge of the bog
next to the road and soil washed down from the surrounding mineral
terrain have affected the lagg vegetation. The intense use of fertilizers
and road salt likely would contribute to this change, especially in the
last few decades. The utilization of these ions by lagg vegetation and
absorption of ions by the peat probably has confined increased salt

concentration to the outer margin of the bog.

The peat samples were obtained from an area extending from about 550 ft. west-south-west of the small bog pond to the approximate centre of the bog. There is a transition of the vegetative types from IEF-EIF, according to the Radforth Coverage classes (Radforth, 1952) at the peripheral sites, to BEI at the more central ones. The peripheral regions are composed of very low hummocks with a thick growth of Sphagnum sp. in the wet hollows. The vegetation on the hummocks from which samples were taken is Chamaedaphne calyculata (L.) Moench, Sphagnum sp. with some Vaccinium oxycoccus L., Polytrichum commune L., and seedling Picea mariana (Mill.) B.S.P. and Larix laricina (Du Roi) K. Koch. The vegetation of the hollows in which samples were taken is primarily Sphagnum sp. with some V. oxycoccus, Calla palustris L., Drosera rotundifolia L., and Sarracenia purpurea L. In the BEI region the microtopography is of the accentuated hummock - hollow type. Here the hummocks are in various stages of development from low rolling wet ones with vigorously growing Sphagnum sp. and large sharp-sided ones with relatively dry tops, to decaying hummocks whose structure is presently deteriorating, showing bare peat. Hummock vegetation where samples were collected is C. calyculata, V. oxycoccus, Sphagnum sp., P. commune on wetter hummocks; C. calyculata, V. oxycoccus, Sphagnum sp., P. commune, and grasses on the dryer hummocks; and, on the degenerating hummocks, mostly P. commune, C. calyculata, various grasses and forbs, and Cladonia sp. The hollows in the BEI region contained standing water in June and little vegetation was present.

These hollows are mostly of bare peat or peat sparsely covered with
Sphagnum sp., _D. rotundifolia_, and _V. oxycoccus_. Gases with the odour
of hydrogen sulphide emanated from these hollows if pressure was
applied to the surface of the peat. The B vegetation of the BEI is
P. mariana and _L. laricina_, which are usually somewhat deformed. For
further information on the floristics of the entire bog the reader is
referred to Stewart (1963, pages 228 to 231).

CHAPTER IV

FIELD SAMPLES

A. Collection and Handling.

Peat samples were removed from hummocks and hollows using 12 oz.
tin containers. These cans were prepared by cutting off both
ends and sharpening the edge of one end.

Excess living vegetation, for example woody branches of
Chamaedaphne sp., was removed from the spot in which the sample was to be
taken. The can was then pushed down into the peat with a short clock-
wise and counter-clockwise twisting motion to cut the fibres present.
With the can at the proper depth, the surrounding peat was removed and
the sample was cut off at its base with a knife. As the can containing
the sample was removed most of the water was retained by placing a
hand under the open bottom. Then the sample was transferred to a glass
jar. About 1 to 2 ml. toluene (Mayboroda, 1961) was added to the sample
and the jar was covered with a plastic lid to prevent loss of water and
excess aeration.

In the laboratory, the gravitational water was allowed to drain
out of the samples. This water was filtered and its pH was determined.
The peat was then squeezed by hand and the water which was extracted
filtered and its pH was determined.

The peat was divided longitudinally into four or more pieces
and allowed to air dry while resting on, and covered with, paper towels

and filter paper in a room in which no ammonia was used.

Once air dried, sufficient peat was taken from this sample to provide subsamples of about 2 g. each. These were then weighed and given the appropriate treatment.

B. Description.

Samples of series A were collected on May 6, 1964, those of series B on June 11, 1964, and those of series C on July 2, 1964.

Site A: EFI hummock in EFI-FEI area I.

1. Samples: A1, B3, C2.

2. Location: top of a well-defined hummock in full sun all day.

3. Vegetation: Chamaedaphne calyculata (L.) Moench, various fine grasses, Sphagnum sp., Polytrichum commune L., Vaccinium oxycoccus L.

4. Moisture condition: damp (very little water able to be squeezed out by hand) to dry-damp (enough water present to prevent peat from becoming powdery when rubbed).

5. Peat description:

   (a) vegetation: about equal amounts of dark brown P. commune and light brown Sphagnum sp. with fine grass and fine-to-medium-fine, long, woody fibres of V. oxycoccus and C. calyculata.

   (b) structure: fibres orientated vertically; sample difficult to separate on a horizontal axis but easy to separate on a vertical axis.

(c) state of humification: mostly little decomposed, H2,

but showing a range from H1 to H3.

Site B: IE hollow in EFI-FEI area I.

1. Samples: A2, B4, C3.

2. Location: hollow immediately south of Site A.

3. Vegetation: mostly darkly coloured bare peat with some

young P. commune, Sphagnum sp., V. oxycoccus,

and, near the base of hummocks, C. calyculata.

4. Moisture condition: very wet (free standing water).

5. Peat description:

(a) vegetation: mostly Sphagnum sp. and P. commune with

pieces of sedge; fine woody fibres of

V. oxycoccus; leaves of C. calyculata and

V. oxycoccus.

(b) structure: amorphous granular peat held in a loose

mossy mesh; some matting on a horizontal plane.

(c) state of humification: mesh: H1 to H3; interstitial

material: H6; considerable range of change

present.

Site C: IE hollow in EFI-FEI area II.

1. Samples: A3, B1, B2, C1,

2. Location: hollow between low and poorly developed hummocks

in a treeless region between the lagg and the BEI

region.

3. Vegetation: mostly Sphagnum sp., with C. calyculata and

<u>V</u>. <u>oxycoccus</u>.

4. Moisture condition: very wet with much free water in May but considerably less in July.

5. Peat description:

    (a) vegetation: two distinct types of peat were present:

        (1) thin surface layer of little decomposed <u>Sphagnum</u> sp. with woody fibres (less than 5.0 mm. in diameter) of <u>V</u>. <u>oxycoccus</u>.

        (2) much more decomposed layer, mostly of indistinguishable plant remains but having woody fibres and leaves of <u>V</u>. <u>oxycoccus</u> and <u>C</u>. <u>calyculata</u>; fine grass, <u>Sphagnum</u> sp.; sedge culms near bottom of sample.

    (b) structure: (1) loose and spongy; (2) dense mesh of very fine fibres holding smaller fragments; matted on a horizontal plane.

    (c) state of humification: (1) very slightly, if at all, changed; H1 to H2.

        (2) much more decomposed with only most resistant parts still recognizable; dark brown in colour drying to light brown with black leaf fragments; H5 to H6.

Site D: EIF hummock in BEF-BFE area III.

1. Samples: A4, B8, C5.

2. Location: top of a well developed hummock (1½ ft. high)

receiving sun throughout the entire day.

3. Vegetation: _Sphagnum_ sp., _C. calyculata_, _V. oxycoccus_, fine grass; growth was not luxurious.

4. Moisture condition: damp to dry-damp.

5. Peat description:

    (a) vegetation: almost entirely _Sphagnum_ sp. with some fine grass; fine fibres of _V. oxycoccus_ and some coarser ones of _C. calyculata_; entrapped leaves of _C. calyculata_ and _V. oxycoccus_.

    (b) structure: typical loose mesh of _Sphagnum_ sp. with some reinforcement with woody fibres.

    (c) state of humification: generally little decomposition of _Sphagnum_ sp. with leaves of other plants exhibiting a great range of decay; H2. Peat light brown with slight reddish tint, drying to light reddish brown.

Site E: hollow in BEF-BFE area III.

1. Samples: B7, C4.

2. Location: hollow, immediately east of hummock at site D.

3. Vegetation: dark bare peat with some _Sphagnum_ sp.; _V. oxycoccus_ present but rooted at the base of surrounding hummocks and not in the hollow.

4. Moisture condition: wet (some free surface water present in June, very little free water present in July).

5. Peat description:

   (a) vegetation: (1) a thin surface layer of _Sphagnum_ sp.
   with woody shoots and leaves of _C. calyculata_
   and _V. oxycoccus_.

   (b) structure: (1) loose mesh of _Sphagnum_ sp.

   (2) loose mesh of fine, non-woody fibres
   reinforced with woody fibres.

   (c) state of humification: (1) light brown _Sphagnum_ sp.,
   very little decomposed; H1 to H2.

   (2) greatly decomposed with more than half of
   the material not botanically identifiable;
   leaves fragmented and black; H5.

Site F: hummock at edge of BEI area IV.

   1. Samples: B6, C11.

   2. Location: large, well-defined, elongated hummock with dense
   growth of _Picea mariana_ (Mill.) B.S.P. at one
   end (end not investigated).

   3. Vegetation: _Sphagnum_ sp., _C. calyculata_, some _V. oxycoccus_,
   and some short "layered" branches of _P. mariana_
   nearby.

   4. Moisture condition: damp.

   5. Peat description:

   (a) vegetation: almost entirely light brown _Sphagnum_ sp.
   with _V. oxycoccus_ and some _C. calyculata_ roots
   and shoots; entrapped leaves of _C. calyculata_

and _V. oxycoccus_.

    (b) structure: loose mesh of _Sphagnum_ sp. with horizontally orientated fine woody fibres.

    (c) state of humification: little decomposed _Sphagnum_ sp.; H2; blackened leaves of _C. calyculata_ and _V. oxycoccus_.

Site G: hollow at edge of BEI area IV.

    1. Sample: B5.

    2. Location: small hollow (8 in. by 12 in. surface area) in hummock at Site F; hollow about 2 ft. below top of hummock.

    3. Vegetation: mostly bare peat with some _Sphagnum_ sp.

    4. Moisture condition: wet, some free surface water.

    5. Peat description:

        (a) vegetation: small amount of _Sphagnum_ sp., mostly leaves and some roots and short twigs of _P. mariana_.

        (b) structure: generally no mesh; peat loose and crumbly when dry.

        (c) state of humification: peat very dark with advanced decomposition; H4 to H5.

Site H: hollow at edge of BEI area IV.

    1. Sample: C12.

    2. Location: small hollow on side of hummock (Site F) opposite Site G; slope of side of hummock very steep.

    3. Vegetation: _Sphagnum_ sp., _Drosera rotundifolia_ L., some _P. commune_.

4. Moisture condition: moist-wet (no free surface water but
much gravitational water in peat).

5. Peat description:

    (a) vegetation: _Sphagnum_ sp., leaves of _P. mariana_,
V. oxycoccus, and _C. calyculata_.

    (b) structure: fine, non-woody fibrous peat; tightly
matted; some fine, long, woody fibres;
separates with some difficulty on a horizontal
axis.

    (c) state of humification: some of the mosses are little
decomposed but generally vegetation is
fragmented and black in colour; H5.

Site I: hummock in BEI area V. (Area of well-defined hummock-hollow
associations).

1. Samples: B9, C6.

2. Location: top of hummock about 2½ ft. high; in mottled shade
of trees much of the day.

3. Vegetation: _Sphagnum_ sp.; fine grass, small _P. mariana_,
and some _V. oxycoccus_; FIE.

4. Moisture condition: damp.

5. Peat description:

    (a) vegetation: _Sphagnum_ sp., fine grass, fine woody shoots of
V. oxycoccus, leaves of _C. calyculata_, and
V. oxycoccus.

    (b) structure: loose mesh of _Sphagnum_ sp., grass shoots,

and roots with scattered woody fibres of
V. oxycoccus.

    (c) state of humification: _Sphagnum_ sp. light reddish-
brown to light grey-brown and little decomposed;
H1 to H2; leaves decomposed almost beyond
recognition.

Site J: hummock in BEI area V.

    1. Sample: B12, C8.

    2. Location: well-defined hummock, southern slope shows
mechanical breakdown and erosion; in full
sunlight throughout the day.

    3. Vegetation: _P. commune_, _C. calyculata_, _V. oxycoccus_,
Cladonia sp.; EIH; growth poor.

    4. Moisture condition: dry-damp to dry.

    5. Peat description:

        (a) vegetation: mostly _P. commune_ with small amounts of
Sphagnum sp.; few woody fibres and leaves of
C. calyculata and _V. oxycoccus_.

        (b) structure: fibres orientated vertically giving pulpy
effect; peat crumbles when dry.

        (c) state of humification: medium-to-dark brown when dry;
decomposition advanced; H4.

Site K: hummock in BEI area V.

    1. Sample: C10.

    2. Location: well-defined hummock south of site J. Top and

southern slope of hummock show mechanical

breakdown and erosion.

3. Vegetation: bare peat with poor growth of P. commune,

C. calyculata, and some brown Sphagnum sp.

4. Moisture condition: dry-damp to dry.

5. Peat description:

(a) vegetation: mostly P. commune with some Sphagnum sp.

and fine grass; few woody fibres and leaves of

C. calyculata and V. oxycoccus.

(b) structure: vertically orientated fibres of P. commune

interwoven with woody fibres; little mesh present;

tends to be spongy when damp but crumbles

easily when air dried.

(c) state of humification: mechanical breakdown advanced;

peat very dark brown with light brown Sphagnum

sp.; leaves fragmented and black; much material

not identifiable; H4 to H5.

Site L: hollow in BEI area V.

1. Sample: B10.

2. Location: elongated hollow immediately north of site I.

3. Vegetation: mostly bare peat and brown Sphagnum sp. with

V. oxycoccus creeping in from the surrounding

hummocks.

4. Moisture condition: very wet.

5. Peat description:

    (a) vegetation: most constituents beyond botanical

        recognition; leaves of <u>C. calyculata</u>, <u>V. oxycoccus</u>,

        and <u>Sphagnum</u> sp.; woody shoots of <u>P. mariana</u>,

        <u>C. calyculata</u> and <u>V. oxycoccus</u> present.

    (b) structure: tightly matted clumps built up of a mesh

        of fine fibres; hard and not spongy when dry;

        much amorphous granular peat present.

    (c) state of humification: wide range of decomposition

        present but most of peat H5 to H6.

Site M: hollow in BEI area V.

    1. Samples: B11, C7.

    2. Location: hollow immediately south of site J.

    3. Vegetation: no living vegetation, only darkly coloured

        <u>Sphagnum</u> sp. and bare peat.

    4. Moisture condition: very wet.

    5. Peat description:

        (a) vegetation: <u>Sphagnum</u> sp.; fragments of leaves of

            <u>V. oxycoccus</u>, and <u>C. calyculata</u>; sedge culms,

            short woody twigs. Much of the vegetation not

            botanically identifiable.

        (b) structure: amorphous granular peat held in a loose

            open mesh of non-woody fibres; dries to form

            very hard mass.

        (c) state of humification: most of the matter well decayed;

        H6.

Site N: hollow in BEI area V.

    1. Sample: C9.

    2. Location: elongated hollow between steeply sloped hummocks.

    3. Vegetation: _Sphagnum_ sp., _P. commune_, _V. oxycoccus_.

    4. Moisture condition: moist-wet.

    5. Peat description:

        (a) vegetation: (1) thin outer layer of _Sphagnum_ sp., and _P. commune_ with woody fibres of _C. calyculata_ and _V. oxycoccus_.

                    (2) thicker under-layer of _Sphagnum_ sp., woody fibres and leaves of _C. calyculata_ and _V. oxycoccus_.

        (b) structure: (1) weak mesh of mosses with some reinforcement with woody fibres.

                    (2) loose discontinuous mesh of non-woody fibres but presence of interwoven woody fibres makes separation of the peat difficult.

        (c) state of humification: (1) medium brown colour with decomposition evident; H3 to H4.

                    (2) leaves black and fragmented; some material not botanically identifiable; H4 to H5.

