CHEMICAL PROPERTIES OF ROOT MATS IN SOME SOUTH COASTAL BRITISH COLUMBIA PODZOLS:

IMPLICATIONS FOR CLASSIFICATION AND GENESIS

by

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### ABSTRACT

Podzols, situated at high elevation within the Coast

Mountains surrounding Vancouver, often have accumulations of organic material within the mineral soil either as mats above an impermeable layer or as channels running obliquely and horizontally through the B horizon. This organic material is "greasy" to the touch with few discernible mineral grains on hand texturing. The mats range in thickness from 1 cm to greater than 40 cm, are situated in seepage zones and are overlain by a well drained sandy loam, often of low organic content. The channels have the gross morphology of roots and are up to 5 cm wide.

Occasional remnants of wood structure are discernable in situ and the cellular nature of the organic material can be seen under the compound microscope.

The majority of the mats could be classified as organic (>17% C), either as an H or an O horizon. If they contained less than 17% C they met the criteria of a Bhf horizon.

Chemically the mats and channels have some unusual properties. They are similar to the surficial humus in carbon to nitrogen ratio and nitrogen to sulphur ratio but much closer to a podzolic B horizon in iron content. The ratio of carbon in humic acids to fulvic acids (Ch/Cf) and polyphenolic to total fulvic acids (Ca/Cf) was also more characteristic of a podzol. The

organic mats had an average Ch/Cf of 0.23 and a Ca/Cf of 0.73. This is in comparison with 2.44 and 0.44, respectively, for the surficial humus and 0.34 and 0.72, respectively, in the organic material of the conventionally situated Bhf horizons.

Both mats and channels had very high concentrations of aluminum, sometimes exceeding 10%. From the organic mats on Burke Mountain, aluminum extracted by acid ammonium oxalate was just slightly higher than that extracted with sodium pyrophosphate and oxalate silicon was low. This implied that most of the aluminum was bound with the organic material. In contrast, the oxalate aluminum of Cypress Park mat samples was often more than double that which was extracted with pyrophosphate and oxalate silicon values were also high. The figures indicated that allophane, with an approximate Al:Si ratio of 2, may make up a high proportion of this horizon.

Morphologically, the mats and channels seem to have originated through root decomposition but chemically, podzolic mechanisms seem to have played an important role. Because of similarities between soils studied in this thesis and soils of the literature found to contain imogolite, a column study was undertaken to test a mechanism whereby decomposing roots could be enriched by the aluminum of proto-imogolite. It was found that the organic material of rotting wood could scavenge aluminum from this positively charged aluminosilicate colloid and that in the process the fulvic acids of the wood were also immobilized. If a mechanism similar to this was operating within a podzol, it could

help explain both the high concentration of aluminum and of fulvic acids in the mats and channels.

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### INTRODUCTION

Many podzolic soils of south coastal British Columbia possess morphological and chemical irregularities which do not "fit" the conventional concept of a podzol (Lewis, 1976) (McKeague, 1979). One unusual feature is typical of soils in very high rainfall environments. These podzols are distinguished by unusual organic accumulations within the B horizon, most notably in layers above a duric horizon or bedrock contact and in channels running vertically and obliquely throughout the entire depth of the mineral soil. The organic matter found in these locations is greasy to the touch and mineral grains may or may not be detectable. The horizontal layers have been called "root mats" in soil survey reports and as the multidirectional channels often have the gross morphology of roots, they are referred to as "root channels" in this paper.

In the Canadian system of soil classification (CSSC, 1978), the root mats can be classified as "organic" if they contain greater than 17% organic carbon. With less carbon, they have often been found to have enough Na-pyrophosphate-extractable iron and aluminum to meet the definition of a podzolic Bhf horizon (H. A. Luttmerding, pers. comm.). If this organic-rich mineral horizon, situated along the contact, is greater than 10 cm thick in an otherwise organic-poor soil, the soil will be classified as a ferro-humic podzol, although the Bhf will not be in the same

position and may not have the same origin as implied in our present understanding of podzol genesis. Recently, however, the view that iron and aluminum owe their solubility within a podzolic soil to metal-complexing organic acids, has been challenged. Anderson et al. (1982) have found evidence that aluminum, at least, may move in an inorganic form and that complexation with organic acids occurs some time after mobilization. Therefore, a better understanding of the processes involved, both in root mat formation and in the genesis of podzolic soils in general, is necessary before deciding if the classification of the root mat as a podzolic Bhf horizon is justified.

The objectives of this study were:

- To characterize chemically and morphologically the organic material within the root mats and root channels.
- 2. To determine if the noted characteristics were different from those of Bhf horizons found directly beneath the Ae.
- To study the mechanisms proposed in the literature for podzol genesis and how these have changed through time, and
- 4. With the use of a column study, to test one of these mechanisms to see if it may apply to the genesis of the root mat horizons.

It was hoped that an historical perspective would serve to show that ideas concerning podzol genesis have always been in a state of flux and that new concepts should be met with an open

mind. It was also hoped that the properties examined would give some clue to the genesis of the organic accumulations and, with the literature review, help determine if the classification of the root mats as podzolic Bhf horizons should be changed.

### CHAPTER 1

# THE CHANGING CONCEPT OF THE PODZOL THROUGH TIME The Lack of a Concensus

### Introduction

Two basic questions have challenged podzol research since the soil was first described by Dokuchaiev in 1879.

- What is a podzol? What characteristics must a soil possess to be included in the podzolic classification?
- What unique environmental conditions and chemical processes led to the genesis of these soils?

The answers to the first question have changed dramatically through the years. Opinions about which horizon is diagnostic, the inclusion or omission of clay-enriched soils, the degree to which the process must occur before the soil meets podzolic classification, and what chemical extractants are best suited to measuring this process, have changed through time and from country to country.

Hypotheses on podzol genesis have been centered around three main themes:

- 1. Iron and aluminum move as inorganic cations.
- 2. Sesquioxides move as humus-protected sols.
- 3. Iron and aluminum are complexed by fulvic acid or simple organic acids and leached from the A horizon in this form.

Although volumes of work have been published on the subjects of podzol genesis and classification, no true consensus has ever been achieved on all aspects of this process and the same questions are still being asked today. As both questions are once again addressed in this thesis, an attempt is made to put this research into historical perspective.

## Early Russian and European Views

According to Joffe (1936), soils similar to podzols were described by Sprengel as early as 1837 and were also noted by Scandinavian and German foresters and geologists of that time. The ash-gray to white material (the Ae horizon in CSSC, 1978) was believed by some to have been carried from surrounding areas by wind and water and deposited on top of the soil as an independant stratum.

In "Cartography of Russian Soils" (1879) Dokuchaev described a podzol as a shallow soil of "6-12 inches, deepening only in places as it approaches bogs." The "external characteristics of the podzol are: an ashy colour, generally with yellowish, bluish or greenish tones," "of a sandy-type and contain[ing] 83-84% silica." "Microscopic analysis shows that samples examined so far consist of phytoliths, diatoms, soft vegetable residues, quartz grains, silty particles, etc." (as quoted in Muir, 1961, p.3). The total podzolic profile in Dokuchaev's view consisted of what Canadians now call the eluvial Ae horizon!

Early Russians did not recognize a zone of deposition.

Dokuchaev described the illuvial B horizon only in noting that

"podzols are underlain by clays, loams or sands: in all these cases the podzol appears to pass gradually into the underlying rock" (after Muir, 1961, p.3). Also, they did not separate soils leached simply of clay in the upper horizons from soils leached also of bases and sesquioxides. All profiles with an eluvial A horizon were classified as podzols.

Dokuchaev summed up the views of his day when he listed four possibilities to account for the genesis of a podzol. He saw the ashy layer arising:

- 1. "Due to [natural] fires.
- Due to the burning of peat.
- 3. From microscopic evidence it might be considered [that podzols were] a simple accumulation of vegetable residues, eg. phytoliths" (Muir, 1961, pp.3-4).
- 4. That podzols were formed as a soil in areas where there was "more moisture, less light and less access of air to the soil" (Muir, 1961, p.4).

Dokuchaev seemed to concur with the latter mechanism, noting that podzols were "formed mainly in forests with a significant participation of bog and forest vegetation" and that these factors worked together to produce a soil with properties in contrast to "the common northern dry-land vegetable loamy and sandy soils" which were "formed in drier places with free access of air and light and the predominance of a dryland herbaceous vegetation" (after Muir, 1961, p. 4).

In 1885, V.P. Amalitskii, a Russian scientist who worked in close collaboration with Dokuchaev, described podzols as "a

product of the modification of local parent material by the combined effect of eluvial processes, atmospheric phenomena and forest vegetation" (as quoted by Ponomareva, 1969, p.5). Russian, A.V. Georgievskii, applied Dokuchaev's soil forming factors in attempting to understand the genesis of podzols. concluded that podzols were differentiated from the underlying subsoil mainly by an abundance of SiO, and a low content of Ca, Mg, Fe and Al. He attributed these modifications to the action of acid organic solutions and concluded that "humic acids are among the most energetic factors of weathering found in nature's laboratory: they are able to extract not only oxides of alkaline and alkali-earth metals, but also those of heavy metals. believe that the podzolic horizon which we are examining and podzols in general, arose through the influence of these particular acids" (1888, as quoted by Ponomareva, 1969, pp. 5-6). Like Dokuchaev, Georgievskii did not recognize the deposition of these weathering products in the underlying subsoil.

### Recognition of the Illuvial Horizon

Various descriptions of soils similar to the Russian "podzol" were published by European authors throughout the 18th century. In these, the bleached eluvial horizon was often designated "Bleicherde" and was linked with an underlying horizon called "Ortstein" (Jenny, 1980). Ortstein was applied both to greyish horizons high in clay and red ferruginous layers in sandier soils. Muir (1961) quotes microscopic evidence presented by P. E. Müller in 1887 which showed that the Bleicherde horizon

was "composed mainly of pure mineral fragments, especially quartz, intermixed with other components of granite" (pp. 15-16). Whereas, ortstein possessed "a quite different constitution: each grain, each solid particle is surrounded by an apparently structureless substance, each encrusted with the brown material which confers its colour to the layer" (Muir, 1961, p.16). Muller also found that "ortstein" horizons of loamy soils were often enriched in clay compared to the overlying and underlying horizons. This, as well as the work of other early Western European soil scientists, pointed the way for the recognition of the illuvial aspect of podzols.

In 1888, P. A. Kostychev, who was probably familiar with the Western European literature, introduced to Russia the concept of a three-membered podzolic profile, including an ortstein horizon. In his view, the decay of organic residues at the surface of podzolic soils produced water soluble acids. As the material of the organic residue had insufficient bases to neutralize these acids, they were washed by rainwater into deeper layers, where they formed salts with metallic bases. This resulted in the leaching of all readily soluble substances from the podzolic horizon into the underlying hardpan (Ponomareva, 1969); however, by what specific chemical process the leaching occurred is not mentioned. The mobile acids were known as "crenic acids" and considered oxidation products of the insoluble humic acid. Further oxidation of crenic acid produced "apocrenic acid". These acids were believed to be biochemically produced by microorganisms in the soil, but their presence was never

conclusively established. The role of fungi in the podzolic process was particularly stressed.

The first Russian soil textbook was written by N. M. Sibirtsev in 1909 (Ponomareva, 1969). In this work he unified much of the early Russian and Western European research to arrive at the following view on the formation of podzols.

An accumulation and translocation of crenic and apocrenic acids occurred in the soil under the conditions of a moderately cold and humid climate in coniferous or mixed forests. With these acids "many mineral substances [were] leached out of the soil, partly as organomineral compounds, i.e., bound with acid and partly as salts of humus acids - apocrenates (K, Na, Ca, Mg, Al, FeO)...Insoluble silica [would] separate out of silicates and chiefly from zeolites; their proportion [would] increase in the soil" (1909, as quoted by Ponomareva, 1969, p.7). Some of the mineral and organic substances leached from the "podzol" would enter the groundwater but the rest, perhaps the majority, would be retained in the underlying soil by the following mechanisms:

- A simple precipitation of salts would occur as incrustations on the surface of sand grains, with no change in the chemical constitution of these salts.
- 2. In some, a chemical changeover from one chemical compound to a less soluble form would result in precipitation. This could include the oxidation of ferrous oxide, the oxidation of crenic acid to apocrenic acid or the formation of iron compounds with phosphoric acid, etc. (Ponomareva, 1969).

In this way, these early Russian scientists, using primarily observation and instinct, arrived at a theory of podzol genesis that touches many of our current concepts.

## Western European Views of the Early 1900's

The term "podzol" was first introduced into the nomenclature of Western Europe by E. Ramann in 1911, but in a much narrower sense than was understood by the Russians. It was applied only to sandy soils that exhibited both a bleached horizon and an accumulation of coloured substances such as humus and/or iron oxides in the ortstein. It did not include soils leached simply of clay. These were to be classified into other categories, mainly the "brown soils", (Braunerden in German) (Peterson, 1976).

A second divergence from Russian views occurred in the early 1900's with the emergence in Western Europe of an alternate theory for podzol genesis (Ponomareva, 1969). The "colloidochemical" theory proposed the movement of iron and aluminum as colloids of inorganic hydroxides rather than as complexes or salts of the "hypothetical" crenic acids. As these hydroxides were positively charged in the pH range of a podzol, to migrate from the negatively charged humus in the A horizon, early researchers suggested they were protected by colloidal humic acids. As a complex sol (a positively charged hydroxide sol surrounded by negatively charged humus sols), the two would migrate to the B horizon where they would be precipitated by higher pH or divalent cations (Deb, 1949; Stobbe and Wright,

1959). Rode (1970) lists a number of early workers who found evidence that these complex sols could exist and so for the next four decades opinion fluctuated between the early Russian theory and this new European concept.

In 1913, using water extracts of peat, B. Aarnio estimated that it would take between 24 and 10 parts of humus to maintain 1 part of  $Al_2O_3$  and between 2.8 to 0.4 parts of humus to maintain 1 part of Fe<sub>2</sub>O<sub>3</sub> as complex sols. This, to many, seemed too high a ratio to explain the high sesquioxide, low organic matter content of the B horizon (Deb, 1949). None the less, Morison and Sothers (1914) studied the colloidochemical theory of podzol genesis, to understand the formation of an iron pan and by extrapolation of laboratory experiments to the real soil, produced the following model. In the accumulating organic matter at the soil surface, substances were produced that exhibited acid properties. These substances would first remove all readily soluble material, probably in true solution. At the same time, colloidal humates of iron, aluminum and calcium oxides would These sols would move downwards in the profile during the wet season, producing a bleached layer at the soil surface. During the dry season, desiccation of the soil would occur to the point of the permanent water table, above which the bulk of the colloids would have accumulated. Upon rewetting in the rainy season, the coagulated and desiccated colloids would not entirely go back into suspension, as the colloid character would have changed during the process of desiccation. This was supported by the laboratory experiments of these authors. Oxidation of the

humus during the dry period would result in most of the iron left in the form of ferric hydroxide, which after many seasons, would form the iron pan (Morison and Sothers, 1914).

In contrast, Jones and Willcox (1929) felt the Russian theory could equally well explain the formation of the pan and presented their own laboratory results to substantiate this. They used the earlier work of Pickering, 1913, which showed that the iron of ferric tartrate, malate and citrate was present in the electronegative portion of the molecule. Jones and Willcox, therefore, assumed that as soil organic acids consist largely of hydroxyacids, compounds were formed on reaction with iron that were similar to the ferric tartrate, malate and citrate studied by Pickering. These compounds, carrying iron in the electronegative portion of the molecule, were leached through the soil, dissolving increasing quantities of sesquioxides until a concentration was reached beyond which the organic-iron compound formed a basic salt and was precipitated. This gave rise to a zone of sesquioxide accumulation and finally a pan (Jones and Willcox, 1929). It seems that a lack of good analytical methods prevented these early workers from knowing exactly what they had produced in their laboratory experiments and, therefore, the results could be argued as proof for either mechanism of podzolization.

The Russian community also took up this debate, with K. D. Glinka and K. K. Gedroits taking the side of the colloidochemical hypothesis and V. R. Vil'yams and I. V. Tyurin supporting movement of Fe and Al through complex formation with organic

acids (Ponomareva, 1969).

Meanwhile, in Western Europe, the colloidochemical theory was supported by a procedure designed to measure the amorphous forms of iron and aluminum in the B horizon assumed to have been translocated from above. This was the acid ammonium oxalate extraction developed by O. Tamm in 1920 (Farmer, 1982). Perhaps because so little of the extracted iron and aluminum oxides were associated with organic matter and because the mobility of the humus protected oxide sol had never been proven in the real soil, Tamm proposed that movement of iron and aluminum in a podzol occurred as an electropositive colloid. He also proposed development of the Bh horizon by migration of unassociated organic colloids through the Ae and their precipitation on to previously deposited inorganic colloids at the top of the B horizon (Farmer, 1982).

A similar mechanism was envisioned by S. Mattson, in publications of the 1930's. By applying the principles of isoelectric weathering to the migration of iron and aluminum hydroxides and organic matter, he found these complex colloids would be the least dispersed and therefore, the least mobile, at a soil pH that corresponded to their isoelectric point. This was the pH where the number of negative charges equalled the number of positive charges and the colloid, as a whole, was neutral. Sesquioxides alone, had a high isoelectric point and therefore, had a positive charge at the pH of a podzol. Peptization by silica or humus decreased the isoelectric point of the complex sol. Below the isoelectric point, a complex colloid would have

more basic groups (positive charges) than acidic groups (negative charges) and would be held in suspension as a cationic colloid. Above the isoelectric point, the negative charges would dominate and an anionic colloid would form. Whether the sol moved as a positive or negative colloid through a podzol depended on the weathering stage of the profile and the proportion of each component (sesquioxides, humus and silica) involved in the complex.

Mattson used isoelectric weathering to explain the formation of deep or shallow pozols, to show how podzol profiles developed from the bottom up and to explain what determined the lower limit of the A horizon (Mattson and Gustafsson, 1937). For these interesting hypotheses, please refer to the original work.

Mattson was virtually ignored in the later review articles. Stobbe and Wright (1959) claimed the pH gradient was not great enough within most podzols for the isoelectric point to be reached and Deb (1949) claimed a positive colloid could not move through the negatively charged humus-rich A horizon. However, Joffe (1936) was sufficiently impressed to write that the "work of Mattson . . . promises to uncover the fundamental principles of the [podzolization] process" p. 293.

Work by Gallagher (1942) may have forced some colloidochemical supporters to reconsider the early Russian views. Gallagher felt that the properties of organic colloids, under the conditions found in a podzol, would be such as to promote the coagulation of sesquioxide sols, rather than their peptization. He also cited the lack of organic accumulation in

the B horizon of many podzols as evidence against the movement of sesquioxides as humus protected colloids. Instead, he supported the concepts of Jones and Willcox (1929) that simple organic acids, such as oxalic acid, played a major role. He felt that more attention had not been given these simple molecules in the past because researchers of the time felt their presence in the soil too transitory. However, Gallagher quoted work of French and German researchers that showed oxalic and citric acids to be the most abundant end-products produced by fungi under nutrient-poor conditions. He felt that because of the abundance of these acids and because podzolization was known to occur most readily on sandy textured soil with free percolation, under leaching conditions, acids of a transitory character could well complex Fe and Al and move them lower in the soil.

Gallagher conducted a column study to determine the effects of leaching simple organic acids through a podzolic B soil. He found that movement of oxalic acid through the column soon produced a strongly leached profile with the upper soil bleached to a depth of 3 cm, an obvious zone of deposition below and clear drainage water. The hydroxy acids of tartaric, citric and lactic formed no such zone of deposition but instead, the drainage soon became highly coloured and contained iron. The poor leaching power of colloidal humus on sesquioxides was demonstrated by the adsorption of humus on the soil surface of a column containing C horizon material.

In the real soil Gallagher saw the iron and aluminum precipitating out in the B horizon first as saturated salts of

organic acids but finally, with continued fungal decomposition, as free hydroxides or hydrated oxides. Colloidal humus was either subsequently or simultaneously leached through the A horizon due to a protective action of colloidal silica, and was coagulated in the B horizon by the sesquioxide gel. Therefore, the role of colloidal humus in podzolization was passive rather than active and this accounted for the wide differences in humus to sesquioxide ratios found in many B horizons (Gallagher, 1942).

In 1946, Bremner et al. studied the extracting power of the neutral salts of some inorganic acids, such as pyrophosphate, on soil organic matter, iron, manganese and copper. Results showed that compounds which were good polyvalent metal extractants and that in fact, formed co-ordination complexes with these metals, also extracted large amounts of organic matter from the soil. This suggested that some of the organic matter in the soil was in the form of co-ordination complexes with the metals, and when these polyvalent cations were removed by the extracting compounds, this organic matter also became soluble. that these metals were in complexed rather than exchangeable form was demonstrated when little organic matter was solublized upon leaching the soil with dilute HCl to remove exchangeable Fe, Mn However, this pretreatment inevitably led to an increase in the amount of these metals and organic matter in the subsequent pyrophosphate extraction. Also, when the pyrophosphate-metal complexes were dialysed from the extracting solution, the remaining organic matter, representing what was originally bound with the metals, was water soluble. Addition of

manganese, copper or iron immediately precipitated this organic matter and the metal-organic complex formed, showed the same solubility characteristics as the original compounds present in the soil. Therefore, the authors proposed that some of the organic matter in the soil formed co-ordination complexes with some of the polyvalent metals and that the presence of these metals rendered the organic-metal complex insoluble. However, they did not attempt to link the presence of these coordination complexes with movement of the metals in this form.

Although the work of Bremner et al. (1946) would steer podzolic research towards chelation chemistry in the 1950's and 1960's, the case for colloidochemical movement of iron and aluminum was still the stronger in the 1940's and its strength was further increased by the work of Deb (1949). Deb attempted to repeat Aarnio's work of 1913 but also wanted to include the effect of pH and concentration on the formation of humus-protected iron oxide sols. Deb found:

- The lower the concentration of iron oxide sol, the smaller was the amount, in proportion, of humus necessary for peptization.
- 2. The amount of humus necessary for peptization varied with the source of the humus.
- 3. The lower the pH, the higher was the amount of humus required for peptization.

In contrast to Aarnio, Deb concluded that humus was able to carry many times its weight in excess iron. He estimated that for concentrations of 100 ppm iron at pH 4.0, not more than

30-40% of the iron oxide (by weight) in humus would be needed for full peptization. Therefore, there was ample humus in the A horizon of podzol profiles to fully peptize any iron formed in this horizon by weathering.

Although Deb found that complex sols could be flocculated in the laboratory by the addition of CaCl<sub>2</sub> to their suspensions, no adsorption took place by these sols on calcium saturated soil. Deb, therefore concluded that exchangeable calcium in the B horizon of a podzol is not sufficient to flocculate the humus-protected iron oxide sol and he implicated microbial decompositon of the humus as an alternative for their precipitation.

Deb (1949) did not repeat these experiments using aluminum to form the complex sol, but if the previous work of Aarnio (1913) had any validity, it would require an order of magnitude more humus to peptize an equivalent amount of aluminum oxide over that required for iron. This mechanism may therefore not work as neatly for this element.

In the 1950's, C. Bloomfield again turned the tide of thinking towards organic acid complexed movement of Fe and Al in a podzol. Most laboratory experiments previous to this time had used organic matter extracted from peat to model organic interactions with sesquioxides. However, as Bloomfield (1951) pointed out, by the very fact of its persistance, peat must have represented a relatively inert fraction of the original organic debris, and the soluble material, which arose either through decomposition or was naturally present as small organic molecules

in the live plant material, may have been more active in mobilizing iron and aluminum. Bloomfield (1951) showed that the ability of raw humus and peat extracts to cause the dissolution of ferric hydroxide was much less than that of the soluble compounds washed from autumn leaves and grass. He then began a 6-part series on podzolization using the soluble products from various tree litters. Aqueous extracts of Scot's pine, Norway spruce, larch, Sitka spruce and Douglas-fir needles were tested for their ability to dissolve iron and aluminum from the co-precipitated sesquioxides (Bloomfield 1953a, 1953b, 1954a, 1954b). Highlights from this work were:

- 1. The extracts were able to reduce much of the ferric oxide to a ferrous form complexed with organic matter. The existance of a complex bond was shown by the ability of the organic molecule to retain much of the iron in solution in the ferrous form, under alkaline oxidizing conditions.
- 2. The organic acids provided much less protection to the aluminum ion as seen by a large precipitation of aluminum when the pH was raised from 3.94 to 6.00.
- 3. The extent to which the sesquioxides were dissolved by the aqueous extract was decreased as the pH of the extracting solution was increased. This effect was most pronounced under aerobic conditions.
- 4. However, even under the adverse conditions of high pH and oxygen, the solution effect was still appreciable. The relatively small changes in pH and degree of

aeration found in a podzolic soil could not have caused the reprecipitation of the oxides in the B horizon. Bloomfield (1953a) suggested microbial assimilation of the organic ligands caused precipitation, although he found he could not explain the segregation of precipitated iron, aluminum and organic matter by this mechanism, nor the consistent order in which they appeared. Later, he found that the acids and iron seemed to be removed from solution by adsorption on to undissolved ferric hydroxide (Bloomfield, 1955).

- 5. The solution of the oxides was non-biological as it proceeded in the presence of toluene and chloroform (Bloomfield, 1953a).
- 6. The extract was separated into a simple organic acid fraction and a polyphenolic fraction using an anion exchange resin. Bloomfield found evidence that the polyphenolic fraction was responsible for the reduction of iron (Bloomfield, 1957).

Although aluminum was included in earlier work, Bloomfield found much less evidence for complex movement of this ion by organic matter. He, therefore, concentrated his later research on reduction and movement of iron, virtually ignoring aluminum.

Similar work by DeLong and Schnitzer (1955) and Schnitzer and DeLong (1955) led these authors to very different conclusions. Aqueous extraction of the autumn leaf fall of poplar, beech, birch, pine and sugar maple from trees growing on podzolized soils, as well as extracts from the forest canopy and

LFH horizon, were mixed with ferric hydroxide. In contrast to Bloomfield, these authors found that as the pH of the extract was raised with NaOH, more iron was held in solution up to an Fe:OM mass ratio of unity at pH 8.5. DeLong and Schnitzer (1955) concluded, like Deb, that a suspending capacity of this magnitude could only be explained if the organic matter was acting as a protective colloid to colloidal iron hydroxide. The authors then supported this reasoning by electrodialysis at pH 5.5 of a 50% saturated poplar extract (Schnitzer and DeLong, 1955). They found that most of the iron moved towards the negative electrode and even the portion which moved positively was explained as being due to organic matter protection. The absorption spectra of the solution present at the anionic cells after electrodialysis, showed no maxima indicative of ferric ions or of soluble complexed iron. They also found no spectrophotometric evidence for chelation (Schnitzer and DeLong, 1955). similarity of these authors results to those of Deb (1949) may indicate that their experimental conditions resulted in the production of colloids of iron oxide rather than iron-organic complexes.

Bloomfield was supported, however, by the work of Coulson et al. (1960a, 1960b). These authors leached columns of soil with the polyphenolic materials, D- and epi-catechin, two of the major extractable components of beech leaves (Fagus sylvatica) grown on mor sites. They found that these compounds could indeed reduce ferric oxide and that either of the compounds leaching at pH 3.72 could remove 10x more iron than a solution buffered to 3.72 but

without the polyphenol, and 5x more iron than the same polyphenol leaching at pH 5.89. This decrease in efficiency in a less acid environment was explained by the lower stability of polyphenolic compounds at higher pH. Experiments showed that under slightly acid or nearly neutral conditions, the polyphenolic compounds were degraded to a number of complex phenolic products, many of which did not combine with iron. The movement of aluminum appeared independant of the polyphenols but correlated negatively with pH.

A third mechanism proposed for sesquioxide movement was the translocation of iron and aluminum as inorganic cations.

According to review articles, this was a theory prevalent thoughout the first half of the twentieth century but on which little experimental work had actually been done. It was believed that organic decomposition in the A horizon produced acid conditions which brought about the solution of sesquioxides, and the higher reaction in the B horizon was responsible for their subsequent precipitation (Stobbe and Wright, 1959). However, Van Schuylenborgh and Bruggenwert (1965) demonstrated, with various assumptions, that the solubility of ferric iron was so low at pH 4.0 that it would require 430,000 years to translocate, in ionic form, the amount of iron that had been removed from the A horizon of the podzol in question. The soils studied were a maximum of 15,000 years old.

In contrast, aluminum ions had a higher solubility. It would have required only 204 years at pH 4.0 and 67,200 years at pH 5 to explain the loss of 3% Al<sub>2</sub>O<sub>3</sub> from the A horizon (Van

Schuylenborgh and Bruggenwert, 1965). Under reducing conditions, iron may be translocated in the ferrous form, as the solubility of this ion is high (Stobbe and Wright, 1959).

## Views of The Modern Era

Despite conflicting evidence, complexed and chelated movement of aluminum and especially iron became the focus of podzolic research throughout the next decade. A chelating agent is an organic ligand which forms two or more coordinate covalent bonds with a metal ion. Movement in this form had been suggested but never established by a number of early workers (Schatz et al., 1954; Barshad, 1955; Schnitzer and DeLong, 1955). Atkinson and Wright (1957) attempted to model podzol formation by leaching a column of calcareous soil with the known chelating agent, EDTA. These authors found that after seventeen months, a profile had formed in the column which resembled a podzolic soil. redistribution of iron was indicated by the formation of a bleached Ae and dark brown B horizons. In contrast, a column leached only with water showed no redistribution of iron. Instead, a dark staining at the top of the column seemed indicative of weathering and the formation, in situ, of hydrated oxides of iron.

At this time, extensive work was undertaken to establish the chemical nature of the organic material actually present in the soil. As humus, both at the soil surface and within the mineral soil, consists of a mixture of organic acids, varying in size and in kinds and numbers of functional groups, it is very difficult

to characterize precisely. Typical research of the early 1960's is exemplified in the following papers presented by the Soil Research Institute, Ottawa. Schnitzer and Desjardins (1962) calculated the number-average molecular weights of organic matter from a podzol by freezing-point depression in sulpholane and cyclohexanol. After ultimate and functional group analyses, molecular formulae were developed to represent the large humic molecules of the Ao (roughly equivalent to the H horizon in the CSSC, 1978) and the much smaller fulvic molecules of the illuvial These authors reported that 61% by weight of extracted organic matter from a Bh was composed of functional groups, and that these contained all of the oxygen of the molecule. number of carboxyls to hydroxyls was 1.0. In contrast, only 23% of the weight of the Ao organics was in functional groups and these contained only half the oxygen of the molecule. The number of carboxyl to hydroxyl groups was only 0.25 (Schnitzer and Desjardins, 1962). Using methods of oxidative degradation in both acidic and alkaline media, Wright and Schnitzer (1963) concluded that the "nucleus" of organic acids within the Bh horizon consisted primarily of aromatic structures, whereas those of the Ao contained appreciable amounts of aliphatic and/or alicyclic structures in addition to the aromatic.

Using these calculated molecules as model compounds,
Schnitzer and Skinner (1963) began a systematic investigation
into the reactions between the organic matter and the metal ions
likely to occur in podzolic soils. Potentiometric and
conductometric titrations, absorption and IR spectroscopy and

flocculation experiments revealed that organic acids formed stable, water-soluble complexes with Fe<sup>+3</sup>, Al<sup>+3</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup>, Cu<sup>+2</sup> and Ni<sup>+2</sup>. More Fe<sup>+3</sup> and Al<sup>+3</sup> could be complexed at pH 5.0 than pH 3.0. The molar ratios of iron and aluminum to the model organic compounds of Schnitzer and Desjardins (1962) varied from 1:1 to 6:1, becoming increasingly water-insoluble as more metal was complexed. The reaction involved at least one carboxyl group per atom of metal and no evidence was found for phenolic hydroxyl participation in complex formation.

Schnitzer and Skinner (1963) also discovered that the power of organic matter to hold sesquioxides in solution seemed much lower for aluminum than for iron. This was substantiated by the reactions of metal:organic complexes prepared in the laboratory. Schnitzer and Skinner (1964) found that iron complexes began to precipitate out at a metal:organic ratio of 3 and complete precipitation occurred at a ratio of 6. Slight flocculation of aluminum complexes occurred at a molar ratio of unity, appreciable and complete flocculation of aluminum complexes occurred at the ratios of 3 and 6, respectively. extrapolation of these results, one might expect iron to move further into the soil than aluminum, a condition not generally found in a podzol (McKeague et al., 1983). However, Wright and Schnitzer (1963) also reported that as little as 0.13 ppm Ca as CaCl<sub>2</sub> and 4.5 ppm Mg as MgCl<sub>2</sub> caused complete flocculation of iron-organic matter complexes but it required 10 and 45 ppm Ca and Mg, respectively, to flocculate Al-organic complexes. Therefore, although the Bh organic matter had a greater

complexing power for iron than aluminum, the Fe-organic matter was much more susceptible to flocculation by Ca and Mg. This led the authors to suggest that the Al-organic complexes may move deeper into the profile than those of iron, as in accordance with field observations. However, it is interesting to note that although Deb (1949) found iron-organic colloids precipitated with ease upon addition of CaCl<sub>2</sub> to their solutions, a soil saturated with calcium could not immobilize organic molecules leached through it.

A review by Mortensen (1963) listed similar research from other laboratories attempting to characterize metal:organic complexes. Petersen (1976) was very critical of the methods used and some of the conclusions drawn in much of this work. pointed out ranges in molecular weights, reported in this literature, that varied by orders of magnitude, even for similar fractions. For example, using different methods the above Ottawa laboratory reported hundred fold discrepancies in the number average molecular weight values of an organic fraction extracted from a single horizon (Wright et al., 1958; Schnitzer and Desjardins, 1962; Hansen and Schnitzer, 1969). As another example, Petersen was critical of a spectroscopic technique originally described by Vosburgh and Cooper (1941) and used by Schnitzer and Skinner (1963). He claimed this technique was only applicable if one complex was formed per molecule. If more than one complex was involved, a modified method not followed by Schnitzer and Skinner, should have been employed. In fact, so many inconsistencies and contradictions occurred within the

1960's research on organic matter characterization that only generalities could be drawn from the work. Nonetheless, Petersen felt there was enough evidence to support a considerable content of acidic groups with structural arrangements able to form complex and chelate compounds with metal ions. This, however, was still only circumstantial evidence for movement of the organic matter and metals into the B horizon together as a complex.

McKeague (1968) and McKeague et al. (1971) found that the molar ratio of pyrophosphate extractable iron and aluminum to fulvic acid within a podzol was in the range of 3-10 for all of the B horizons tested. If fulvic acid began to precipitate at a metal:organic ratio of 1-3 and complete precipitation occurred at a ratio of 6 (Shnitzer and Skinner, 1964), how could complexes with these high ratios form, especially as more fulvic acid would have subsequently leached down and lowered the apparent molar ratio of the complex? McKeague et al. (1971) felt that this raised some old questions concerning the genesis of these horizons.

To this time most evidence in support of proposed podzolic models was gained through laboratory experimentation. Few studies actually looked at what was happening in the real soil. However, by centrifugation, Bruckert (1970) was able to collect the soil solution from a podzol and show that the dominant organic constituents moving through this soil were the aliphatic acids, citric and oxalic, and the small molecular weight aromatic acids, vanillic and p-hydroxybenzoic. All had the ability to

complex iron, although the simple aliphatic compounds were able to complex 3x more of this element than the aromatic. The highest concentration of these acids was collected from the litter and the concentration decreased rapidly with depth.

A later review article by Vedy and Bruckert (1979) reported that the small aliphatic acids were specifically in the "bound" water adsorbed on to soil surfaces and held within small pores. This would be the fraction Bruckert (1970) had removed by centrifugation and its presence was consistent with the proliferation of microorganisms in this environment. contrast, the "gravitational" water in the larger pores contained predominantly high molecular weight polymeric materials that were brownish yellow in colour and related to fulvic acids. were much more stable to biodegradation than the low molecular weight compounds. Vedy and Bruckert (1979) suggested that the small aliphatic acids within the "bound" water, affected the weathering of certain soil minerals and formed stable and unstable complexes with the metals released during this process. Upon soil drainage, the small aliphatic acid complexes entered the "gravitational" water and were either rapidly biodegraded in this aerated medium or integrated into the larger "fulvic acids". It was in the latter form that iron and aluminum were transported through the soil.

Throughout the 1970's, the lysimeter became an important tool used to monitor podzolization processes. Schnitzer and Desjardins (1969) found that the leachate moving through the Ae horizon of a humus podzol had many chemical and spectral

properties similar to the fulvic acids extracted from the soil but seemed to have a lower number average molecular weight.

Ugolini et al. (1977) using lysimeters, measured the concentration of certain elements moving through the soil solution of a podzol situated in the central Cascade Mountains of Washington. Their results divided this ecosystem into two distinct horizontal compartments, the first extending from the forest canopy to the bottom of the IIB2hir (approximately equivalent to the Bhf, CSSC, 1978) and the second from this horizon down through the IVB32 (Bf, CSSC, 1978). Rainwater passing through the canopy and forest floor became enriched in basic cations, N, P, Fe, Si and Al and except for silica their maximum concentration in the the soil solution was reached at the bottom of the O horizon (H, CSSC, 1978). The concentration of these elements dropped slightly in the A2 and reached a minimum at the bottom of the IIB2hir. The concentration of the mobile fulvic acid fraction also dropped 60-70% within the IIB2hir. Below this horizon, the soil solution again became enriched in basic cations, Al and N. Singer et al. (1978) attributed the latter enrichment to the renewed carrying capacity of soil water within the IIB2ir horizon. This was due to the precipitation of much of the water's ionic content in the horizon above. et al. (1977) called the upper solum where fulvic acids were active, the biopedological compartment and the lower solum, the geochemical compartment. Although the concentration of aluminum in the "geochemical" compartment nearly equalled that passing through the A2, no attempt was made to characterize the form in

which the aluminum occurred. However, the authors noted that little aluminum was carried out of this compartment into the ground water.

The molecular weights of the soluble organic compounds moving through this soil were 837-845 by gel filtration and infrared analysis indicated the presence of aromatic hydroxy carboxylic acids. Interaction of this leachate with material from the IIB2ir horizon demonstrated how effective reactive sesquioxides were in adsorbing the soluble organic compounds within the soil solution (Dawson et al., 1978).

In 1976, L. Petersen completed an exhaustive work on podzols and podzolization. In this, it is interesting to note how many aspects of podzol genesis remain in question despite a century of research on the subject. Although western classification schemes have removed soils with B horizons enriched in layer silicate clays from the podzol great group, Russians still contend that the two should be united. They see the clay enrichment as due to neosynthesis of layer silicates within the B horizon, from raw materials translocated from above (Ponomareva, 1969). However, Lowe (1980) showed that organic matter, as well as clay enrichment, distinguished a Bt horizon from a Bf horizon. He found that the ratio of polyphenolic fulvics to total fulvics (Ca/Cf) was consistently much lower in luvisolic B horizons.

Organic matter extraction from the litter and mineral soil is still accomplished by methods used in the early 1900's. The resulting organics must be considered at least slightly modified by the extracting procedures and although we have obtained a

general idea of the types of molecules present, the wide variety of organic compounds within the soil humus make it impossible to characterize precisely. As a result, Petersen (1976) still lists circumstantial evidence for the formation of complex bonds between organic acids and metals and he finds it is also difficult to prove chelating compounds actually exist in the soil.

Even the mechanisms of podzol genesis are still in question. Petersen shows through thermodynamic calculations, that it is impossible to rule out the movement of aluminum as an inorganic cation. He believes movement of colloidal sesquioxides protected by humus could also be possible, although Petersen can not visualize the means by which solutions of these colloids would form in the soil. Complex formation between water soluble organic compounds and metal cations is the most popular candidate for translocation of iron and aluminum within a podzol, but arguments still exist as to whether the most active compounds are the simple organic acids or the polyphenolic fulvic acid precursors. Petersen finds it difficult to explain how simple acids would precipitate out in the B horizon. Decomposition of the small organic acids is most often implicated but this author questions why the organisms responsible would be particularly abundant at this level in the soil. Petersen, therefore, favors transport of iron and aluminum by polyphenolic acids and the deposition of this complex when the amount of iron and aluminum taken up exceeds a certain limit.

Original research by Petersen also added to the bulk of

knowledge. He found, by centrifugation of moist soil and from aqueous extractions, that dissolved organic carbon was present in the soil solution throughout the profile. A high carbon content was found in extracts from the AO, Al and Bl and, although the amount decreased with depth, appreciable carbon was still found in the colourless soil solution of the C horizon. Soluble iron and aluminum also decreased with depth but although the C/Al value in solution dropped noticeably from the A2 to the Bl, variation in the C/Fe value was less regular. In laboratory reactions between metal ions and a soil organic extract, Petersen found that acids and metals remained soluble until a certain amount of metal had been added and then complete precipitation of both took place. Like Schnitzer and Skinner (1963, 1964), Petersen found that this precipitation occurred at a lower concentration of aluminum ions than ferric iron.

As with the rest of the temperate world, researchers of southwestern British Columbia have also attempted to address the question of genesis and classification of podzolic soils but unlike many of the past situations, soils here are not the "classical" podzol of the literature. The classical model consists of a thick, light-coloured eluviated horizon over a B horizon, approximately comparable in thickness to the Ae and enriched with translocated sesquioxides and organic matter. Instead Lewis (1976) found that the podzols of Vancouver Island often contained no Ae or a thin discontinuous horizon over a very thick, very sesquioxide-rich B horizon. The amount of sesquioxides extracted from this horizon usually decreased with

depth except for oxalate aluminum, which frequently attained its maximum immediately overlying the C horizon. The soils also had large accumulations of organic matter both at the soil surface and randomly distributed throughout the mineral soil. Lewis suggested that the discrepancies between the classical model and these soils were a function of climate and a base-rich parent material. Heavy rainfall ensured that in situ weathering was a dominant force in soil genesis and as a consequence, the translocation of sesquioxides was limited when the charges on complexing organic acids were neutralized near the surface by the abundant iron and aluminum oxides. Also, the randomly distributed organic material within the B horizon resulted from the periodic uprooting of large trees. These buried large amounts of organic debris which subsequently decomposed.

Lewis (1976) suggested that the current concept of podzol genesis, which centered on the translocation of sesquioxides as a complex with organic matter, should be broadened to include genesis by:

- In <u>situ</u> weathering and negative enrichment of iron and aluminum; and
- Anti-horizonation processes such as physical turbation and the biocycling of elements.

Lewis believed that all three processes were active in all podzols and that the different podzol morphologies found throughout the world resulted from the dominant environmental forces under which the soils developed.

Also on Vancouver Island, podzol-like soils were studied by

Moon (1981). These soils occurred over a climosequence, created by an increase in elevation. With the aid of lysimeter data, soil morphology and chemical extractions this author was able to derive a simple, linear model to account for the genesis of these soils and to find evidence that some of the mechanisms suggested by Lewis (1976) actually occurred. One of the most interesting aspects of Moon's work was that he was able to relate the generalized processes of soil formation - addition, loss, transformation and translocation - to real soils in the field. He believed that the balance of these processes resulted in the unique character of the soil at each site. Although all processes played a role in all soils, under the light rainfall conditions of lower elevations, weathering and negative enrichment of iron and aluminum were the dominant processes acting in the formation of the  $\mathrm{B}_1$  horizon. However, under the higher rainfall of mid- and high elevation sites, the illuviation of iron and aluminum from the A horizon and forest floor with subsequent precipitation in the B, was the mechanism most responsible for the development of the sesquioxide-rich horizon. The latter two sites were separable primarily on the rate of profile development, with the high biological activity of the mid-elevation soils resulting in the greatest morphological expression of podzolic characteristics and the highest acid ammonium oxalate iron and aluminum value. However, the sodium pyrophosphate-extracted sesquioxides of the site were low, presumably because a high decomposition rate quickly released the metals from the organic complex and therefore, the soil could not be classified as a podzol under the criteria established by the CSSC, 1978. In situations such as these, methods of podzol classification are still in question today.

In conclusion, all research from the past century has contributed to our knowledge today and forms the basis of the two models of podzol genesis presented in Chapter 2. The first of these is the most widely accepted "classical" model and the second, a recent divergence based most closely to the work of Tamm (1920, as read in Farmer, 1982) and Mattson and Gustafsson (1937). In both models many questions remain to be answered before the proposed mechanism of podzol formation can be accepted. Future research may prove the truth lies somewhere between the two extremes or in another direction altogether.

### CHAPTER 2

### MODERN MODELS OF PODZOL GENESIS

## The Movement of Iron and Aluminum as an Organic Complex

Concepts of podzol formation evolved with the research of the 1960's and 1970's into an accepted biochemical mechanism, outlined by both DeConinck (1980) and Duchaufour (1982), as follows. Leaching of soluble bases from the soil by rainwater, and a conifer-dominated vegetation which by rooting habits returns few of these bases to the soil surface, results in the formation of an acid "mor" humus (Duchaufour, 1982). The low pH and nutrient content restrict bacterial activities. Simple organic acids, formed both with and without the aid of fungal decomposition, are leached from the litter layer. These by complexolysis, weather the minerals of the A horizon, reduce any free iron present and with the aid of larger fulvic acid precursors, carry this ion as well as aluminum, in complex form, into the B horizon (Duchaufour, 1982). Through various mechanisms, the iron and aluminum are precipitated in the B horizon as hydroxides (DeConinck, 1980; Duchaufour, 1982). amorphous silica, which has moved from the A horizon in a soluble form, precipitates with the Fe and Al hydroxides, forming a mixed gel similar to the allophane of andosols. All that remains in the eluvial horizon is detrital quartz and a few clay minerals resistant to acid weathering (Duchaufour, 1982).

DeConinck (1980) relies on two principles of colloid chemistry to give a more complete account of this podzolization mechanism:

- 1. Organic substances may form hydrophilic colloids with surface charges.
- 2. The hydrophilic character and negative surface charges determine the dispersibility of the colloids.

The organic substances involved in iron reduction and complex formation are the small aliphatic and aromatic acids of Bruckert (1970) and also larger fulvic acid precursors with molecular weights of 2500-3000 (Duchaufour, 1982). These have structures of aliphatic chains and benzene rings substituted with different radicals such as -COOH, phenolic-OH, alcoholic-OH, NH2 and quinones. The polar nature of these radicals attracts water molecules. Also, if the carboxyl groups form the strongest acid in the soil environment, they may dissociate releasing an H+ ion and imparting a negative charge to the molecule. The charge and hydrophilic nature of the primary compounds cause them to repel each other and form discrete particles surrounded by water molecules (DeConinck, 1980).

DeConinck (1980) lists four characteristics of the organic compounds that determine their mobility within the soil:

- 1. The size of the compounds.
- 2. The ratio of hydrophilic to hydrophobic parts, the latter being the benzene rings and aliphatic chains without replacement radicals.
- 3. The charges present on the compounds.

4. The way in which these charges are neutralized.

The negative sites present on the organic molecules attract cations of monovalent, divalent and trivalent character present in the environment. As monovalent cations are unable to form strong covalent or co-ordinate covalent bonds with the organic radicals, their neutralization powers are exclusively physical or electrostatic. If, as found in podzols, the monovalent cation concentration is low, the cations adopt a distribution in a thick double layer around the organic anion. This layer repels the other organic acids, also surrounded by a thick double layer and the acids remain dispersed. Divalent and trivalent cations, on the other hand, are able to form chemical bonds of strong co-ordinate covalent character with the organic anion. organo-metallic bond is in the form of a chelate or other type of In this way, the cations are chemiabsorbed without a complex. well-developed double layer and no repulsion occurs (DeConinck, 1980).

The stability of the organic-polyvalent bond increases with charge and with declining size as follows:

 $A1^{+3} > Fe^{+3} > Fe^{+2} > Mg^{+2} > Ca^{+2}$  (DeConinck, 1980)

Duchaufour (1982) sees complex formation occurring at low pH (4), in periods of heavy rainfall in which temporary waterlogging occurs in the soil. The Eh at this time is at a minimum at the H/Ae boundary and so the iron is generally complexed in the ferrous state. These complexes are very stable, able to resist the rise in pH and Eh which can occur at the bottom of the Ae. In contrast, the salt complexes formed under conditions of better

aeration, are not as mobile or stable and precipitation occurs more rapidly. Also, according to Duchaufour (1982, p. 318, p. 77), the reason why aluminum moves further into the B horizon than iron is because aluminum-organic complexes are the more soluble. However, very little evidence is given by Duchaufour to support this claim and the results of past research, listed in chapter 1, seem contradictory to this.

Iron and aluminum in complex form with the organic acids, move downwards through the soil until the mobility of the complex is lost through three different processes (DeConinck, 1980):

- 1. During their migration, additional cations may be complexed by the organic colloids. The divalent and trivalent cations may neutralize the negative charge to the point where the organic acids can approach one another. Also, a polyvalent cation may bind two primary organic molecules together, bringing about polymerization of the ligands. Precipitation occurs through the lack of charge and increased size.
- 2. The organic colloids may precipitate out of solution under conditions of higher ionic concentration or a soil reaction that is different from where they were mobilized.
- 3. Desiccation of the soil may increase ionic concentration, resulting in contraction of the double layer surrounding the complex and expulsion of water molecules from voids.

When immobilized, the primary compounds are still surrounded

by water of hydration. Also, during formation of the larger particles, many water molecules and cations present in the surrounding solution are locked inside the voids. As a result, the complex is in a gel state rather than a solid state. The water is lost through gradual dehydration (DeConinck, 1980).

Various authors, quoted by Duchaufour (1982), have demonstrated the ease with which clay is destroyed in the A horizon by the complexing ability of simple organic acids. However, owing to the rapid mineralization of aliphatic acids, their effectiveness as weathering agents is restricted to the surface horizons. At lower levels the aliphatic acids are replaced by phenolic polymers which act mainly as carriers of iron and aluminum rather than as weathering agents. Biological activity at the top of the B horizon may biodegrade a portion of these complexing anions, reducing the anion:cation ratio and freeing part of the iron and aluminum. The metals may then in turn neutralize the charge on other organic complexes and bring about their immobilization. Duchaufour specifically cited the work of Bruckert (1970) which illustrated how biological decarboxylation, occurring in the B horizon, was one initial cause of soluble complex precipitation.

Despite an abundance of organic acids, weathering within a well-developed podzol is often not as great as is commonly believed. This is because of a lack of weatherable minerals within the A horizon, and within the B horizon, because of the protection afforded minerals by a covering of precipitated, surface-derived amorphous material. The production of this

amorphous material by polymerization of the iron and aluminum complexes and/or silica is much more important than clay formation in the B horizon of a podzol (Duchaufour, 1982).

According to Duchaufour (1982), the formation of a Bh horizon occurs at first simultaneously with the development of the Bs, as small aromatic acids move to a greater depth within the profile than larger molecules. After precipitation, the acids gradually polymerize to form humic acids, dominant in the Bh and fulvic acids, dominant in the Bs. As the podzol develops, the amount of free iron responsible for insolubilization of the organic complexes increases in the soil, particularly in the Bh horizon. As a result, eventually all complexes, regardless of size, are insolubilized in the Bh. This forms an absolute chemical barrier that cannot be crossed by mobile complexes. Duchaufour substantiates this with the carbon 14 determinations of Guillet (1972) which show that the mean age of the Bs is always greater than that of the Bh. Later remobilization of organic acids and sesquioxides within the eluvial horizon may result in a thickening of the B horizon (Duchaufour, 1982).

In general terms regarding organic matter, Duchaufour reports that the stabilizing effect of iron on organic compounds is minimal. All the humic compounds precipitated by iron remain susceptible to biodegradation. Their biological turnover is rapid and they do not accumulate in acid forest mulls. In contrast, amorphous alumina has a great stabilizing effect against microbial biodegradation of organic matter. This is illustrated especially well in andosols where amorphous alumina

is the active part of the allophanes prevalent in these soils. The aluminum bonds strongly with the organic molecules, particularly the precursor compounds and this results in an almost immediate insolubilization and stabilization of the organic matter. Duchaufour cites work by Hetier (1975) which showed that a considerable portion of the organic matter in the central part of the allophane-humus aggregates accumulating in an andosol, was of the same age as the soil, (up to 4000 years old). This is one factor behind the second model of podzol genesis now to be presented.

## Movement of Aluminum (and Iron) as Inorganic Proto-imogolite

A reassessment of podzol formation was made by Anderson et al. (1982) based on work by V. C. Farmer and coworkers at the Macauley Institute for Soil Research in Scotland. These researchers discovered in podzolic B horizons, imagolite, a mineral related to allophane.

Allophane is a series name applied to naturally occurring hydrous aluminosilicate clays characterized by a short-range order and by the predominance of Si-O-Al bonds (Wada, 1977). Because allophane is a weathering product of volcanic ash, many past studies have emphasized its importance in andosols, but allophane is also found in a variety of other soils. It is formed from basic igneous rocks by intense tropical weathering, from acid rocks by podzolization, by the physical process of glacial grinding and from solution in areas with ground waters high in dissolved silica and alumina (Brown et al., 1978).

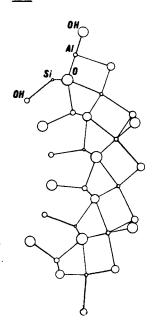
Yoshinaga and Aomine (1962a) found that by dispersing a volcanic ash soil first at the high pH of 10.5-11.0 then subsequently, by dispersing the residue at the low pH of 3.5-4.0, they could separate two distinct < 0.2 micron fractions. The first was x-ray amorphous and determined to be pure allophane; the second had broad, relatively intense 14.5 Å and 7.6 Å diffractions and a weak peak at 5.5 Å. This mineral had never before been described. The authors proposed the name "imogolite" after imogo, a brownish yellow layer in volcanic ash soils of the Kuma basin in Japan, in which imogolite was first found. Until recently, this colloid was considered exclusive to the weathering of volcanic ash.

Under the electron microscope, Yoshinaga and Aomine (1962b) found that imogolite appeared to be of thread-like shape with a relatively uniform size. This uniformity in shape seemed to suggest some regularity of atomic arrangement within the imogolite particles. Further work determined the imogolite fibers to be 20 Å in outside diameter (Wada et al., 1970) and electron diffraction indicated a repeat distance along the fiber axis of 8.4 Å and a repeat distance perpendicular to this axis of 22-23 Å. The 8.4 Å repeat distance was tentatively assigned to a gibbsite-like chain or ribbon (Wada and Yoshinaga, 1969; Russell et al., 1969). As well, Cradwick et al. (1972) presented strong evidence for the presence of an orthosilicate group in imogolite. These authors then proposed that imogolite had a "tube" structure, the outer walls like a single sheet of gibbsite with orthosilicate groups replacing the inner hydroxyl surface of the

gibbsite sheet. The binding of silica to this free hydroxyl surface shortens the O-O distances between hydroxides from about 3.2  $\mathring{\rm A}$  in gibbsite to less than 3  $\mathring{\rm A}$  in imagolite, appropriate to the edges of a SiO<sub>4</sub> tetrahedron. This would account for the curling of the gibbsite sheet and therefore, the tube structure of imagolite (see figure 2-1).

This structure would require an empirical formula of  $(HO)_3Al_2O_3SiOH$  and this would also be the sequence of atoms encountered on passing from the outer to the inner surface of the tube (Farmer et al., 1977).

Figure 2-1: Proposed Structure of Imogolite (Cradwick et al., 1972).

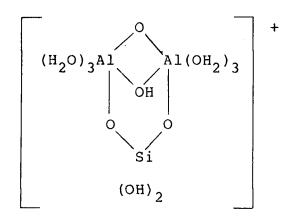


Imogolite occurred in volcanic ash soils as a gel film coating weathered pumice particles but, in contrast to allophane, could not be found within the weathered particles themselves

(Wada and Harward, 1974). This suggested to Farmer et al. (1977) that natural imogolite formed from solution. Using this evidence and assuming the molecular arrangement as determined above was correct, Farmer et al. (1977) set out to synthesize imogolite, using an infrared band at 348 cm<sup>-1</sup>, distinctive to this mineral, to monitor their success. A dilute solution containing hydroxy-Al cations and orthosilicic acid, with Al:Si atomic ratios of about 2:1, was adjusted to pH 4.5 and heated to 96-100°C. After maintaining the solution at this temperature for one day, imogolite was detectable and after five days a maximum yield was attained. This synthetic imogolite had an IR spectrum and electron diffraction pattern which indicated a product only slightly less regular than the best natural specimens and its fibrous morphology could be seen under the electron microscope.

The imogolite precursor, present before heating, was an hydroxyaluminum orthosilicate sol called "proto-imogolite" (Farmer, 1981). Proto-imogolite formed colloidal suspensions which were water-clear and stable indefinately. The freeze-dried suspension gave an infrared spectrum similar to that of synthetic imogolite but whereas imogolite had electron diffraction patterns at 1.4 Å, 2.1 Å and 4.2 Å, proto-imogolite showed none of these or only a diffuse ring at 1.4 Å. Proto-imogolite was, therefore, considered to consist of small fragments of the imogolite structure, the smallest possible building unit is shown in figure 2-2 with a charge dependant on the ionization of Al(OH<sub>2</sub>) groups (Farmer, 1981).