CHAPTER V

METHOD

A block of predominantly Sphagnum peat, which had been air dried

in the laboratory for more than ten years, was selected for the

development of a method to be used for nitrogen determinations and

ammoniating procedures. The faces were trimmed and discarded. Shavings,

tending to uniformity in colour, texture, and plant composition, were

removed from the remaining block of peat. After the few woody fibres

were removed, the shavings were blended in a Waring Blender for 5

minutes. The blended peat was then placed in a jar and shaken. Samples

from this jar were reblended. These reblended samples were transferred

to another jar and reshaken. About 60 grams of air dried peat was

prepared in this way. The largest plant remains which were recognizable

without magnification in this sample were individual Sphagnum sp. leaves.

Samples for analyses were composed of a sufficient number of small batches

of about 0.2 grams each of which was removed from the jar using a small

spatula.

This peat was light brown in colour and very little decomposed.

Although no water was present the degree of humification was estimated

to be about H2 on the von Post Humification Scale (Healey, 1961).

A second bulk sample was prepared from fresh amorphous granular

type peat which had been collected in the fall of 1963 in a bog north of

Parry Sound, Ontario, and had been air dried in the laboratory. This

when wet was dark olive-to-black amorphous granular peat with occasional light coloured non-woody fibres and occasionally a woody fibre. On the von Post Humification Scale this peat was H9. When air-dried the peat formed a dark brown-to-black, very hard mass. Thin lenses and layers of charcoal were present in the peat.

This sample was blended and mixed in the manner already described. The resulting fine-to-medium-fine powder with some small, short, non-woody fibres was stored in a tightly capped bottle.

In the digestion of peat by the Kjeldahl method, 1 to 2g., preferably 2g. (Malmer and Sjörs, 1955), samples of weighed peat were placed in a 500ml. Kjeldahl flask with 10.0g. K_2SO_4, 1.0g. $HgSO_4$, and 30 ml. concentrated H_2SO_4 (Wilson and Wilson, 1958). These chemicals and all others used were Fisher "Certified" Reagents. The flask contents were mixed and gently heated, with the flask tilted at a 45^0 angle. When frothing ceased the intensity of the heat was increased until full heat was applied and the mixture boiled vigorously. During heating the flask contents were swirled to flush down organic matter lodged on the wall of the flask above the boiling mixture. Heating was continued for the required period of time after the mixture "cleared". With the amorphous granular peat the digestion progressed to a stage at which the mixture was still faintly coloured and opaque but no change in these visible characteristics occurred with further heating. This characterized the "cleared" condition.

Comparisons of Kjeldahl nitrogen contents of digestions of blended peats were made for digestion periods of 2 and 3 hours after clearing.

Comparisons of nitrogen contents of digestions of blended

samples were made for digestion periods of 2 hours (Wilson and Wilson,

1958), with or without modification to include "azo or nitro derivatives"

(Willard, Furman and Bricker, 1956, page 161) and with or without the

addition of hydrogen peroxide to assist in digestion. For Kjeldahl

digestion to include the nitro derivatives (Paech and Tracey, 1955,

Vol. I), a 2 g. peat sample was placed in a 500ml. Kjeldahl flask with

10ml. of a solution containing 0.430 g. salicylic acid for every 100 ml.

of concentrated H_2SO_4. The sample was then thoroughly mixed with this

solution and allowed to stand for at least thirty minutes. Then 0.70 g.

sodium thiosulphate was added and the contents were heated for 1 minute

longer after copious white fumes were produced. The contents of the

flask were allowed to cool and then 10.0g. K_2SO_4, 1.0 g. $HgSO_4$, and 30 ml.

concentrated H_2SO_4 were added. When the effect of H_2O_2 was being

investigated, 1-2 ml. of 30% H_2O_2 was added to the flask contents after

the above chemicals. The heating was carried out in the manner previously

described.

When the period of time after clearing was completed the digested

mixture was allowed to cool. During the cooling process and during

storage small beakers were placed over the ends of the flasks to prevent

contamination. The flask contents were then slowly diluted with 200 ml.

of distilled water, and the contents were shaken until most of the salts

went into solution.

Several boiling chips were added and the flask with its contents

was connected directly to a distillation apparatus (Fig. 8).

After connection of the distillation apparatus, the drawn glass
tube was immersed as deeply as possible in a solution of 25.0 ml. of
0.10 N H_2SO_4 and several drops of indicator contained in a 250 ml.
Erlenmeyer flask which was tilted to make the acid solution as deep as
possible (Fig. 8). When required, 50.0 ml of the 0.10 N H_2SO_4 was used
when the peat sample contained more equivalents of nitrogen than were
contained in 25 ml. of this acid. The acid was measured by either a
25.0± 0.03 ml. or 50.0± 0.05 ml. Corning, Class A, NBS-C 602 transfer
pipet. A 45% solution of NaOH was placed in the separatory funnel and
was added to the flask contents dropwise. Excess of this base was
added to make the flask contents basic. Care was taken that there was
always some alkaline solution left in the separatory funnel to detect
any loss of ammonia through this passage. As the final base was added,
gentle heat was applied. Until the first distillate began to flow
bubbles were emitted by the drawn tube in the collecting acid. After
distillate had begun to collect the heat was regulated so that bubbling
in the acid collector no longer occurred. Distillation was continued
until 125 ml. of distillate was collected. Heating was stopped then
and the stopcock on the separatory funnel was opened to prevent the
drawing back of the distillate and acid into the condenser.

The acid of known volume and concentration was then back titrated
with NaOH with a normality of 0.05-0.06 to a methyl red/methylene blue
end point of grey. This indicator was prepared by dissolving 0.0636 g.
methyl red and 0.0319 g. methylene blue in 70ml. of 95% ethanol
(Ponomareva and Nikolayeva, 1961). This NaOH solution was prepared

according to the procedure recommended for the preparation of carbonate free decinormal sodium hydroxide solution in the chapter concerning standard solutions for Volumetric Analysis in the Handbook of Chemistry and Physics (1963, page 1660). This base was then titrated with 0.10 N H_2SO_4 (Fisher Scientific SO-A-220) to the phenolphthalein end point (fist sign of pink).

For all chemical procedures a reagent blank was used. This involved using all the same amount chemicals and following all steps of the procedure with the exception of the presence of peat. One reagent blank was used with every group of Kjeldahl digestions made at any one time.

For oven dried peat, the samples were spread out evenly on open glass petri dishes and placed in an electric oven at $105^{o}C$ (Malmer and Sjörs, 1955, Tibbetts, 1963) or some other desired temperature. Oven dried samples were stored in a desiccator with $CaSO_4$ as the desiccant.

Preliminary analysis of the blended samples was done with distilled water, but analysis of the Copetown Bog samples was done with "equilibrium water". Air was bubbled through dilute sulphuric acid to remove traces of ammonia, then through water to remove droplets of acid spray, and then it was passed through a cylinder of glass wool to remove dust. This "purified air" was then bubbled through the distilled water for 6 hours. This produced distilled water with a CO_2 content in equilibrium with the air (Kolthoff and Sandell, 1959).

For the ammoniation of samples using NH_4OH, concentrated NH_4OH solution was placed in a petri dish, containing glass wool, in the

bottom of a vacuum desiccator jar. The sample on a petri dish rested on a porous disc shelf. The jar was slightly evacuated using a water filter pump. The samples were then left a desired period of time.

Ammoniation of the samples using gaseous ammonia was done in the apparatus shown in figure 9 .

Samples were ammoniated in this apparatus by spreading the sample over the bottom of the 200 l. flask and immersing this in the water bath and leaving the ammonia-air mixture passing through it for 6 hours. Ammonia-air mixture was then passed slowly through the system with the flow controlled by a needle valve on the gas regulators attached to the air and ammonia tanks. The flow of ammonia and air was controlled according to predetermined rates and allowed to continue for 6 hours. At the end of ammoniation period the ammonia flow was stopped and the filter pump was connected to the acid ammonia trap outlet. While partial vacuum was applied, air was allowed to flow through the system. This was done to allow as little ammonia as possible to escape into the room when the peat sample was removed. The ammonia sample was placed in a glass container covered with filter paper, and placed in the fume cupboard until the odour of ammonia was no longer present.

The sample was then subdivided, weighed, and stored in individual 50 ml. beakers which were tightly covered with polyethylene sheeting. If the sample was not used immediately, it was reweighed just before being analysed. The samples were individually mixed with distilled water (50 ml./g. peat) and washed with another 100 ml. of distilled water in small volumes to remove free and readily available ammonia. This

filtrate was discarded.

Exchangeable ammonia was extracted with KCl. The damp sample was then mixed with 1M KCl (1 g. peat to 25 ml. 1M KCl) (Kaila, Koylijarvi, and Kivinen, 1953) for 30 minutes (Harper, 1924; Kaila, Koylijarvi, and Kivinen, 1953), filtered, and the residue washed with an additional 25 ml. 1M KCl in small amounts and then with 50 ml. of distilled water. A drop of HCl was added to the filtrate to prevent escape of ammonia.

The total filtrate was distilled with an additional 150 ml. distilled water and 2.0g. MgO (Harper, 1924; Nommik, 1957; Kaila, Koylijarvi, and Kivinen, 1953) to make the solution basic. Boiling chips were added and the distillate was collected in the same manner as that used for Kjeldahl distillations. There were 125 ml. (Harper, 1924) of distillate collected in 25.0 or 50.0 ml. 0.10 N H_2SO_4 and titrated to the methyl red/methylene blue end point with the base used for titrating distillates of the Kjeldahl digestions.

A Kjeldahl digestion was done on the residue from the KCl extraction. The filter paper used in the previous filtration was included in the digestion. A similar filter paper, with the same procedure applied to it except for the addition of peat, was included in the digestion with the reagent blank.

The amount of nitrogen initially present in the samples was calculated as:

1 equivalent weight of NaOH reacts with 1 equivalent weight of H_2SO_4 in the titration.

1 equivalent weight of NH_3 reacts with 1 equivalent weight of

H_2SO_4 in the distillation.

Therefore the number of equivalent weights of NH_3 neutralizing a certain

amount of H_2SO_4 is the same as the number of equivalent weights of NaOH

neutralizing this same amount of H_2SO_4.

x ml. of y N NaOH contains

$$39.999 \times \frac{x \ ml.}{1000 \ ml.} \times y \times \frac{1}{39.999} \quad \text{equivalent weights}$$

of NaOH which is equivalent to the same number of

equivalents of NH_3 and also of N.

This amount of NaOH is then equivalent to

$$39.999 \times \frac{x \ ml.}{1000 \ ml.} \times y \times \frac{1}{39.999} \times 14.008 \ g. \ Nitrogen$$

The number of equivalents of NaOH in the x ml. is the same number

of equivalents of NH_3 distilled and is arrived at by subtracting the

volume of base required to neutralize the remaining acid in the distillate

from the volume of base required to neutralize the acid from the reagent

blank distillation. The above equation then may be multiplied by the

distillation correction factor. The distillation correction factor was

determined by distilling a known weight of dried ($105^\circ C$ until constant

wt.) $(NH_4)_2 SO_4$, using the above described procedure, and determining

the amount of nitrogen present by back titration of the distillate

collected in acid of known concentration and volume. The distillation

correction factor was then:

$$\frac{\text{actual weight of Nitrogen in } (NH_4)_2SO_4 \text{ used}}{\text{weight of Nitrogen present calculated by titration}}$$

This factor may be included to compensate for lack of complete

efficiency in the nitrogen recovery in the distillation procedure. The distillation was carried out in association with a reagent blank. Weights of $(NH_4)_2 SO_4$ used were selected to determine the range of the weight of nitrogen used.

The general equation applied to the calculation of amount of nitrogen present in a sample was:

base volume difference x base normality x 14.008 x 10^3

x Distillation correction factor. This gave the amount of nitrogen present in grams.

The nitrogen present was expressed as a percentage of the sample weight as:

$$\frac{g. N.}{g. wt. of sample} \times 100$$

The amount of nitrogen determined in the sample before ammoniation was termed the initial Kjeldahl nitrogen content, N^O Kjeldahl. The amount of nitrogen determined by distillation of the KCl extract of the ammoniated sample gave the amount of readily exchangeable NH_4^+ and free NH_3 in the sample. Nitrogen present in the residue digested after the KCl extraction was given the term N^A Kjeldahl.

The amount of ammonia fixed, N_f^A, by the peat sample was determined by subtracting the initial Kjeldahl nitrogen content from the Kjeldahl nitrogen content of the ammoniated sample.

$$N_f = N^A \text{ Kjeldahl} - N^O \text{ Kjeldahl}$$

The ash content and alkalinity were determined in the following manner. A sample of the peat being investigated was oven dried at $105^O C$ to constant weight (Malmer and Sjörs, 1955; Tibbetts, 1963). This

weighed sample was then placed in a weighed, clean, moisture-free porcelain crucible. The covered crucible with its contents was heated gently until smoking stopped. The heat was then increased until the crucible was red and ashing was continued. The crucible containing its ash was then transferred to a desiccator jar. The crucible and ash were weighed after being allowed to reach room temperature (in excess of 2 hours). The ashing was continued until constant weight of the crucible and its contents was obtained.

The ash was then mixed with 25.0 ml. 0.10 N HCl (Gorham, 1953) filtered, and the filtrate and washings were back titrated with dilute NaOH of known normality to the phenolphthalein end point. A reagent blank was always done. The ash alkalinity or excess base was expressed as milliequivalents of base per 100 g. oven dry peat (Puustjärvi, 1957; Koutler-Andersson, 1960).

CHAPTER VI

RESULTS OF ANALYSIS OF PEAT SAMPLES FROM COPETOWN BOG

A. <u>pH Determinations of Water Extracted from Samples</u>.

Sufficient water was not available in the samples taken from tops of hummocks to make pH determinations with the equipment available.

The filtered gravitational water taken from the samples collected in hollows had a range in pH from 4.30 to 5.53 with an average of 4.74 (see Table 4).

The pH of the water squeezed out of the samples by hand, after the gravitational water was drained off, varied from 4.32 to 5.20, with an average of 4.69.

In all but two samples, C7 and C9, the pH of the water squeezed out was lower than the pH of the gravitational water.

B. <u>Ash content of Samples</u>.

The ash content of samples collected from hummocks varied from 4.76 to 23.2% (of oven dry weight). Within this range samples from eroded hummocks (Sites J and K) varied from 9.48 to 23.2% and the samples from non-eroded hummocks varied from 4.76 to 12.2%.

The ash content of samples collected from hollows (see Table 5) varied from 12.3 to 28.6%.

C. <u>Ash Alkalinity (Excess Base) of Samples.</u>

The ash alkalinity of the ashed samples collected from hummock tops varied from 19.4 to 33.0 milliequivalents per 100g. oven dry peat (see Table 5). The values of this property for peats from hollows was 1.57 to 35.9 m.e. per 100g. oven dry peat.

D. <u>Initial Nitrogen Content of Samples.</u>

The content of exchangeable (KCl extracted) nitrogen of samples before ammoniation was very low (see Table 6). Two samples from hummock tops had values of 0.020 to 0.024% with an average of 0.022% nitrogen of air dry weight.

Seven samples from hollows had an average of 0.019% nitrogen with a range of 0.012% to 0.027%. One sample, C8, from an eroded hummock at site J had an initial exchangeable nitrogen content of 0.018%. These concentrations were regarded as negligible, being less than 4% of the lowest Kjeldahl nitrogen content of the samples investigated.

E. <u>Initial Kjeldahl Nitrogen Content of Samples.</u>

As a percentage of oven dry weight of peat the range for initial Kjeldahl nitrogen was:

       hummocks (except J and K) :   0.580 to 1.02%

       hollows   -   :   0.852 to 1.50%

       eroded hummocks (J and K) :   0.879 to 1.40%

In Table 6 these values are also given as a percentage of air dry weight and of loss on ignition.