Figure 2-2: The Smallest Possible Building Unit of the Imagolite Structure (Farmer, 1981)



Within the podzolic model crediting fulvic acids with the transport of aluminum, are many mechanisms accounted for only by circumstantial evidence. Much more of the iron and aluminum enriching podzolic Bf horizons can be extracted with acid ammonium oxalate than with pyrophosphate, indicating that most is present in an amorphous inorganic form rather than as a complex with organic matter. McKeague et al. (1971) felt this implied that iron and aluminum were either transported with organic matter which was subsequently biodegraded or that these minerals were translocated as hydrous oxide sols. Farmer (1981) felt the first suggestion to be unlikely because of the high stability from microbial decomposition of organic complexed aluminum and iron in volcanic ash soils, specifically the 10,000 year+ age of organics in buried Al horizons (Wada and Higashi, 1976; Higashi and Wada, 1977). Farmer (1981) also felt the second suggestion to be unlikely because of the low solubility of Fe and Al

hydroxides and the readiness with which Al hydroxides of low salt content crystallize to form gibbsite. Gibbsite is not a typical constituent of podzols. In fact, evidence for the movement of iron and aluminum as fulvic acid complexes concentrated on properties near the top of the B horizon where much of the iron and aluminum was tied up with organic matter. Anderson et al. (1982) argued that these complexes could have formed in situ when soluble fulvic acids precipitated on inorganic sesquioxide coatings. They felt this would also explain the higher humic to fulvic ratio of Bh horizons in comparison with Bf horizons, as the more mobile fulvic acids could penetrate further into the mineral soil than the less mobile humic acids.

Earlier work had found that much of the x-ray amorphous clays in podzolic soils consisted of aluminum silicates related to allophane (Mitchell and Farmer, 1962; Kirkman et al., 1966; Brydon and Shimoda, 1972). In these, the allophane was assumed to have formed in situ. Imogolite had been detected by electron microscopy of the clay fraction in Scandinavian and German soils, developed on dune sand and on a quartz parent material, respectively, but no further proof of its presence had been offered (Tait et al., 1978). However, by dispersing the clay fraction of Scottish podzols at pH 4.0, Tait et al. (1978) concentrated the allophanic materials, and imogolite was positively identified by electron microscopy. These soils were located on parent materials unaffected by recent volcanic activity. The discovery of imogolite was significant because, if indeed this mineral could only form from solution, the precursor

could well have been proto-imogolite. As proto-imogolite is fully mobile in the positively charged B horizon, aluminum could move through the soil in this inorganic form (Farmer, 1981).

In further studies, Farmer et al. (1980) isolated imogolite in three additional Scottish soils. In one of these, an imogolite-like material was the dominant component of the acid-dispersible clay fraction of the  $B_2$  horizon but although electron microscopy showed that a considerable amount of well-ordered imogolite was present, the infrared spectrum was intermediate between imogolite and proto-imogolite. The clay was, therefore, considered to be a mixture of both components.

In subsequent papers imagolite was detected again and again in podzolic environments. Anderson et al. (1982) found this mineral in the Bs horizon of a number of Scottish podzols but it was not found in the Bh horizons of these soils. Childs et al. (1982) located imagolite in non-volcanic soils of New Zealand and it was also found in Canadian podzols by Ross and Kodama (1979) and by McKeague and Kodama (1981). In two of these last three situations, imagolite appeared to form the cement of indurated horizons located within the soils (Childs et al., 1982; McKeague and Kodama, 1979).

The deposition of an allophane with an infrared spectrum and composition of proto-imogolite was also seen in household water pipes where the water supply had a pH of 4.5 (Farmer, 1981, from unpublished data) and an allophane with a high Al:Si ratio rapidly accumulated in a field drain at the Rothamsted Experimental Station, England (Ormerod and Brown, 1978).

Farmer (1981) studied the effect of various organic acids on the liberation of aluminum and silica from imogolite. that the strong complexing acids, malonic, tartaric and salicylic decomposed proto-imogolite completely while mono-carboxylic acids such as acetic, did not decompose proto-imogolite and did not impede its formation. At pH 4.5, fulvic acid behaved as a strongly complexing acid, completely decomposing imagolite to a soluble Al-fulvate plus silicic acid when the molar ratio of fulvate-COOH to Al exceeded about 8. Fulvate and proto-imogolite formed precipitates at lower ratios of COOH: Al and complete coprecipitation of all aluminum and all fulvate from solution occurred at a molar ratio of unity with partial liberation of silica from the proto-imogolite. At ratios of COOH: Al of less than 0.3, most of the proto-imogolite remained soluble and maintained fulvate in solution by adsorption on the proto-imogolite sol. Farmer (1981) also estimated that the equilibrium concentration of silica necessary to prevent the decompositon of imogolite to boehmite was 1 ppm SiO, at 25°C. Further calculations led to the conclusion that "there is ample SiO, in most soil solutions to ensure that imogolite rather than aluminum hydroxides form when a reactive aluminum species is liberated by the weathering of minerals" (Farmer, 1981).

The high proportion of iron and aluminum organic complexes in the Bh, the very low proportion of iron and aluminum in organic form in the Bs and the fact that imogolite was so frequently found in podzolic horizons unaffected by volcanic activity led Farmer and coworkers to propose a model for podzol

genesis which included translocation of aluminum as proto-imogolite (Farmer, 1981; Anderson et al., 1982). In this model, the authors did not question the role of colloidal chemistry, as proposed by DeConinck (1980), in the mobilization and subsequent immobilization of organic acids, rather they questioned the role these acids played in the transportation of iron and aluminum. Small organic acids, released by the vegetation, were still considered important in the weathering of soil minerals but Farmer (1981) quoted work by Aristovskaya and Zykina, 1977, which found microorganisms present in the soil capable of decomposing these lactic, tartaric and citric acid-complexes of aluminum and excreting the metal. (1982) felt that when sufficient silica was present in the soil solution, the aluminum released by the organic acids would form proto-imogolite rather than an aluminum hydroxide. At pH below 5.0, proto-imogolite is soluble and should move through the positively charged B horizon as a positive sol.

Proto-imogolite would precipitate out of the soil solution when the pH rose above 5.0, when the positively charged sols were neutralized by adsorbed anions or when they encountered negatively charged surfaces such as smectites, illites or vermiculite. If conditions were right, the sols might eventually crystallize to form imogolite. However, in acidic soils, proto-imogolite might be transported completely out of the profile (Farmer, 1981).

Farmer saw podzolization occurring in stages. During early development of the soil, before differentiation of an Ae horizon,

alumina and silica were abundant in the soil solution and any fulvic acid formed either precipitated in situ near the top of the profile or was carried downwards as a sorbed phase on proto-imogolite. Later, when fulvic acid was in excess, it began to transport aluminum as an acidic complex. The complex precipitated out on the imogolite and allophanes of the B horizon, complexing the aluminum and releasing silica. This interaction in situ between organic acids or colloidal organic matter and aluminum, resulted in the formation of a Bh horizon, a reaction similar to that which produced the humus-rich A horizons of andosols (Farmer, 1981).

Farmer (1982) pointed out that the two stages of podzol development - migration of the inorganic components followed by the separate movement of organic components - may not be widely separated in time. Proto-imogolite could be the dominant transport of aluminum during periods of high biological activity in summer and the migration of organic colloids dominant during periods of heavy rainfall.

Later, Farmer and Fraser (1982) included in their model, a mechanism for the movement of iron. These authors found that no compound analogous to proto-imogolite could be formed when  ${\rm Fe}({\rm ClO}_4)_3$  was mixed with  ${\rm Si}({\rm OH})_4$  at pH 3.7, because hyroxyiron species have less affinity for silica than do hydroxyaluminum species. However, when iron is partially substituted for aluminum in proto-imogolite, the resulting  ${\rm Al}_2{\rm O}_3{\rm -Fe}_2{\rm O}_3{\rm -SiO}_2{\rm -H}_2{\rm O}$  sols are almost as stable as pure proto-imogolite, up to an Fe:Al ratio of 1:1 (Farmer, 1982). Beyond this, the stability declines

rapidly. Farmer and Fraser (1982) conclude that iron could move inorganically in podzols as this mixed sol. Iron does not, however, appear to substitute for the aluminum in imagolite or allophane (Farmer, 1982).

Possible support for the movement of aluminum through a podzol as proto-imogolite was presented by Farmer et al., (1984). Prepared thin sections of concretions within Australian podzols revealed that the clear, yellow, glassy, isotropic or weakly anisotropic cement of these structures was deposited in layers as if from solution. By infrared spectroscopy and oxalate and pyrophosphate extraction, the concretions were estimated to contain between 1 and 5 % proto-imogolite allophane with only minor amounts of iron and organic carbon. In contrast, no imogolite was detectable in the surrounding loose mineral soil. Farmer et al. (1984) envisioned the deposition of proto-imogolite from solution during the successive drying episodes typical of this climate. Local concentrations of secondary gibbsite and kaolinite seemed to suggest by their position that allophane is a possible precursor to these minerals.

Stronger evidence that proto-imogolite allophane may actually form the cement within many podzol B horizons was found in Scottish soils by Farmer et al., 1985. Translucent, pale yellow, strongly fluorescent, gelatinous deposits could be seen in thin sections as coatings surrounding skeletal sand and silt and forming thick deposits filling voids. Electron-probe analysis of these deposits gave atomic ratios averaging 15i:2.48Al:0.29Fe. This aluminum to silicon ratio fell within

the range typical of proto-imogolite sols formed at silicic acid concentrations near the lower limit of their stability (Farmer and Fraser, 1982).

Farmer et al. (1985) did not detect the fibrous morphology of imagolite within thin sections nor by scanning electron microscopy of air-dry lumps of soil. However, fibrous structures with a Si:Al ratio similar to that of the cement in the thin sections, were visible on fractured surfaces of soil subject to critical point drying. Also, in local areas the allophanic deposits in the thin sections exhibited weak, striated birefringence perhaps caused by co-migration and deposition of layered silicates and gibbsite or from the alignment of imagolite tubes associated with the allophane.

No support was found for the contention that this allophanic material arose in situ either from the weathering of minerals within the B horizon or from the individual translocation of iron and aluminum fulvates and silicic acid. Indeed, examination of mineral grains by the light and scanning electron microscopes revealed that weathering of minerals was at a maximum in the eluvial and Bhg horizons and at a minimum in the Bs and C horizons. Also, silicon to aluminum ratios were often lower inside the voids than on the organic-stained surfaces, a fact contrary to the idea of Al-fulvate enrichment (Farmer et al., 1985).

Root residues within the gelatinous allophanic deposit seemed to have their cell structure preserved by allophane-impregnation. The cell structure exhibited the colour,

fluorescence and lack of birefringence typical of the allophanic gel but atypical of cellulose. Also, electron probe analysis gave Si:Al:Fe ratios similar to that obtained for the gel deposits (Farmer et al., 1985).

Farmer (1981) and Anderson et al. (1982) were supported by the findings of Yoshinaga et al. (1984). By electron microscopy, these authors discovered fibrous imagolite as gel films associated with allophane in fresh fractures of a shattered sandstone parent material beneath a brown forest soil. was unaffected by volcanic activity. The gel films ranged from a few to 20 mm across, were found more often near the top of the sandstone than at depth, and were situated in such a position as to appear to have arisen from the overlying soil. However, neither imagolite nor allophane could be separated from the clay fraction of the brown forest soil nor were they found in old fractures of the parent material. As postulated by Yoshinaga et al., this was because interfering materials such as layer silicate clays and organic matter were present at these locations. It is doubtful whether the imogolite found in the fresh fractures could have arisen in situ from the separate migration of silica and aluminum because the Si:Al ratio in the soil solution was so large that a high-silica type allophane would have been formed. Also, the virtual absence of organic carbon in the soil solution may rule out the movement of aluminum to this location as a fulvic complex (Yoshinaga et al., 1984).

### Conclusions

Each of the two models presented for podzol genesis relies heavily on circumstantial evidence for support. The model favoring movement of iron and aluminum in an organic complex (DeConinck, 1980; Duchaufour, 1982), accounts fairly well for properties visible near the surface of the soil and examination of the soil solution seems to support this hypothesis (Bruckert, 1970; Ugolini et al., 1977). However, only supposition can account for the high proportion of amorphous, inorganic iron and especially aluminum, found at depth.

Farmer and coworkers also rely on circumstantial evidence to support their model. This is the presence of imogolite in the soil, its formation from solution in the laboratory and the solution-deposited "look" of proto-imogolite cement. They have not found proto-imogolite actually moving through the soil in lysimeter work.

These models are examined in Chapter 6 as to how they could possibly relate to the formation of root mats and root channels in podzolic soils of southwestern British Columbia.

#### CHAPTER 3

#### SOIL CLASSIFICATION IN CANADA

## Introduction

Taxa in the Canadian System of Soil Classification (CSSC, 1978) are defined on the basis of observable and measurable soil properties chosen so that taxa at higher levels "reflect broad differences in soil environments that are related to differences in soil genesis" (CSSC, 1978). This is in contrast to the American system of classification based on specific properties which often, but not necessarily, reflect processes by which the soil was formed. The emphasis away from soil genesis in the United States:

- Enables soils rather than soil-forming processes to be classified.
- Puts the focus on the soil itself rather than on related sciences such as geology and climatology.
- 3. Allows soils of unknown genesis to be classified.
- 4. Ensures that all soil scientists, regardless of how they view the origins of a soil, classify it in the same manner (Brady, 1974).

This difference in emphasis between the two systems means that in Canada, class criteria are under constant modification as more information is gathered about the processes behind soil formation, whereas, in the U.S., modification of the system to

fit current concepts of soil genesis is not always necessary.

The need for constant fine tuning in the Canadian system is well illustrated by past revisions made in the classification of podzolic soils. It is interesting to note how these revisions echo the changing concepts of podzol genesis listed in Chapter 1.

# Early History of the Classification System

Soil surveys, designed to identify and map the different soils of Canada, began in 1914 using the classification scheme of the U. S. Bureau of Soils. This system had such a broad concept of the soil "series" that only nine different series were mapped throughout southwestern Ontario. From the 1920's to mid 1940's, soil survey was a strictly provincial undertaking with each province developing its own system of mapping and classification. In Manitoba, systematic soil survey did not begin until 1927 when J. H. Ellis undertook a reconnaissance soil survey of the area west of the Red River extending to the U. S. boundary. During this initial project he developed a system of soil classification based on discussions with C. C. Nikiforoff, of the Russian school of soil science, who was conducting a soil survey immediately across the Manitoba-U. S. border. This system proved so useful in designating soil mapping units that it is still in use today in some Canadian provinces and in Scotland. It wasn't until the first meeting of the National Soil Survey Committee (NSSC) in 1945 that surveyors from across the country got together to compare systems and discuss ways to bring about greater uniformity between the provinces in all aspects of soil survey

work. At this meeting a tentative Canadian field classification scheme was first proposed by P. C. Stobbe. This system was based on that developed by Ellis (McKeague and Stobbe, 1978).

The first Canadian taxonomic system was presented at the third meeting of the NSSC in 1955. A taxonomic rather than strictly field method of classification was deemed necessary at that time because:

- 1. The knowledge of Canadian soils had greatly increased between 1945 and 1955.
- 2. A need had arisen to order this information.
- 3. The U. S. taxonomic system was seen as too complicated and too tentative for Canadian needs.

The Canadian system consisted of six categoric levels corresponding to order, great group, subgroup, family, series and type. The orders were named Chernozemic, Halomorphic, Podzolic, Forested Brown, Regosolic, Gleisolic and Organic. After several revisions, the system was officially adopted in 1960 (McKeague and Stobbe, 1978).

## Some Modifications in the Classification of Podzols

By the 6th meeting of the NSSC in 1965, the names of the orders had been changed to Chernozemic, Solonetzic, Podzolic, Brunisolic, Regosolic, Gleysolic and Organic. Like the Russian system, the Podzolic order consisted of both soils on coarse textured parent material leached of sesquioxides and soils on heavier parent materials leached primarily of clay. The eluvial A horizon was diagnostic. As a result, the Acid Brown Wooded

Great Group of the Brunisolic order could have a podzolic Bf horizon but because the Ae horizon was less than one inch thick or absent, these soils were not included in the podzolic order (NSSC, 1965).

At the 7th meeting, in 1968, soils of high base saturation with B horizons enriched in illuviated layer silicate clays, were removed from the Podzolic order and placed in their own order, the Luvisolic. The Ae horizon was no longer considered diagnostic and, therefore, the Brunisolic Acid Brown Wooded soil could now become a great group of the Podzolic order. sesquioxide-enriched B horizon was characterized by the oxalate-extractable Fe+Al value, a procedure developed by Tamm (1920), and the percent organic matter. As acid ammonium oxalate extracted both organic and inorganic amorphous forms of iron and aluminum; its use in the 1960's may still have reflected the earlier belief, prevalent when the classification scheme was developed in the 1940's and 50's, that podzols form through the migration of humus protected sesquioxide sols. pyrophosphate, an extractant specific for organic complexed iron and to a lesser extent aluminum, was tested by McKeague et al. These authors found pyrophosphate was better able to separate podzolic from brunisolic, gleysolic and luvisolic B It also reflected the concept current at that time, horizons. that iron and aluminum were leached in complex form with organic acids. The extractant was, therefore, adopted to define podzolic B horizons in the Canadian System of Soil Classification, 1978. Moon (1981) questioned the wisdom of this decision while

examining the soils of a climosequence on Vancouver Island. He found that the soil with the greatest podzolic morphological expression did not meet the chemical criteria of 0.6% sodium pyrophosphate extractable Al+Fe. He believed this was due to a rapid decomposition of the organic ligands under the optimum environmental conditions and with the aid of a derived model and lysimeter data, showed that the translocation of iron and aluminum from higher in the profile was the dominant force responsible for the formation of the sesquioxide-rich B horizon.

Other podzolic criteria established at the 1968 meeting were those of the Ferro-humic great group. "The upper four inches (10cm) of the B horizon contains more than 10% organic matter and the oxalate-extractable Fe+Al exceeds that of the C horizon by 0.8% or more...a Bh horizon less than 4 inches (10 cm) thick may overlie the Bhf horizon or the Bhf may directly underlie the Ah or Ae" (NSSC, 1968, p. 51). However, in the proceedings of the eighth meeting (1970) this organization, now known as the Canadian Soil Survey Committee (CSSC), recommended the above criteria be changed so the Bhf horizon "usually ... is the uppermost B horizon, but in some soils the Bhf may be overlain by a Bfh or Bf horizon" (CSSC, 1970, p. 126). If the Bhf horizon was thick enough, the profile would be classified a Ferro-humic podzol, no matter at what depth the organic-rich horizon appeared in the profile.

This latter revision soon became a problem in the classification of podzolic soils as seen by a recommendation of the Expert Committee on Soil Survey (1981), that research be

carried out to characterize organic matter occurring at depth in some British Columbia podzols. Profiles with Bhf horizons that do not seem to fit the concept of podzol genesis, as outlined by McKeague et al. (1976), are influencing the classification of these soils. These podzols have their highest accumulation of organic material above a root restricting layer such as a duric horizon rather than directly beneath the Ae or forest floor. accumulations meet the criteria of a podzolic Bhf horizon when they have less than 17% organic carbon and are greater than 10 cm thick. If they are the only podzolic Bhf horizon in the profile, they will change the classification of the otherwise organic-poor soil from a humo-ferric to a ferro-humic podzol although the organic content may owe its origins more to root decomposition than to illuviation. One purpose of this thesis is to characterize this organic material, so that determinations can be made as to whether the classification system should be modified once again.

# Characterization and Classification of Soil Organic Matter

In the past, objective properties of the organic matter have rarely been included in the classification criteria of soils both because meaningful relationships had not yet been established and because the analyses were too time consuming to be employed on a regular basis. However, a number of studies have indicated that certain chemical and morphological procedures, performed on the soil organic material, may indeed be useful in separating some problematic soils into the major taxonomic groups (Kumada, 1965;

Kononova, 1966; Lowe, 1980; DeConinck, 1980; Righi, 1984).

The organic matter of the soil consists of three major components; undecomposed plant and animal debris, partially decomposed material and stable humus, a generally dark coloured, amorphous, colloidal substance relatively resistant to further decomposition. Humus, itself, is a mixture of large, complex polymers, simpler phenolic compounds and polysaccharides. The polymers are rich in aromatic rings with attached side chains and reactive functional groups - no two may be exactly alike. The polysaccharides may account for 10-30 % of the humus and contain more than ten major sugar types (Martin and Haider, 1971) including hexoses, pentoses, deoxyhexoses, amino sugars, sugar alcohols and uronic acids bound together into some of the highest molecular weight organic molecules found in the soil.

Exactly how the organic matter is studied depends upon the major organic component to which it belongs. Undecomposed plant remains can be examined and even botanically or zoologically classified with the naked eye. A compound microscope can help to identify partially decomposed organic material from distinct cellular remnants of the vascular system, pollen grains, faecal pellets etc. Characterization of the humus is more difficult as it first must be separated from undecomposed material and from the mineral soil. Even when this is accomplished, the amorphous and complex nature of humus makes it impossible to distinguish morphologically. Instead, humus is examined and classified as to how it reacts chemically.

Humus may be extracted from the soil with 0.1-0.5 N NaOH

and/or Na pyrophosphate and fractionated by acidification with  $\mathrm{H_2SO_A}$  into the precipitated "humic acid" and still soluble "fulvic acid". A third fraction, "humin", because of a high molecular weight, lack of hydrophilic functional groups or because of a stable association with the mineral fraction, does not dissolve in alkali. Included in the humin are also the undecomposed plant remains. Each fraction consists of compounds with a wide range of chemical properties but in general, fulvic acids have a lower molecular weight, a higher functional group content, and have a lower carbon and nitrogen but a higher oxygen content than humic acid. Decomposed humin appears similar to humic acid but for reasons mentioned above, does not dissolve in alkali (Schnitzer, 1978). The fulvic acid "fraction" also contains large polysaccharides. These can be separated from the remaining phenolic component by adsorption of the polyphenols on PVP (Lowe, 1975).

The proportion of the organic material soluble only in alkali to that which is soluble in both alkali and acid is described as the humic/fulvic ratio, normally expressed Ch/Cf, on the basis of carbon content. Lowe (1980) found that this ratio and the ratio of polyphenolic fulvic acids to total fulvic acids (Ca/Cf) was diagnostic for a number of different great group horizons. For example, a luvisolic Bt could be discriminated from a podzolic Bf horizon by how its organic matter separated into the different extracted fractions. Methods such as these may be valuble in assisting with the classification of many mineral horizons.

Organic horizons are defined in the Canadian System of Soil Classification (CSSC, 1978) as one with an organic carbon component of 17% or greater - a value approximately equal to 30% organic matter. Once the carbon requirement is met, a horizon is then classified into one of two major groups: LFH or O. An O horizon is developed mainly from mosses, rushes and woody materials and an LFH horizon, primarily from an accumulation of leaves, twig and woody materials. Usually, LFH horizons are not saturated. From this description of the component vegetation and the usually unsaturated state of the LFH, we can surmise that the LFH is the upland organic horizon of most mineral soils and that O horizons are found in a semi-terrestrial (wetland) environment. However, this is not stated specifically in the classification scheme and according to Klinka et al. (1981) it is sometimes difficult to determine into which organic group a horizon should be assigned, given the present definitions and criteria. specific example is seen in a rainforest environment where the litter layer beneath the trees is deep, usually water saturated and may contain a large component of moss. Is this an LFH or O horizon? Another example is a root mat horizon, usually saturated with water, of high organic carbon value, found at depth within the mineral soil. This horizon does not fit into either group well. Perhaps the classification scheme for organic soils should be made more specific, with chemical or physical tests able to separate the two groups.

Another problem concerns the 17% carbon cutoff point between mineral and organic soils. Does this have any relevance to soil

behavior? The American system classifies water saturated horizons with little clay into the organic order if they have only 20% organic matter, a value corresponding to approximately 12% organic C.

#### CHAPTER 4

## DESCRIPTION OF THE STUDY AREA

## General Description of the Soils

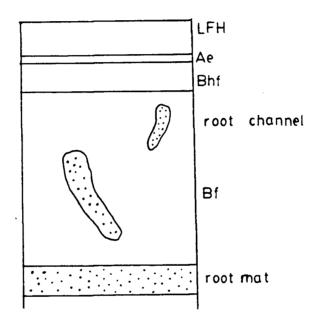
Some podzolic soils of south coastal British Columbia differ from the "classical" podzols of the literature in that they have concentrations of organic matter in vertical and oblique channels and in horizontal layers throughout the depth of the B horizon (see Figure 4-1). The concentration is especially prominent in seepage zones above and parallel to a root impermeable layer, such as a hardpan or bedrock. These are called "root mats" in soil survey reports, although live roots are often few in number or may not be present at all. Instead, the organic material appears amorphous, greasy to the touch, often without detectable mineral grains and with little rubbed fibre content.

Occasionally, remnants of wood structure are discernible in situ but when removed from the profile, are easily crushed between the fingers and found to be greasy and well decomposed.

The root mats are found at depths of up to and greater than 1 m and range in thickness from 1 cm to more than 40 cm. The colour of the organic matter is usually dark reddish brown (5 YR 2/2) but lighter and darker materials are also found. The primary structure is massive, the secondary structure is subangular blocky. In a few localized areas the structure appears granular but on closer inspection looks like short pieces

of decomposed fine roots. Short pieces of dead but undecomposed roots of large diameter are found near the bottom of a few of the pits.

Figure 4-1: Diagramatic Representation of a Root Mat and Root Channel in a Podzolic Soil



The organic material in the root channels is similar in morphology, texture and structure to the root mats but in situ wood structure is perhaps more common and when present tends to fill the entire channel. The mineral soil surrounding the organic material is of a sandy loam texture and well drained.

Soils of the above description occur side by side with soils with no unusual organic accumulations. It is obvious that the root mats are found in pockets, perhaps in dips of the bedrock or pan along which seepage water runs. If these indeed arise from

roots, the channels and horizontal layers may be remnants of root balls. Numerous very large cedar stumps and fewer large hemlock stumps are found throughout the forest of the Burke Mountain sampling site, although second growth hemlock is the dominant tree today.

### Locations Where These Soils Are Found

Soils with "root mat" organic accumulations are found in the high elevation podzols of the Coast Mountains that surround Vancouver. They are seen specifically on Mt. Seymour, Fromme Mountain, Burke Mountain, in Cypress Park, on the higher slopes of the U.B.C. Research Forest and have been reported from the Seymour watershed (Luttmerding, 1981). Root mats are located at lower elevations near Holberg, on the north-west tip of Vancouver They have also been reported along the west coast of the island, in soil survey reports (Goldstream series, RAB, 1977), and more recently by Sanborn (pers. comm. 1984). Somewhat similar soils were studied on Vancouver Island by Lewis (1976). Root mats have also sometimes been found in the rainforests near Revelstoke in the B.C. interior (H. A. Luttmerding, pers. comm., 1985). All these locations have in common a high annual rate of precipitation, approaching 5000 mm in some localities and soils that do not freeze in the winter. They are all within the Coastal Western Hemlock or Mountain Hemlock Biogeoclimatic Zones (Krajina, 1969). A root restricting layer along which seepage water runs may also be essential for the development of these soils. With respect to other factors - elevation, length of

growing season, and perhaps bedrock geology - the environments appear quite diverse.

Soils studied in this thesis were from the Whonnock soil series which is classified as a Duric Ferro Humic Podzol. Sampling locations were found between 700 and 730 m on Burke Mountain in Port Coquitlam  $(49^{\circ}\ 19^{\circ}\ N\ 122^{\circ}\ 44^{\circ}\ W)$  and at 920 m near the downhill ski parking lot in Cypress Bowl, West Vancouver,  $(49^{\circ}\ 24^{\circ}\ N\ 123^{\circ}\ 12^{\circ}\ W)$ .

## General Environment of the Coast Mountains

### A. Vegetation

The vegetation found on the windward mountain slopes surrounding Vancouver is determined both by the mild, wet climate and by the elevation. Below 914 m, the Coastal Western Hemlock Zone (CWH) is dominant and the vegetation of the Burke Mtn. site is representative of the wet subzone (CWHb) (Krajina, 1969). Western hemlock (Tsuga heterophylla, (Raf.) Sarg.) makes up 90% of the modern overstory but the abundant large cedar stumps indicate a much more dominant role played by western red cedar (Thuja plicata, Donn.) in the past. Pacific silver fir (Abies amabilis, (Dougl.) Forbes) is also fairly common.

At the higher elevation in Cypress Park, vegetation is typical of the forest subzone of the Mountain Hemlock Biogeoclimatic Zone (MHa). (Krajina, 1969) Here, mountain hemlock (Tsuga mertensiana, (Bong.) Carr.), yellow cedar (Chamaecyparis nootkatensis, (D. Don) Spach) and pacific silver fir form the overstory.

Hemlocks are noted for their surficial rooting habit, the preference of ammonium or amino acids over nitrates as a nitrogen source and the need for steady yet low concentrations of the other essential cations (Brooke et al., 1970). According to Krajina (1969), neither species of hemlock grows well in nutrient-rich soil and in seepage and hydric moisture regimes they are limited to drier humps of organic debris or boulders covered with humus. In contrast, Krajina feels that both yellow and western red cedar have a high nutrient requirement and will attain optimum growth in soils affected by continuous nutrient-rich seepage water. Pacific silver fir requires a steady supply of water even during the winter months and like cedar favors nutrient-rich soils and nitrates as a nitrogen source (Krajina, 1969). It is an edaphic species in the CWHZ, limited to the highest rainfall areas or to seepage environments (Brooke et al., 1970)

Krajina (1969) assumes by their distribution, that none of the dominant conifers prevalent in the coastal subalpine can tolerate having their roots frozen and so are limited to soils that do not freeze. Deep snow, which is common on the coast, can insulate the ground and provide these milder temperatures, as well as a steady seepage of melt water through the soil until mid-summer. The deep snow in the Revelstoke wet belt near Mica Dam also ensures that the soil does not freeze. As a result, mountain hemlock is abundant in this location, but this time found with Engelmann spruce (Picea engelmannii Parry) and subalpine fir (Abies lasiocarpa (Hook.) Nutt.) (Krajina, 1975).

The low temperatures and high moisture content promote slow decomposition of organic matter in the subalpine soils. Brooke et al. (1970) found that leaves remained intact and only slightly decomposed nearly a year after they had fallen from the tree.

#### B. Air and Soil Climate

The Pacific Ocean has a moderating effect on the climate of the British Columbian coast. In the winter, the Kuroshio current keeps water temperatures warmer than air temperatures. The Aleutian Low dominates and the Vancouver area is hit by a succession of storms with heavy cloud and precipitation. In summer, the North Pacific High brings clear skies and warm temperatures but even these are moderated by cooler ocean temperatures due to cold water upwelling off the west coast (Brooke et al., 1970).

Frequently throughout the year, moisture laden clouds from the Pacific Ocean move eastward towards the Coast Mountains. As they rise over these mountains their moisture cools and condenses, dropping as rain or snow. Precipitation increases with elevation at least up to the level of the cloud base (Walker, 1961). Table 4-1 illustrates the increase in precipitation with elevation from the North Shore waterfront to the top of Grouse Mountain, as reported by Environment Canada (1980).

Table 4-1: Change in precipitation with change in elevation in North Vancouver

location	elevation	rainfall (mm)	snowfall (cm)	Total pptn (mm)
N. Vanc wharves	6 m	1720.0	51.9	1763.5
N. Vanc-Holyrood	183m	1857.8	72.3	1943.1
N. Van-Grouse Mt	1128m	1773.7	816.5	2564.6

(extracted from Environment Canada, 1980)

In addition, daily average temperatures decrease with elevation, resulting in heavy snow falls at higher levels from November to April. The deep snow insulates the ground and the soil seldom freezes, even in mid-winter. This, combined with air temperatures which can rise above 0°C at any time of year, produces a dense and saturated snow pack. The water equivalent ratio of fresh snow is 10.0; 10 cm of snow melts to 1 cm of water. Brooke et al. (1970) quote statistics collected by the Seymour Mountain Snow Course which show a snow to water equivalent ratio of 2.36 at the first of February and 1.98 on May 15th. This snow pack does not completely melt until mid-June or July.

All this ensures that soils have a high moisture content throughout the year in the Mountain Hemlock Zone. Brooke et al (1970) found that soils of the Mt. Seymour watershed were at or above field capacity during all months in the lower subalpine. In this case, field capacity was measured indirectly with a Colman fiberglas moisture unit and was considered to be the moisture content of the soil a few days following two separate

heavy rainfall events and under conditions in which the surface soil would not be excessively dried by evaporation. In addition, these authors found that the maximum in soil moisture occurred some time after all the snow pack had melted. This suggests that lateral movement of water from higher elevations keeps the soils charged with water until well into July.

Burke Mountain, at a lower elevation, obtains a smaller percent of its total precipitaion as snow. However, the insulation is not needed as under the milder air temperatures the soils do not freeze. The high rainfall levels plus seepage from higher elevations along the duric horizon keep the soils permanently moist. All this water in well drained profiles imparts a high leaching potential to the soils.

Table 4-2 shows monthly mean temperatures, average highs and lows and the daily precipitation recorded from the climate station on Hollyburn Ridge (Environment Canada, 1980). This is located close to the Cypress Bowl sampling site. As no climate station is near the profiles described on Burke Mountain, the data presented are taken from the station on Coquitlam Lake at a lower elevation.

C. Surficial Geology and Bedrock of the Sampling Sites

The Whonnock soil series consists of greater than one metre of moderately coarse-textured glacial till over bedrock (Luttmerding, 1981). The subsoil has been cemented into a duric horizon with a hydraulic conductivity measured by McKeague and Sprout (1975) of 0.1 to a few millimetres per hour.

Table 4-2: Climatic Data Obtained from Stations Close to the Burke Mountain and Cypress Park Sampling Sites (Environment Canada, 1980)

HOLLYBURN RIDGE 49° 22'N 123° 12'W 951 m														
Daily Maximum Temperature	0.5	3.1	3.4	6.6	10.8	14.3	18.5	17.7	15.7	9.7	3.9	1.2	8.8	В
Daily Minimum Temperature	-5.1	-2.9	-3.0	-0.8	1.8	4.9	7.8	8.0	5.7	2.2	-1.7	-37	1.1	8
Dally Temperature	-2.3	0.1	0.2	2.9	6.3	9.6	13.2	12.9	10.7	6.0	1.1	-1.3	5.0	8
Standard Deviation, Daily Temperature	2.3	2.0	1.4	1.2	1.2	2.1	1.5	2.0	1.9	1.3	1.4	2.1	0.6	3
Extreme Maximum Temperature	17.8	16.7	15.6	20.0	26.7	31.7	33.3	31.7	30.0	26.7	22.2	12.8	33.3	
Years of Record	20	20	20	19	19	19	20	19	20	20	19	19		
Extreme Minimum Temperature	-21.7	-15.0	-15.0	-8.3	-4.4	-2.2	0.6	0.6	-3.9	-7.8	-13.9	-26.7	-26.7	
Years of Record	19	20	19	19	19	20	20	20	20	20	19	19		
Raintall	177.5	147.8	112.4	1.17.4	130.3	124.1	106.9	128.3	193.3	329.4	306.0	260.9	2134.3	2
Snowfall	169.2	145.8	146.6	67.0	11.1	0.2	0.0	0.0	0.2	21.0	85.2	173.9	820.2	2
Total Precipitation	346.7	293.5	259.0	184.3	141.4	124.3	106.9	128.3	193.5	350.4	391.2	434.8	2954.3	2
Standard Deviation, Total Precipitation	162.6	120.3	100.6	81.3	87.8	62.4	90.6	92.6	104.5	193.6	147.6	126.4	431.6	2
Greatest Rainfall in 24 hours	162.1	100.3	77.7	111.0	133.1	71.4	167.4	115.8	137 2	174.5	153.4	125.0	174.5	
Years of Record	25	26	26	25	26	26	25	26	26	26	24	25		
Greatest Snowfall in 24 hours	66.0	53.3	50.8	42.4	19.8	3.8	0.0	0.0	1.5	40.1	60.5	61.0	66.0	
Years of Record	25	26	26	25	26	26	26	26	26	26	25	25		
Greatest Precipitation in 24 hours	162.1	100.3	86.4	111.0	133.1	71.4	167.4	115.8	137.2	174.5	153.4	125.0	174.5	
Years of Record	25	26	26	25	26	26	25	26	26	26	24	25		
Days with Rain	8	8	7	11	12	13	8	10	11	16	14	11	129	2
Days with Snow	15	12	13	9	2	•	0	0	•	2	8	14	75	2
Days with Precipitation	19	18	17	16	13	13	8	10	11	17	19	21	182	2

COQUITLAM LAKE 49° 22'N 122° 48'W 161 m														
Daily Maximum Temperature	2.7	5.1	7.1	11.5	15.9	16.5	22.0	21.3	16.1	12.7	7.1	4.3	12.2	1
Daily Minimum Temperature	-1.5	-0.1	0.3	26	5.9	8.9	11.1	11.2	9.0	5.6	2.0	0.1	4.6	1
Delly Temperature	0.6	2.5	3.7	7.0	10.9	13.7	16.6	16.3	13.6	9.2	4.5	2.2	8.4	1
Standard Deviation, Daily Temperature	1.9	1.5	1.2	1.1	1.3	1.7	1.5	1.5	1.2	1.1	1.3	1.4	0.6	1
Extreme Maximum Temperature	13.3	14.4	21.1	26.1	32.8	33.3	36.7	34.4	31.7	25 0	18.9	13.3	36.7	
Years of Record	45	44	45	45	45 .	43	45	43	45	46	46	45		
Extreme Minimum Temperature	-21.1	-16.7	-12.2	-5.6	-2.2	1.7	3.3	4.4	-0.6	-5.0	-178	-22.8	-22.8	
Years of Record	45	45	45	45	45	45	44	43	45	46	46	45		
Raintall	445.5	374.6	<b>3</b> 34.5	236.5	140.5	130.9	86 4	108 8	204 4	403.0	474.1	529.2	3468 4	1
Snowfall	62.6	23.2	15.9	1.0	0.0	0.0	O.O	0.0	0.0	0.0	6.3	39.2	148.2	• 1
Total Precipitation	508.0	397.8	350.4	237.4	140.5	130.9	86.4	108.2	204.4	403.0	480.6	568.4	3616.0	1
Standard Deviation, Total Precipitation	268.7	168.5	129.6	110.8	70.9	78.5	65.8	79.5	108.3	225.7	187.7	189.2	640.7	1
Greatest Rainfall in 24 hours	190.5	152.4	127.8	145.5	113.8	98.0	128.8	98.6	136.4	176.5	203.2	194.3	203 2	
Years of Record	56	57	55	57	57	56	56	55	57	55	56	57		
Greatest Snowfall in 24 hours	66.0	43.2	26.7	16.5	0.0	0.0	0.0	00	0.0	1.3	27.9	48.3	66.0	
Years of Record	55	57	56	57	57	57	57	57	57	57	57	57		
Greatest Precipitation in 24 hours	190.5	152.4	127.8	145.5	113.8	98.0	128.6	98.6	136.4	176.5	203.2	194.3	203.2	
Years of Record	56	57	55	57	57	56	56	55	57	. 55	56	57		
Days with Rain	18	17	19	17	13	13	8	11	13	19	20	20	188	2
Days with Snow	6	3	2	•	0	0	0	0	0	0	1	4	16	1
Days with Precipitation	21	18	19	17	13	13	8	11	13	19	21	22	195	2

Bedrock beneath the study site on Burke Mountain consists of quartz diorite, with hornblende more abundant than biotite. The bedrock of Cypress Park is granite, and hornblende is the only mafic material present in appreciable amounts (Roddick, 1965). Other bedrocks common in the Coast Mountains near Vancouver are granodiorite, diorite, gabbro and migmatite. As till may consist of stones carried from considerable distance, a mixture of the above lithologies may be present in the surficial materials at both locations. However, Brooke et al. (1970) found that most rocks sampled from the till on Mt. Seymour resembled the underlying bedrock, an indication that material may not have been carried by the glaciers as far as expected. Brooke and coworkers also found that rocks collected from the soil showed considerable chemical weathering and oxidation and that ash, identified as Mazama, was present in several of the profiles.

#### CHAPTER 5

MORPHOLOGICAL AND CHEMICAL CHARACTERIZATION OF THE SOILS

### Field Sampling

Nine soils were sampled from a road cut on Burke Mountain and eighteen pits were located and sampled from both Burke Mountain and Cypress Park. Because root mats and root channels were found only in very localized areas not easily recognized by surface morphology, the placement of pits was difficult. Therefore, pits were dug wherever convenient between the numerous fallen logs and dead trees, and those pits which contained no root mats or channels in the B horizons were rejected. In addition four pits, located at two lower elevations along the Burke Mountain road, were sampled in order to compare the properties of the root mat podzols with podzols which contained more "classical" features.

Pits and roadcuts were sampled to the depth of the duric horizon unless circumstances in the pit did not allow it. The road cuts were cleared back one half to one metre to expose a fresh surface. Where possible, all horizons were sampled. The surficial humus along the road cut on Burke Mountain was only sampled when it was overhung with forest vegetation. Organic material in root channels and root mats was sampled separately from the mineral material, except in some B horizons where root channels were too fine to remove.

Soil texture, coarse fragment content and Munsell colour were determined in the field. Pits were described for depth and thickness of horizons, structure, consistence, presence of mottles, location, size and abundance of roots and presence of cementation.

Most of the pits containing root mats and root channels were located on flat to gently sloping microtopography, often at the bottom of a steeper hill. However, a few soil pits located on steeper slopes also contained large organic accumulations above the duripan and therefore, no conclusion could be reached about how topography affects the probability of root mat formation.

Several of the pits contained more than one horizontal organic-rich layer. In this case, both were considered root mats. From the 31 sites sampled, 30 root mat and 20 root channel samples were collected.

# Laboratory Methods on Field Collected Samples

The soils were air-dried at 21°C, aggregates crushed with a wooden rolling pin and the soils sieved through a 2 mm screen to remove the coarse fragments. A subsample was ground to 60 mesh and a subsample of this ground to 100 mesh. A portion of each air-dried sample was oven-dried overnight at 105°C, cooled in a desiccator and weighed to determine moisture loss as a percentage of air-dried weight. From this, chemical data were adjusted as a percent of the oven-dried weight. Samples were analyzed for total carbon by a Leco Induction Furnace and Carbon Analyser, model numbers 521 and 572, respectively, according to the method

described in the Leco manual. Carbon analysis was done on 60-mesh samples with sample weights varying from 0.07 g for highly organic samples to 0.50 g for horizons containing little organic material.

Total nitrogen was measured by semi-micro Kjeldahl, following Bremner (1965). Sample weight varied from 0.2 to 2.0 g depending on carbon content. Both nitrogen and carbon values were measured in duplicate and the mean of each recorded.

Total sulphur was measured on a Fisher Sulphur Analyzer and High Temperature Furnace models 475 and 472, respectively, in accordance with the Fisher manual.

Soil reaction was determined in both water and 0.01 M CaCl<sub>2</sub>. For water, a 1:1 soil:water suspension was used for mineral horizons, a 1:2 ratio for root channels and root mats and a 1:4 ratio for surface organic horizons. Reaction in 0.01 M CaCl<sub>2</sub> was determined using ratios of 1:2, soil:0.01 M CaCl<sub>2</sub> for mineral horizons, root mats and root channels, and a ratio of 1:4 for surface organic horizons. The pH was measured using a Radiometer PHM 62 standard pH meter.

Iron, aluminum and silicon were extracted from soil ground to 100 mesh using:

- 1. 0.1 M sodium pyrophosphate (pH 10.0) (Bascomb, 1968).
- Acid ammonium oxalate (McKeague and Day, 1966).
- 3. Citrate-bicarbonate solution (pH 7.3) (Weaver et al, 1968; Mehra and Jackson, 1960).

The ppm of each element within each extractant was measured using atomic absorption spectrophotometry on a Perkin-Elmer 306

spectrophotometer. These elements were them calculated as a percent of the total soil. Iron was measured in an air-acetylene flame while aluminum and silicon were determined using the higher temperature nitrous oxide-acetylene flame: It should be noted that the values read on the atomic absorption unit for iron, aluminum and silicon in citrate-bicarbonate solution, were very unstable, affecting the percent accuracy of these numbers. Also, the silicon standards were prepared separately from standards containing both iron and aluminum, as silicon interferes with iron. Presence of the two elements in the same standard solution will badly overestimate the iron values in the soil.

Humic and fulvic acids were extracted from soil samples in 0.1 M sodium pyrophosphate:0.1 M NaOH following the methods of Lowe (1980) except that the Sorvall Model RC2B centrifuge was set at a speed of 6000 rpm instead of 5000 rpm (Schuppli and McKeaque, 1984). A soil to total extractant ratio of 0.75 - 1.0 g carbon to 300 mL extractant was used. The fulvic acids were separated into polyphenolic and polysaccharide-rich fractions by adsorption of the polyphenolic acids on to polyvinyl pyrrolidone The total carbon of the humic acid, total fulvic (Lowe, 1975). acid and the polysaccharide fractions was determined by the Walkley-Black wet oxidation procedure (Allison, 1965). percent C in the polyphenolic fraction was found by subtraction of the polysaccharide carbon from the total fulvic carbon. Ratios of humic carbon to fulvic carbon (Ch/Cf), and ratios of polyphenolic carbon to total fulvic carbon (Ca/Cf) were calculated. The percentage of the total carbon in the soil that

was extracted by the Na pyrophosphate: NaOH solution was estimated from the ratio:

The micromorphology of the root mats and channels was studied using the Wilde-Lietz Dialux 2 phase contrast microscope. Slides were prepared by teasing small fragments of the organic material into distilled water forming a suspension dilute enough to allow the passage of light.

### Column Study

The method used to synthesize proto-imogolite was adapted from Wada et al. (1979) but with a molar ratio of 0.516 Si:Al instead of 0.497. Farmer et al. (1977) reported that a slight excess of silica over the theoretical value was necessary to inhibit boehmite formation. Reagents required were as follows:

- 1. 4% tetraethyl orthosilicate stock solution: 40g of  $(CH_3CH_2O)_4Si$  was added to 1 litre of ethanol
- 2. AlCl<sub>3</sub>:6H<sub>2</sub>O
- 3. 0.1 M NaOH

Solution A was prepared by dissolving 0.900 g of AlCl<sub>3</sub>:6H<sub>2</sub>O into 400 mLs of distilled water. Solution B was prepared by measuring 10 mL of the tetraethyl orthosilicate stock solution into 400 mL of distilled water. Solution A was then immediately mixed with solution B. With a burette 0.1 M NaOH was slowly dripped into the mixture over several hours, until the pH read between 4.5 and 5.0 (preferably 4.8, as the pH will drop slightly

over the next 12 hours). This will require 80-90 mLs NaOH per litre of proto-imogolite. The resulting solution was made up to 1 litre. It was opalescent if the 0.1 M NaOH had been added fairly quickly but cleared on standing overnight, as reported by Farmer (1981).

The eluent for the "no-imogolite" control columns was prepared by measuring 10 mLs of ethanol and 90 mLs of 0.1 M NaOH into 800 mLs of water. The pH was then adjusted with acetic acid, to correspond to the pH of the proto-imogolite solution and made up to 1 litre with distilled water.

The columns were set up as follows:

- 1. Rotted wood was collected from a Douglas-fir (Pseudostuga menziesii (Mirbel) Franco) stump in Lynn Valley, North Vancouver. This material had a colour of 2.5YR 3/4 and although wood structure was seen in place, this structure was crushed with slight pressure between thumb and forefinger into a "greasy" mass with no fibrous content.
- 2. In the laboratory, this moist organic material was ground to pass a 2 mm sieve. The moisture content was then determined by drying the rotted wood overnight in an oven set at 105°C. In all of three replicates, the moisture content was 70%.
- 3. Ottawa sand was washed as follows. After soaking in 2 N HCl for several hours, the sand was filtered using suction filtration and washed twice with 0.1 N HCl. It was then rinsed 6 times with distilled water.

- 4. Carl Schleicher and Schuell Co. No. 289 Ash-free Analytical Filter Pulp was washed with 0.1 N HCl, filtered with suction and then rinsed approximately four times with distilled water. The filter paper was oven-dried, overnight, at 105°C
- netting were cut to fit over the holes in the bottom of the column. A piece of 100% cotton, loosely woven material was then cut to the same size and placed over the matting. One cm of glass beads was layed down over these materials. Sixty grams of air-dry Ottawa sand formed the next tier. Over this was placed 35 g moist organic matter from the rotted stump, mixed in water with 2.5 g oven-dried filter pulp. The upper most layer consisted of 100 g air-dry Ottawa sand. See Figure 5-1. As material was laid down, the whole column was saturated with water to remove air bubbles.

The "no-organic matter" control columns were set up as above, except 2.5 g of filter paper mixed with Ottawa sand replaced the organic layer. See Figure 5-1.

Column study No. 1 was conducted as follows.

Proto-imogolite was slowly dripped through nine columns

containing organic matter, and through three control columns with

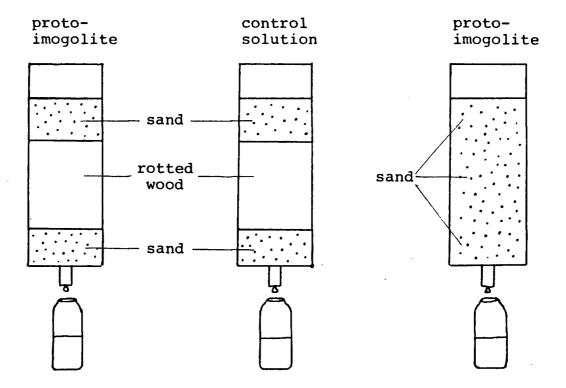
no organic matter tier, at the rate listed in Table 6-1. The

"no-imogolite" eluent, at the same rate as the proto-imogolite,

was dripped through three additional control columns, each

containing an organic tier.

Figure 5-1: Set Up of Column Study



After one month, three of the proto-imogolite-organic columns were removed from the study, an additional three columns and the control columns were removed after two months. The final three proto-imogolite-organic columns were retained to be used in the second column study.

The column materials were air-dried and the organic tier ground to pass through a 100 mesh sieve. The filter paper, used primarily to improve the structure of the column, was too fibrous to pass through the sieve, so was removed from the organic and mineral soil and weighed separately for analysis.

The three tiers of all columns were extracted with sodium pyrophosphate and acid ammonium oxalate, and the percent aluminum and silicon measured by atomic absorption.

A second column study was set up to measure exactly how much aluminum and silicon was absorbed from each addition of proto-imogolite and how much carbon was released after each treatment in the "no-imogolite" control columns. Six columns containing an organic tier and three columns containing only sand and filter paper, were set up as in Column study No. 1. A total of four litres of proto-imogolite was dripped through three of the organic-filled columns and the three mineral columns, at the rate shown in Table 6-2. The "no-imogolite" eluent was dripped through an additional three organic columns at the same rate.

As each 250 mL of leachate passed through the columns it was analyzed by atomic absorption for ppm Al and Si, and its pH was recorded.

The ppm carbon in the leachate of the "no-imogolite" control

column was measured by the Walkley-Black method (Allison, 1965) with the carbon found in the eluent subtracted from the leachate value. However, the carbon in the imogolite column leachate could not be determined by this method because of its high chloride content (Allison, 1965). It was, therefore, estimated from the absorbance of light by the leachate at 600nm wavelength in a Bausch and Lomb Spectronic 20. This value was then compared with absorbance values of a "no-imogolite" control leachate when the acetic acid in the eluent had been replaced with 0.1 M HCl and the exact carbon value had been measured on the Astro Total Carbon Analyzer, model 1850.

In addition, the three remaining proto-imogolite-organic columns from column study No. 1 were treated as follows:

- A further four litres of proto-imogolite were dripped through one of the columns at the rate shown in Table 6-2. This column, therefore, was treated with proto-imogolite for a total of 3 months.
- 2. Fulvic acids, extracted with distilled water from rotting wood were dripped through another of the columns previously treated for two months with proto-imogolite. The fulvic acids were also leached through a column containing organic matter with no previous proto-imogolite treatment. The carbon of the extracted fulvic acids and of the leachate, were measured by Walkley-Black analysis.
- 3. The eluent solution used in the "no-imogolite" controls was dripped through the third column, previously leached

with two months proto-imogolite. The leachate was analyzed for Al and Si.

### Results and Discussion

Based on percent carbon, twenty-two of the thirty root mats were classified as organic horizons (Oh) and the remaining eight classified as mineral (Bhf). Seventeen of the twenty root channels also contained greater than 17% carbon and of the remaining three, all had between 15 and 17% C. The highest value for a root mat was 31.3% C and for a root channel was 28.7% C. This is compared to values of 30-51% C for humus of the LFH, indicating that although mineral grains were often not detectable by hand texturing, much of the organic accumulations in the B horizon did indeed contain inorganic material. See Table 5-1.

Horizons immediately surrounding the root mats usually had very low percent carbon values. For example, often this organic accumulation rested on the duric horizon, which contained less than 1% C and the horizon immediately above had so little carbon it could be classified a Bf horizon. Mineral material through which the root channels ran also tended to have low carbon values. This may not always be reflected in the results as it was sometimes difficult to separate out the fine root channels from the mineral soil.

Total nitrogen was relatively low as judged by a carbon to nitrogen ratio averaging 28 for rootmats. However, as the C/N of the surficial humus was within a similar range, see Table 5-1, a ratio this wide seems appropriate for this forested situation.

Nitrogen to sulphur ratios ranged from 5 to 7 and averaged 5.9 and 6.2 for the root mats and root channels, respectively.

See Table 5-1 for actual sulphur values. These are slightly lower than ratios reported for the humus of the LFH of the U.B.C. Research Forest by Carter(1983). He reported mean ratios ranging from 7.1 to 8.3 but with Douglas-fir as the dominant overstory tree.

Note the similarity between the root mat and root channel samples in the results listed in Table 5-1, and the differences between these and the surficial humus.

Table 5-1 - Average and Range of Percent Carbon, Nitrogen and Sulphur Values found in the Root Mats, Root Channels and Surficial Humus Horizons Studied

	Root mats	Root channels	Surficial humus
% carbon average	20.46	20.28	42.73
% carbon range	10-31	15-29	30-51
<pre># samples analyzed</pre>	30	20	21
% nitrogen average	0.740	0.777	1.536
% nitrogen range	0.438-	0.447-	0.917-
	1.562	1.611	1.974
C/N average	28	27	26
C/N range	16-39	18-34	21-37
# samples analyzed	28	20	12
% sulphur average	0.127	0.130	
% sulphur range	0.0804-	0.0861-	
	0.190	0.223	
# samples analyzed	17	10	

Soil reaction in all horizons was acid and extreme values occurred near the top of the profile. Values of 3.0 - 4.0, in distilled water, were common in the litter and eluvial horizons on Burke Mountain and even the pH of the lower B horizon was usually well below 5.0. In Cypress Park, the A horizon was also very acid but the upper B horizon had a pH  $(H_2O)$  greater than 4.6 and the lower B horizon and root mat had a pH value between 5.0 and 5.5. See Appendix A. Carter (1983) found extremely acid reactions in surficial humus of the U.B.C. Research Forest, an area which is similarly situated to Burke Mountain, but slightly further east along the Fraser Valley. Thomas (1967) noted that pH values less than 4.0 indicated the presence of free inorganic acids, as the mineral soil is buffered by  $Al(OH)^{2+}$  to pH 5 (Bohn et al., 1979) and organic matter is buffered to pH 4-5 by the dissociation constant of carboxyl groups (Bruckert and Rouiller, Free inorganic acids usually arise from the oxidation of sulphides and nitrites and this may imply that the soils of the Coast Mountains are influenced by acid rain. Data collected by Environment Canada (Nikleva, 1982) seem to refute this. ion concentration and conductivity were measured in rainfall collected at stations around the lower mainland after 12 major storms between January and March, 1982. Results listed in Table 5-2 show that rainfall pH is lowest in downtown Vancouver and increases with elevation in the Coast Mountains. In addition, the conductivity of rainfall is highest in the city and the concentration of ammonium, sulphate and nitrate ions is 2.5 - 5.0 times higher here than in the mountains.

As this is only a preliminary study with limited data, these results do not exclude the possibility of nitrogen and sulphur emissions being responsible for some of the acidic properties of the soil. For instance, the amount of rainfall which fell in each area was not included in the report. The lower ion concentration and conductivity found in rainfall of the mountains may simply be a product of dilution. As it rains harder and more often on Grouse and Seymour Mountains and in Port Moody, more total acids may be deposited in the soils.

Table 5-2 - pH, Conductivity and Ionic Concentration of Rainfall in the Lower Mainland

	downtown Vancouver	Pt. Moody	Grouse	Mt. Seymour
рН	4.54	4.74	5.01	4.91
conductivity	18.2	11.1	7.6	9.8
(AS/CM)				
ion concentration	on			
NH <sub>4</sub> +	0.382		0.0	0 73
so <sub>4</sub> -2	1.32		0.5	5
· NO3	1.356		0.	475

selected data from Nikleva, 1982

Soil reaction was measured in both distilled water and in 0.01 M CaCl<sub>2</sub> after John Omueti (1984, unpublished data) reported anomalous results from two profiles also included in this study. The pH values obtained on soil suspensions in distilled water are

usually a consistent number of pH units higher than those of the same samples measured in a salt solution. Therefore, it is often considered a waste of time to perform both operations (Thomas, 1967). However, Omueti found that although surficial horizons of profiles 28 and 29 were the expected half a pH unit higher in distilled water than in salt solution, the values converged lower in the profile until soil reaction immediately above the duric horizon was identical in the two supernatants.