F. <u>Potassium Chloride Extracted Nitrogen Content of Ammoniated Samples</u>.

The amounts of nitrogen extracted from ammoniated samples by potassium chloride solution are listed in Table 7 as percentages of air dry weight, of oven dry weight, and of ignition loss. Ranges of values of this property as a percentage of oven dry weight are:

hummocks	:	0.479 to 1.29%
hollows	:	0.458 to 0.990%
eroded hummocks	:	0.781 to 0.912%

G. <u>Kjeldahl Nitrogen Content of Ammoniated Samples</u>.

In Table 8, are listed the values of Kjeldahl nitrogen from ammoniated peat samples. These values are given as a percentage of oven dry weight, of air dry weight, and of ignition loss weight. Ranges of Kjeldahl nitrogen content from ammoniated samples expressed as a percentage of oven dry weight are:

hummocks	:	1.01 to 1.44%
hollows	:	1.14 to 1.96%
eroded hummocks	:	1.18 to 1.33%

H. <u>Total Nitrogen Content of Ammoniated Samples</u>.

The total nitrogen content extracted from each ammoniated sample is recorded in Table 9 as a percentage of air dry weight and of oven dry weight and as a percentage of ignition loss of peat. Ranges of the total nitrogen content of the ammoniated samples expressed as a percentage of oven dry weight are:

hummocks	:	1.49 to 2.38%
hollows	:	1.59 to 2.93%

eroded hummocks   :   1.96 to 2.24%

I. <u>Fixed Nitrogen in Ammoniated Samples</u>.

The maximum range and average value by the peat samples investigated are listed in Table 10. These are expressed as percentage nitrogen of air dry weight, of oven dry weight, and of ignition loss of peat. The total range of nitrogen fixed by peats of specific topographic locations as a percentage of oven dry weight is:

hummocks   :   0.21 to 0.76%

hollows   :   0.39 to 0.96%

eroded hummocks   :   0.02 to 0.45%

CHAPTER VII

DISCUSSION

A. Expression of Chemical Concentration

It was thought that to facilitate comparisons of quantitative values of different properties of the samples a common referable property should be selected. The oven dry weight (105° C. for 24 hours) of the peat was chosen for this purpose. Units of concentration were given as a percentage of oven dry weight. Cursory inspection revealed that the concentration is comparable whether the property is expressed in proportion to 100 grams oven dry peat (for example: grams per 100 grams oven dry peat) or as a percentage. Both of these two units of concentration are common in the literature on peat (Waksman and Stevens, 1928a; Mattson and Koutler-Andersson, 1954; Sjörs, 1955; Puustjärvi, 1957; Gorham, 1961). Because in this work, nitrogen content was determined in air dry peat the concentrations were given also as a percentage of air dry weight. Sjörs (1961, page 17) has expressed concentrations of different chemical constituents of peat as a percentage of ignition loss because "loss on ignition represents the content of organic matter fairly well [in 'more', 'mull', and peat] ". This method did involve ash determinations which others may not require or obtain. Concentrations have also been given on the basis of percentage of ignition loss but results for individual samples differ little with respect to one another for the different peat samples studied.

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B. Evaluation of Procedures.

1. Preparation of a Uniform Sample.

To compare procedures for examination of chemical properties of peat either a sample which will always give reproducible results if the same conditions are applied, or an accepted quantitative reference for these properties is required. Neither is available. The heterogeneity of peat, with respect to many of the chemical properties, often is responsible for the existence of ranges in values which are wider among portions of a single sample than among samples from different locations.

An attempt was made to prepare a sample of peat, from which sub-samples could be taken, which in turn would give values for nitrogen content that would approach uniformity when analysed under similar conditions. Such a sample was prepared by the sorting and blending technique described in the "Method". Table 1 shows results of seven Kjeldahl analyses representing a precision of more than ninety-nine per cent. The variation was attributed primarily to determinate errors although some indeterminate errors possibly still occur.

2. Digestion Procedure.

Digestion of the Copetown samples was continued for two hours after clearing. This time was chosen on the basis of results obtained for the investigation on the blended peat samples. Because very little difference in concentrations of nitrogen took place between periods of two and three hours of digestion time the shorter period was chosen.

Decreasing by one half the amounts of potassium sulphate and mercuric sulphate used in the Kjeldahl digestions produced no change in the concentration of nitrogen of the blended samples. The smaller concentration was therefore used. The 30 millilitre volume of concentrated sulphuric acid was retained because smaller volumes brought about an increase in problems resulting in frothing and an extension in the digestion time before clearing. Even with this volume of acid, the immersed material tended to force the peat above up into the neck when heat was applied. Larger volumes of acid were not used because of the increased volume of base required to neutralize the acid before distillation.

Modification to include nitro derivations was examined. This involved the use of salicylic acid and sulphuric acid to change the nitro form to the nitrated derivative which was then reduced, by sodium thiosulphate, to an amino derivative, then finally to ammonium sulphate by the sulphuric acid (Willard, Furman and Bricker, 1956). This modification brought about no change in the nitrogen content of the blended samples (Table 2) and was therefore not included in the Kjeldahl digestions of the Copetown samples.

The addition of several drops of 30 per cent hydrogen peroxide, prior to digestion of the peat sample, was continued for the analysis of Copetown samples because it appeared to assist in mechanical breakdown of the peat. No variation in nitrogen concentration resulted from the use of this chemical (see Table 2).

3. <u>Efficiency of Distillation Apparatus and Procedure</u>.

The apparatus, as illustrated in Figure 8, was used for all required distillations. It was believed that with the use of this apparatus the flask contents could be make alkaline without any danger of the loss of ammonia. More base or distilled water could be added during distillation to the flask contents without any problem arising. This modification was found to be very useful when serious "bumping" of the contents occurred as distillation was nearing completion. An attempt was made to use a fritted glass gas dispersion tube in place of a glass tube drawn to a fine point. Leggett and Moodie (1962, page 161) emphasized the importance of the use of "multiperforated delivery tubes" in place of "open end tubes". "Small but significant amounts of NH_3 escape sortion by the acid in large bubbles released from an open end delivery tube" (Ibid). With the use of a sintered glass delivery tube a build up of an initial pressure inside the apparatus before the first bubbling occurred either forced apart the individual pieces of the apparatus resulting in a leakage of ammonia or sprayed some of the collecting acid out of the flask with a rapid release of bubbles, thereby ruining the determination.

Efficiency of the distillation procedure was determined by distilling known amounts of ammonium sulphate. Comparison of the results of nitrogen determined by distillation was made with the amount of nitrogen initially present in the dried, weighed sample. Results of this examination were as follows. For a 2.7×10^{-3} g. sample of $(NH_4)_2SO_4$ recovery was 95.73± 0.56% of the weighed sample (two determinations);

for a 20 x 10^{-3} g. sample, recovery was 96.91%; and for a 40 x 10^{-3} g. sample, 98.53%.

Several determinate errors were involved in this investigation. The electric balance used was found to be inaccurate when small portions were extracted from the larger samples. The balance consistently gave heavier readings for these small portions than if they were weighed alone. The distillation apparatus was therefore probably more efficient than the above results indicate. Other determinate errors which would account for the variation are: errors in pipetting and titrating, and loss of ammonia in large bubbles. Because of the doubt of the validity of these results of ammonia sulphate distillations, the values of nitrogen concentrations recorded in the tables were not corrected with the distillation correction factor. This had very little effect on the relative nitrogen concentrations. Consideration was given however when the ranges of nitrogen concentrations of Copetown samples were compared with those of the literature.

4. <u>Ammoniation.</u>

Blended samples were ammoniated to obtain some idea of the properties of ammoniated peat, to compare procedures for the extraction of exchangeable ammonia, and to determine ranges in concentrations of fixed ammonia. Ammoniation of blended samples was done using ammonium hydroxide solution because the ammoniating equipment utilizing gases was not operable at that time. This preliminary procedure was not satisfactory because the moisture in the closed jar caused caking of the surface of the peat and controlled proportions of

ammonia to air were not possible. The equipment used for the
ammoniation of the Copetown samples overcame these two problems and in
addition constantly renewed the gas which was in contact with the peat.
Analyses were not made to determine if all the peat in each ammoniating
vessel did come in contact with this gas mixture under similar
conditions but precautions were taken to prevent packing of the peat
in these containers to allow free gas movement.

The accurate determination of rate of flow of gases was not as
important with the techniques of nitrogen analysis used here as with
methods used by other workers (cf. literature review: Mattson and
Koutler-Andersson, 1943; Allison and Roller, 1955). The rate of flow was
about 50 litres of air and 5 litres of anhydrous ammonia per hour.
The proportion of air to ammonia was therefore 10 to 1. The rate of
flow and proportion of gases were reproducible for the ammoniation of
all Copetown samples.

Samples of B9 and C6 were ammoniated on July 4 and July 9
respectively. The values of nitrogen concentration of these samples
show less variation than the values of nitrogen concentrations of
subsamples of B7 which were taken from one ammoniated sample (Table 9).
Duplicate values of this property for samples A1, B5, and B12 were
determined in the same manner as those of B7. These results tend to
discount any variation due to differences in flow rates of gases in
the ammoniating apparatus on different days or they show that small
variations in flow rates do not affect the fixation of ammonia by these
peats.

5. <u>Ash Alkalinity.</u>

A problem arose in the back titration of the filtered acid with
which the ash had been mixed. During the titration with dilute sodium
hydroxide solution a flocculent, white precipitate formed which tended to
obscure the first sign of pink of the phenolphthalein indicator. This
precipitate formed as neutrality of the mixture was approached (from the
acid side). Puustjärvi (1957, page 192) reported that the solution and
precipitation of aluminium and iron caused considerable inaccuracy in
this method [of Gorham (1953) and the one used by this author] .
Puustjärvi (Ibid) recommended that the hydrochloric acid be replaced by
"an ammonium acetate buffer solution adjusted to pH 4.5 with HCl. The
acidity of pH 4.5 was chosen for the reason that aluminium cannot yet go
into solution at this reaction". This modification is recommended for
future work on ash alkalinity.

6. <u>pH Determinations.</u>

The pH determination of the peat water filtrates were made on a
Beckman Zeromatic (electric) pH meter using separate glass and calomel
electrodes. Du Rietz (Sjörs, 1950, page 245) reported that "the pH
determinations had to be corrected for a salt error which was mainly due
to difference in ionic strength (of cations) in the sample and in the
comparison buffers". This correction varied with specific electrical
conductivities and whether or not calcium was the dominant cation (Ibid).
Sjörs (1950, page 246) stated: "It is evident that +0.3 is the proper
correction to apply in strongly acid dilute waters" if proper measurements
cannot be taken to determine the exact correction. These measurements of
quantitative and qualitative analysis of cation were not available for

the Copetown Bog. The values recorded in Table 4 are not corrected for
the "salt error".

7. Addition of Toluene to Fresh Samples.

Less than two millilitres of toluene was added to the fresh
samples as they were collected in the field to discourage microbiological
activity (Mayboroda, 1961). Waksman and Stevens (1929, page 336) have
determined that "the treatment of peat with toluene, even without the
removal of the toluene extract, but merely allowing the solvent to
evaporate, more than doubled the rate of peat decomposition". The
extent of this phenomenon was not investigated in the present work. The
volume of toluene used here was quite small in relation to the volume,
about 600 cubic centimetres, of peat. Waksman and Stevens did not state
the volumes of toluene with which they were concerned. All the fresh
samples collected had equal opportunity to decompose with respect to use,
both of this chemical and the analytical procedures. The values given
for the initial Kjeldahl nitrogen content in Table 6 for sample A4 were
obtained in chronological order over a period from May 19 to June 18.
Subsamples of A1 examined for initial nitrogen content did show an
increase in this property over the period of time from May 19 to July 3
(see Table 6). If the nitrogen content does increase, the loss must be
less than the gain of this element. Waksman and Stevens (1928b, page 250)
reported that on the drainage of bogs there is a "rapid liberation from
peat complexes, of nitrogen, in the form of ammonia". Nikonov and
Minkina (1961, page 67) reported: "The intense mineralization of
organic substances is not accompanied by any substantial losses of

nitrogen". This increase in nitrogen then could be due to this latter explanation (Ibid) or to possible fixation of ammonia from the air in the laboratory. Because of the small amount of the peat obtained from each site, subsamples were not analysed to determine the extent of ammonia fixation during exposure to the air in the laboratory.

8. Sample Size.

A 2.0 to 2.5 gram amount of dry peat was selected as the appropriate size for analysis in this investigation. Malmer and Sjörs (1955, page 48) stated: "a little more than 2 g. [of peat and fresh plant material] is the desirable minimum for analysis". In the present work the size stated is considered optimum for showing basic trends for purposes of comparisons and yet it is capable of showing diversity of chemical reaction within the peat.

Decreasing sample size decreases precision of duplicates (Sjörs, 1961). Small samples collected side by side at a site, which appears to be uniform in all features, may show as much variation in any of the chemical properties investigated as between samples collected from different sites. This is due to a change in importance of individual physical components of the peat relative to one another. For example, a small woody twig is not as likely to impose its own chemical properties on the total properties in a block of peat in which it represents less than one per cent of the mass than if it is in a very small sample in which it may represent thirty per cent of the mass. The twig is present in both samples but its relative importance is different. This example is particularly pertinent if the nitrogen concentration of the sample is

being investigated.

If larger samples are used, sufficient peat may not be available to make the desired number of analyses. With some of the little decomposed, air dry, mossy peats (especially if they have not been compacted during handling) a two gram amount may represent a sample volume *in situ* of about 200 cubic centimetres. Not very many samples of this size can be taken from the top of a hummock or from a small patch of *Sphagnum* sp.

In the present work three - two gram subsamples were required for analyses. One was for initial nitrogen content determination, one was for ammoniation, and one was for ash content and excess base determinations. Even with a sample of this size not all of the desired analyses could be done on each sample, as can be seen from the tables. This is due to losses of samples by frothing during digestion, contamination, and equipment breakdown.

9. Oven Drying of Samples Before Initial Nitrogen Determination.

In Table 3 are recorded the results of analyses of the initial Kjeldahl nitrogen content of peat samples, after these samples had been oven dried at 105° C. in excess of 20 hours. The sample which was prepared by blending peat comprised of *Sphagnum* sp. showed a loss of weight of 10.4 to 14.5% of the air dry weight. The average weight loss increased with the increased period of heating. The Kjeldahl nitrogen content of these two sets of samples differed. Those heated for 43 hours showed a distinct decrease in this property while those heated for one week showed little change in this property. It is assumed that

those samples heated for one week had lost some nitrogen also in the same amount of time as those heated for 43 hours but this loss must have been compensated for by a gain in nitrogen over this one week period. This replenishment could have come only from the air by way of ammonia fixation by the peat. No further investigation was made into this phenomenon on the basis of fixation in proportion to time.

The two Copetown samples (A2, A3) showed a definite loss of approximately 20 per cent in initial Kjeldahl nitrogen after 21 hours of oven drying.

Unfortunately no chemical investigations are known to have been done of the sample comprised of Sphagnum sp. when it was fresh. Kjeldahl nitrogen content of this blended peat is somewhat below the concentration range of this element for Sphagnum peat samples recorded in the literature (Mattson and Koutler-Andersson, 1943; Gorham, 1961; Sjörs, 1961). A nitrogen loss could have taken place over a period of years. Oven drying may have just accelerated this process in the fresh sample. Kaila et al (1953, page 45) reported that loss of organic matter and of total nitrogen from peat was almost negligible at temperatures below 150^{0} C. They reported that the forms (nitrate-nitrogen, organic-nitrogen, and ammonia) in which nitrogen occurs may vary with temperature but the total nitrogen content remains almost constant. "Heating of moist samples at 75^{0} C for two hours brings about a marked accumulation of ammonia nitrogen. The treatment with dry heat was less effective except when the temperature was raised to 200^{0} C in which case carbonation of peat took place" (Ibid, page 45). "The volatization of ammonia from a medium

more acid than pH 6.5 occurs at a very slow rate" (Ibid, page 41). The
peat samples examined had a pH value less than 6.0. In addition "a
fairly regular decrease in the pH values with increasing temperature
can be demonstrated within the range from 50° to 150°" (Kaila et al,
1953, pages 43-44). In association with this, these workers (Ibid,
page 41) point out that "the possible fixation of ammonia.... may
deserve some attention".

The results of analysis of initial nitrogen content of peat
samples oven dried and recorded in Table 3 appear as contradictions of
the work of Kaila et al.

The results obtained in the present work may be anomalies
but this could only be determined by analysis of more samples.
The occurrence of possible changes in nitrogen concentrations in the
peat samples with oven heating led the author to make all nitrogen
analyses on air-dried samples.

C. Discussion of Results of:

   1. pH Determinations.

   The pH values of the gravitational water of the peat samples
were somewhat high for an ombrogenous bog. Gorham (1961, pages 104 to
105) reported pH values of an ombrogenous bog peat to be from 3.3 to 4.7
with a mean of 3.8. These results were obtained by direct insertion of a
glass electrode into the wet peat. "It should be pointed out that
direct insertion of a glass electrode into fresh peat measures not only
free acid in solution but also some of the ions adsorbed by peat colloids"
(Ibid, page 103). Sjörs (1950, Figure 3, page 250) graphed the ranges
in pH which he had found for "different kinds of mire communities".
Here he gave normal ranges of pH values as: "mosses 3.7-4.2; extreme poor
fens 3.8-5.0; transitional poor fens 4.8-5.7; intermediate fens 5.2-6.4;
transitional rich fens 5.8-over 7; extreme rich fens about 7-about 8.4"
(Ibid, pager 251). Sjörs indicated that "these figures are significant
only in North Sweden, and only for determinations made by the same
methods" (Ibid).

   Two important features of pH analyses of peat for purposes of
ecological studies have come forward here. Exact pH correlations with
surface vegetation do not exist and different methods of analysis
produce different results.

   The pH results in Table 4 showed no trend in variation with
different times of collection. The "C" samples were collected when the
water level was much lower than when the "A" samples were collected.
Sjörs (1961) stated that acidity increases as peat dries. Apparently
this reaction does not occur with a mere decrease in content of

gravitational water or, if it does, other variations may also occur
which obliterate the trend in change.

   2. Ash Determinations.

        The results of ash determinations of peat samples, as recorded
in Table 5, showed that peat collected from hollows had a much higher
ash content than peat collected from hummocks. This phenomenon has
been observed by others (Mattson and Koutler-Andersson, 1954; Malmer and
Sjörs, 1955; Gorham, 1961). Gorham (1961, page 104) attributed this
variation in ash content between hummocks and hollows to differences in
"degree of decay", the peat of the hollows generally being more decayed.
This feature was observed for samples collected from the Copetown Bog.

        The ash content of peat of Copetown samples, particularly those
of hollows, was considerably higher than the range of this property
recorded in the literature for ombrogenous bogs (Mattson and Koutler-
Andersson, 1954, Table 6 and 8; Sjörs, 1961, Table 4; Gorham, 1961,
Tables 1 and 2). These authors reported ash contents in ombrogenous
bogs to be less than 9% for hollows and less than 5% for hummocks.
Gorham (1961, Table 2) reported mean ash contents as:

Ombrogenous Sphagnum Bog Peat	3.2% (of dry weight)
Lacustrine Bog Peat	11.6%
Reedswamp and Carex Fen Peat	20%

The total determinate errors did not account for much of the variation
in ash content which existed between results of the present work and
results recorded in the literature.

        The ash content of samples taken from Area II revealed another
phenomenon. Two completely different classes of peat were found in

very close contact (see "Description of Samples"). The upper layer of peat was greatly decomposed. Sample Clb was composed only of the lower layer of peat. The ash content of this sample approximated that of peat from hollows having little surface vegetation. Samples A3, B1, and B2 were composed of peat from both layers. Graph 1 showed that these samples contained a considerable range of ash content, (from about 12 to 25 grams ash per 100g. peat). Samples collected from any other site did not show this much variation in this property.

The ash content increased with increasing decomposition. Area II had two peats at two different stages of decomposition. The upper peat would therefore be expected to have a low ash content and the lower peat, a high ash content. Mixtures of these two layers in various proportions should have resulted in ash contents which lie between the values of these peats, if each would have been analysed separately. The upper layer of peat was less than one inch thick. Peat which was decomposed very little tended to be very light in weight. The samples were of a size that sufficient peat of the upper layer was not available to form a two gram sample. Because of this, all samples of peat of Area II contained a significant amount of the denser peat of the lower layer. If this was so the peat of the upper layer must have had a very low ash content to have brought about a change from 25 grams (for peat from the lower layer) to 12 grams ash per 100 grams peat. The ash content of the upper layer of peat would then have approximated that of peat collected from tops of hummocks. Wide ranges in concentration were found for initial nitrogen content, ash alkalinity, and Kjeldahl nitrogen content of ammoniated samples indicating the above explanation to have been possible.

The sharp transition from one layer to the other in different properties indicated a sudden change in development from stagnation of growth to rapid growth. This phenomenon was observed at no other place in the bog but it is known not to be uncommon.

3. Ash Alkalinity.

The range of excess base (ash alkalinity) in samples from Copetown Bog agreed very closely with those of Puustjärvi (1957, Table 4) and Mattson and Koutler-Andersson (1954). Results listed in Table 5 showed no clear distinction between values for hummock peat and values of peat from hollows although peat from hollows had an ash alkalinity range which extended below that of hummock tops (see Graph 4). There was also a tendency, for the values of this property, for peats from hummock tops to be grouped together in the approximate middle of the total range. Mattson and Koutler-Andersson (1954, Table 6) gave values of excess base for peats from a hummock top of 13.38 m.e. per 100g. and of a hollow (depression) of 9.52 m.e. per 100g. dry weight. These workers found that peat samples selected at different depths within the hummock had an ash alkalinity content which varied between 8.56 and 13.51 m.e. per 100 grams dry weight. This range was slightly lower than that found in the present investigation. Puustjärvi (1957) reported average values of ash alkalinity for different peat types as:

Bryales - sedge	30.6 m.e. / 100g.
Eutrophic Sphagnum-Carex	44.8 m.e. / 100g.
Forest sedge	31.0 m.e. / 100g.
Carex	16.7 m.e. / 100g.
Sphagnum-Carex	12.9 m.e. / 100g.
Carex-Sphagnum	10.7 m.e. / 100g.

Forest Sphagnum   8.2 m.e. / 100g.

Sphagnum   11.5 m.e. / 100g.

This table of results is very difficult to accept if variation with topography of bog surface as great as that found in the present study is not an anomaly. Although some error may have been due to the formation of precipitate during titration (see "Discussion of Methods") in the present work, the values obtained should not be totally disregarded.

4. Initial Kjeldahl Nitrogen Content of Samples.

The range of values for initial nitrogen content of samples from Copetown Bog (Table 6) agreed with that range reported by Mattson and Koutler-Andersson (1954, Table 6), Gorham (1961, Table 1) and Sjörs (1961, Table 4).

Samples from hummock tops had an initial nitrogen content lower than that of samples taken from hollows (Graph 1). Samples taken from the tops of eroded hummocks had values which lie in the region between the ranges of the other two sites. Mattson and Koutler-Andersson (1954), Gorham (1961), and Sjörs (1961) have found similar relationships in this property between peat of hummocks and hollows. (No references have been found in the literature for eroded hummocks). This relationship is attributed to the fact that hummock peat is usually less decomposed (Gorham, 1961). Nitrogen contents were reported lowest under "regenerating Sphagnum" (Ibid, page 106). The results of the present work tended to support this. Site C had the most luxurious growth of Sphagnum sp. and its initial nitrogen content was relatively high. This however was due to the inclusion of more decomposed peat below the Sphagnum sp. peat.

High initial nitrogen content is "an expression of stagnation
of growth " (Mattson and Koutler-Andersson, 1954, page 357). In this
investigation highest initial nitrogen contents were found in hollows
having little or no living vegetation surface cover, thereby supporting
Mattson's explanation.

5. <u>Nitrogen Content of Ammoniated Samples</u>.

Although Mattson and Koutler-Andersson (1954) investigated the
amounts of total nitrogen and fixed ammonia in ammoniated samples of peat
taken from a profile of the Ramna Bog, no references could be found in the
literature for these properties of peat samples collected from the surface
of a bog. Comparison of results of investigation of these properties of
peat collected from hummocks and hollows, in this study, with the results
of others is therefore not possible.

From Mattson and Koutler-Andersson's results (1954, Table 3)
ranges of properties of ammoniated peat can be obtained. They found that
total nitrogen (after ammoniation) varied from 2.65 to 4.83% nitrogen of
organic matter. Total nitrogen of ammoniated samples taken from Copetown
Bog varied from 1.68 to 4.11% nitrogen of matter lost during ignition
(ignition loss) (Table 9). Using the wet ammoniation method, Mattson
and Koutler-Andersson (Ibid) found concentrations of fixed nitrogen to
have been from 1.17 (near the surface) to 3.92% nitrogen of organic
matter. Their lower concentration had about 0.3% nitrogen more than the
highest found in samples from the Copetown Bog. This difference in
concentrations may have been due to differences in methods of ammoniation.
These authors reported (Ibid, 1943) that "ammonia fixation amounted to
4.00% nitrogen by the wet method and 3.44% by the dry method" for a

particular sample being investigated. Although their "dry method" of ammoniation was quite different from that used here, the resulting difference in amount of ammonia may still apply. No comparison was made for samples of lower nitrogen concentration so that the difference in fixed nitrogen between Copetown samples and those of Mattson and Koutler-Andersson's (1954) work could be due either to differences in ammoniating technique or differences due to the peat itself.

Results of potassium chloride solution extracts of ammoniated samples showed the concentrations of this exchangeable ammonia to be approximately equal (Table 7) irrespective of sample location. No correlation could be found between the variations in concentration of exchangeable ammonia and any other property investigated of these samples. Ranges in concentrations of Kjeldahl nitrogen of the ammoniated samples differed for peat from hummock and hollow (Table 8). Ammoniated peats taken from hollows contained larger amounts of Kjeldahl nitrogen than ammoniated peats from hummocks. Samples from eroded hummocks differed little from those of other hummocks with respect to values of this property.

Peat collected from hollows tended to fix more ammonia than peats from hummocks (Table 10). Peat from eroded hummocks fixed the least amount of ammonia. This phenomenon was clearest if per cent nitrogen of ignition loss was examined. In this way the nitrogen was expressed essentially as a percentage of organic matter.

D. Correlation of Nitrogen Content of Ammoniated Samples with Other

Properties Investigated.

Values in Graph 3 indicated an approximation to linear correlation
between ash content and Kjeldahl nitrogen of ammoniated samples exists.
Linear correlation was more nearly approached between the initial
Kjeldahl nitrogen content and the ash content of the peat samples
investigated (Graph 1). The slopes of these two lines were very
similar. The position of these lines was selected visually.

Analysis of Graph 3 showed that all samples of peat did not
have the same potential for fixing ammonia although samples from specific
locations designated by topography tended to group together. The
presence of these groups of values suggested that a topographic factor
was associated with chemical properties of the peat.

Graph 1 showed closer correlation of nitrogen content with ash
content for peat from hummocks than for peat from hollows. This result
combined with the unusually high ash content could have been attained
through influence of wind erosion of the surrounding fields and
subsequent settlement of the wind-borne matter onto the surface of the
bog. In spite of this high ash content, correlation between ash content
and nitrogen content was not lost. The addition of this wind-borne
matter to the bog surface was likely to have less effect on the ash
content of peat from hummocks than from hollows because there was more
opportunity for the particles to have been washed off the hummocks into
the hollows. Here it tended to accumulate. This substantiates Sjörs'
(1948) findings that vertical water movement occurred less in hollows
than in hummocks. Lateral surface movement of water was believed to have

been negligible except perhaps during flooding. Very little ash
therefore would have been distributed very far laterally on the surface
of the bog.

Ash content was not as closely correlated with Kjeldahl nitrogen
content of ammoniated peat as it was with initial Kjeldahl nitrogen
content (refer to Graphs 1 and 3). This was most obvious with peat from
hummocks. Not only was the proximity of the values to the regression line
decreased but considerable horizontal rearrangement of points relative to
one another has occurred for values of peat from hummocks. Rearrangement
has not occurred to the same extent for values of peat from hollows.
Determination of ash content was of less value for prediction of total
potential nitrogen content for peat from hummocks than for peat from
hollows. In contrast, ash content analysis did enable one to make closer
predictions of the initial nitrogen content of peat from hummocks than
of peat from hollows.

Koutler-Andersson (1960, page 35) emphasized that "a distinct
negative correlation between total nitrogen and excess base in ash" was
characteristic of bog profiles, with some exceptions, especially in the
upper part of the profiles. Graph 4 showed that a possible inverse
relationship between ash alkalinity and total nitrogen of the ammoniated
sample may exist for peat near the surface but until more values are
available conclusion on this point is tentative.

E. Comparisons of Selected Properties of Peat From Hummocks and Hollows.

Many have examined certain aspects of hummock-hollow association
in bogs (Kulczynski, 1949; Mattson and Koutler-Andersson, 1954; Sjörs,
1949, 1961; Gorham, 1961; and others). Kulczynski (1949) reported that

R. Sernander and L. von Post were the first to propose the "lenticular regeneration of Sphagnum peat". H. Osvald extended this idea and developed a theory concerning the "regeneration complex" which joins together associations of the raised bog into an "association complex". Kulczynski (1949, page 67) stated: "Today the theory of the lenticular regeneration of Sphagnum peat stands among the most beautiful and well grounded achievements of bog science".

Basically this hummock-hollow regeneration cycle involves development of two ecologically diverse Sphagnum types - (1) the hydrophilous Sphagna and (2) the semiterrestrial Sphagna - and the changes they bring about enabling other plants to develop. Oswald [reported by Mattson and Koutler-Andersson (1954, page 356)] describes, with reference to species, the development of vegetation beginning in a wet depression and ending in a fully developed hummock. Osvald (Ibid) continues:

> "After the hummock has grown to a certain height
> it gets too dry for the mosses which dry out and
> are replaced by heather and lichen. But then the
> growth is inhibited, and as the surrounding parts
> simultaneously grow in height a day will eventually
> come when the former hummock is drowned, heather and
> lichen rot away and their place in the wet depression
> is again invaded by Sphagnum cuspidatum. A new cycle
> has started."

The role of each species and associations of species has been studied in this sequence (Kulczynski, 1949; Mattson and Koutler-Andersson, 1954; Gimingham et al, 1961). Chemical analyses of certain properties of peat have been studied in hummocks and hollows (Mattson and Koutler-Andersson, 1954; Sjörs, 1949, 1961; Gorham, 1961). In agreement with

the results of these workers, the results of this investigation of
the properties selected do show a difference in ranges of values of
peat of hummocks and of hollows. These properties which have distinct
ranges are: initial nitrogen content, total and Kjeldahl nitrogen content,
and ash content. No differences were found to exist between peat of
hummocks and hollows in loss of weight on oven drying, ash alkalinity,
and exchangeable ammonia. Although there is considerable overlap of
ranges, the concentration of fixed ammonia may differ for peat of hollows
and hummocks.

The higher nitrogen and ash contents, of the hollows indicate
that there is a stagnation of growth. The initial nitrogen content
is believed to be higher than that of peat from hummocks because the
hollows contain more peat which is more humified or decomposed. As
humification occurs all plant remains do not break down at the same rate.
Lignin being a more resistant compound, tends to increase in proportion
to the total organic matter. Mattson and Koutler-Andersson (1943, 1954)
stated that lignin is not the only component which is capable of fixing
ammonia but it is one of the most important. Therefore, relative
increases in lignin in peat lead to an increase in the initial nitrogen
content which is expressed as a percentage nitrogen of peat weight.
Comparison of the results listed in Table 6 with assessed von Post
Humification numbers supports this explanation. Further evidence is
that total nitrogen after ammoniation varies with the state of the
peat.