In this thesis only some of the soils followed the above pattern. Soil reaction in profiles 28 and 29 remained consistently higher in water than in salt solution throughout the entire depth of the soil, however, a number of different profiles did exhibit trends similar to those found by Omueti, see pH data of profiles 14 and 20 in Appendix A. According to Thomas and Hargrove (1984) these anomalous results can be explained by the sesquioxides coating the mineral grains of the soils. When pH is measured with a salt solution, the cation is able to replace the Al<sup>+3</sup> on the exchange complex and increase the hydronium ion concentration in the supernatant by the subsequent hydrolysis. However, at the same time the anion of the salt solution will exchange with the hydroxyl groups of the sesquioxides and the total effect of salt addition is minimized.

The pH governs many of the chemical reactions and biological activities in the soil and so ultimately controls the forms and solubility of the ionic species present. Chemically active aluminum can exist in a variety of forms within a podzol, the proportions of which are controlled by the pH and mineralogical

composition of the system. At a pH below 5.0 aluminum is exchangeable on negative soil colloids as hexa-aqua aluminum  $(Al(H_20)_6^{+3})$ . At a pH below 4.7 this is the predominant form of aluminum in the soil (Barnhisel and Bertsch, 1982; Bohn et al., 1979). As the pH increases, the  $Al^{+3}$  react progressively with the hydroxyl ions to form monomeric and polymeric hydroxyaluminum complexes such as  $Al(OH)^{+2}$  and  $Al(OH)_2^{+}$ . These forms are predominantly non-exchangeable, and they coat the clay particles in a monolayer, lowering the cation exchange capacity. They may even impart a net positive charge to the soil (Coleman and Thomas, 1967).

Aluminum may also be present in the soil as an organic complex, as complex hydroxy polymeric compounds occupying the interstitial space of 2:1 layer silicates and as discrete amorphous or crystalline phases of oxides and hydroxides (Barnhisel and Bertsch, 1982). In podzols, free aluminum oxides and hydroxides are present only in small amounts, possibly due to their instability in the presence of silicic acid (Russell, 1973; Guillet and Souchier, 1982).

Chemically active iron can also exist as amorphous oxides and hydroxides forming discrete particles but not monolayers on the surface of clays. Iron readily forms complexes with organic acids. In addition, iron can be reduced to a divalent cation at low pH and/or under waterlogged conditions. Ferrous iron can be held by the cation exchange complex but because it is much more soluble than Fe<sup>+3</sup>, under reducing conditions, iron is easily leached from the soil. Ferric iron is not found in the Fe<sup>+3</sup> form

at a pH greater than 3.0 and so does not sit on the exchange sites of most podzolic soils (Guillet and Souchier, 1982).

Chemically active silica can be found in podzols as the soluble monosilicic acid or precipitated in an amorphous form as silica gel or in bioopals (phytoliths). Precipitated silica gel rarely remains in the free state. It is either adsorbed on the surface of very finely divided quartz or by electropositive gels such as Al(OH)<sub>3</sub> or Fe(OH)<sub>3</sub>. Silica gels adsorbed by alumina may lead to the neoformation of allophanes in spodic horizons (Guillet annd Souchier, 1982).

The three extractants used to extract iron, aluminum and silicon each removed a different fraction of these elements from the soil. Sodium pyrophosphate (abbreviated "Pyro" in the tables) is considered selective for organically-complexed iron, acid ammonium oxalate (Ox) extracts this fraction as well as amorphous forms of inorganic iron, and citrate bicarbonate dithionite (CBD) extracts all of the above plus the crystalline iron oxides (McKeague et al., 1971). In reality the demarcation between the three extractants is not this clear cut. For instance, oxalate removes more iron from magnetite and olivine than does CBD (McKeaque, 1978). Also, the organic-complexed iron of this study, as represented by pyrophosphate extraction, may be slightly higher than actually occurs in the soil. because, during the pyrophosphate operation, a centrifugation speed was used that was too low to spin down microcrystalline iron oxides peptized by the extractant (Jeanroy and Guillet, 1981). The case for aluminum is somewhat different. Organic

complexed aluminum is removed by sodium pyrophosphate but this extractant also removes 5% of the aluminum from allophane (Parfitt, 1983). Oxalate is the best extractant for inorganic amorphous forms of aluminum, removing all the aluminum from the oxides, hydroxides and from allophane. It also removes the organic complexed aluminum (Farmer et al., 1983; Parfitt, 1983). CBD extracts organic-complexed aluminum, inorganic amorphous and some crystalline aluminum oxides and hydroxides but is only a partial extractant of the aluminum from allophane (Parfitt, 1983; Farmer et al., 1983). In a few horizons CBD values are slightly lower than pyrophosphate. This is attributed to the instability of the CBD measurement on atomic absorption which made the operation much less reproducible.

The silicon extracted by acid ammonium oxalate is believed by Parfitt (1983) to be solely from the silicon of allophane-like material.

From this, the amount of specific forms of iron and aluminum can be estimated, as in Table 5-3.

In the mineral soils of Burke Mountain and Cypress Park, iron values in all extracts were highest near the top of the B horizon. Here they commonly ranged between 1 and 2%, but dropped fairly quickly to low values in the Bf above the root mat. Iron usually, but not always, increased in this underlying organic-rich layer. No increase in iron was noted in root mats of Cypress Park (see Appendix A, profiles 11-15). Extractable iron in root channels usually reflected the position of the channel in the soil. More iron was extracted from channels near

Table 5-3 - Estimations of the Forms of Iron and Aluminum in the Soil Using Various Extractants

Fraction	Extractant
1. Organic-complexed Fe	pyrophosphate Fe <sup>a</sup>
2. Inorganic amorphous Fe	Ox. Fe - Pyro. Fe <sup>a</sup> , <sup>c</sup>
3. Crystalline Fe oxides	CBD Fe - oxalate Fe <sup>a</sup> , <sup>c</sup>
and hydroxides	
4. Allophane Al	Ox. Al - Pyro. Al <sup>b</sup>
5. Allophane Al/Si ratio	Ox. Al - Pyro. Al x AtWt Si oxalate Si AtWt Al
6. Allophane content	Oxalate Si <sup>b</sup> %Si in soil allophanes(ca. 14%)

a = McKeague et al., 1971

the top of the profile than near the bottom, although an increase was often noted in the root mat horizon up to the level found in the Bhfl. High extractable iron values were found in channels running through mineral soil also high in iron. An increasing percent iron was removed from the soil by sodium pyrophosphate, acid ammonium oxalate and CBD as expected.

Profile 30 on Burke Mtn. contained the only root mat with an iron value above 2%. Iron values of 2-5% were seen in root channels of profiles 9, 28, and 30. A value of 6% pyrophosphate extractable iron was taken from a root channel in profile 16 but

 $b = Parfitt, \overline{1983}$ 

c = only true in soils with low magnetite
 concentrations

this high value corresponded to the high iron also extracted from the mineral soil of this profile. All other root mats, root channels and mineral soil had relatively low extractable iron values.

For a comparison of the average iron, aluminum and silicon extracted by pyrophosphate and acid ammonium oxalate from root mats and channels on Burke Mountain and Cypress Park, see Table 5-4.

Table 5-4 - Average and Range of Pyrophosphate and Oxalate Extractable Fe, Al and Si in root mats and root channels

		RM Burke Mt.	RC Burke Mt.	RM (+RC) Cypress Pk.
1.	Pyrophosphate			
	%Fe average	1.23	2.07	0.45 (RM only)
	%Fe range	0.56-3.70	0.34-5.79	0.23-0.82
	%Al average	6.62	6.30	1.86
	%Al range	2.38-9.74	3.74-10.03	1.52-2.17
	%Si average	0.43	0.44	0.09
	%Si range	0.08-1.18	0.04-1.40	0.08-0.10
2.	Oxalate			
	%Fe average	1.30	2.05	0.50 (RM only)
	%Fe range	0.62-3.70	0.34-5.92	0.26-0.94
	%Al average	7.24	6.52	8.50
	%Al range	2.61-10.52	3.94-10.39	8.01-8.88
	%Si average	0.62	0.48	2.79
	%Si range	0.07-2.19	0.02-1.59	2.40-3.15

Aluminum results were surprising. Although pyrophosphate aluminum values often increased from the top to the bottom of the profile they had usually dropped to or were at 1-1.5% Al in the horizon immediately overlying the root mat. In the root mat, values increased dramatically, as up to 10.5% Al was removed by pyrophosphate. Aluminum values were also high in the root channels and in contrast to iron, the percent extracted increased from the top to the bottom of the channel. Immediately below the root mat in the duric horizon, pyrophosphate aluminum values were very low. See Appendix A for profile data.

Acid ammonium oxalate aluminum values were higher than pyrophosphate, but in Bhf horizons, root mats and root channels on Burke Mountain, the increase was on the whole, slight. In these highly organic materials, most of the aluminum was bound with the organic matter or was at least in a form both extractants could remove. Also in these horizons, the CBD aluminum approximately equalled the aluminum extracted with pyrophosphate, and silicon values were low.

In B horizons with low carbon values on Burke Mountain, in the root mat of profile 10 and in all horizons regardless of organic content in Cypress Park, the aluminum extracted by oxalate was often more than double that extracted with pyrophosphate, implying that a large proportion of amorphous inorganic aluminum was present (see Table 5-5). As CBD values in these horizons were lower than oxalate but higher than pyrophosphate, much of the oxalate minus pyrophosphate aluminum may be present as allophane-like constituents, only a portion of

which CBD can extract. This is substantiated by the oxalate extractable silicon values which are much higher in horizons where the gap between pyrophosphate and oxalate Al values is wide. In fact, thoughout the study, the larger the difference between pyrophosphate and oxalate Al, the higher in proportion to the aluminum was the oxalate silicon value. According to Parfitt (1983), allophane is responsible for the silicon extracted by oxalate.

This is illustrated well in Table 5-5. The Bhfl horizon of profile 2 has a high %C; pyrophosphate, oxalate and CBD extractable Al are approximately the same and silicon extracted by oxalate is low. The Bhf2 horizon has a lower %C, the oxalate Al is much higher than pyrophosphate or CBD and the silicon extracted by oxalate is high. It is interesting to note that where oxalate silicon values are high (>1%) but pyrophosphate silicon is low, the pH of that horizon is above 4.8. See for example Cypress Park profiles, Appendix A.

Table 5-5

Profile 2 - A Bhfl horizon with a high %C and the underlying Bhf2 horizon with a lower %C.

	&C		%A1			%Si	
horizon		pyro	Ox	CBD	pyro	Ox	CBD
Bhfl	9.97	1.29	1.36	1.23	0.10	0.11	0.15
Bhf2	5.42	1.41	5.18	1.37	0.08	1.44	0.17

In addition to the pH and mineral constituents, the chemical properties of the soil are also determined by its organic In turn, the amount and exact composition of soil organic matter depends on the physical and chemical environment under which the soil was formed, as well as the origin of the organic debris. Organic matter added to a tropical soil has a different fate from that of a prairie soil and both from that of a podzol. Even within a podzol, organic material found in the litter layer is normally quite different in appearance to that of the B horizon and this difference is also reflected in the chemical properties of each horizon. Lowe (1980) found that upon chemical extraction of the organic matter with NaOH:Na pyrophosphate, one could discriminate between the LFH, Ah and Bf horizons by how the carbon of the extract fractionated upon In general, Lowe found that the humic to fulvic acidification. ratio (Ch/Cf) of the litter was high, averaging 3.25 in the F and FH horizons tested and greater than 8.0 in the H horizon alone. In these same horizons the polyphenolic fulvic to total fulvic (Ca/Cf) was low, always less than 0.5. In contrast, Lowe found that podzolic B horizons had low Ch:Cf ratios, averaging 0.21 and the Ca/Cf averaged 0.61, meaning more than 60% of the total fulvics were polyphenolic. The Ah horizons measured had a Ch/Cf value between the two extremes and a Ca/Cf similar to the litter These figures make sense when we consider the conditions of genesis of podzolic soils. In temperate regions, podzols are formed under a cold, high rainfall environment conducive to slow

and incomplete decomposition of organic material. The biological breakdown of the coniferous forest litter releases negatively charged organic acids whose mobility in the acid soil solution depends upon their size, their ratio of hydrophilic to hydrophobic parts and the presence of neutralizing cations. Those that are mobile are leached by excess rainwater into the B horizon where upon polymerization into larger molecules or upon charge neutralization on reaction with inorganic cations they become insoluble. The immobile compounds synthesized during decomposition are left behind at the soil surface along with a much higher proportion of polysaccharides than found in the B horizon. Upon chemical extraction of the organic matter, the fulvic acid fraction (Cf) is considered to consist of the once acid-soluble acids of decomposition plus the polysaccharides. The humic acid fraction (Ch) is associated with the acid-insoluble organic acids.

If root decomposition is the main factor in the genesis of the root mats and root channels, one might expect the resulting organic material to behave in a pattern similar to that outlined by the above model:

As the roots decompose, small organic acids would be released that are soluble in the rainwater leaching through the soil. These would then be removed to the mineral soil or ground water and the acid-insoluble organic molecules, abundant upon decomposition of the root's lignin, would remain in the channel with any polysaccharides undecomposed in this acid, perhaps anaerobic, low nitrogen environment.

Upon chemical extraction of the organic matter, the Ch/Cf and Ca/Cf of the root mats and root channels would be similar to that of the litter layer.

Results were just opposite to those predicted by the model described. The Ch/Cf value was low, always less than 0.5 and often near 0.2, indicating abundant fulvic acids and little humics. The Ca/Cf value was high - greater than 70% of the fulvic acids were polyphenolic rather than polysaccharide in character. No difference was noted between the organic characteristics of the root mats as compared to root channels.

McKeague (1981) reported a humic:fulvic ratio of a root mat in the Goldstream series on Vancouver Island which is in contrast to the above and in fact, does seem to support the expected He obtained a Ch/Cf value of 1.8 indicating that most of the extracted organics were large humic molecules. He concluded that this was an indication of in situ root decomposition. McKeague had obtained his sample from the B.C. Ministry of Environment, another sample of this horizon was obtained from H. A. Luttmerding and reanalysed in this thesis. Results obtained were very different from McKeaque's and they agreed instead with the root mats of Burke Mtn. and Cypress Park. A Ch/Cf of 0.26 and a Ca/Cf of 0.66 indicate most of the extracted organics were polyphenolic fulvic acids. In an attempt to explain the discrepancy, McKeague sent his sample to be analysed by an independant technician in the U.B.C. lab. This technician obtained a Ch/Cf and Ca/Cf value of 0.26 and 0.67, respectively. A comparison of methods showed the Ottawa laboratory used a

larger sample weight to extractant ratio and did not wash the humic acids by redissolving them in alkali and reprecipitation in acid, two factors that will significantly affect results (Schuppli and McKeague, 1984). Perhaps the concentration of organic matter in the McKeague extractant was so high, the smaller fulvic molecules were occluded by the precipitating humic molecules and the two fractions were never washed clean by redissolution and reprecipitation. McKeague did report that his analysis of a Bhf horizon above a duric horizon in the Sarita series had a Ch/Cf of 0.2, the same as the overlying Bf horizon (pers. comm). Perhaps a smaller %C to extractant ratio was used in this case. In addition, McKeague's laboratory reanalyzed the Goldstream rootmat and obtained a value below 0.5, although method differences still prevented identical results in the Ottawa and Vancouver laboratories.

The percent of the root mat carbon extracted by NaOH-pyrophosphate (%Ce) was always high, sometimes apparently greater than 100%. Very little carbon remained in the "humin" fraction. The high values indicate both a high degree of decomposition of the organic material and that false assumptions were used in calculating the Walkley-Black percent carbon values. It would appear that more carbon was oxidized during analyses than expected by the efficiency factor of 1.25 and/or that the assumed average change in oxidation state from C<sup>O</sup> to C<sup>+4</sup> was incorrect. If the efficiency factor was at fault, the carbon in the root mats and channels was likely in a more "active" form than normally encountered in organic horizons (Allison, 1965).

The humic to fulvic and polyphenolic to total fulvic ratios for the Bf and surficial Bhf were as expected for a podzol and in the same range as that of the root mats. It is doubtful the root mats could be statistically differentiated, on the basis of extracted organic matter ratios, from a normal podzolic Bhf horizon. See Table 5-6.

Table 5-6 - Average and range of humic to fulvic acid ratios (Ch/Cf), polyphenolic fulvic to total fulvic acid ratios (Ca/Cf) and percent of total carbon extracted (%Ce)

	Ch/Cf	Ca/Cf	%Ce
Surficial humus (H1)	2.44	0.44	62
range	0.60-4.71	0.24-0.68	50-73
Upper Bhf horizon	0.34	0.72	83
range	0.16-0.64	0.49-0.79	65-99
Podzolic Bf	0.11	0.62	75
range	0.08-0.14	0.45-0.72	56-91
Root Mats (H2)	0.23	0.73	97
range	0.13-0.39	0.66-0.81	81-115
Root Mats (Bhf)	0.32	0.66	76
range	0.11-0.47	0.53-0.77	61-92
Root channels	0.22	0.70	93
range	0.17-0.28	0.61-0.79	61-107

The extracted carbon data showed some variation between sites. For example, the root mats of Cypress Park appeared to be

less well decomposed than those of Burke Mountain. This would explain the higher proportion of polysaccharides to polyphenolic fulvic acids, the lower percent extracted carbon, and a humic to fulvic ratio in one of the root mats of 0.47. The numbers could also be explained by a smaller relative contribution of illuviated fulvic acids vs in situ decomposition in the formation of the organic material making up the root mats. Some of the more conventional B horizons of Cypress Park showed similar results to the Cypress Park root mats. These may also be under the influence of root decomposition.

The Ch/Cf ratios of organic material in the LFH was always well above 1.0, except for the H layer of a localized area sampled east of the Burke Mountain road cut. The H1 horizon of profiles 18, 19, 20, 22, 23, 24, was much thicker than the other sampled soils, very black and amorphous. It appeared to be an excellent example of a well developed surface organic, however, its chemical properties were unusual. The surficial humus in pits numbered 18 and 19 had Ch/Cf values of 0.88 and 0.60, respectively, and the Ca/Cf values were high. These H layers also had much higher oxalate extractable Al than other surficial organic horizons, approaching 5%, compared to less than 0.5%. In fact, it had properties approaching a root mat!

Under the microscope the cellular nature of the organic material filling the mats and channels could be determined. Refer to photographs in Appendix c. In one horizon pollen grains of Abies spp. were found within a clod of organic matter taken from a depth of 78 cm. This would indicate that at least some

surficial material contributed to the organic matter within the root channels and mats.

In summary, the properties exhibited by the root mats and root channels seem full of apparent contradictions. Morphological characteristics point to genesis by root decomposition and chemical properties credit podzolization for the origin of these organic accumulations. The root channels show the gross morphology of large branching roots, the tips of which often extend into the root mat horizon. Occasionally, above the duric horizon, a short piece of undecomposed root of large diameter can be found within the organic material. mineral grains can be detected in most channels or mats by hand texturing and under the phase contrast microscope the cellular nature of the material is easily seen. In addition, wood structure can sometimes be distinguished in situ, although, when this structure is removed from the profile, and crushed between the fingers, its well decomposed state is revealed. ratio of the root material is in the same range as that of the surficial humus.

In contrast, no wood structure can be seen in most of the organic matter accumulations. Instead, the material appears dark and amorphous and the few live roots found are fine to very fine rather than the 1-5 cm in diameter indicated by the size of the root channels. Why would large, coarse roots have grown to the duric horizon in the past, yet no trace of these could be found today?

The chemical properties of the organic material were

completely opposite to what might be expected for decomposing wood, if the humus of the LFH was used as a model. Oxalate extractable aluminum was high - up to half the %C value, and much higher than that extracted from the surrounding mineral soil. This large increase was not mirrored by the extractable iron values, however. The humic to fulvic ratios and polyphenolic fulvic to total fulvic ratios put the properties of the extracted organic much closer to those of a podzolic Bf than to the decomposing wood of the LFH. In fact, the chemical properties make the root mats and root channels much more "podzolic" in character than the conventional Bhf and Bf horizons, with Fe + Al values an order of magnitude larger than those required to meet podzolic classification.

While genetic history of these soils cannot be established by laboratory studies alone, several possible explanations for the formation of root mats and channels with the above properties are presented in Chapter 6. With the aid of a column study, one of these models is then tested.

## Classification of the Root Mats

As a root mat is "a layer of mineral or organic soil or soil material approximately parallel to the land surface that has characteristics altered by processes of soil formation" (CSSC, 1978, p. 22) it is a soil horizon, and as such should be classified. If it has greater than 17% organic carbon it is an organic horizon by the Canadian classification system (CSSC, 1978). When organic, it has been labelled H2 in bulletins

published by the Ministry of Environment, Victoria, but as organic soil classification is somewhat problematic, classification as an H and as an O horizon will be considered Because a root mat is composed of woody materials and is nearly always saturated with water it may meet the classification criteria of an O horizon. If put into this grouping it should be classified as follows. Root mats studied on Burke Mountain and in Cypress Park are all well decomposed. They have less than 10% by volume of rubbed fiber and the pyrophosphate index is 3 or They rate 9-10 on the von Post scale, as there is very little recognizable plant structure and nearly all the peat escapes between the fingers. As such these root mats would be classified as Oh. On the other hand, because the water moving through these materials may be well aerated and because the root mats are associated with a forest environment, they may be more appropriately classified H2.

If a rootmat contains less than 17% organic carbon it can be classified as a Bhf horizon as all root mats have a hue of 7.5YR or redder, contain at least 0.6% pyrophosphate extractable Al + Fe, have a ratio of pyrophosphate extractable (Fe + Al) to clay (<0.002 mm) of more than 0.05 and have an organic C content greater than 5% (CSSC,1978). It can not be classified a Bh horizon when the pyrophosphate extractable iron is greater than 0.3%. The root mat will meet the criteria of a "podzolic Bhf" if its minimum thickness is greater than 10 cm. However, the root mats do differ from the conventional Bhf horizons found directly beneath the LFH or Ae horizons by the amount of pyrophosphate and

oxalate aluminum found within their materials. See Table 5-7.

Table 5-7 - Average Percent Carbon and Percent Pyrophosphate and Oxalate Extractable Fe and Al in the Root Mat Bhf Compared to More Conventional Bhf Horizons Found Near the Top of the Profile

	Conventional Bhf	Root Mat Bhf		
	avg. range	avg.		
% C	7.36 5.27-13.16	13.63		
% Fe (Pyro)	1.22 0.11- 4.85	0.68		
% Fe (Ox)	1.35 0.13- 5.05	0.80		
% Al (Pyro)	1.41 0.55- 2.60	3.60		
% Al (Ox)	1.91 0.57- 4.55	6.73		

It should be noted that little morphological or chemical differences were detected between root mats with a carbon content greater than 17% and those with slightly less than 17% organic carbon. In this case the cutoff point between the two classifications seems very artifical. The American system, which classifies soils low in clay as organic if they have greater than 20% organic matter, may better separate root mats with few discernable mineral grains from those with a more obvious mineral component.

Using the system as it now stands, it is very important that classification of these soils be made on an oven-dried basis.

Air-dry root mats and channels averaged 23% and 20% moisture, respectively, compared to 7% moisture in conventional Bhf

horizons, 5% in Bf horizons and 13% in the humus of the LFH. One root mat still held 30% moisture after air-drying, a probable function of both the organic and aluminum content. Correction for oven-dried weight "bumped" most of the problematic Bhf horizons into the organic classification.

The root channels are not horizontal layers and therefore, do not need to be classified. Rather, they should be described under additional notes in soil survey reports.

#### CHAPTER 6

### POSSIBLE ORIGINS OF THE ANOMOLOUS ORGANIC MATERIAL

## Proposed Models of Root Mat/Channel Genesis

During this study, four possible hypotheses emerged to account for the presence of organic matter in channels throughout the B horizon and in mats above the duric horizon.

- 1. Roots of mature forest trees grew down through the coarse textured mineral soil, seeking the water that collected along the hardpan during periods of drought. The roots had the force to push mineral grains up and apart. The roots died and decomposed leaving a greasy organic horizon.
- 2. This horizon developed through a classically "podzolic" process. Fulvic acids carrying Fe and Al moved from the litter layer and upper horizons to precipitate out along the hardpan.
- 3. Particulate matter, originating from the surface litter was washed down root channels and other favored pathways. It was suspended in the water moving laterally through the coarse textured soil above the hardpan and eventually collected in pockets.
- 4. A combination of the above hypotheses, acting together.

  Hypotheses 1 and 3 require an additional mechanism to

  account for the enrichment of the organic material with iron and

especially aluminum. At least three possibilities can be put forward and not surprisingly, these correspond to the suggested mechanisms of podzol genesis listed in Chapter 1.

- 1. Iron and aluminum move independantly as inorganic cations from the mineral soil into the organic-rich horizons. Van Schuylenborgh and Bruggenwert (1965) and Petersen (1976) found that at pH 4.0, the solubility of Al<sup>+3</sup> was high enough to account for podzol formation. Also, the solubility of iron, under reducing conditions, is high (Stobbe and Wright, 1959). This is a less satisfactory mechanism in soils with reactions above 5.0 because solubility of both elements at this pH is very low.
- 2. Aluminum and perhaps some iron move into the organic-rich layers as the positively charged colloid, proto-imogolite.

In both the above cases, aluminum and iron would precipitate out in the organic horizon through reaction with negatively charged organic acids.

and mats has been enriched with illuviated iron and aluminum-organic complexes. These precipitate out specifically in the root mats and channels due to a change in soil pH, ionic concentration or due to cationic bridging by Fe<sup>+3</sup> and Al<sup>+3</sup> to organic molecules already present in these organic-rich zones. The latter mechanism may cause the insolubility of the organic complex through increase in

size and neutralization of charge.

It has been shown that many conifers growing on acidic soils not only have a tolerance to high aluminum levels in the soil but also actually take this element up into their foliage (Messenger et al., 1978). Messenger (1975) found that eastern hemlock (Tsuga canadensis (L.) Carr.) was an effective foliar aluminum accumulator and that a high concentration of extractable aluminum was also present in the humus-rich surface soils beneath forest stands dominated by this species. These forest floor environments also had a large capacity for the production of "crenic acid", the name given by the early Russian researchers to coloured organic molecules, released from vegetation, able to dissolve and chelate metals.

As the litter is decomposed, the aluminum may be released in combination with a mobile acid. David and Driscoll (1984) measured the aluminum passing through a spodosol subject to atmospheric acid deposition at hardwood and conifer sites in the Adirondack Mountains, New York. They found lower solution pH values and higher total aluminum concentrations in the soil solution of the conifer site. Furthermore, 85% and 65% of the aluminum in the B horizon soil solution at the hardwood site and the conifer site, respectively, was in the soil solution of the litter layer before coming in contact with the mineral soil. Aluminum in this acid soil seemed to be taken up by plant roots and later released into the litter layer upon decomposition of the leaves. However, especially with surficial rooting species such as hemlocks (Krajina, 1969) cycling may mean exactly that,

cycling. The same population of aluminum, released from the foliage through decomposition, may be once again picked up by the tree roots.

On forested sites in this study, aluminum may be absorbed by roots of hemlock trees, transported to the leaves, released upon decomposition and washed down favored pathways, such as root channels, in combination with organic acids. The aluminum may then bind with other organics in the channel, and through decomposition the carbon to aluminum ratio decreased with time.

### How these Suggested Models Fit the Properties Found

It appears that at least part of the organic matter in channels and mats on Burke Mountain and in Cypress Park arose through the decomposition of roots. Many channels had the gross morphology of large branching roots. Much of the organic matter filling the channels and in localized areas of the mats had the fibrous morphology of wood in situ, although the "wood" was too decomposed to maintain its fibrous nature when crushed between the fingers. This "wood" often filled the channels completely and a darker area could be seen along the edge of the channel which resembled "bark". The granular structure of some of the organic material looked like short pieces of decomposed fine roots. Short pieces of dead, but undecomposed roots of large diameter were occasionally found at depth within the mat and, the cellular nature of the decomposed material could be seen under the microscope. In addition, the mats were located in areas where roots were likely to concentrate. They were found above a

hardpan along which seepage water ran, beneath a fairly coarse textured, well-drained soil. In times of drought it would be advantageous for a tree to be able to collect seepage water and dissolved nutrients moving along the pan from higher elevations. The distribution of organic matter was by no means uniform. Thin channels of organic material were surrounded by soils with a very low %C value and the root mat profile as a whole was often surrounded by soil with no unusual organic accumulations, a distribution easily attributable to the preference of rooting habit.

Why large roots can not be found to this depth today may be due to the predominance of hemlock in the second growth forest. Hemlock is known for its surficial rooting habit and preference for nutrients in steady but low concentrations (Krajina, 1969). The large cedar stumps prevalent in the forest of Burke Mountain indicate a larger role played by cedar in the past. Cedar and Pacific Silver Fir both have a high nutrient requirement and achieve optimum growth in soils affected by nutrient-rich seepage water (Krajina, 1969).

Other evidence for a root-derived origin of the organic material is found in the thickness of some of the root mats, up to 40 cm with few detectable mineral grains. Where did the mineral material go? It would require the active pressure of roots, or a landslide over surficial material, the latter of which there is no evidence, to create the space the organic materials fill.

Surficial material may have later contributed to the organic

mass in the channels, washing down paths of least resistance created by decomposing roots. Evidence for this was given by pollen grains found in the root mat of Profile 25. It should be noted however, that on Burke Mountain and in Cypress Park, most channels did not obviously extend to the surface and that no empty "pipes" were found.

It seems probable that the organic material within these soils was secondarily enriched with aluminum, and to a lesser extent, iron. If live tree roots were capable of absorbing and storing up to 10% aluminum, surely this would have been noted in previous studies. Also, as the percent aluminum is often up to half the percent carbon value, the high aluminum could be due to the relative decomposition of carbon. However, the cellular nature of the organic matter and the residual wood structure in some of the material makes this much decomposition seem doubtful.

The low reaction of the soils on Burke Mountain would allow aluminum to sit on the exchange sites as Al<sup>+3</sup>(Bohn et al., 1979). This element is also somewhat soluble within the soil solution at this pH. Driscoll et al. (1984) found that inorganic monomeric aluminum levels increased in stream systems of the Adirondack Mountains, as pH values decreased. Under the conditions of low soil pH found on Burke Mountain, Al<sup>+3</sup> could move with percolating rainwater into the root channels when the soils are saturated, as the channels are the pathways of least resistance in the soil. The positive cation might react with the negatively charged acids released from decomposition of roots or surficial material, and both become neutralized and insoluble. In addition, live hemlock

roots could absorb  ${\rm Al}^{+3}$  from the exchange complex or as it moves within the soil solution. Messenger (1975) found that the eastern hemlock had especially high levels of aluminum in its foliage. A high aluminum level in the  ${\rm H}_1$  horizon of one localized area on Burke Mountain suggests some mechanism must be bringing aluminum to the soil surface.

This mechanism less easily explains the high aluminum level of root mats on Cypress Park and beneath some of the mineral horizons on Burke Mountain. Here, mineral soil pH is in the range of  $4.7-5.4~(\mathrm{H_2O})$ , and although the aluminum content of the root mat reaches as high as 9%, the soil is too basic for high solubility of the aluminum cation (Bohn et al., 1979) Also, roots on Cypress Park seem concentrated in the LFH. Few extend far enough into the B horizon to absorb large quantities of the aluminum weathered from the mineral soil.

Farmer (1981) felt that the aluminum released by weathering in a podzolic soil had a high enough affinity for the silicon in the soil solution that it would react to form proto-imogolite rather than aluminum hydroxides. This positively charged proto-imogolite sol would be fully mobile at a pH less than 5.0 and could move through the positively charged B horizon. It would precipitate out of solution when the pH rises above 5.0, when its charge was neutralized by adsorbed anions or when its positive charges encountered negatively charged surfaces.

Using electron microscopy, infrared spectroscopy and x-ray diffraction, McKeague and Kodama (1981) detected imagolite in the cement of the duric horizon of the Whonnock soil series on Burke

Mountain. They felt that movement of proto-imogolite through the acid mineral soil was plausible and, as the stability of the proto-imogolite sol decreased above 5.0 (Farmer and Fraser, 1982), the high reaction of the basal till could result in the precipitation of proto-imogolite and perhaps the eventual cementation of the horizon.

Childs et al. (1983) found that imogolite was also present in the cement of indurated horizons in New Zealand podzols. such soil had properties somewhat similar to the Whonnock soil series of this study. The One Tree Point profile contained little volcanic ash, had indurated horizons with very firm consistence, and had low weathered Fe to weathered Al ratios. Ιt also possessed a root mat at a depth of 62 cm with an organic carbon content of 20% and an aluminum value of over 9%. Like root mat horizons in Cypress Park, pyrophosphate aluminum was much lower than oxalate aluminum and oxalate-extractable silicon was high. The presence of proto-imogolite allophane was detected throughout the profile by these authors and it was found that predictions of this mineral by oxalate extractable silicon values (after Parfitt, 1983) and by infrared spectroscopy (Farmer et al., 1980), showed good agreement in the horizons tested. estimated a value of 18% proto-imogolite allophane in the root mat horizon by the high oxalate extractable silicon. addition, up to 5% fully crystallized imagolite was detected by electron microscopy in the clay sample of the Bs horizon. Proto-imogolite appeared to cause induration of the mineral horizons by filling the available pore spaces.

If imogolite is responsible for the cement of the duric horizon immediately underlying the root mat horizons (McKeague and Kodama, 1981) and if indeed, imogolite can only form from a solution of proto-imogolite (Farmer and Fraser, 1978), perhaps this mobile aluminosilicate can also contribute to the aluminum concentration of the organic-rich mats and channels.

It is interesting to note that in the present study, whenever the pyrophosphate aluminum level of B horizons and organic accumulations is substantially less than the oxalate aluminum level, the oxalate silicon level is always high (see especially the Cypress Park root mat horizons). In addition, Al(ox)-Al(pyro)/Si(ox) is approximately 2, although often a slightly higher ratio is found. Farmer (1984) reported that the excess aluminum in the ratio could arise from extraction of this element from interstratified hydroxyaluminum species. He felt that the oxalate-soluble Si value alone, is a surer basis for an estimation of the percent allophane present. In the root mats of Cypress Park, levels of allophane were calculated by the method of Parfitt (1983). Values ranged between 17 and 23 percent allophane.

# Column Study Testing the Proto-imogolite Model

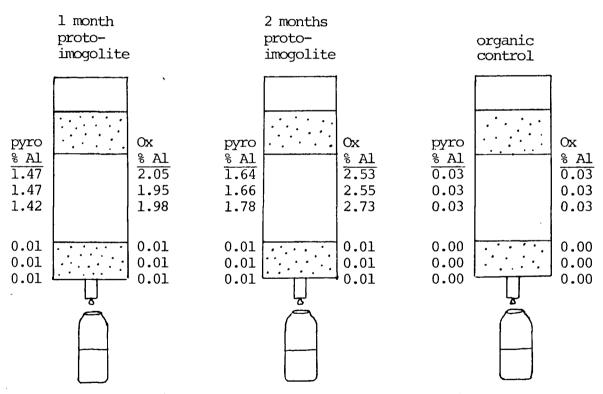
A column study was undertaken to test a mechanism by which decomposing roots could become enriched with high aluminum levels, through adsorption from proto-imogolite. For periods ranging from 2.5 weeks to 3 months a solution of 0.01 M proto-imogolite was slowly leached through a column of rotting

wood sandwiched between layers of Ottawa sand. Two controls were also set up. The first was identical with the proto-imogolite column but leached with a solution of the same pH and approximate ionic concentration but without the aluminum and silicon. In the second control, the proto-imogolite solution was dripped through columns filled only with the Ottawa sand. To simulate rainfall events, periods of proto-imogolite leaching were alternated with periods ranging from 16 hours to 3 days, when no solution was added.

Results were encouraging. After the first 250 mLs of proto-imogolite were leached through the organic-filled column, the leachate was the yellow-brown of fulvic acids. The proto-imogolite was simply replacing the distilled water used to make up the columns. The next 250 mLs of proto-imogolite immediately immobilized the fulvic acids in the column and the leachate was as clear as distilled water. It remained clear throughout the duration of the experiment. In contrast, the leachate from the organic control was still stained yellow-brown and continued to show at least some colour even after it was leached for three months with water. See photographs in Appendix D.

The organic matter and sand were removed from the columns, air-dried and analyzed for pyrophosphate and acid ammonium oxalate extractable aluminum. After 1 month of leaching, the organic matter of the columns contained 2% oxalate extractable aluminum and after 2 months, the organic material consisted of

Figure 6-1: Percent Aluminum, Extracted from Organic Matter and Sand, by Acid Ammonium Oxalate and Na Pyrophosphate After 1 and 2 Months Treatment with Proto-imagolite



Aluminum values of all 3 replicates are given

2.5% oxalate aluminum. Duplicate columns showed good agreement and pyrophosphate aluminum values were also high. See Figure 6-1. Neither the Ottawa sand nor the organic matter of the controls contained significant aluminum. Oxalate-extractable silicon values averaged 0.57% and 0.80% for 1 and 2 months proto-imogolite treatment, respectively, and corresponded with pyrophosphate-extractable silicon values averaging 0.43% and 0.48% for the same periods. The fulvic acids of the decaying wood seemed capable to some extent of scavenging aluminum from the aluminosilicate solution and releasing silicon.

After each 250 mL of solution was added to the column, the leachate was analyzed by atomic absorption for ppm aluminum and The starting concentration of the laboratory synthesized proto-imogolite was 100 ppm Al and 54 ppm Si. the first few days, the organic matter in the columns adsorbed all of the aluminum added. The leachate contained 0 ppm aluminum and 20 ppm silicon. Upon each addition the pH dropped from approximately 4.5 in the proto-imagolite eluent to 3.3 in the subsequent leachate, indicating that the adsorbed aluminum was exchanging with hydrogen ions on the organic material. amount adsorbed decreased with time but still averaged 50-60% (A1) after 2.5 weeks and 4 litres of 0.01 M proto-imagolite had leached through the column. See Table 6-1. Even after an organic-filled column had been treated for 2-3 months with proto-imogolite, the organic matter was still able to adsorb an average of 10% aluminum from the eluent.

It is interesting to note that the amount of aluminum adsorbed by the organic matter increased with time between leaching periods. For example, only 50% of the aluminum from proto-imogolite was adsorbed on April 24, a day after 500 mLs had been put through the column. On April 27, after a 3 day period when no leaching took place, 60% aluminum was adsorbed. Table 6-1. Also, the colour of the water control leachate corresponded exactly with the higher adsorption values. The more aluminum adsorbed, the darker was the water leachate, see Table 6-1 for ppm C data. This indicates that fulvic acid-like Material was being constantly released. It built up during the period of inactivity and more was available to react with the aluminum or to be leached out by the water in the control columns. Carbon released from the proto-imogolite organic columns was estimated by the percent absorbance of light at 600 nm wavelenth. This indirect method seemed to indicate that less than 1 ppm carbon was found in this leachate.

A concentration of 100 ppm aluminum is of course very high for a real soil solution and organic immobilization may be due to neutralization of acidic charges by this high concentration of cations. In contrast, the aluminum in a proto-imogolite solution of very low concentration may instead be complexed by the acids and the two move out of the root layer as a mobile complex. For this reason, a solution with only 5 ppm aluminum was dripped through an organic column and the aluminum of the leachate measured by atomic absorption. Although the experiment was only continued for a few days with a total of 1 litre proto-imogolite

Table 6-1 - Percent Aluminum and Silicon Adsorbed From Proto-imogolite by Organic Columns and ppm Carbon released by the Control Columns (3 replicates)

Date April	mL p-im* (or H <sub>2</sub> O)	Proto-: % i adso	Al .	ite Colu % Si adson	i		Cont om C Leas	2	;
10	500	100	)	83			90		
11	750	100 10	100	67 61	61	59	50	5 4	
11	1000	100 100	100	80 80	76	13	14	10	
12	1250	98 99	97	46 52	48	35	3 4	36	
12	1500	87 9	l 86	65 69	6 7	9	8	10	
15	1750	99 10	98	22 22	22	58	6 4	65	
15	2000	88 8	4 83	61 61	59	14	10	10	
16	2250	80 8	L 79	46 44	44	19	20	19	
18	2500	72 8	75	24 28	26	26	28	30	
18	2750	61 6	0 65	35 35	35	7	8	9	
19	3000	68 6	3 6 <u>8</u>	31 31	33	14	13	16	
23	3250	73 7	4 72	30 30	30	42	44	45	
23	3500	46 4	1 50	31 30	33	7	8	9	
24	3750	49 5	51	30 28	30	13	12	14	
27	4000	66 6	56	30 26	28	24	23	20	

<sup>\*</sup> cumulative mL proto-imogolite or water added

solution put through the column, no aluminum was found in the leachate and its colour indicated much less carbon than was present in the water control. The organic acids did not appear to peptize the proto-imogolite sol nor carry the aluminum out in complex form. It is also important to keep in mind that there would likely be much more fulvic acids available for reaction in the previously "protected" rotting wood collected for the column study than from roots slowly decomposing in a seepage environment.

To see if the root mats could be subsequently enriched with fulvic acids leaching from the soil surface, acids were extracted with distilled water from rotting wood. The resulting yellow-brown liquid was dripped into a column previously leached for 2 months with proto-imogolite. According to Figure 6-1 the organic matter should contain 2.5% Al. As a control, fulvic acids were also leached through an organic column with no previous proto-imogolite treatment and therefore, with a very low aluminum concentration.

Although the organic acids extracted from the rotting wood had coloured the distilled water a yellow-brown, after passing through a column previously treated with proto-imogolite, the leachate was as clear as distilled water. The aluminum-organic matter had immobilized the coloured organic acids. The leachate of the control was the same colour or much darker than the added extracted fulvic acids and the ppm C of the leachate was usually much higher. See photographs in Appendix D and Table 6-2.

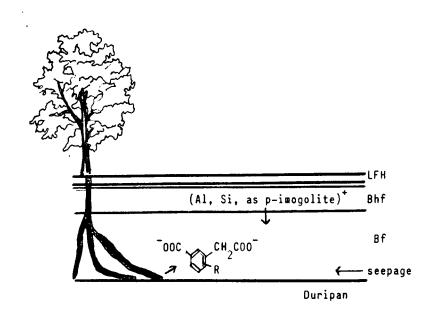
Table 6-2 - ppm C in Fulvic Acid Prior to and Subsequent to Their Leaching Through Two Organic Columns; The First Previously Treated With Proto-imagolite and the Second Not

Date April	ppm C in fulvic acid	ppm C in leachate #1	ppm C in leachate #2
1,1	45.44	4.73	76.98
11	45.44	4.57	35.65
12	49.86	7.01	45.98
16	64.81	9.43	107.90
18	72.94	5.31	43.81
19	35.61	4.84	54.56
19	35.61	3.17	31.81
23	37.05	6.56	55.97
23	37.05	3.66	35.90
24	44.25	4.03	38.44
27	61.02	6.80	57.67

leachate #1 is the leachate from the column previously
 treated for 2 months with proto-imogolite
leachate #2 is the leachate from the control column with no
 previous proto-imogolite treatment and no aluminum

The above results seem to indicate that if indeed proto-imogolite is moving through these soils, the organic material of decomposing wood could adsorb aluminum from this colloid and release at least a portion of the silicon. The mechanism by which this would operate is illustrated in Figure 6-2. Because neither the aluminum nor the fulvic acids are leaving the root mat environment the percent aluminum would increase and the Ch/Cf decrease with time. In addition, fulvic acids leaching from the soil surface could react with the aluminum already held by the decomposing roots and precipitate out in this environment. Of course, if small fulvic acids were themselves carrying aluminum, this element and fulvic acids in the root mats and channels would be further enriched.

Figure 6-2: Diagramatic Representation of Inorganic Proto-imogolite Moving Through the Soil and Reacting with Fulvic Acids Released by Decomposing Roots



The proto-imogolite theory of podzolization as envisioned by Farmer (1980) has come under criticism from various sources. Buurman and van Reeuwyk (1984) feel the presence of imogolite within B horizons can be explained by its neoformation from silica percolating within the soil solution and from aluminum released by decomposition of organic complexes. The authors question the turnover rate of Al-humus complexes as quoted by Farmer et al. (1980) and also feel that simple organic acids such as citric, lactic, oxalic, malic, succinic, glucuronic, vanillic, p-coumaric and p-hydroxybenzoic may resist decompositon for a long enough period to be an important agent in the transportation of aluminum through to the B horizon.

Chesworth and Macias-Vasquez (1985) analyzed the problem of an organic vs inorganic mechanism responsible for podzol genesis, in terms of the range of pH and electrode potential (pE) common in podzolic soils and in terms of the solubility of various forms of iron, aluminum and silicon at these pH and pE levels. They found that if amorphous aluminum and iron hydroxides were used to determine the solubilities of the metals in the soil solution and that if quartz was responsible for the solubility of silica, a geochemical fence could be constructed that accounted for precipitation of amorphous phases within the B horizon. It could not account, however, for the formation of the Ae horizon under all but the most acid conditions. By adding the effect of organic matter to their pH-pE diagram, they were able to construct a geochemical fence separating conditions under which an albic horizons would form consistent with those found in the

real soil. In contrast, Chesworth and Macias-Vasquez could find no evidence that imogolite could control the mobility of aluminum under the pH and pE of a pozolic soil, to form the Ae horizon but found that once Al had been mobilized by another mechanism, imogolite could control its precipitation within the B horizon.

In fairness to Farmer, however, his theory of podzolization does not depend on the solubility of imogolite within the albic horizon. Imogolite is a mineral he sees forming within the lower B horizon, if conditions are right, from "proto-imogolite".

Proto-imogolite, itself, would form from the aluminum released upon the decomposition of small acids and from the silica in the soil solution and it would not precipitate immediately out of solution, if the soil pH is below 5.0 and if negative surfaces are not available to adsorb it. Instead it would travel through the subsoil and precipitate when conditions change, such as under the higher pH of the lower B horizon.

#### Conclusions

From the evidence gathered on Burke Mountain and in Cypress Park all hypotheses proposed for the genesis of the root mats and channels may have some validity. The predominant force responsible in an individual area may be dependent upon the prevalent environmental conditions, such as soil pH, texture and mineralogy, interacting with the tree species growing on the site.

Morphological evidence suggests that large tree roots play an important role in pushing aside the soil and creating the

initial space for organic materials to fill. However, particulate matter percolating down paths of least resistance from the soil surface, must also contribute to the organic material, as evidenced by pollen grains found within one profile at a depth of 78 cm. As the roots are further decomposed, the role of particulate matter infilling the channels may become even more important.

High aluminum levels imply that podzolic mechanisms must also contribute to the bulk of material within the channels and mats and support can be found for both mechanisms of podzol genesis presented in Chapter 2.

If proto-imogolite does indeed move through these well weathered soils, perhaps the root mats and channels on Burke Mountain and in Cypress Park are at different stages of development. As the roots decompose, they release fulvic acids which precipitate with the proto-imogolite migrating at a pH below 5.0. As more fulvic acids are released they scavenge the aluminum from the proto-imogolite and release the silica. If roots grow down into the B horizon they may be able to absorb the aluminum from proto-imogolite moving through the soil, from Al<sup>+3</sup> sitting on the exchange, and upon decomposition from organic complex. The aluminum would then be cycled upwards where it would be released to enrich the LFH and the root channels closer to the surface.

It will require the research of the next few years to determine if the proto-imogolite theory of podzolization has any validity and therefore, if it can be applied to the genesis of aluminum rich root mats and channels.

#### SUMMARY AND CONCLUSIONS

Mats and channels of high organic content within podzols of the Coast Mountains surrounding Vancouver were characterized for a number of morphological and chemical properties. Based on these analyses the following conclusions could be drawn:

- 1. The mats tended to sit above a hardpan or particle size discontinuity, ranged from 1 cm to more than 40cm thick and were located at depths of approximately one metre under a relatively coarse textured mineral soil. The channels ran obliquely and vertically through the soil, often had the gross morphology of roots and were up to 5 cm wide. Both channels and mats contained organic material that was "greasy" to the touch and had a cellular nature under the microscope. Occasionally remnants of wood structure could be determined in situ but when removed from the profile the structure was easily crushed between the fingers, often with no residual fiber content.
- 2. Most of the channels and mats of Burke Mountain contained greater than 17% organic carbon on an oven-dried basis and few mineral grains could be detected. Carbon values in Cypress Park tended to be lower, mineral grains were obvious and the roots appeared less well decomposed. Percent total nitrogen and sulphur values were relatively low at both sites but C/N and N/S ratios were fairly typical for organic material of a forested site. Soil reaction of surface organic horizons was extremely

low but values increased with depth. The pH of the lower horizons of Cypress Park were notably higher than those of Burke Mountain.

Iron extracted with sodium pyrophosphate, acid ammonium oxalate and citrate bicarbonate dithionite was usually highest near the top of the B horizon, where values commonly ranged between 1 and 2%, but dropped to fairly low values with depth. Within the root mats, extractable iron sometimes increased again, up to the level found near the top of the B horizon, although no increase was noted at sites sampled in Cypress Park. Extractable iron in root channels usually reflected the amount of iron in the surrounding mineral soil.

In contrast to iron, aluminum in all extractants increased dramatically in the mats and channels over values found in the mineral soil. In some root mat horizons, greater than 10% aluminum (often more than half the percent carbon value) could be extracted by acid ammonium oxalate. In most soils on Burke Mountain, pyrophosphate aluminum levels almost equalled oxalate aluminum, oxalate silicon was low, the humic to fulvic ratio was well below 0.5 and the polyphenolic to total fulvic ratio was high. This suggested that most of the aluminum was bound with the organic material.

Data gathered from Cypress Park sites presented a slightly different picture. While oxalate aluminum levels averaged greater than 8%, pyrophosphate extractable aluminum levels were much lower than oxalate aluminum and oxalate silicon values were high. The ratio of [oxalate Al - pyrophosphate Al/oxalate Si]

was approximately 2 indicating the presence of a mineral similar to the proto-imogolite allophane found by Childs et al. (1983) in an indurated New Zealand podzol. This New Zealand soil also had a root mat with 20% carbon, 9% aluminum and a high oxalate silicon value. The humic to fulvic ratios were sometimes higher and the polyphenolic fulvic to total fulvic ratios were lower than those found on Burke Mountain.

At both sites, root mats and root channels have similar values in all chemical extractants except for those of iron. In the latter case the mats and channels seem to reflect their position in the mineral soil.

3. The root mats could either be classified as organic or mineral depending on their percent carbon content. It was very important that classification be made on an oven-dried basis as the highly organic mats and channels retained relatively more water on air-drying than surficial organic horizons and the surrounding mineral soils. If the carbon content was greater than 17%, the horizons met both the classification criteria of an O and of an H horizon. They have been classified as H2 in this report as this designation seems to better reflect their association with a forested environment. The Canadian system should be more strongly clarified and less subjective in regards to organic horizon classification.

When the root mat contained less than 17% carbon, pyrophosphate extractable iron plus aluminum was more than an order of magnitude greater than that required to meet podzolic classification. It also met the criteria of a "podzolic Bhf"

when it was greater than 10 cm thick. On soil description forms, root channels should be described under additional notes.

It seems certain that at least initially, root decomposition was involved in the genesis of the organic-rich Particulate organic matter, percolating down paths of zones. least resistance (decomposing root channels) may also add to the bulk of material in the mats and channels, as seen by pollen grains found at depths of 78 cm. Podzolic processes must also play a role but just as the mechanisms of podzol genesis in the mineral soil are still somewhat unclear, so too are the means of iron and aluminum enrichment of the accumulated organic material. On Burke Mountain, chemical properties suggest the transport of aluminum in organic complex. The pH is so low in these soils that the exchange complex must be covered with Al<sup>+3</sup>. As roots are plentiful within the top of the B horizon and within the root channels of many profiles, these could be cycling the metals to the surface and from here the complex may move down the root channels. Also, at an acid pH, enrichment from Al +3, soluble in the soil solution, cannot be ruled out.

In contrast, the chemical properties of Cypress Park soils suggest that a large portion of the aluminum within the root mats is present as allophane with an Al:Si ratio close to that found in imogolite. In addition, many of the B horizons on both Burke Mountain and Cypress Park have a much higher oxalate aluminum than pyrophosphate aluminum, a high oxalate silicon value and a number are partially cemented. On Burke Mountain the strong cement of the duric horizon has been shown to consist of aluminum

and silicon (McKeague and Kodama, 1981).

Cypress Park soils differed from soils of Burke Mountain in several other respects. They had a higher pH at which the solubility of aluminum would be very low and its importance on the exchange complex would be much less. The roots of the profiles examined on Cypress Park were concentrated within the litter layer and did not venture far into the B horizon. All of this suggests a smaller amount of aluminum would be cycled by vegetation. The remains of roots were fairly obvious within the root mat and this is reflected in humic to fulvic and polyphenolic fulvic to total fulvic ratios that are often not as extreme as those of Burke Mountain. These ratios could also be interpreted as having a smaller influence by percolating fulvic acids.

A column study demonstrated that if proto-imogolite was indeed moving through the mineral soil, it could react with fulvic acid-type molecules, released upon decomposition of organic materials, and both aluminum and fulvic acid would precipitate. Research reported by Farmer (1981) suggested that if the fulvic acid concentration was much higher than that of the proto-imogolite, the fulvic acid would scavenge the aluminum from the positive colloid and release silicon. Co-precipitation would occur at a lower ratio of COOH:Al.

Which ever mechanisms of podzolization are found in the future to be valid, it seems reasonable to assume that similar mechanisms to those operating in the mineral soil, are enriching the root mats with Fe and Al. Therefore, root mats with carbon

contents less than 17% are correctly classified a "podzolic" Bhf horizon.

To truly understand the genesis of these soils, lysimeter work should be undertaken at both the Cypress Park and Burke Mountain sites.

# LITERATURE CITED

- Allison, L. E. 1965. Organic carbon. <u>In</u> C. A. Black (ed.). Methods of Soil Analysis. Agronomy 9:1346-1366.
- Anderson, H. A., M. L. Berrow, V. C. Farmer, A. Hepburn, J. D. Russell and A. D. Walker. 1982. A reassessment of podzol formation processes. J. Soil Sci. 33:125-136.
- Atkinson, H. J. and J. R. Wright. 1957. Chelation and the vertical movements of soil constituents. Soil Sci. 84:1-11.
- Barnhisel, R. and P. M. Bertsch. 1982. Aluminum. <u>In A. L. Page</u> (ed.). Methods of Soil Analysis. Agronomy 9:275-300.
- Barshad, I. 1955. Soil development. <u>In</u> F. E. Bear (ed.). Chemistry of the Soil. Reinhold Publ. Co., New York. pp 1-52.
- Bascomb, C. L. 1968. Distribution of pyrophosphate extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19:251-268.
- Bloomfield, C. 1951. Experiments on the mechanism of gley formation. J. Soil Sci. 2:196-212.
- Bloomfield, C. 1953a. A study of podzolization. 1. The mobilization of iron and aluminium by Scots Pine needles. J. Soil Sci. 4:5-17.
- Bloomfield, C. 1953b. A study of podzolization. II. The mobilization of iron and aluminium by the leaves and bark of Agathis australis (Kauri). J. Soil Sci. 4:17-24.
- Bloomfield, C. 1954a. A study of podzolization. III. The mobilization of iron and aluminium by Rimu (Dacrydium cupressinum). J. Soil Sci. 5:39-46.
- Bloomfield, C. 1954b. A study of podzolization. IV. The mobilization of iron and aluminium by picked and fallen larch needles. J. Soil Sci. 5:46-50.

- Bloomfield, C. 1955. A study of podzolization. VI. The immobilization of iron and aluminium. J. Soil Sci. 6:284-293.
- Bloomfield, C. 1957. The possible significance of polyphenols in soil formation. J. Sci. Food Agricult. 8:389-393.
- Bohn, H. L., B. L. McNeal and G. A. O'Connor. 1979. Soil Chemistry. John Wiley and Sons, New York. 329pp.
- Brady, N. C. 1974. The Nature and Properties of Soils, 8th ed. McMillan Publishing Co., New York. 639pp.
- Bremner, J. M. 1965. Total Nitrogen. <u>In</u> C. A. Black (ed.). Methods of Soil Analysis. Agronomy 9:1149-1178.
- Bremner, J. M., P. J. G. Mann, S. G. Heintze and H. Lee. 1946. Metallo-organic complexes in soil. Nature 158:790-791.
- Brooke, R. C., E. B. Peterson, V. J. Krajina. 1970. The subalpine mountain hemlock Zone. Subalpine vegetation in southwestern British Columbia, its climatic characteristics, soils, ecosystems and environmental relationships. Ecology of Western North America 2:147-349.
- Brown, G., A. C. D. Newman, J. H. Rayner and A. H. Weir. 1978.