The amount of nitrogen fixed by peat collected from eroded
hummocks encourages speculation. The initial Kjeldahl nitrogen content

of this peat falls within the range of values for this property of peat

from hollows. The total nitrogen content of ammoniated peat of eroded

hummocks lies within the range of values for this property of peat

from hummocks. From this it appears that the ammonia fixing

constituents of peat from eroded hummocks differ little from those of

less decomposed peat from non-eroded hummocks. The author believes that

peat from the eroded hummocks investigated has a higher initial nitrogen

content because this peat is more exposed to the atmosphere. The eroded

hummocks have surface vegetation which is less dense and luxurious and

they have peat which has a looser, crumbly structure than non-eroded

hummocks. The eroded hummocks tend to be drier on top probably because

of the breakdown on fine capillaries with the development of a coarser

structure. These features very likely allow for freer movement of air

in and out of eroded hummocks than of non-eroded hummocks. Some samples

from eroded hummocks fixed little or no ammonia during ammoniation,

possibly because they had already effected fixation to their capacity.

A longer period of ammoniation then would have brought about no further

change in the final nitrogen content.

The peat from these eroded hummocks are more decomposed than

peat from non-eroded hummocks but are less decomposed than the peat

of most hollows. If ammonia fixation increases as decomposition of

peat increases the peat of eroded hummocks should be expected to have

a total nitrogen content after ammoniation which is somewhere between

the values of this property for peat of hummocks and that for peat of

hollows. This does not occur. To account for this phenomenon one could

believe that either the ammonia fixing constituents have not increased

yet in relative importance or that some of the ammonia fixing constituents have been lost during decompostion.

In addition, the very wide range of values of initial nitrogen content and ash content of these samples is somewhat confusing because there does not appear to be a wide range of decomposed peat present. A possible answer arises after an examination of Tables 6 and 9. Sites L and M were hollows immediately adjacent to the eroded hummocks of sites I and J. Peat from sites L and M, particularly M, has an initial nitrogen content which is among the highest found. Peat from these two hollows had the highest nitrogen content after ammoniation. In addition they had a very high ash content. It is possible that a constituent of peat which is capable of fixing ammonia has moved from the tops of the eroding hummocks down into the nearby hollow, perhaps under the influence of moisture during precipitation. The exact substance is not known but is probably either small solid particles or a water-soluble substance. The latter is possible because Mattson and Koutler-Andersson (1943) reported water soluble matter in peat which was capable of fixing ammonia. If the substance was soluble it would be leached out of all hummocks and into the hollows. The end result would be an inverse correlation between peat of hummocks and peat of nearby hollows with respect to ammonia fixing capabilities. This was not found. This substance must therefore become mobile after decomposition of peat reaches a more advanced stage.

The very high ash content of peat of site M cannot be attributed to wind blown matter because this site was very near the middle of the

bog. Neither surface courses nor vertical movements of mineralized water is apparent in this area. The only likely source then is mineral matter washed out of the nearby eroded hummock. This mineral matter would become mobile during mineralization of organic material of the hummock. This lends support to the view that the nitrogen fixing substance may be released in greater proportions during peat decomposition.

Another phenomenon characterized by peat from sites L and M is their very low concentration of excess base (ash alkalinity). The base-binding capacity of peat was reported to a very inversely with nitrogen content and with huminosity (Mattson and Koutler-Andersson, 1954). The peat from these sites illustrates this inter-dependency very well for here the highest initial nitrogen contents and lowest concentrations of excess base were encountered.

The possibility of the above described and explained changes of properties of peat, during the dying and erosion of a hummock, being an anomaly due to analytical errors is poor. The inter-dependency of the investigated properties of peat still exists for peat from eroded hummocks.

F. Implications Arising From Results.

Ranges of values are considered to be more reliable than specific values where chemical constitution of peat is involved. Averages of certain properties of peat of specific sites designated by topographic location are useful for approximations, but knowledge of the range of values for the pertinent property provides the context of reference.

Thus, Graphs 1, 2, 3, and 4 can be used for determining approximations of values. This is done by determining the equation of the

regression line, (for example the equation for this line in Graph 1 is:
Ash content = 24 (Initial nitrogen content) - 9.8), and substituting a
value for one of the unkown properties and solving the equation for the
other. The resulting value for this property is an approximation but
it is likely to be close enough to the possible value to determine at
least whether the sample came from a hummock or a hollow.

With a material as heterogeneous as peat, for the chemical
properties investigated, and very likely for some others, application
of statistics could be difficult and dangerous. Sjörs (1950, page 242),
after examining concentrations of dissolved salts, emphasized: "Even
if it were possible to obtain statistically good results by some method,
some rare but interesting combination of [water] conditions might be
overlooked". In conjunction with this, samples of peat which appear to
be outliers should not be discarded for the sake of procuring better
approximations. The worker must be aware these samples do exist and they
really may not be anomalies.

Because of the tedious and time consuming processes involved in
the study of cores of profiles of a bog, there is a tendency to examine
only one core per bog and to base all conclusions and predictions on the
results obtained from that core. The variations in results obtained in
the present investigation readily show a shortcoming of the single core
investigation. Here values of some of the properties have doubled within
a lateral distance of just one foot. No reason is known why this
variation would be completely destroyed as depth of samples in the bog
increases. As long as peat retains its heterogeneity, and the present
work shows how difficult it is to prepare a homogeneous sample, no

possible prediction can be made for changes in vegetation and certain chemical properties with respect to time and peat deposition which could apply to the entire bog. At the most only the sequence of events for that site, which have been recorded in the core examined, can be ascertained.

The results of the present investigation also indicate that the use of an average value of a certain property to represent the conditions existing for that property in a specific type of bog is of little practical use. Averaging the results of hummocks and hollows together of most of the individual properties investigated in the present study merely gives a hypothetical concentration for this property and says little about the conditions which exist in the bog at this time.

Peat may be heterogeneous but the diversity of concentrations of certain properties can still be handled to obtain useful and meaningful results if approximate ranges are determined and if changes in influence of relative components with changing sample size is recognized and considered. (This was illustrated previously with the example of a woody twig in a block of peat composed mostly of a moss).

Results of this work lend further evidence to the argument that hummocks and hollows are real identities having their own chemical properties in addition to their own plant associations. It is possible then that other visible topographic features of bogs have chemical characteristics specific for them. Investigation of these other features from this aspect may lead not only to a better knowledge of their distribution, but also to factors which affect the initiation and conclusion of their existence. The author wishes to caution the reader that although specific ranges of chemical characteristics exist for

topographic features there is no reason to suppose that any single factor should determine the differentiation of these features. This differential is very likely the result of co-variation of several factors.

The author is aware of some of the problems of microbiological activity in bogs and the effect on changes in certain properties of peat and of the restrictions certain properties of peat impose on the activity of microorganisms and development of higher plants, but examination and discussion of this has not been considered an integral part of the present investigation although it may prove worthy of study in the light of the results of the present work.

SUMMARY AND CONCLUSIONS

To compare methods of analysis of initial nitrogen content a sample of peat, which was almost uniform in this property, was required. A sample of sufficient uniformity was prepared by a sorting and blending technique. Methods shown to be satisfactory by the use of this blended peat presented few problems when used on fresh samples.

Before assessment of the phenomenon of ammonia fixation could be made properties initially present in the peat were examined. The air dry samples investigated contained very little exchangeable nitrogen. Although the concentration of this property was not uniform, it did not vary with any of the other properties investigated. A wide range in concentration of the initial Kjeldahl nitrogen content was found with the values of peat from hummocks being lower than those of hollows. The values of this property for peat from eroded hummocks extended, with some overlap, from the values of initial nitrogen content of non-eroded hummocks to those of hollows. Subsamples taken from a sample collected from any of the sites investigated varied as much in initial Kjeldahl nitrogen content as samples collected from the same site at different times.

Peat collected from the hollows investigated was characterized by a range in ash content which was higher than that of peat from the hummocks investigated. The range of amounts of ash content of peat from eroded hummocks extended, with some overlap, from the lower to the higher range of values of the other two site types.

The values of pH of gravitational water and of water squeezed from the sample were high for ombrogenous bogs and they varied with none of the other properties investigated. In all but two samples the gravitational water had a lower pH than the water squeezed from the sample.

The range ash alkalinity content of the samples investigated was greater than that recorded in the literature for ombrogenous bogs.

The results of the present work have substantiated the reported phenomenon that ammonia is absorbed and fixed to some extent by peat. Results indicated that ammonia from the atmosphere may have been fixed by the peat samples while they were air drying. Gaseous ammonia, in concentrations greater than in the atmosphere, was fixed by peat during ammoniation. The degree of ammonia fixation was governed by the amount of ammonia previously fixed, the total potential of the peat for ammonia fixation, and the amount of ammonia available. All peat did not have the same potential for fixation of ammonia.

That ammonia which was not removed from the peat by water washings but was removed by 1 M. potassium chloride solution was defined as exchangeable ammonia. The exchangeable ammonia content varied, but in no predictable manner, with the samples investigated.

The concentration of total nitrogen after ammoniation tended to be higher for peat from hollows than for peat from hummocks. The concentration of this nitrogen in peat from eroded hummocks differed little from that of peat from non-eroded hummocks.

Peat from hollows tended to fix more ammonia than peat from non-eroded hummocks. Peat from eroded hummocks fixed the least amount of ammonia and some of this peat fixed no ammonia at all during ammoniation. It is possible that peat from eroded hummocks had fixed atmospheric ammonia almost to their full potential while they were still in situ. This was possible because of the greater air movement possible in the loose structure of peat of eroded hummocks than in the vegetation-covered, non-eroded hummocks and the water-soaked, denser peat of hollows.

The concentration of ammonia fixed during ammoniation was always less than the amount of nitrogen initially present and was also less than the amount of exchangeable ammonia, for each sample investigated.

Correlation has been found between nitrogen content of peat, before and after ammoniation, with certain other properties of the peat investigated.

Peat collected from both hummocks and hollows was characterized by a straight line relationship between the initial Kjeldahl nitrogen content and the ash content of the samples and also between initial Kjeldahl nitrogen content and Kjeldahl nitrogen content after ammoniation. This was supported by an approximation to a straight line relationship between Kjeldahl nitrogen content of the ammoniated sample and ash content of the samples. Here then were three properties which varied together. Approximations of the concentration of any one of these properties could be made if values of any of the other two properties and the equation of the regression line are known.

There was evidence in the present work to suspect that total nitrogen content of the ammoniated sample may have varied inversely with the ash alkalinity. This relationship has been observed in peat profiles of bogs by others.

Analysis of results of the present investigation has suggested that phenomena related to the properties studied have occurred.

The ash content of peat of both hummocks and hollows has been found to be considerably higher than that found in the literature for ombrogenous bogs. This increased ash content was attributed to a settling of wind-borne mineral matter onto the surface of the bog. This should be considered in areas where much cultivation is common. In spite of this high ash content the relationship between total nitrogen content and ash content of the peat was still present.

There appeared to be an accumulation of substances, capable of fixing ammonia, and of mineral matter in hollows, particularly those near eroded hummocks. Water movement was the most likely method of transportation of these substances. This tended to substantiate the claim of Sjörs that water movement is more extensive in hummocks than in hollows.

Results have shown that although peat is heterogeneous, with respect to the properties investigated, fairly distinct ranges of concentrations of these properties existed and were characteristic of peat of both hummocks and hollows. This then was further evidence that hummocks and hollows are real entities having their own chemical characteristics as well as having their own plant associations.

Averages of any of the properties investigated are useful and meaningful only if they are considered in context with the ranges in concentrations of these properties. Neglection of these ranges is neglection of the presence of the heterogeneity of peat with respect to certain properties. In light of this, use of results, obtained from single core analysis, to explain past conditions and general development of the bog as a whole is subject to serious error. For the same reason representation of a certain property of an entire bog by an average value is not likely to be of much value for depicting the actual conditions existing in the bog at that time. Because statistics very often involves the establishment of means and averages, attempts to enforce its use may lead to serious errors by causing the worker to overlook unusual situations which may arise.

BIBLIOGRAPHY

ADDOMS, R. M. and MOUNCE, F. C.
1931   Notes on the nutrient requirements and histology of the cranberry (<u>Vaccinium macrocarpon</u> Ait.) with special reference to mycorrhiza. Plant Physiol. 6: 653-666.

ALEXANDER, M.
1961   Introduction to Soil Microbiology. John Wiley and Sons, Inc., New York.

ALLISON, F. E. and ROLLER, E. M.
1955   A comparison of leaching and distillation procedures for determining fixed ammonium in soils. Soil Sci. 80: 349-362.

ANGSTRÖM, A. and HÖGBERG, L.
1951   On the content of nitrogen (NH_4-N and NO_3-N) in atmospheric precipitation. Tellus (Swed. Quart. Jour. of Geophysics) 3: 31-42.

ANGSTRÖM, A. and HÖGBERG, L.
1952   On the content of nitrogen in the atmospheric precipitation in Sweden. Tellus 4 (4): 271-279.

ATLAS OF THE COUNTY OF WENTWORTH (AN)
1959-1960   Hamilton Wentworth Planning Area Board, Hamilton.

BLACK, W. A. P., CORNHILL, W. J. and WOODWARD, F. N.
1955   A preliminary investigation on the chemical composition of Sphagnum moss and peat. Jour. Appl. Chem. 5: 484-492.

BOND, G.
1951   The fixation of nitrogen associated with the root nodules of <u>Myrica gale L.</u> with special reference to its pH relations and ecological significance. Annals of Botany 15 (60): 447-459.

BOND, G.
1963   The root nodules of non-leguminous angiosperms. Symposia of the Society for General Microbiology, No. XIII, Symbiotic Associations.

BOTAN, E. A., MILLER, J. J. and KLEEREKOPER, H.
1960   A study of the microbiological decomposition of nitrogenous matter in fresh water. Arch. Hydrobiol. 56, No. 4: 334-354.

BREMNER, J. M.
1949   Studies on soil organic matter. Part I: The nature of soil organic nitrogen. Jour. of Agric. Sci., XXXIX: 183-193.

BREMNER, J. M.
1952   The nature of soil-nitrogen complexes. Jour. Sci. Food Agric. 3: 497-500.

CLIMATE OF CANADA (THE)
1962   Meteorological Branch, Air Services, Dept. of Transport, Toronto. Roger Duhamel, Queen's Printer and Controller of Stationery, Cat. No. T56-162, Ottawa.

DASHEVSKIY, D. I.
1960   Improved method for determining adsorbed ammonia in soil. Soviet Soil Sci. (Pochvovedenie) No. 8: 885-891 (trans.).

DASHEVSKIY, D. I.
1962   Method of extracting adsorbed NH_4^+ from soils. Soviet Soil Sci. (Pochvovedenie) No. 11: 1260-1262 (trans.).

DHARIWAL, A. P. S. and STEVENSON, F. J.
1958   Determination of fixed ammonia in soils. Soil Sci. 86: 343-349.

ENCYCLOPAEDIA BRITANNICA
1957   Encyclopaedia Britannica Inc., Chicago.

ERIKSSON, E.
1952   Composition of atmospheric precipitation. I: Nitrogen compounds. Tellus Vol. 4, No. 3: 215-232 (Inst. Pedology, Roy. Agric. Coll. Sweden, Uppsala).

FERNALD, M. L.
1950   Gray's Manual of Botany. 8th ed. American Book Co., New York.

FEUSTEL, I. C. and BYERS, H. G.
1933   The decomposition of hydrolytic peat products including ammoniated peat. U.S.D.A. Tech. Bull.No. 389: 1-32.