  The structure and chemistry of soil clay minerals. In C. J. Greenland and M. H. B. Hayes (eds.), The Chemistry of Soil Constituents. John Wiley and Sons, New York. pp 29-178.
- Bruckert, S. 1970. Influence des composes organiques solubles sur la pedogenese en milieu acide. Ann. Agron. 21:421-452.
- Bruckert, S. and J. Rouiller. 1979. Mechanisms regulating the pH of soils. In M. Bonneau and B. Souchier (eds.), Constituents and Properties of Soils. Academic Press, London. pp 399-411.
- Brydon, J. E. and Shimoda, S. 1972. Allophane and other amorphous constituents in a podzol from Nova Scotia. Can. J. Soil Sci. 52:465-475.
- Buurman, P. and L. P. Van Reeuwyk. 1984. Proto-imogolite and the process of podzol formation: a critical note. J. Soil Sci. 35:447-452.
- Canada Soil Survey Committee. Proceedings of the meeting in 1970.

- Canada Soil Survey Committee, Subcommittee on Soil Classification. 1978. The Canadian System of Soil Classification. Can. Dep. Agric. Publ. 1646. Supply and Services Canada, Ottawa, Ont. 164pp.
- Carter, R. E. 1983. Forest floors under second growth Douglas-Fir stands: their chemical variability and some relationships to productivity. M. Sci. thesis, U.B.C. 89pp.
- Chesworth, W. and F. Macias-Vasquez. 1985. pe, pH and podzolization. Amer. J. Sci. 285:128-146.
- Childs, C. W., R. L. Parfitt and R. Lee. 1983. Movement of aluminum as an inorganic complex in some podzolized soils, New Zealand. Geoderma 29:139-155.
- Coleman, N. T. and G. W. Thomas. 1967. The basic chemistry of soil acidity. <u>In</u> R. W. Pearson and F. Adams (eds.), Soil Acidity and Liming. Agronomy 12:1-41.
- Coulson, C. B., R. I. Davies and D. A. Lewis. 1960a.
  Polyphenols in plant, humus and soil. I. Polyphenols of leaves, litter and superficial humus from mull and mor sites. J. Soil Sci. 11:20-29.
- Coulson, C. B., R. I. Davies and D. A. Lewis. 1960b.
  Polyphenols in plant, humus and soil. II. Reduction and transport by polyphenols of iron in model soil columns. J. Soil Sci. 11:30-44.
- Cradwick, P. D. G., V. C. Farmer, J. D. Russell, C. R. Masson, K. Wada and N. Yoshinaga. 1972. Imogolite, a hydrated aluminium silicate of tubular structure. Nature Physical Science 240:187-189.
- David, M. B. and C. T. Driscoll. 1984. Aluminum speciation and equilibrium in soil solutions of a haplorthod in the Adirondack Mountains (New York, U.S.A.). Geoderma 33:297-318.
- Dawson, H. J., F. C. Ugolini, B. F. Hrutfiord and J. Zachara. 1978. Role of soluble organics in the soil processes of a podsol, Central Cascades, Washington. Soil Sci. 126:290-296.
- Deb, B. C. 1949. The movement and precipitation of iron oxides in podzol soils. J. Soil Sci. 1:112-123.
- DeConinck, F. 1980. Major mechanisms in the formation of spodic horizons. Geoderma 24:101-128.

- DeLong, W. A. and M. Schnitzer. 1955. Investigations on the mobilization and transport of iron in forested soils. I. The capacities of leaf extracts and leachates to react with iron. Soil Sci. Soc. Amer. Proc. 19:360-363.
- Driscoll, C. T., J. P. Baker, J. J. Bisogni, and C. L. Schofield. 1984. Aluminum speciation and equilibria in dilute acidic surface waters of the Adirondack region of New York State. In O. R. Bricker (ed.), Acid Precipitation: Geological Aspects. Ann Arbor Sci., Ann Arbor, MI, pp. 55-75.
- Duchaufour, P. 1982. Pedology. George Allen and Unwin, London. 448pp.
- Environment Canada, Atmospheric Environment Service. 1980. Canadian Climate Normals. Temperature and precipitation 1951-1980. British Columbia. 268pp.
- Expert Committee on Soil Survey. Proceedings of the meeting in 1981.
- Farmer, V. C. 1981. Possible roles of a mobile hydroxyaluminium orthosilicate complex (proto-imogolite) and other hydroxyaluminium and hydroxy-iron species in podzolization.

  In Migrations Organominerales dans les Sols Temperes.

  Colloques Internationaux du CNRS. No. 303:275-279.
- Farmer, V. C. 1982. Significance of the presence of allophane and imagolite in podzol Bs horizons for podzolization mechanisms: A review. Soil Sci. Plant Nutr. 28:571-578.
- Farmer, V. C. and A. R. Fraser. 1982. Chemical and colloidal stability of sols in the Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system: Their role in podzolization. J. Soil Sci. 33:737-742.
- Farmer, V. C., A. R. Fraser, L. Robertson and J. R. Sleeman. 1984. Proto-imogolite allophane in podzol concretions in Australia: Possible relationship to aluminous ferrallitic (lateritic) cementation. J. Soil Sci. 35:333-340.
- Farmer, V. C., A. R. Fraser and J. M. Tait. 1977. Synthesis of imogolite: A tubular aluminium silicate polymer. J. Chem. Soc. Chem. Comm. 13:462-463.
- Farmer, V. C., W. J. McHardy, L. Robertson, A. Walker and M. J. Wilson. 1985. Micromorphology and sub-microscopy of allophane and imogolite in a podzol Bs horizon: Evidence for translocation and origin. J. Soil Sci. 36:87-95.

- Farmer, V. C., J. D. Russell and M. L. Berrow. 1980. Imogolite and proto-imogolite allophane in spodic horizons: Evidence for a mobile aluminium silicate complex in podzol formation. J. Soil Sci. 31:673-684.
- Farmer, V. C., J. D. Russell and B. F. L. Smith. 1983. Extraction of inorganic forms of translocated Al, Fe and Si from a podzol Bs horizon. J. Soil Sci. 34:571-576.
- Gallagher, P. H. 1942. The mobile colloidal humus of podsolic soils and its relationship to the process of podsolisation. Proc. Royal Irish Acad. 48(B):213-230.
- Guillet, B. and B. Souchier. 1982. Amorphous and crystalline oxyhydroxides and oxides in soils (iron, aluminium, manganese, silicon). In M. Bonneau and B. Souchier (eds.), Constituents and Properties of Soils. Academic Press, London. pp.21-42.
- Hansen, E. H. and M. Schnitzer. 1969. Molecular weight measurements of polycarboxylic osmometry. Anal. Chim. Acta 46:247-254.
- Higashi, T. and K. Wada. 1977. Size fractionation, dissolution analysis and infrared spectroscopy of humus complexes in Ando soils. J. Soil Sci. 28:653-663.
- Jenny, H. 1980. The Soil Resource. Springer-Verlag, New York. 377pp.
- Jeanroy, E. and B. Guillet. 1981. The occurrence of suspended ferruginous particles in pyrophosphate extracts of some soil horizons. Geoderma 26:95-105.
- Joffe, J. S. 1936. Pedology. Rutgers University Press, New Jersey. 575pp.
- Jones, H. T. and J. S. Willcox. 1929. Studies in soil genetics I. J. Soc. Chem. Ind. 48:304-308.
- Kirkman, J. H., B. D. Mitchell and R. C. Mackenzie. 1966.
  Distribution in some Scottish soils of an inorganic gel system related to "allophane". Trans. Roy. Soc. Edin. 66:393-418.
- Klinka, K., R. N. Green, R. L. Trowbridge and L. E. Lowe. 1981. Taxonomic classification of humus forms in ecosystems of British Columbia. Ministry of Forests, Land Management Report #8, Victoria. 54pp.
- Kononova, M. M. 1961. Soil Organic Matter. Its nature, its role in soil formation and in soil fertility. Pergamon Press, New York. 450pp.

- Krajina, V. J. 1969. Ecology of forest trees in British Columbia. In Ecology of Western North America 2:1-146.
- Krajina, V. J. 1975. Some observations on the three subalpine biogeoclimatic zones in British Columbia, Yukon and Mackenzie District. Phytocoenologia 2:396-400.
- Kumada, K. 1965. Studies on the colour of humic acids. Part I. On the concepts of humic substances and humification. Soil Sci. Plant Nutr. 11:11-16.
- Lewis, T. 1976. The till-derived podzols of Vancouver Island. PhD dissertation, U.B.C. 158pp.
- Lowe, L. E. 1975. Fractionation of acid-soluble components of soil organic matter using polyvinyl pyrrolidone. Can. J. Soil Sci. 55:119-126.
- Lowe, L. E. 1980. Humus fraction ratios as a means of discriminating between horizon types. Can J. Soil Sci. 60:219-229.
- Luttmerding, H. A. 1981. Soils of the Langley-Vancouver Map Area. RAB bulletin 18, British Columbia Soil Survey, report # 15, 6 volumes.
- McKeague, J. A. 1978. Manual on Soil Sampling and Methods of Analysis, 2nd ed. Canadian Society of Soil Science. 212pp.
- McKeague, J. A. 1981. Organo-mineral migration some examples and anomolies in Canadian soils. <u>In Migrations</u>
  Organominerales dans les Sols Temperes. Colloques
  Internationaux du CNRS 303:341-348.
- McKeague, J. A., J. E. Brydon and N. M. Miles. 1971.

  Differentiation of forms of extractable iron and aluminum in soils. Soil Sci. Soc. Amer. Proc. 35:33-38.
- McKeague, J. A. and J. H. Day. 1966. Dithionite and oxalate extractable iron and aluminum as aids in differentiating various classes of soils. Can. J. Soil Sci. 46:13-22.
- McKeague, J. A., F. DeConinck and D. P. Franzmeier. 1983. Spodosols. <u>In</u> L. P. Wilding, N. E. Smeck and G. F. Hail (eds.), Pedogenesis and Soil Taxonomy II. The Soil Orders. Elsevier Science Publishers, Amsterdam. pp217-253.
- McKeague, J. A. and H. Kodama. 1979. Imagolite in cemented horizons of some British Columbia soils. Geoderma 25:189-197.

- McKeague, J. A., G. J. Ross and D. S. Gamble. 1976. Properties, criteria of classification and concepts of genesis of podzolic soils in Canada. In W. C. Mahaney (ed.), Quaternary Soils. Geo. Abstracts, Norwich. pp27-60.
- McKeague, J. A. and P. N. Sprout. 1975. Cemented subsoils (duric horizons) in some soils of British Columbia. Can. J. Soil Sci. 55:189-203.
- McKeague, J. A. and P. C. Stobbe. 1978. History of Soil Survey in Canada 1914-1975. Research Branch Canada Dept. of Agriculture Historical Series #11. 30pp.
- Martin J. P. and K. Haider. 1971. Microbial activity in relation to soil humus formation. Soil Sci. 111:54-63.
- Mattson, S. and Y. Gustafsson. 1937. The laws of soil colloid behavior: XIX The gel and sol complex in soil formation. Soil Sci. 43:453-475.
- Mehra, O. P. and M. L. Jackson. 1960. Iron Oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays and clay minerals 7:317-327.
- Messenger, A. S. 1975. Climate, time and organisms. Soil Sci. Soc. Amer. Proc. 39:698-702.
- Messenger, A. S., J. R. Kline and D. Wilderotter. 1978.
  Aluminum biocycling as a factor in soil change. Plant and Soil 49:703-709.
- Mitchell, B. D. and V. C. Farmer. 1962. Amorphous clay minerals in some Scottish soil profiles. Clay Minerals 5:128-144.
- Moon, D. E. 1981. The genesis of three podzol-like soils occurring over a climatic gradient on Vancouver Island. PhD dissertation, U.B.C. 146pp.
- Morison, C. G. T. and D. b. Sothers. 1914. The solution and precipitation of iron in the formation of iron pan. J. Agric. Sci. 6:84-97.
- Mortensen, J. L. 1963. Complexing of metals by soil organic matter. Soil Sci. Amer. Proc. 27:179-186.
- Muir, A. 1961. The podzol and podzolic soils. Advances in Agronomy 13:1-56.
- National Soil Survey Committee. Proceedings of the meetings in 1965 and 1968.

- Nikleva, S. 1982. Progress report to western LRTAP committee of AES Pacific Region Program Atmospheric Environment Services, Pacific Region, Environment Canada. Report No. PAES 82-6. 5pp.
- Omerod, E. C. and G. Brown. 1978. Deposits found in field drains. Rothamsted Exp. St. Rep. 1977 1:287.
- Parfitt, R. L. 1983. Identification of allophanes in inceptisols and spodosols. Soil Taxonomy News 5:11.
- Petersen, L. 1976. Podzols and Podzolization. Royal Veterinary and Agricultural University, Copenhagen. 293pp.
- Ponomareva, V. V. 1969. Theory of Podzolization biochemical aspects. Israel Program for Scientific Translations, Herusalem. 387pp.
- Ramann, E. 1928. The Evolution and Classification of Soils. Translated by C. L. Whittles. W. Heffer and Sons, Ltd, Cambridge. 128pp.
- Righi, D. 1983. Utilisation du fractionnement des acides fulviques par le polyvinyl pyrrolidone pour la caracterisation des sols acides du Plateau de Millevaches. Science du Sol No. 1:27-36.
- Roddick, J. A. 1965. Vancouver North, Coquitlam and Pitt Lake Map Areas, British Columbia with Special Emphasis on the Evolution of the Plutonic Rocks. Canada, Dept. Mines and Tech. Surveys, Geol. Survey of Canada. Memoir 335. 276pp.
- Rode, A. A. 1970. Podzol-Forming Process. Israel Program for Scientific Translations, Jerusalem. 387pp.
- Ross, G. J. and H. Kodama. 1979. Evidence for imagolite in Canadian soils. Clays and Clay Minerals 27:297-300.
- Russell, E. W. 1973. Soil Conditions and Plant Growth. Longman, London. 849pp.
- Russell, J. D., W. J. McHardy and A. R. Fraser. 1969.

  Imogolite: a unique aluminosilicate. Clay Minerals 8:87-99.
- Schatz, A., N. D. Cheronis, V. Schatz and G. S. Trelawny. 1954. Chelation (sesquestration) as a biological weathering factor in pedogenesis. Pennsylvania Academy of Science 28:44-51.

- Schnitzer, M. 1978. Humic substances: chemistry and reactions. In M. Schnitzer and S. U. Khan (eds.), Soil Organic Matter. pp1-64.
- Schnitzer, M. and W. A. DeLong. 1955. Investigations of the mobilization and transport of iron in forested soils. II. The nature of the reaction of leaf extracts and leachates with iron. Soil Sci. Soc. Amer. Proc. 19:363-368.
- Schnitzer, M. and J. G. Desjardins. 1962. Molecular equivalent weights of the organic matter of a podzol. Soil Sci. Soc. Amer. Proc. 26:363-365.
- Schnitzer, M. and J. D. Desjardins. 1969. Chemical characteristics of a natural soil leachate from a humic podzol. Can. J. Soil Sci. 49:151-158.
- Schnitzer, M. and S. I. M. Skinner. 1963. Organo-metallic interactions in soils: 1. Reactions between a number of metal ions and the organic matter of a podzol Bh horizon. Soil Sci. 96:86-94.
- Schnitzer, M. and S. I. M. Skinner. 1964. Organo-metallic interactions in soils: 3. Properties of iron- and aluminum-organic-matter complexes prepared in the laboratory and extracted from a soil. Soil Sci. 98:197-203.
- Schuppli, P. A. and J. A. McKeague. 1984. Limitations of alkali-extractable organic fractions as bases of soil classification criteria. Can. J. Soil Sci. 64:173-186.
- Singer, M., F. C. Ugolini and J. Zachara. 1978. <u>In situ</u> study of podzolization on tephra and bedrock. Soil Sci. Soc. Amer. Proc. 42:105-111.
- Stevenson, F. J. 1982. Humus Chemistry. Genesis, Composition, Reactions. John Wiley and Sons, New York. 443pp.
- Stobbe, P. C. and J. R. Wright. 1959. Modern concepts of the genesis of podzols. Soil Sci. Soc. Amer. Proc. 23:161-164.
- Tait, J. M., N. Yoshinaga and B. D. Mitchell. 1978. The occurrence of imogolite in some Scottish soils. Soil Sci. Plant Nutr. 24:145-151.
- Thomas, G. W. 1967. Problems encountered in soil testing methods. In Soil Testing and Plant Analysis Part 1. Soil Testing. Soil Sci. Soc. Amer. Special Publication #2:37-54.
- Thomas, G. W. annd W. L. Hargrove. 1984. The chemistry of soil acidity. <u>In</u> F. Adams (ed.), Soil Acidity and Liming, 2nd ed. Agronomy 12:3-56.

- Ugolini, F. C., R. Minden, H. Dawson and J. Zachara. 1977. An example of soil processes in the <u>Abies amabilis</u> zone of central Cascades, Washington. Soil Sci. 124:291-303.
- Van Schuylenborgh and M. G. M. Bruggenwert. 1965. On soil genesis in temperate humid climate. V. The formation of the "albic" and "spodic" horizon. Neth. J. Agric. Sci. 13:267-280.
- Vedy, J. C. and S. Bruchert. 1982. Soil Solution: composition and pedogenic significance. In M. Bonneau and B. Souchier (eds.), Constituents and Properties of Soils. pp184-213.
- Vosburgh, W. C. and G. R. Cooper. 1941. Complex ions. I. The identification of complex ions in solution by spectrophotometric measurements. J. Amer. Chem. Ssoc. 63:437-442.
- Wada, K. 1977. Allophane and imogolite. <u>In</u> J. B. Dixon and S. B. Ween (eds.), Minerals in Soil Environments. Soil Sci. Soc. Amer., Madison, Wisconsin.
- Wada, S. I., A. Eto and K. Wada. 1979. Synthetic allophane and imagolite. J. Soil Sci. 30:347-355.
- Wada, K. and M. E. Harward. 1974. Amorphous clay constituents of soils. Adv. Agron. 26:211-260.
- Wada, K. and T. Higashi. 1976. The categories of aluminum- and iron-humus complexes in Ando soils determined by selective dissolution. J. Soil Sci. 27:357-368.
- Wada, K. and N. Yoshinaga. 1969. The structure of imogolite. Amer. Miner. 54:50-71.
- Wada, K., N. Yoshinaga, H. Yotsumoto, K. Ibe and S. Aida. 1970. Clay Minerals 8:487-489.
- Walker, E. R. 1961. A synoptic climatology for parts of the western Cordillera. McGill Univ. Artic Meteorology Research Group, Meteorological Publication # 35, Science Report #8. 218pp.
- Weaver, R. M., J. K. Syers and M. L. Jackson. 1968.

  Determination of silica in citrate-bicarbonate-dithionite extracts of soil. Soil Sci. Soc. Amer. Proc. 32:497-501.
- Wright, J. R. and M. Schnitzer. 1963. Metallo-organic interactions associated with podzolization. Soil Sci. Soc. Amer. Proc. 27:171-176.

- Wright, J. R., M. Schnitzer and R. Levick. 1958. Some characteristics of the organic matter extracted by dilute inorganic acids from a podzolic B horizon. Can. J. Soil Sci. 38:14-22.
- Yoshinaga, N. and S. Aomine. 1962a. Allophane in some Ando soils. Soil Sci. Plant Nutr. 8:6-13.
- Yoshinaga, N. and S. Aomine. 1962b. Imogolite in some Ando soils. Soil Sci. Plant Nutr. 8:22-29.
- Yoshinaga, N., M. Nakai, T. Minagawa and T. Henmi. 1984. Formation of imogolite and allophane in shattered sandstone underlying brown forest soil. Soil Sci. Plant Nutr. 30:555-567.

Appendix A: Chemical Properties of the soils at the Burke Mountain and Cypress Park Sampling Sites

Profile 1 - Road cut on Burke Mountain

Horizon	Depth	Texture	%C <sub>m</sub>	%N <sub>√</sub>	C/N	<b>%</b> 5		% Fe			% A1			% Si		p!	1	ext	racted	đ
	(cm)		T	T	•		Pyro	Οx	CBD	Pyro	Οx	CBD	Pyro	Ох	CBD	H <sub>2</sub> O	CaCl <sub>2</sub>	Ch/Cf	Ca/Cf	%Ce
LF	10-04	٥.														2	2			
Н	04-00	0	42.29	1.60	26						0.55					3.56	3.03	3.11	0.24	50
Ae	00-02	LS	2.10	0.084	25											3.79	3.29			
Bhf	02-36	SL	5.63	0.180	31		1.60	1.61	1.84	1.64	1.86	1.64	0.14	0.20	0.19	4.60	4.12			
Bf1	36-61	SL	2.55	0.084	30		0.21	0.55	0.54	0.97	1.99	1.23	0.08	0.54	0.20	4.76	4.41			
Bf2	61-89	SL	1.71	0.050	34		0.21	0.59	0.57	0.77	1.24	0.96	0.09	0.29	0.25	4.72	4.56			
Н2	89-95	0	22.02	0.738	30	0.1278	0.77	0.83	0.76	8.72	9.24	8.71	0.62	0.62	0.62	4.73	4.29	0.17	0.74	102
Ccq	95+	FSL	0.60	0.014	42		0.04	0.41	0.44	0.30	0.75	0.32	0.06	0.28	0.00	4.96	5.03			
RC T	44-60	0	25.58	0.928	28	0.1461	1.39	1.54	1.59	8.62	8.99	8.61	0.55	0.60	0.53	4.38	4.31	0.23	0.72	107

- 1. The root channel had the shape of a live branching root and extended from 25 cm to 10cm above the H2 horizon.
- 2. The sampled root channel was 6 cm wide.
- 3. The C horizon was strongly cemented
- 4. The Hl was sampled slightly back from the road cut, in the forest.

Profile 2 - Road cut on Burke Mountain

Horizon	Depth (cm)	Texture	*c <sub>T</sub>	₹N <sub>T</sub>	C/N	%S	Pyro	% Fe Ox		Pyro	% Al	CBD	Pyro	% Si Ox		н <sub>2</sub> о	H CaCl <sub>2</sub>		tracte Ca/Cf	
LFH	25-00	0														_	-			
Ae	00-05	ĹS	1.45	0.062	23											3.54	3.01			
Bhf	05-26	SL		0.327			1.55	1.57	1.67	1.29	1.36	1.23	0.10	0.11	0.15			0.44	0.79	94
Bhf2	26-43	SL		0.195						1.41								•••		
Bf	43-70	SL		0.070						0.85										
Н2	70-73	ō		0.808						8.27								0.21	0.68	97
Cog	73+	FSL	0.56																	
RC	45-65	0	24.92	0.843	30	0.1513	0.75	0.85	0.80	8.63	8.93	8.42	0.80	0.84	0.75	4.47	4.27	0.28	0.74	100

- 1. The profile was a heterogeneous mixture of 60% "red" Bf soil and 40% Bhf material.
  2. In places, the H2 split vertically into two 2 cm horizons separated by 10 cm of Bf matrix.
  3. No suitable H1 horizon was available to sample.
- 4. The root channel was 2 cm wide.

Profile 3 - Road cut on Burke Mountain

Horizon	Depth	Texture	%C <sub>m</sub>	8N_T	C/N	%S		% Fe			% A1			% Si		pl	H	ex	tracte	d
	(cm)		T	Т	,		Pyro	Ох	CBD	Pyro	Ox	CBD	Pyro	Ox	CBD		CaC12	Ch/Cf	Ca/Cf	%Ce
LF	10-05	0																		
H	05-00	0	33.73	1.122	30			0.33			1.05			0.02			3.41			
Ae	00-03	SL	2.74	0.123	22											3.48	2.99			
Bhf	03-10	SL	8.63	0.346	25		1.52	1.59	.1.71	0.59	0.59	0.55	0.05	0.05	0.14	3.58	3.20	0.51	0.75	71
B£1	10-30	SL	3.05	0.113	27		0.16	0.75	0.84	0.96	3.21	1.52	0.07	0.85	0.22	4.83	4.70	0.10	0.63	70
Bf2	30-52	SL	4.95	0.164	30		0.36	0.77	0.82	1.39	2.18	1.70	0.12	0.38	0.20	4.62	4.20			
H2	52-68	0	29.34	0.971	30	0.1529	0.56	0.62	0.66	7.12	7.45	7.03	0.28	0.29	0.24	4.45	4.19	0.39	0.73	81
Bfc	68-92	SĻ	3.92	0.113	35		0.46	0.67	0.84	1.51	2.66	2.00	0.14	0.60	0.35	4.77	4.42			
Ccg	92+	SL	0.79	0.022	35		0.10	0.39	0.35	0.33	0.75	0.38	0.05	0.24	0.08	4.84	4.69			

- Very thick H2 horizon.
   Moderate cementation in the Bfc, strong in the duric horizon.

Profile 4 - Road cut on Burke Mountain

Horizon	Depth (cm)	Texture	&С <sub>Т</sub>	%N <sub>T</sub>	C/N	%S	% Fe Pyro Ox CBD	Pyro	% Al Ox CBD	% Si Pyro Ox CBU	рН Н <sub>2</sub> О CaCl <sub>2</sub>	extracted Ch/Cf Ca/Cf %Ce
LF H Ae	20-05 05-00 00-01	0 0 SL	30.45	0.917	33		1.38		1.19	0.00	3.87 3.38	2.86 0.53 72
Bf1 Bf2 H2 Ccg	01-30 30-71 71-74 74+	SL SL O FSL	3.54 25.68	0.192 0.101 0.850 0.010	35 30	0.1382	1.36 1.40 1.58 0.60 0.72 0.80 2.05 2.09 2.10 0.06 0.30 0.39	1.28 7.40	1.36 1.22 7.76 7.34	0.09 0.12 0.1 0.20 0.24 0.2	5 <b>4.46 4.20</b> 7 <b>4.45 4.16</b>	0.08 0.72 88 0.17 0.73 100

Notes:
1. The Ae was too thin to sample.

Profile 5 - Road cut on Burke Mountain

Horizon	Depth	Texture	%C <sub>m</sub>	%N <sub>m</sub>	C/N	%S		% Fe			% A1			% Si		р	Н	e x	tracte	đ
	(cm)		1	1			Pyro	Ox	CBD	Pyro	Ох	CBD	Pyro	Οx	CBD	H <sub>2</sub> O	CaC1 <sub>2</sub>	Ch/Cf	Ca/Cf	%Ce
LFH	18-00	0																		
Ae	00-04	SL																		
Bf1	04-33	SL	4.58	0.165	28		0.60	0.98	1.11	1.30	3.16	1.77	0.09	0.74	0.22	4.47	4.26			
Bf2	33-91	SL	2.75	0.090	30		0.35	0.39	0.54	1.29	1.50	1.31	0.17	0.25	0.22	4.65	4.53	0.10	0.65	88
Н2	91-99	0	23.89	0.855	28	0.1417	0.99	1.13	1.04	9.45	10.19	9.18	0.78	0.82	0.78	4.46	4.19	0.18	0.69	103
Ccg	99+	FSL	0.42																	
URC1	11-13	0	21.15	0.679	31		1.76	1.75	1.93	6.76	7.03	6.80	0.33	0.33	0.35	4.38	4.20	0.18	0.74	99
LRC1	32-35	0	19.83	0.686	29		0.34	0.34	0.36	8.06	8.18	7.64	0.67	0.73	0.73	4.46	4.34	0.21	0.68	103
RC2	25-28	0	18.97	0.640	30	0.1105	1.13	1.57	1.54	7.80	8.32	7.74	0.88	1.02	0.86	4.43	4.41	0.17	0.65	96

- 1. Two samples were taken from root channel #1 the upper channel (URC) and the lower channel (LRC) to compare the properties of each.
- 2. The Ae and LFH were too high on the road cut to sample.

Profile 6 - Pit in the forest behind profile 5 on Burke Mountain

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	%S	Pyro	% Fe Ox		Pyro	% Al Ox CBD	Pyr	% Si Ox		н <sub>2</sub> о			tracte Ca/Cf	
LF	33-04	0																	
H	04-00	0	47.54	1.877	25						0.23		0.00	)	3.17	2.56	2.86	0.25	55
Ae	00-04	SL	2.25	0.105	21										3.62	3.21			
Bhf	04-05	SL																	
Bfl	05-37	SL	4.01	0.120	33		0.43	0.95	1.01	1.22	3.65 1.8	7 0.0	4 1.06	0.23	4.84	4.58			
Bf2	37-92	LS	4.96	0.166	30		0.47	0.71	0.81	2.16	3.12 2.7	3 0.2	5 0.55	0.45	4.61	4.33		•	
Н2	92-94	0	18.06	0.541	33	0.0998	1.19	1.36	1.34	8.28	8.92 8.3	8 0.8	6 0.93	0.89	4.62	4.38	0.14	0.66	115
Ccg	94+	SL	0.65																
RC	46-49	0	19.35	0.672	29		1.32	1.33	1.45	4.40	4.62 4.4	4 0.1	9 0.22	0.22	4.38	4.05			

- 1. The vast majority of roots were in the litter layer. Very few roots were found in the Bhf and the top of the Bfl.
- 2. Abundant coarse but few fine roots were present in the lower Bfl. Only a few coarse roots were found in the Bf2.
- 3. The Bhf was too thin to sample.