GIMINGHAM, C. H., MILLER, G. R. and SLEIGH, L. M.
1961   The ecology of a small bog in Kinlochewe Forest, Wester Ross. Trans. Bot. Soc. Edinb. 39, II: 124-147.

GORHAM, E.
1953   Notes on the acidity and base status of raised and blanket bogs. Jour. Ecol. 41: 153-156.

GORHAM, E.
1957   The development of peat lands. Quart. Rev. Biol. 32: 145-166.

GORHAM, E.
1961   Water, ash, nitrogen and acidity of some bog peats and other organic soils. Jour. Ecol. 49: 103-106.

HANWAY, J. J. and SCOTT, A. D.
1956   Ammonium fixation and release in certain Iowa soils. Soil Sci. 82: 379-386.

HARPER, J. V.
1961   The determination of ammonia in soils. Soil Sci. 18: 409-418.

HEALEY, J. V.
1961   Organic terrain reclaimation in Newfoundland. L. von Post Humification Scale. Appendix "i" Proc. 7th Muskeg Res. Conf. April 1961. Tech. Memo. No. 71, N.R.C., Ottawa, 1961.

HEINSELMAN, M. L.
1963.   Forest sites, bog processes, and peatland types in the Glacial Lake Agassiz Region, Minnesota. Ecological Monographs, 33: 327-374.

HODGMAN, C. D.
1963   Handbook of Chemistry and Physics. Chemical Rubber Publishing Co., Cleveland, 1963.

JOFFE, J.
1949   Pedology, Pedology Publications, New Brunswick, New Jersey.

KAILA, A., KOYLIJARVI, J. and KIVINEN, E.
1953   Influence of temperature upon the mobilization of nitrogen in peat. Maataloustieteellinen Aikakauskirja (Jour. Sci. Agric. Soc. Finland) 25 (2): 37-46.

KIVEKAS, J.
1958   The effect of drying and grinding peat samples on
                        the results of analysis. Maat. Aik. 30: 1-9.

KOLTHOFF, I. M. and SANDELL, E. B.
1959   Textbook of Quantitative Inorganic Analysis.
                        Macmillan Co., N.Y.

KOUTLER-ANDERSSON, E.
1960   Geochemistry of a raised bog. Part 3: Correlation
                        between total nitrogen and ash alkalinity in bog-
                        peats. Annals of the Royal Agric. Coll. of Sweden
                        Vol. 26: 33-40.

KULCZYNSKI, S.
1949   Peat Bogs of Polesie. Mem. Acad. Sci. Cracovie,
                        Ser. B: 1-356.

LEGGETT, G. E. and MOODIE, C. E.
1962   The aeration-recovery method for determining ammonium
                        fixation by soils under moist conditions. Soil Sci.
                        Soc. Amer. Proc., Vol. 26, No. 2: 160-163.

MACFARLANE, I. C.
1957   Guide to a Field Description of Muskeg (Based on
                        the Radforth Classification System) National
                        Research Council, Canada, Associate Committee on
                        Soil and Snow Mechanics. Tech. Memo. 44, N.R.C.
                        4214, Ottawa.

MAKSIMOW, A. and GRUDZINSKI, Z.
1950   Sorption of gaseous ammonia and ionic ammonia by
                        peat. Roszniki Gleboznawcze V. I: 131-148.

MAKSIMOW, A., MACIAK, F. and LIWSKI, S.
1963   Direction of chemical investigations of peat soils in
                        Poland. Int. Peat Cong., Leningrad.

MALMER, N. and SJÖRS, H.
1955   Some determinations of elementary constituents in
                        mire plants and peat. Botaniska Notiser Vol. 108:
                        46-80.

MALO, B. A. and PURVIS, E. R.
1964   Soil absorption of atmospheric ammonia. Soil Sci.
                        Vol. 97, No. 4: 242-247.

MASON, B.
1960   Principles of Geochemistry. John Wiley & Sons, N.Y.

MATTHEWS, B. C. and BARIL, R. W.
    1960   The soils of the Great Lakes - St. Lawrence
                          Lowlands. In "A Look at Canadian Soils".
                          Agric. Inst. Review Vol. 15, No. 2: 37-40.

MATTSON, S. and KOUTLER-ANDERSSON, E.
    1943   The acid-base condition in vegetation, litter, and
                          humus: VI. Ammonia fixation and humus nitrogen.
                          Annals Royal Agric. Coll. Sweden, Vol. 11: 107-134.

MATTSON, S. and KOUTLER-ANDERSSON, E.
    1954   Geochemistry of a raised bog. Part 1. Annals
                          Royal Agric. Coll. Sweden. Vol. 21: 321-366.

MATTSON, S. and KOUTLER-ANDERSSON, E.
    1955   Geochemistry of a raised bog. Part 2: Some
                          nitrogen relationships. Annals Royal Agric. Coll.
                          Sweden. Vol. 22: 219-244.

MAYBORODA, N. M.
    1961   Determination of ammonium in the soil by acid
                          extract method. Soviet Soil Sci. (Pochvovedenie)
                          Feb. 1961: 206-208 (trans.).

McELROY, W. D. and GLASS, B. (ed.).
    1956   A Symposium on Inorganic Nitrogen Metabolism.
                          Sponsored by McCollum-Pratt Inst. of John Hopkins
                          U., John Hopkins Press, Baltimore.

MEINZER, O. E. (ed.).
    1942   Hydrology. McGraw-Hill Book Company, New York.

MINNESOTAS PEAT MISSION TO EUROPE.
    1958   A report of the Minnesota Technical Mission to the
                          U.S.S.R. and other European nations. Iron Range
                          Resources and Rehabilitation, St. Paul, Minn.

MORTLAND, M. M.
    1955   Adsorption of ammonium by clays and muck. Soil
                          Sci. 80: 11-18.

NIKONOV, M. N. and MINKINA, T. I.
    1962   Nature of change in peat under influence of
                          aeration. Soviet Soil Sci. (Pochvovedenie)
                          (trans.). 1961 (1): 63-68.

NÕMMIK, H.
    1957   Fixation and defixation of ammonium in soils. Acta
                          Agric. Scandinavica VII: 395-436.

OXFORD UNIVERSAL DICTIONARY.
        Third edition, revised. Oxford University Press, London.

PAARLAHTI, K. and VARTIOVAARA, U.
1958   Observations concerning the microbial populations in virgin and drained bogs. Communicationes Instituti Forestalis Fenniae 50 (4): 1-38.

PAARLAHTI, K.
1959   Changes in the edaphic factors on some bog types by draining. Suo 10: 13-18. Supplied by the Commonwealth Bureau of Soils in "Bibliography on Vegetation and Chemical Compostion of Bog Soils". Nov., 1962.

PEACH, K. and TRACY, M. V.
1955   Modern Methods of Plant Analysis. Springer-Verlag, Berlin, 1955.

PONOMAREVA, V. V. and NIKOLAYEVA, T. A.
1961   Methods of studying organic matter in peat-bog soils. Soviet Soil Sci. (Pochvovedenie) 5: 548-554 (trans.).

PUTMAN, D. F. and CHAPMAN, L. J.
1938   The climate of Southern Ontario. Sci. Agric. 18.

PUUSTJÄRVI, V.
1957   On the base status of peat soils. Acta Agric. Scandinavica Vol. VII: 190-223. Stockholm.

PUUSTJÄRVI, V.
1960   The luxuriance of a bog in its original state as an index to the quality of its peat. Maat. Aik. (Jour. Sci. Agric. Soc. Finland) 32 (1): 7-26.

RADFORTH, N. W.
1952   Suggested Classification of Muskeg for the Engineer. Engin. Jour. Vol. 35, No. 11, Nov. 1952.

SJÖRS, H.
1948   Mire vegetation in Bergslagen, Sweden. Acta Phyogeographica Suecica 21: 1-340. Uppsala.

SJÖRS, H.
1950   On the relation between vegetation and electrolytes in the north Swedish mire waters. Oikos 2, 2: 241-258.

SJÖRS, H.
   1959   Forest and peatland at Hawley Lake, Northern Ontario.
                      Nat. Museum of Can., Bull. No. 171, Contributions to
                      Botany. Roger Duhamel, Queen's Printer.

SJÖRS, H.
   1961   Some chemical properties of the humus layer in Swedish
                      natural soils. Bulletin of the Royal School of
                      Forestry, Stockholm, Sweden. Nr. 37.

SOHN, J. B. and PEECH, M.
   1958   Retention and fixation of ammonia by soils. Soil
                      Sci. 85: 1-9.

SPENCER CREEK CONSERVATION REPORT.
   1960   Department of Commerce and Development, Conservation
                      Branch, Toronto.

STATZY, G. and MORTENSEN, J. L.
   1957   Effect of crop residues and nitrogen addition on
                      decomposition of an Ohio muck soil. Soil Sci. 83:
                      165-174.

STEVENSON, F. J.
   1959   C:N relationships in soils. Soil Sci. 88: 201-208.

STEWARD, F. E. (ed.).
   1963   Plant Physiology. Vol. III: Inorganic Nitrition
                      of Plants. Academic Press, New York.

STEWART, J. M
   1963   Interpretation of organic terrain by the cuticular
                      components of peat. Unpubl. Ph. D. Thesis,
                      McMaster University, Hamilton.

STOJANOVIC, B. J. and BROADBENT, F. E.
   1960   Recovery of ammonium-nitrogen from soils. Soil
                      Sci. 90: 93-97.

SUTCLIFFE, J. F.
   1962   Mineral salts absorption in plants. International
                      Series of Monographs on Pure and Applied Biology,
                      Plant Physiology Division, Volume I, Pergamon
                      Press Ltd., London.

THOMAS, M.
   1958   Plant Physiology. J. & A. Churchill Ltd., London.

TIBBETTS, T. E.
   1963   Evaluation of peat bogs for peat moss production.
                      Int. Peat Congr. Leningrad.

VALLENTYNE, J. R.
1962   Solubility and decomposition of organic matter in nature. Arch. Hydrobiol. 58, No. 4: 423-434.

VIDAL, H.
1963   The importance of north-west and central European bogs as regulators of water balance and climate. Int. Peat Congr., Leningrad.

WAKSMAN, S. A. and STEVENS, K. R.
1928a   Contribution to the chemical composition of peat: I. Chemical nature of organic complexes in peat and methods of analysis. Soil Sci. 26: 113-137.

WAKSMAN, S. A. and STEVENS, K. R.
1928b   Contributions to the chemical composition of peat: II. Chemical composition of various peat profiles. Soil Sci. 26: 239-252.

WAKSMAN, S. A. and STEVENS, K. R.
1929   Contributions to the chemical composition of peat: V. The role of microorganisms in peat formation and decomposition. Soil Sci. 28: 315-340.

WAKSMAN, S. A.
1942   Nature and origin of peat - The peats of New Jersey and their utilization, Part A. Dept. of Conserv. and Develop., State of N.J., in co-op. with N.J. Agric. Expt. Sta., Rutgers U., Bull. 55, Geologic Series.

WALSH, L. M. and MURDOCK, J. T.
1960   Native fixed ammonium and fixation of applied ammonium several Wisconsin soils. Soil Sci. 89: 183-193.

WELCH, L. F. and SCOTT, A. D.
1960   Nitrification of fixed ammonium in clay minerals as affected by added potassium. Soil Sci. 90: 79-85.

WILLARD, H. H., FURMAN, N. H. and BRICKER, C. E.
1956   Elements of Quantitative Analysis. D. Van Nostrand Co., Inc., Toronto.

WILSON, C. L. and WILSON, D. W.
1958   Comprehensive Analytical Chemistry. D. Van Nostrand Co., Inc., Toronto.

YEFIMOV, V. N.
   1962   Forms of accumulation and migration of substances
               in bog soils. Soviet Soil Sci. (Pochvovedenie)
               1961 (6): 643-650.

Figure 1.

Vertical aerial photograph of Copetown Bog. Highway 52
skirts the western boundary and the T.H. & B. R.R. the
eastern boundary of the bog. Sample areas are marked by **X**.
Enlarged photograph was made from R.C.A.F. aerial
photograph #60134-82 obtained from the Wentworth Planning
Board, Hamilton.

Scale: 1in.: 240 ft.

Figure 2.

View of the general region around area II in
Copetown Bog. Photograph taken from embankment
of Highway 52 facing south-east. Vegetation in
foreground is D of the lagg, middle ground is
EFI-FEI, background is BEF-BFE.

Figure 3.

Area I, EFI-FEI in foreground and middle ground.
Photograph taken towards south-east.
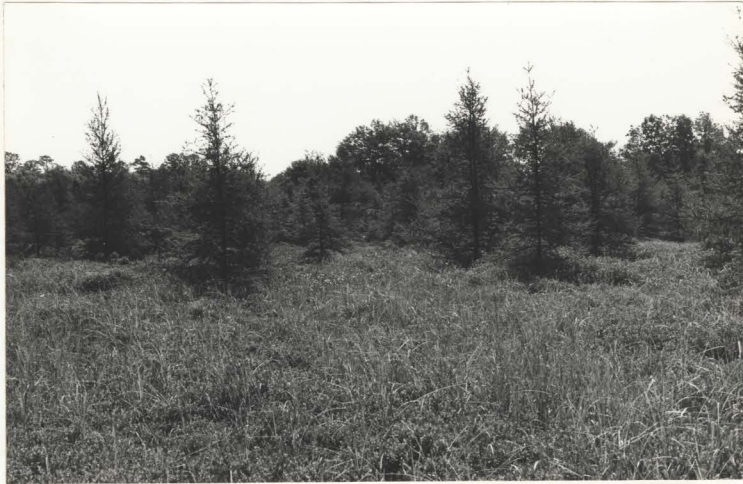
Figure 4.

Area II, EFI-FEI, in foreground. Photograph taken
towards east-south-east.

Figure 5.

Area III, BEF-BFE, in fore and middle ground.
Photograph taken towards north-north-east.

Figure 6.

Area IV, BEI, in middle ground. Photograph taken
towards east-south-east.

Figure 7.

Area V, BEI. Photograph taken towards north-east.
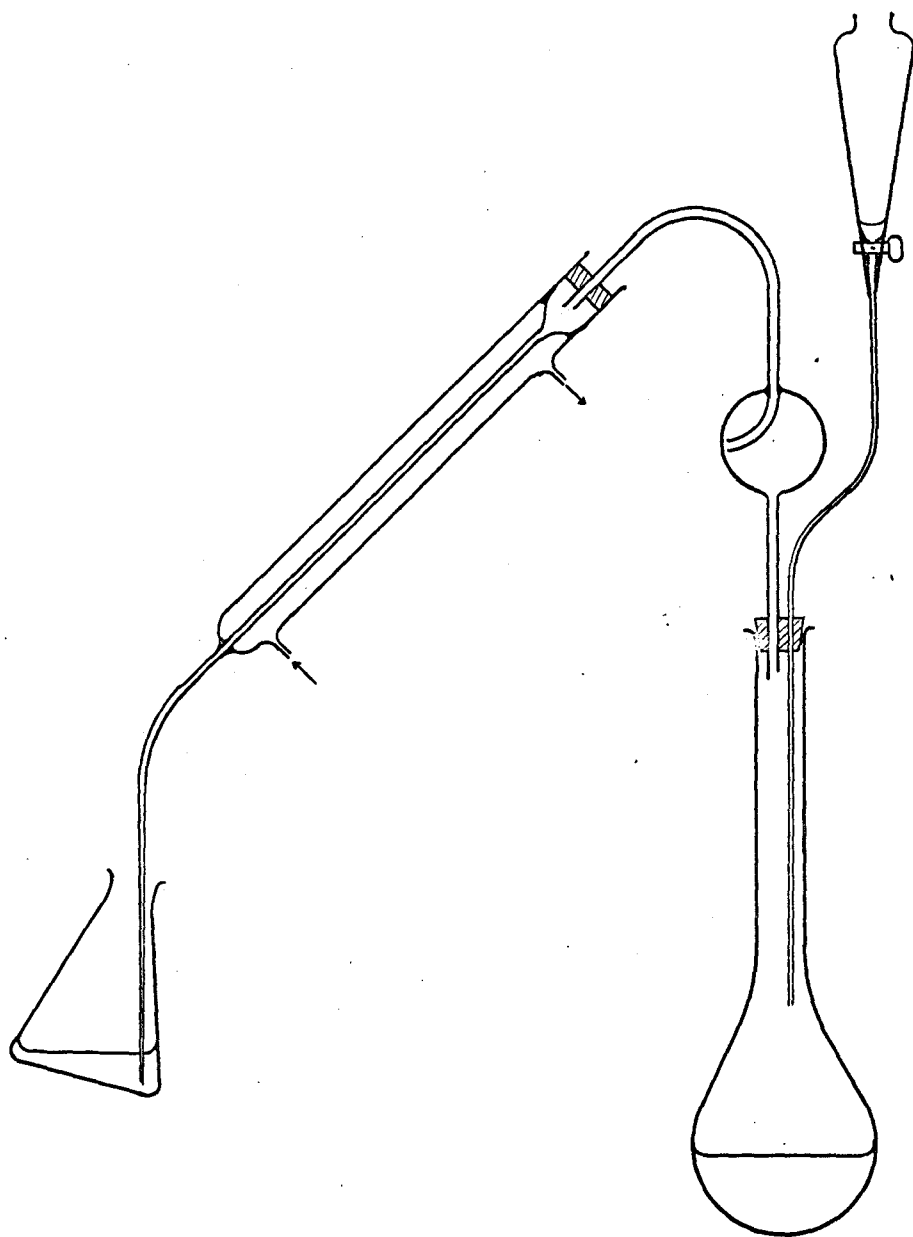
Figure 8.

DIAGRAM OF DISTILLATION APPARATUS
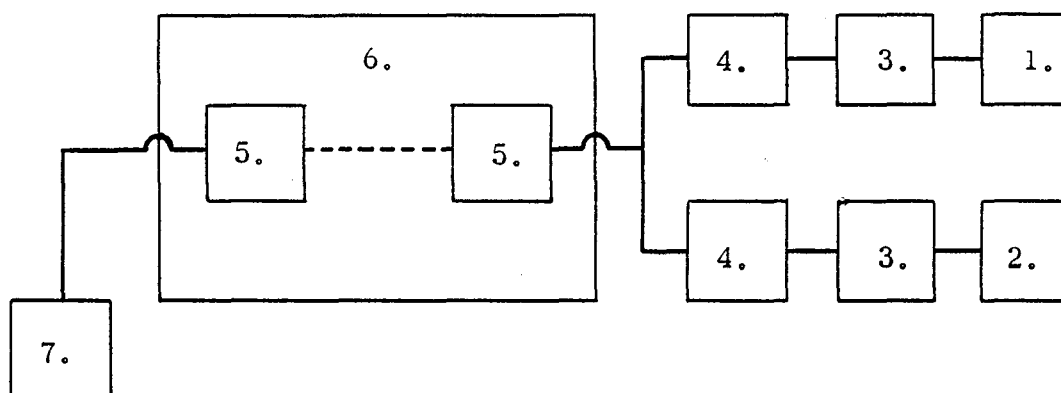
Figure 9.

DIAGRAM SHOWING SEQUENCE OF APPARATUS USED
FOR AMMONIATING SAMPLES OF PEAT

1. Compressed air tank fitted with guages and valves (Matheson of Canada Ltd.).

2. Tank of anhydrous ammonia with Regulator No. 12-240 check valve, and line needle valve (Matheson of Canada Ltd.).

3. Pyrex Flowmeters, model 5960 (Corning Glass Works).

4. "U" tube manometers, 3mm. outside diameter.

5. Sample container(s), 3 to 5 connected in series with entry tube near bottom and outlet tube at the top of each container (Pyrex test tubes 290 x 30 mm.), or a single 250 ml. Erlenmeyer flask.

6. Constant temperature bath containing about 0.07 m^3 of water. The tank was insulated with styrofoam sheets on all surfaces. A Precision Scientific Company "Porta-Temp" was used to circulate and maintain the temperature of the water at $27.0 \pm 0.1^\circ C$.

7. Container of dilute acid used to trap the ammonia at the end of the gas line.

TABLE 1.

The Effect of Duration of Digestion After Clearing on Kjeldahl Nitrogen

Content of Blended _Sphagnum_ sp. Peat Sample..

Number of hours after clearing digestion continued	Kjeldahl Nitrogen content as a percentage of air dry weight of sample
2	0.440
2	0.439
2	0.445
3	0.438
3	0.444
3	0.448
3	0.438

Average value for 2 hour period: 0.441%

Average value for 3 hour period: 0.442%

TABLE 2.

Effect of Variation of Digestion Period For Time After Clearing,
Addition of 30% H_2O_2, and Inclusion of Nitro derivatives on Initial
Kjeldahl Nitrogen Content of the Blended _Sphagnum_ sp. Peat Sample

	Nitro Derivatives Included		Nitro Derivatives Excluded	
	2 hour	3 hours	2 hours	3 hours
Addition of H_2O_2	0.443	0.442	0.445	0.450
Exclusion of H_2O_2	0.442	0.444	0.449	0.443

Nitrogen content as a percentage of air dry weight of peat sample.

TABLE 3.

Effect of Oven Drying the Sample at $105^{\circ}C$ on the Initial Kjeldahl Nitrogen Content

Sample	Period of Oven Drying	Oven Dry wt. as a percentage of Air Dry wt.	N^{o} Kjeldahl as a percentage of Oven Dry wt.	N^{o} Kjeldahl as a percentage of Air Dry wt.	N^{o} Kjeldahl of unheated samples.
Blended Sphagnum sp. Peat	43 hr.	89.6	0.433	0.388	
	.43 hr.	86.6	0.450	0.346	0.441
	1 week	87.6	0.526	0.460	$\pm 0.02\%$
	1 week	85.5	0.506	0.433	
Average		86.6	0.479	0.409	0.441
A2	21 hr.	80.2	0.897	0.719	1.08
A3	21 hr.	80.9	0.934	0.756	0.965

TABLE 4.

pH of Water from Samples.

Site	Sample	pH of Gravitational Water	pH of water squeezed out of Sample
B	B4	4.80	4.59
	C3	5.00	4.79
C	A3	5.35	4.83
	B1	4.60	----
	B2	4.90	----
	C1	4.89	4.70
E	B7	4.53	----
	C4	4.63	4.57
G	B5	4.53	----
H	C12	4.50	4.32
L	B10	4.37	----
M	B11	4.98	----
	C7	4.99	5.20
N	C9	4.30	4.48

TABLE 5.

Ash Content and Ash Alkalinity of Peat Samples

Area	Site	Topography and Sample Number	Weight of Ash grams 100g. Oven Dry Weight of Peat	Ash Alkalinity as milliequivalents per 100g. Oven Dry Weight of Peat at (105°C, 24 hr.)
I	A	top of hummock		
		A1	6.67*	-----
		B3	5.43	19.4
		C2	7.90	33.0
I	B	hollow		
		A2	18.0*	-----
		B4	15.9	25.0
		C3	20.2	8.89
II	C	hollow		
		A3	14.1**	-----
		B1	12.3	35.9
		B2	15.9	18.8
		C1b	25.3	10.4
III	D	hummock top		
		A4	12.2*	-----
		B8	12.2*	-----
		C5	12.2	23.5
III	E	hollow		
		B7	18.9	-----
		C4	15.0	12.5
IV	F	hummock top		
		B6	4.76	18.2
		C11	4.76*	-----
IV	G	hollow		
		B5	18.9	10.5
IV	H	hollow		
		C12	-----	-----
V	I	hummock top		
		B9	5.60	14.0
		C6	7.26	17.4
V	J	hummock top		
		B12	9.48	-----
		C8	17.8	24.6
V	K	hummock top		
		C10	23.2	15.7
V	L	hollow		
		B10	22.8	4.56
V	M	hollow		
		B11	28.6	1.57
		C7	28.6*	-----
V	N	hollow		
		C9	18.0	5.52

*   indicates sample not ashed, value calculated from average of others at that site.

**   value is an average of B1 and B2; C1b not included in average.

----- indicates value not obtained.

TABLE 6.

Nitrogen Extracted from Peat Samples by Kjeldahl Digestion (N^o Kjeldahl) Before Ammoniation.

| Site | Sample | N^o Kjeldahl as a Percentage of: | | |
		Air Dry Weight	Oven Dry Weight	Ignition Loss
A	A1	0.581	0.622	0.705
		0.645	0.690	0.782
		0.681	0.730	0.827
	B3	0.525	0.596	0.635
	C2	0.697	0.790	0.898
B	A2	1.13	1.37	1.51
		1.02	1.25	1.38
	B4	0.922	1.03	1.22
		0.870	0.970	1.15
	C3	1.03	1.12	1.29
C	A3	0.905	1.05	1.21
		1.02	1.19	1.36
	B1	0.797	0.897	1.02
		0.756	0.852	0.971
	B2	1.10	1.36	1.61
		1.11	1.37	1.63
	C1	0.876	0.953	1.28
		1.01	1.10	1.47
D	A4	0.693	0.791	0.901
		0.647	0.738	0.841
		0.737	0.842	0.959
		0.640	0.730	0.832
		0.609	0.695	0.792
	B8	0.891	1.02	1.16
		0.903	1.03	1.17
	C5	0.789	0.900	1.03
E	B7	1.14	1.27	1.56
		1.07	1.21	1.42
		1.20	1.37	1.46
F	B6	0.524	0.580	0.609
	C11	0.554	0.613	0.643
G	B5	0.928	1.01	1.24
		0.998	1.08	1.33
H	C12	0.932	1.07	----
I	B9	0.615	0.677	0.717
	C6	0.697	0.752	0.838
J	B12	0.803	0.879	0.971
	C8	1.01	1.16	1.41
K	C10	1.33	1.40	1.83
L	B10	1.07	1.15	1.49
M	B11	1.34	1.49	2.09
	C7	1.34	1.50	2.10
N	C9	1.13	1.24	1.51

TABLE 7.

Nitrogen Extracted from Ammoniated Peat Samples by KCl Solution (N^A_{KCl})

Site	Sample	N^A_{KCl} as a percentage of:		
		Air Dry Weight	Oven Dry Weight	Ignition Loss
A	A1	0.447	0.479	0.543
		0.561	0.553	0.627
	B3	0.843	0.956	1.02
B		————	————	————
C	B1	0.407	0.458	0.522
	B2	0.541	0.670	0.796
D	A4	0.875	0.999	1.14
	B8	0.700	0.799	0.911
		0.747	0.852	0.971
E	B7	0.661	0.735	0.906
		0.733	0.815	1.00
F	B6	1.17	1.29	1.36
G	B5	0.776	0.841	1.04
		0.663	0.718	0.885
H		————	————	————
I	B9	0.671	0.738	0.782
	C6	0.845	0.930	1.02
J	B12	0.714	0.781	0.863
		0.834	0.912	1.01
K		————	————	————
L	B10	0.758	0.817	1.06
M	B11	0.888	0.990	1.09
N		————	————	————

TABLE 8.

Nitrogen Extracted from Ammoniated Peat Samples by Kjeldahl Digestion.
(following aqueous and KCl solution extractions). (N^A Kjeldahl)

| Site | Sample | N^A Kjeldahl as a percentage of: | | |
		Air Dry Weight	Oven Dry Weight	Ignition Loss
A	A1	0.941	1.01	1.14
		1.03	1.10	1.25
	B3	1.16	1.31	1.40
B		----	----	----
C	B1	1.01	1.14	1.30
	B2	.1.47	1.81	2.15
D	A4	1.12	1.28	1.45
		1.22	1.40	1.59
	B8	1.09	1.24	1.41
E	B7	1.64	1.83	2.25
		1.75	1.95	2.40
F	B6	0.985	1.09	1.14
G	B5	1.36	1.47	1.81
		1.37	1.48	1.83
H		----	----	----
I	B9	1.31	1.44	1.53
	C6	1.18	1.30	.1.42
J	B12	1.07	1.18	1.30
		1.22	1.33	1.47
K		----	----	----
L	B10	1.56	1.68	2.18
		1.82	1.96	2.55
M	B11	1.74	1.94	2.72
N		----	----	----

TABLE 9.

Total Nitrogen Extracted from Ammoniated Peat Samples (N_T^A)

| Site | Sample | N_T^A as a percentage of: | | |
		Air Dry Weight	Oven Dry Weight	Ignition Loss
A	A1	1.39	1.49	1.68
		1.55	1.65	1.88
	B3	2.00	2.27	2.42
B		----	----	----
C	B1	1.41	1.59	1.82
	B2	2.01	2.48	2.95
D	A4	2.00	2.12	2.59
	B8	1.79	2.04	2.32
E	B7	2.30	2.57	3.16
		2.48	2.77	3.40
F	B6	2.16	2.38	2.50
G	B5	2.14	2.31	2.85
		2.03	2.22	2.72
H		----	----	----
I	B9	1.98	2.18	2.31
	C6	2.03	2.23	2.42
J	B12	1.78	1.96	2.16
		2.05	2.24	2.48
K		----	----	----
L	B10	2.32	2.50	3.24
M	B11	2.63	2.93	4.11
N		----	----	----

TABLE 10.

Amount of Ammonia Fixed (N_f) by Samples After Ammoniation.

N_f expressed as percentage of:

| Site	Sample	Air Dry Weight		Oven Dry Weight		Ignition Loss	
		RANGE	AVERAGE	RANGE	AVERAGE	RANGE	AVERAGE
A	A1	0.35 - 0.45	0.40	0.28 - 0.48	0.38	0.31 - 0.55	0.43
	B3	0.64	0.64	0.71	0.71	0.77	0.77
	Max.	0.24 - 0.64	0.44	0.22 - 0.71	0.47	0.24 - 0.77	0.50
B	Max.	----	----	----	----	----	----
C	B2	1.4	1.4	0.44 - 0.45	0.45	0.52 - 0.54	0.53
	Max.	0.71 - 1.4	1.1	0.44 - 0.96	0.70	0.52 - 1.2	0.85
D	A4	0.43 - 0.61	0.52	0.44 - 0.71	0.57	0.49 - 0.80	0.64
	B3	0.19 - 0.20	0.19	0.21 - 0.22	0.22	0.24 - 0.25	0.25
	Max.	0.19 - 0.61	0.40	0.21 - 0.71	0.46	0.24 - 0.80	0.52
E	B7	0.50 - 0.61	0.56	0.56 - 0.68	0.62	0.69 - 0.84	0.77
	Max.	0.44 - 0.68	0.56	0.46 - 0.74	0.60	0.69 - 0.98	0.83
F	B6	0.65	0.65	0.51	0.51	0.53	0.53
	Max.	0.62 - 0.65	0.64	0.48 - 0.51	0.49	0.50 - 0.53	0.52
G	B5	0.36 - 0.44	0.40	0.39 - 0.47	0.43	0.48 - 0.59	0.54
	Max.	0.36 - 0.44	0.40	0.39 - 0.47	0.43	0.48 - 0.59	0.54
H	Max.	----	----	----	----	----	----
I	B9	0.70	0.70	0.76	0.76	0.81	0.81
	C6	0.48	0.48	0.55	0.55	0.58	0.58
	Max.	0.48 - 0.70	0.59	0.55 - 0.76	0.66	0.58 - 0.81	0.70
J	B12	0.27 - 0.422	0.34	0.30 - 0.45	0.38	0.33 - 0.50	0.42
	Max.	0.06 - 0.42	0.24	0.02 - 0.45	0.24	0.00 - 0.50	0.25
K	Max.	----	----	----	----	----	----
L	B10	0.49 - 0.75	0.62	0.53 - 0.81	0.67	0.69 - 1.1	0.88
	Max.	0.49 - 0.75	0.62	0.53 - 0.81	0.67	0.69 - 1.1	0.88
M	B11	0.40	0.40	0.45	0.45	0.63	0.63
	Max.	0.40	0.40	0.44 - 0.45	0.45	0.62 - 0.63	0.63
N	Max.	----	----	----	----	----	----

EXPLANATION OF SYMBOLS ON THE FOLLOWING GRAPHS

To facilitate comparisons of samples taken from different
locations the following symbols have been used:

    O   indicates the value of a sample taken from the
           top of a hummock.

    ◒   indicates the value of a sample taken from the
           top of a hummock which was eroded.

    ●   indicates the value of a sample taken from a
           hollow.

O——O indicates a range of values which resulted from
           more than one analysis, of the type indicated,
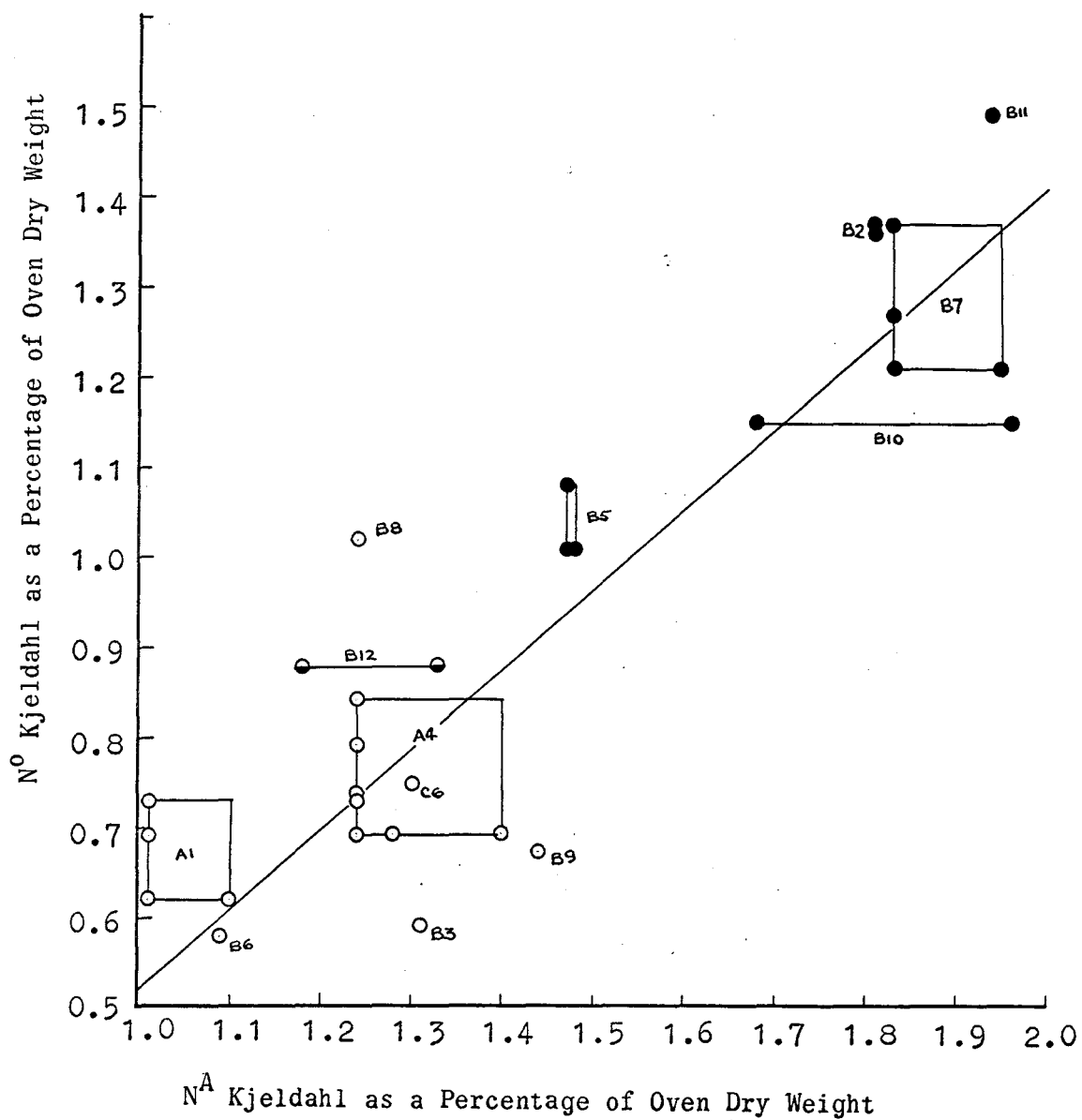   of any particular sample.

GRAPH 1.

Ash Content in Relation to Initial Kjeldahl Nitrogen
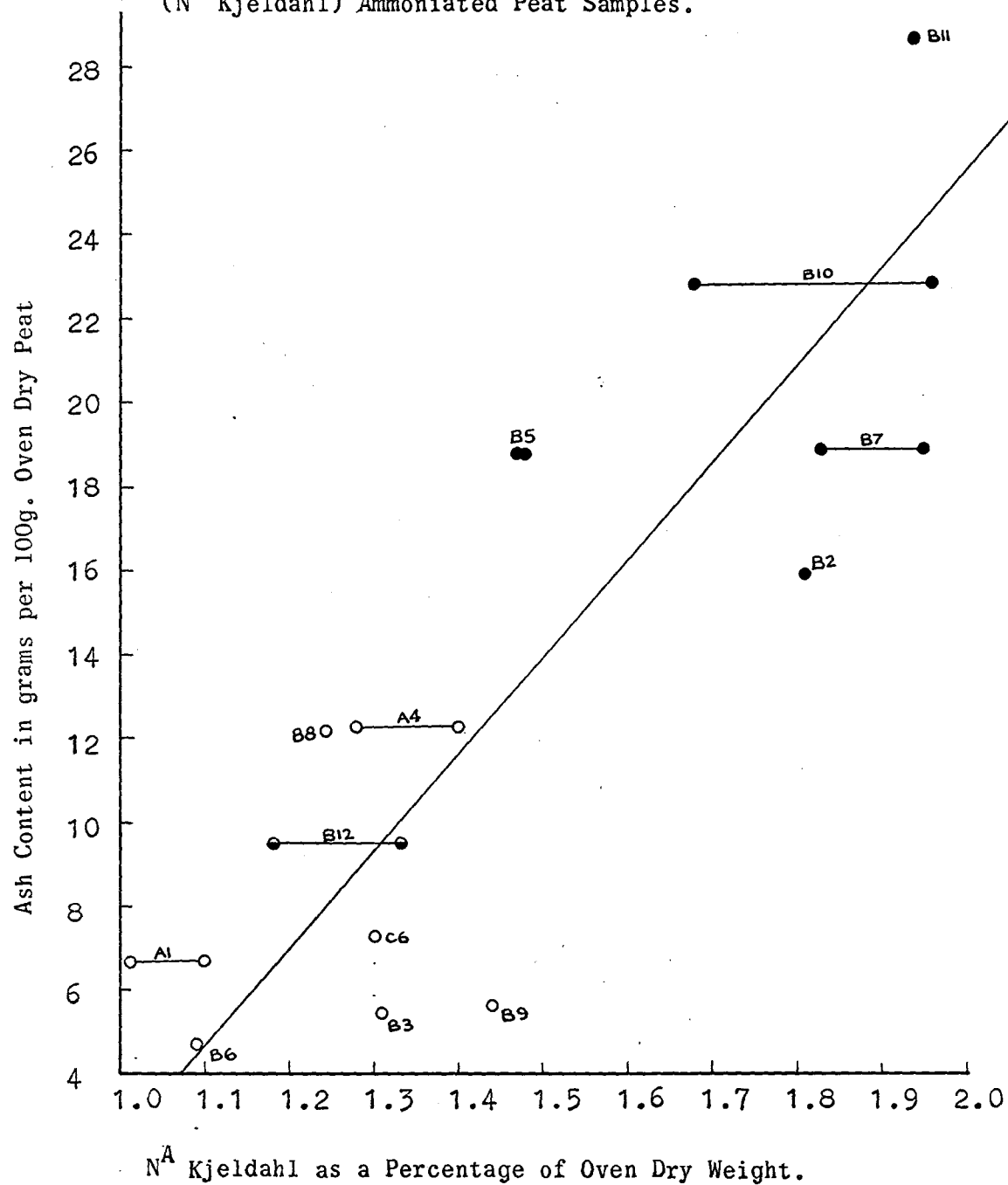Content (N^0 Kjeldahl) of Peat Samples.

N^0 Kjeldahl as a Percentage of Oven Dry Weight of Peat.
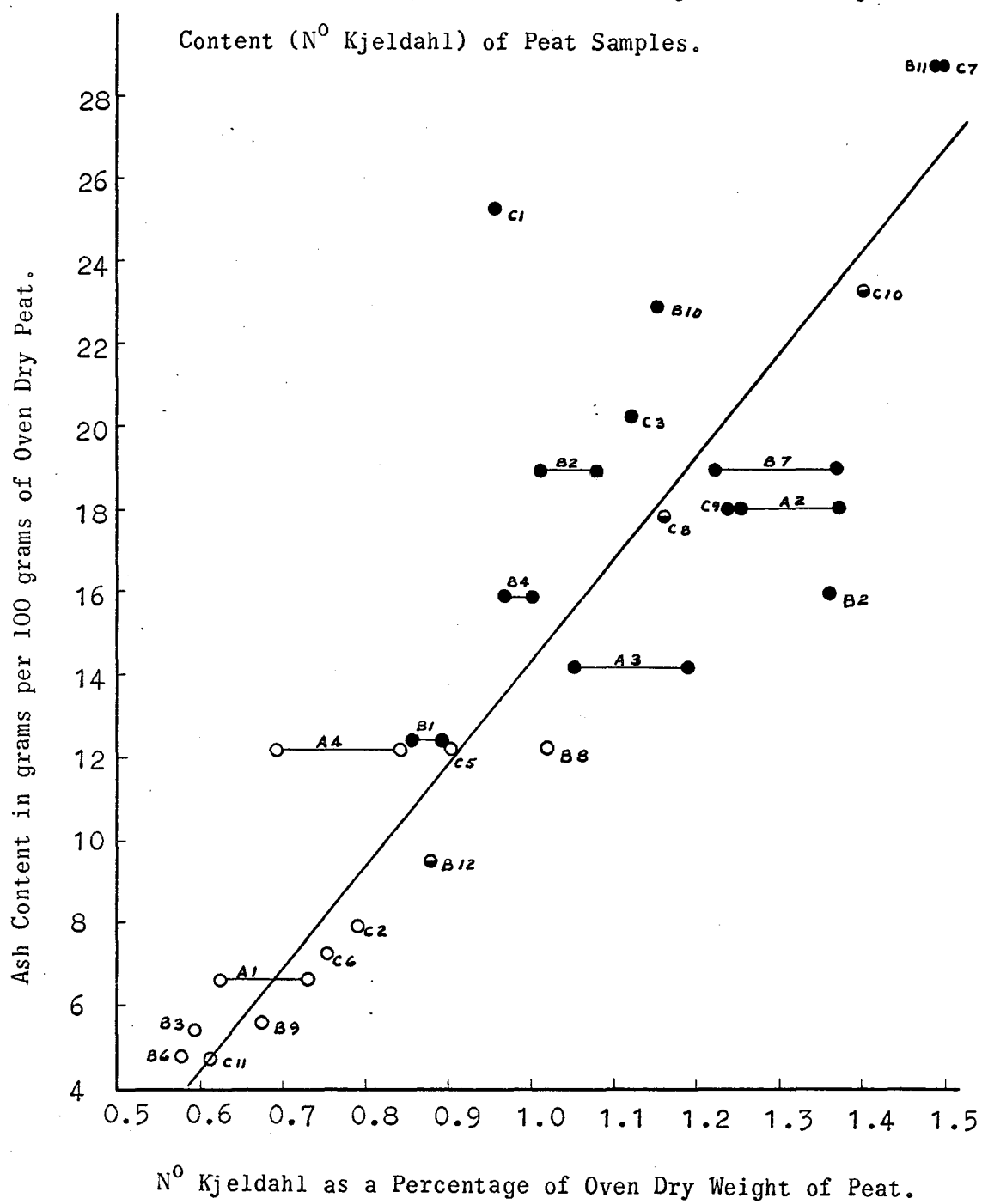
GRAPH 2.

Initial Kjeldahl Nitrogen (N^O Kjeldahl) in Relation
to Kjeldahl Nitrogen (N^A Kjeldahl) Ammoniated Peat
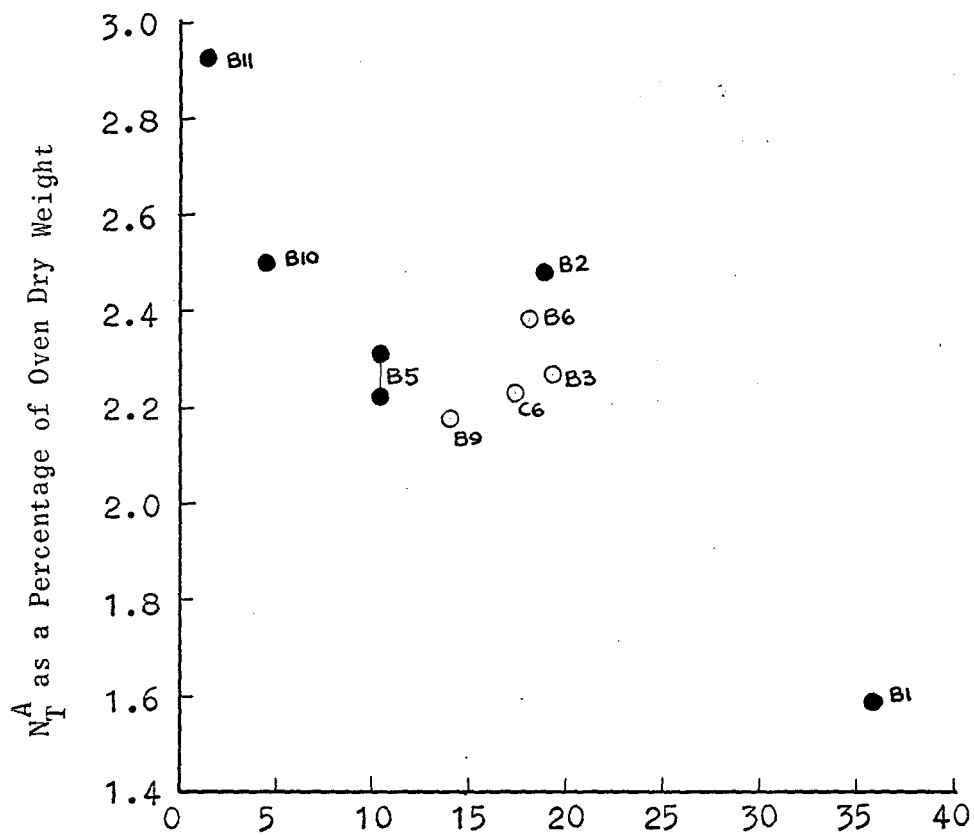Samples, Both as a Percentage of Oven Dry Weight of
the Sample.

GRAPH 3.

Ash Content in Relation to Kjeldahl Nitrogen Content

(N^A Kjeldahl) Ammoniated Peat Samples.

GRAPH 4.

Total Nitrogen Content (N_T^A) of Ammoniated Peat Samples

in Relation to Ash Alkalinity.

Ash Alkalinity in milliequivalents per 100g. Oven Dry Peat.

ADDENDUM

The author wishes to point out that the term "hummock" used in this work is synomic with the term "mound" used by Dr. N. W. Radforth in his work. Both terms occur in the literature.