Profile 8 - Road cut on Burke Mountain

Horizon	Depth	Texture	&C_	%N <sub>∞</sub>	C/N	<b>%</b> S		% Fe			% A1			% Si		$\mathbf{p}^{1}$			tracted	
	(cm)		T	ľ			Pyro	Ox	CBD	Pyro	Ox	CBD	Pyro	Ох	CBD	H <sub>2</sub> O	CaCl <sub>2</sub>	Ch/Cf	Ca/Cf	%Ce
LFH	12-00	0																		
Åе	00-03	SL	1.31	0.052	25											3.82	3.57			
Bf1	03-13	SL	4.06	0.137	30		0.50	1.04	1.18	1.53	3.06	2.25	0.16	0.76	0.37	4.63	4.44	0.08	0.69	87
Bf2	13-44	SL	2.66	0.064	28		0.22	0.99	1.09	0.75	2.71	1.30	0.06	0.88	0.22	5.23	4.76			
Bhf	44-65	SL	8.05	0.230	27	0.0458	1.04	1.15	1.19	1.07	1.19	1.02	0.05	0.08	0.13	4.26	3.83	0.53	0.75	80
Bf3	65-85	SL	4.10	0.155	26		0.30	0.66	0.74	1.48	3.05	2.29	0.12	0.70	0.37	4.61	4.54	0.12	0.61	91
Н2	85-87	0	18.13				0.98	1.07	0.96	7.85	9.70	8.54	1.05	1.62	1.42	4.75	4.45			
BC	97+	ST.																		

- 1. The soil would be classified as a Ferro-humic podzol although the Bhf horizon was not directly beneath the Ae.
- 2. There were abundant coarse and plentiful fine roots in the Bhf. This horizon may actually have been a root mat forming over the partially cemented Bf3.
- 3. The structure is partially cemented throughout the profile.

Profile 9 - In the forest, 10 m behind profile 3

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	ъN <sub>Т</sub>	C/N	<b>%</b> S	Pyro	% Fe Ox	CBD	Pyro	% Al Ox CBD	Pyro	% Si Ox		н <sub>2</sub> о		extract Ch/Cf Ca/	
LF	05- 03	0																
H	03- 0	0	49.23															
Аe	00- 01	SL																
Bf1	01- 31	SL	4.95	0.212	23		1.14	1.70	2.02	1.51	2.90 2.0	2 0.14	0.63	0.28	4.57	4.33		
Bf2	31-62	SL	3.07	0.112	27		0.38	0.79	1.09	1.02	2.12 1.3	4 0.06	0.48	0.19	4.72	4.49		
Bf3	62-100	SL	4.12	0.136	30		0.91	1.08	1.27	1.92	2.21 2.1	2 0.20	0.31	0.29	4.63	4.33		
Bf4	100-140	SL	4.17	0.129	33		0.83	1.00	1.04	1.98	2.35 2.1	2 0.22	0.29	0.33	4.70	4.39		
Bhf*	140-142	SL	13.41	0.438	31			1.07			8.00		2.00	)				
Cc	142+	SL									•							
RC	61- 63	0	20.75	0.815	25		3.43	3.31		6.68	6.82	0.25	0.26	i	4.55	4.23		

- 1. Water seeped quickly into the bottom of the pit making the Bhf\* very difficult to sample.
- 2. There were many dead, decomposing coarse roots in the Bf3 and Bf4 but no live roots.
- There were plentiful medium and coarse roots in the LFH, Ae, and Bfl, few to very few roots in the Bf2.

Profile 10 - Road cut on Burke Mountain

Horizon	Depth (cm)	Texture	&CT	%N <sub>T</sub>	C/N	<b>%</b> S	Pyro	% Fe Ox		Pyro	% Al Ox	CBD	Pyro	% Si Ox		р! Н <sub>2</sub> 0	H CaCl <sub>2</sub>		tracted Ca/Cf	
LF H Ae	10-04 04-00 00-02	0 0 st	48.66																	
Bhf Bf Bhf2	02-07 07-12 12-40 40-70	SL SL SL SL	4.37 6.99	0.234	34		0.87 0.92	1.03 1.04	1.91 1.21 1.26 0.78	1.18 2.54	1.86 2.91	1.63 2.61	0.10 0.32	0.38	0.19 0.35 0.46	4.50 4.46	4.17 4.29	0.20	0.70	79
Bfg H2 Ccg	70-74 74+	O SL	17.30	0.665	26		1.91	1.73	1.63	5.27	10.52	7.23	0.18	2.19	0.94	4.81	4.44			
URC1 LRC2	15-17 34-37	SL O		0.447 0.672	34 28	0.0861 0.1363	1.83 1.32		2.00 1.74		5.42 7.69		0.50 0.81		0.61		4.27 4.28	0.20	0.68	85

- 1. The upper 40 cm of the profile was very blotchy with the Bf and Bhf material actually too intermixed to sample separately.
- 2. The upper root channel runs into the profile within a matrix of Bf material.
- 3. The lower root channel runs across the profile.

Profile 11 - Cypress Park, forest near downhill ski parking lot

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	%S	Pyro	% Fe Ox	CBD	Pyro	% Al Ox CBD	% Si Pyro Ox CBD	H <sub>2</sub> O CaCl <sub>2</sub>	ext: Ch/Cf (	racted Ca/Cf	d ∜Ce
LF H Ae	30-05 05-00 00-05	0 0 SL		1.284 0.135							1.23	0.00	3.57 3.14 3.91 3.53	2.06	0.44	56
Bhf1 Bhf2 Bhf3* Bf	05-24 24-30 30-42 42+	SL SL SL	6.75 9.86 13.42	0.240 0.433	28 23 23	0.0824	0.96 0.82	1.38 0.94	1.81 1.44	1.91 2.17	7.26 3.34 8.01 3.55	0.07 1.50 0.28 0.10 2.30 0.31 0.10 2.65 0.23 0.06 1.37 0.15	4.77 4.54 4.89 4.68 4.99 4.75	0.34 (	0.49 0.53	65 61

- 1. Many decomposing root remains were still visible in the Bhf3\*, only very few fine roots were alive in this horizon at the present time.
- 2. The Bhf2 looked actually to be a gradual transition from the Bhf1 with little root remains to the Bhf3\*.
- 3. Some of the root channels in the Bhf3 and the few present in the Bf were the red of decomposing wood.
- 4. There were many gravels and cobbles present in the Bf. The roots seemed to have grown over these.

Profiles 12 and 13 - Cypress Park, Bhf horizons with no underlying root mat

Horizon	Depth	Texture	%C_	%N.π	C/N	₹S		% Fe			% A1			% Si		q	H	e x l	racted	đ
Horizon	(cm)		1	1			Pyro	Ox	CBD	Pyro	Оx	CBD	Pyro	Ох	CBD	н <sub>2</sub> о	CaC12	Ch/Cf	Ca/Cf	%Ce
12 Bhf	04-13	SL	6.53	0.238	27		0.62	0.78	1.36	0.97	1.07	0.98	0.10	0.12	0.09	4.12	3.71	0.64	0.79	82
13 Bhf	03-13	SL	5.31	0.314	17		0.11	0.13	0.25	1.09	4.16	1.57	0.08	1.43	0.22	5.16	4.57	0.48	0.69	71

1. Both profiles had abundant roots in the LFH but few roots in the underlying mineral soil.

Profile 14 - Cypress Park, near profile 11

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	%S		% Fe Ox	CBD	Pyro	% Al Ox CBD	% Si Pyro Ox CBD	pH H <sub>2</sub> O CaCl <sub>2</sub>	extracted Ch/Cf Ca/Cf %0	Ce
LFH	30-00	0													
Ae	00-03	SL	9.12	0.315	29								3.68 3.30		
Bhf	03-20	SL	7.19	0.232	31		0.73	1.15	1.52	1.89	4.07 2.72	0.07 0.80 0.33	4.61 4.21		
B£	20-41	SL	2.88	0.104	28		0.28	0.64	0.98	0.79	3.31 1.33	0.06 1.15 0.21	4.83 4.80		
Bhf2*	41-46	SL	12.23	0.564	22	0.0804	0.23	0.26	0.43	1.90	8.84 3.10	0.08 3.15 0.23	5.16 4.91	0.11 0.58	66
Cc	46+	SL													
RC	20-41	0	18.52	0.628	29			1.93			8.27	2.40			

- Found the Bhf2 by following a root channel within the "firm" Bf. This led directly to the root mat.
   Bf seemed slightly cemented.
   Abundant roots in the LFH, only a few in the Bhf, none below 20 cm.
   Root channel was 1.5 cm wide.

Profile 15 - Cypress Park, .5 km east of profiles 11 and 14

Horizon	Depth (cm)	Texture	${^{\boldsymbol{\mathcal{g}}}}^{\mathbf{T}}$	<b>%</b> N <sub>Т</sub>	C/N	<b>%</b> S		% Fe Ox	CBD	Pyro	% Al Ox	CBD		% Si Ox		рі Н <sub>2</sub> о	H CaCl <sub>2</sub>		tracted Ca/Cf	
LFH Ae Bhfl Bf Bhf2* Cc	32-00 00-03 03-23 23-40 40-41 41+	O SL SL SL SL	2.94	0.280 0.141 0.597	21		0.17	0.31	0.58	0.74	2.84 3.47 8.88	1.22	0.06	1.32	0.19	5.12		0.29	0.73	83

- 1. The Bhf2\* contained no live roots but many root remains (outer bark, etc.) and white fungal mycelia.
- 2. The Bhfl and Bf contained many decomposing root channels, some were quite large in the Bfl.
- 3. There were abundant live roots in the LFH, none in the Ae or Bf, few, fine in the Bhfl.

Profile 16 - Road Cut on Burke Mountain

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	°вN <sub>Т</sub>	C/N	₹S	% F Pyro Ox		Pyro	% Al Ox CBD	% Si Pyro Ox CBD	рН Н <sub>2</sub> О СаС1 <sub>2</sub>	extracted Ch/Cf Ca/Cf %Ce
LFH Ae Bhfl Bhf2	20-00 00-01 01-14 14-53	O SL SL	6.15	0.498	26		2.96 2.9	8 3.27	1.48	1.57 1.42	0.12 0.10 0.21 0.09 0.07 0.14	4.48 4.20	
Bf Ccg RC	53-94 94+ 46-54	LS FSL O		0.078	-	0.1032					0.14 0.27 0.28 0.26 0.22 0.39		0.26 0.61 61

- 1. There was a very thin root mat at contact with Ccg (not samplable).
- Many small decomposing root channels were present in the Bhfl and Bhf2. Can identify "gross" root morphology.
- 3. The colour of the root channels were "brick" red and black.

Profile 17 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth	Texture	%С <sub>Т</sub>	%N <sub>T</sub>	C/N	%S		% Fe		_	% A1	_	% Si		р	н		racted	
	(cm)		-	_			Pyro	Ox	CBD	Pyro	Ox CBD	Pyro	Ох	CBD	H <sub>2</sub> O	CaCl <sub>2</sub>	Ch/Ct	Ca/CI	₹Ce
LF	20-10	0																	
H	10-00	0	50.54					0.17			0.25		0.00		3.44	2.86			
Ae	00-01	SL																	
Bhfl	01-13	SL	7.51	0.302	25		1.15	1.24	1.36	1.79	1.96 1.70	0.16	0.21	0.22	4.14	3.83			
Bhf2	13-44	SL	6.70	0.225	31		0.91	0.95	1.16	2.03	2.22 2.11	0.17	0.22	0.26	4.44	4.14	0.25	0.69	84
Н2	44-45	0	25.51	1.562	16		0.77	0.79	0.84	4.07	4.17 3.90	0.10	0.07	0.15	4.37	4.02			
Bhf3	45-76	SL	6.44	0.215	30		0.73	0.76	0.98	1.41	1.47 1.34	0.07	0.07	0.14	4.30	4.10			
н3	76-80	0	24.77	0.850	27	0.1339	1.59	1.69	1.65	6.43	6.43 5.88	0.19	0.20	0.20	4.28	4.01	0.30	0.78	99
Bfc	80+	LS	3.82	0.125	31		0.50	0.61	0.68	1.39	1.44 1.28	0.09	0.17	0.16	4.66	4.18			

- 1. Abundant roots in the LFH, plentiful coarse roots in the Bhfl and Bhf2. Few fine roots in H2 and only very few below.
- 2. Cedar codominant with hemlock.

Profile 18 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth	Texture	%C_	%N_	C/N	<b>%</b> S		% Fe			% Al			% Si		p	H	ex	tracted	3
	(cm)		Т	Т	·		Pyro	Ox	CBD	Pyro	Ox CB	D Py	yro	Ox	CBD	н20	CaCl <sub>2</sub>	Ch/Cf	Ca/Cf	<b>%</b> Се
LF	37-23	0																		
Н	23-00	0	38.95	1.814	21						4.00			0.00		4.20	3.77	0.88	0.68	73
Bh f l	00-19	SL	5.68	0.253	22		0.76	0.80	1.02	1.35	1.43 1.	35 0.	.12	0.15	0.19	4.37	3.88	0.34	0.74	86
Bhf2	19-41	SL	6.27	0.268	23		0.69	0.72	0.91	1.55	1.70 1.	53 0.	.17	0.19	0.16	4.28	3.85			
H2	41-42	0	23.92	0.923	26	0.1340	0.99	1.05	1.07	3.81	4.05 3.	61 0.	.08	0.08	0.13	4.16	3.87			
Bhf3	42-71	SL	5.97	0.234	26		0.56	0.66	0.81	1.65	1.90 1.	68 0.	.20	0.25	0.23	4.25	3.95			
Bh £ 4	71-79	SL	5.70	0.220	26		0.46	0.55	0.70	1.60	1.89 1.	77 0.	.12	0.21	0.20	4.38	4.12			
Bfc	79+	LS	3.10	0.085	36		0.21	0.44	0.50	1.18	1.68 1.	36 0.	.10	0.29	0.17	4.42	4.24			

- 1. Some remains of undecomposed dead roots in H2 and near bottom of the pit.
- 2. Very thick, black Hl, (unusual compared to previous pits).
- 3. Abundant roots in LFH, plentiful, medium but only few fine roots in Bhfl and Bhf2, few to very few below.
- 4. Bhf3 and Bhf4 had many root channels in a mineral matrix, but they were too small to sample separately.

Profile 19 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	%S	Pyro	% Fe Ox	CBD			CBD		% Si Ox		р: Н <sub>2</sub> О	H CaCl <sub>2</sub>		tracte Ca/Cf	
																2	2			
LF	31-25	0																		
Н	25-00	0	33.72	1.201	28			1.55			4.90			0.02		4.29	3.87	0.60	0.72	69
Bhfl	00-11	SL	5.29	0.208	25		0.67	0.71	0.97	1.28	1.36	1.29	0.06	0.13	0.10	4.24	3.93			
Bhf2	11-32	SL		0.185			0.65	0.61	0.86	1.33	1.34	1.32	0.10	0.12	0.14	4.22	3.96			
						0.1067				4.33								0.30	0.01	0.6
Н2	32-46	. 0	20.00	0.003	31	0.1007									-			0.30	0.01	86
В£	46-55	SL	4.27	0.128	33		0.48	0.55	0.66	1.28	1.31	1.16	0.09	0.10	0.11	4.34	4.07			
н3	55-63	0	28.62	0.813	35	0.1346	1.30	1.45	1.45	7.92	8.67	8.01	0.13	0.16	0.16	4.28	3.92	0.14	0.80	100
Bfc	63+	LS	3.67	0.117	31		0.35	0.45	0.54	1.25	1.28	1.14	0.08	0.10	0.10	4.57	4.11			

- 1. Abundant roots in LFH, plentiful, medium but very few fine roots in Bhfl, very few roots below Bhfl.
- One root channel continues from the surface to the H2.
   The H1 is very thick and black.

Profile 20 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth	Texture	%C_	%N	C/N	<b>%</b> S		% Fe			% A1			% Si		p			tracted	
	(cm)		ľ	1			Pyro	Οx	CBD	Pyro	Ox	CBD	Pyro	Ox	CBD	H <sub>2</sub> O	CaCl	Ch/Cf	Ca/Cf	%Сe
LF	44-15	0					-			_						2	2			
H	15-00	0	34.67					0.27			1.95			0.00		4.17	3.57			
Bhfl	00-15	SL	6.07	0.224	27		0.56	0.59	0.74	1.30	1.43	1.31	0.11	0.16	0.17	4.32	3.95	0.38	0.77	80
Bhf2	15-45	SL	8.60	0.330	26		0.67	0.78	0.99	2.08	2.06	2.18	0.13	0.18	0.16	4.36	3.92			
Bhf3*	45-47	SL	16.43	0.609	27		0.91	0.97	1.07	5.05	4.98	5.02	0.20	0.23	0.27	4.21	3.99			
Bf	47-75	SL	4.78	0.130	37		0.38	0.48	0.60	1.70	1.95	1.76	0.15	0.22	0.21	4.26	4.27			
H2	75-78	0	21.44	0.549	39	0.1028	1.37	1.61	1.69	8.87	9.36	9.05	0.96	1.04	0.97	4.42	4.14			
Bfc	78+	SL																		

- Can see veins of mineral in Bhf3\*.
- 2. There is seepage at the bottom of the pit above the Bfc.
- 3. Bf had small root channels and many cobbles. Bhf3\* sits along top of cobbles.
- 4. Abundant roots in LFH, abundant coarse and medium roots in Bhf1 and Bhf2, few to very few roots below.

Profile 21 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth	Texture	8C_	%N <sub>m</sub>	C/N	%S		% Fe			% Al			% Si		p	Н	ex	tracted	đ	
	(cm)		1	1	-		Pyro	Оx	CBD	Pyro	Ox	CBD	Pyro	Ox	CBD	H20	CaCl	Ch/Cf	Ca/Cf	%Ce	
LF	07-05	0														2	2				
H	05-00	0	46.74					0.14			0.28			0.00		3.43	2.87				
Bhfl	00-26	SL	7.83	0.309	25		0.74	0.74	0.93	1.29	1.39	1.24	0.07	0.08	0.15	4.31	3.92	0.47	0.77	73	
Bhf2	26-57	SL	7.04	0.230	31		0.80	0.90	1.08	2.01	2.30	2.08	0.14	0.19	0.21	4.33	3.95				
H2	57-60	0	26.47	0.866	31	0.1442											3.91			90	
Bhf3	60-88	SL	8.53	0.276	31		0.66	0.70	0.84	2.42	2.67	2.48	0.15	0.18	0.20	4.27	4.05	0.16	0.79	93	
Bh £4	88-90	L	9.07	0.282	32		0.42	0.45	0.54	3.19	3.41	3.14	0.17	0.22	0.23	4.45	4.10				
Bfc	90+	SL	1.86	0.051	37		0.11	0.37	0.29	0.76	0.88	0.70	0.08	0.14	0.11						

- 1. Found a piece of coarse, dead root at 35cm which extended to the duric horizon.
- 2. Abundant roots in LFH and Bhfl, very few fine roots in Bhf2.

Profile 22 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth	Texture	%C_	%N_m	C/N	<b>%</b> S		% Fe						% Si		р		extracted
	(cm)		1	1			Pyro	Оx	CBD	Pyro	Ox	CBD	Pyro	Οx	CBD	H20	CaCl,	Ch/Cf Ca/Cf %Ce
LF	32-26	0														2	2	
H	26-00	0	34.83	1.650	21			0.89			3.07			0.00		4.29	4.00	
Bh £ l	00-09	SL	7.97	0.340	23		0.73	1.02	1.08	2.25	2.70	2.53	0.18	0.40	0.28	4.53	4.28	
Bf1	9-30	SL	4.28	0.138	31		0.27	0.51	0.53	1.70	1.78	1.81	0.16	0.25	0.21	4.76	4.43	
B£2	30-39	SL	2.08	0.062	34		0.21	0.41	0.42	1.00	1.25	1.06	0.15	0.26	0.20	4.71	4.42	
Bhf2*	39-40	SL	15.61	0.589	27		0.76	0.88	0.85	8.21	8.28	8.22	0.92	1.10	0.90	4.51	4.25	
Cc	40+	SL	0.93	0.019	48		0.06	0.43	0.29	0.46	0.67	0.52	0.07	0.18	0.12	5.26		

- 1. Small root channels throughout B horizons.
- 2. The upper horizons looked churned in part of the profile.
- 3. Abundant coarse and medium roots in Bhf, few, medium and very few fine roots in Bfl.
- 4. Thick, black H1. A section of the upper profile appeared churned.

Profile 23 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth (cm)	Texture	$^{\$C}_{\mathbf{T}}$	%N <sub>T</sub>	C/N	%S		% Fe Ox		Pyro	% Al Ox			% Si Ox		р Н <sub>2</sub> 0	H CaCl		tracted Ca/Cf	
LF	17-12	0					-			_			_			2	Z			
H	12-00	0																		
Аe	00-02	SL	2.11	0.115	18															
Bhfl	02-17	SL	8.33	0.321	26		1.80	1.99	1.93	0.98	0.99	0.90	0.08	0.06	0.10	4.03	3.60			
Bhf2	17-46	SL	6.36	0.237	27		0.66	0.74	0.88	1.59	1.68	1.57	0.11	0.14	0.14	4.57	3.92			
Bhf3*	46-52	SL	12.84	0.491	26		0.86	0.91	1.05	2.38	2.61	2.49	0.12	0.14	0.17	4.40	3.92	0.38	0.77	86
Bhf4	52-77	SL	6.03	0.223	27		0.50	0.57	0.65	1.83	1.78	1.72	0.15	0.21	0.22	4.35	3.98			
Н2	77-79	0	21.91	0.700	31		0.79	0.83	0.82	5.84	6.20	6.04	0.24	0.27	0.27	4.40	3.99			
Cc	79+	SL	1.05	0.026	39		0.08	0.44	0.29	0.48	0.73	0.52	0.06	0.23	0.14	5.17	4.66			
													- 1							

- 1. Bhf3\* appeared closer to an F than an H in state of decomposition, (not greasy).
- 2. Abundant medium and few fine roots to the Bhf3\*. Pit was close to trees.
- 3. The H1 horizon was 22 cm deep on one side of the pit, extending down into the mineral soil.

Profile 24 - Pit in the forest on the east side of the Burke Mountain road cut

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	<b>%</b> S		% Fe Ox C	BĎ !	Pyro	% Al Ox			% Si Ox		р1 Н <sub>2</sub> О	H CaCl		tracted Ca/Cf	
LF	27-18	0					-			-			-			2	2			
H	18-00	0	36.95	1.623	23	0.1948		0.47			3.68			0.01		4.11	3.64			
Аe	00-02	SL																		
Bhf	02-21	L	8.11	0.262	31		1.23	1.24 1	.47	1.61	1.68	1.48	0.09	0.09	0.12	4.58	4.07	0.29	0.66	69
Bfl	21-56	SL	4.80	0.164	29		0.59	0.64 0	.86	2.15	2.30	2.01	0.20	0.24	0.24	4.53	4.38			
Bf2	56-72	SL	2.48	0.085	29		0.38	0.44 0	.69	0.97	1.62	1.23	0.07	0.35	0.24	4.82	4.49			
C	72+	SL	0.52	0.016	32		0.06	0.32 0	.38	0.24	0.66	0.29	0.06	0.20	0.04	5.08	4.66			
RC1	18-19	SL	16.38	0.540	30		1.57	1.78 1	.86	6.82	6.91	6.89	0.46	0.52	0.50	4.58	4.24			
RC2	30-56	SL	16.38	0.619	26	0.0894	1.23	1.28 1	.44	4.34	4.36	4.43	0.13	0.15	0.23	4.56	4.12			
RC3	66-69	0	18.39	0.668	28		1.01	1.15 1	.20 1	0.03	10.39	9.84	1.40	1.59	1.29	4.60	4.37			

- 1. Many small root channels throughout that were too small to separate from the mineral soil.
- 2. Abundant roots in LFH, abundant medium, very few fine roots in Bhf, only few, medium roots below.
- 3. C horizon was not cemented and no organic layer was found above it.
- 4. RCl lies horizontally, RC2 branches at its base and has the gross morphology of a root.
- 5. Charcoal was obvious in Hl and RC1.

profile 25 - Pit in the forest on the west side of the Burke Mountain road cut

Horizon	Depth (cm)	Texture	&C <sup>™</sup>	$\mathbf{T}^{N\mathscr{E}}$	C/N	%S Pyro	% Fe Ox	CBD	Pyro	% Al Ox	CBD	Pyro	% Si Ox		р Н <sub>2</sub> О	H CaCl <sub>a</sub>		tracte Ca/Cf	
LF	21-16	0													2	2			
H	16-00	0	47.22				0.20			0.23			0.00		3.40				
Ae	00-01	SL																	
Bfc1	01-22	SL	4.29	0.133	32	1.27	2.24	1.97	1.48	2.24	1.97	0.13	0.37	0.31	4.78	4.27	0.12	0.62	71
Bfc2	22-42	SL	2.17	0.071	30	0.14	0.71	0.94	0.78	3.01	1.24	0.04	0.95	0.15	4.93	4.87			
В£	42-64	SL	2.36	0.077	30	0.28	0.49	0.68	0.87	1.12	1.05	0.09	0.23	0.25	4.59	4.59			
Bfc3	64-78	SL	3.50	0.116	30	0.38	0.83	0.97	1.64	2.67	2.05	0.17	0.51	0.35	4.70	4.44			
Н2	78-85	0	19.03	0.737	26	1.16	1.28	1.29	8.36	8.33	8.26	0.72	0.84	0.68	4.36	4.29	0.18	0.67	107
Bfc4	85+	SL	1.11	0.033	33	0.14	0.42	0.29	0.57	0.67	0.56	0.07	0.15	0.15	5.35	4.62			
RC	42-45	0	17.93	0.566	32		0.84			6.31			0.41						

- 1. Many small root channels throughout that were too small to separate from the mineral soil.
  - 2. Bfc1 and Bfc3 were very "red" (7.5YR 4/4). They resembled an Ortstein.
  - 3. Bfc4 is the duric horizon.
  - 4. All horizons but the Ae, Bf and H2 are weakly cemented.
  - 5. Abundant roots in LPH and Bfcl, plentiful medium roots in the Bfc2 and Bfc3, only few, fine roots in H2.

Profile 26 - Pit in the forest on the west side of the Burke Mountain road cut

Horizon	Depth	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	<b>%</b> S	% Fe	% A1	% Si	рН	extracted
	(cm)		•	•			Pyro Ox CBD	Pyro Ox CBD	Pyro Ox CBD	H <sub>2</sub> O CaCl <sub>2</sub>	Ch/Cf Ca/Cf %Ce
LF	33-14	0								2 2	
H	14-00	0	49.67				0.14	0.32	0.00	3.14	
Аe	00-03	SŁ	3.24	0.103	31					4.25 3.85	
Bh <b>f l</b>	03-26	SL	7.53	0.283	27		1.47 1.55 1.60	1.74 1.77 1.63	0.06 0.09 0.15	4.37 3.92	0.26 0.76 90
Bhf2	26-46	SL	8.45	0.323	26		0.84 0.91 1.10	2.27 2.39 2.28	0.15 0.16 0.18	4.49 3.97	0.24 0.75 95
Bhf3*	46-56	SL	15.24	0.603	25		0.89 1.04 1.17	3.98 4.23 3.91	0.27 0.31 0.26	4.52 3.98	0.30 0.77 92
Bf	56-86	SL	3.36	0.107	32		0.32 0.46 0.53	1.52 1.77 1.66	0.18 0.31 0.29	4.56 4.33	
H2	86-92	0	21.83	0.693	31	0,1299	0.91 0.99 1.00	9.74 10.01 9.36	1.18 1.21 1.13	4.56 4.32	
Cc	92+	SL	1.15	0.029	39		0.21	0.67	0.18		
RC	63-66	0	19.54	0.790	25	0.1129	0.74 0.85 0.92	5.16 5.52 5.24	0.30 0.33 0.30	4.53 4.00	0.26 0.79 96

- 1. Bf horizon was slightly cemented.
- 2. Abundant roots in LFH, plentiful medium and coarse roots in Bhfl, plentiful fine and very fine roots in Bhf3\* but no roots below.
- 3. RC and Bhf3\* organic matter is composed of many fine, broken decomposed roots that give a granular appearance to the organic matter.

Profile 27 - Pit in the forest on the west side of the Burke Mountain road cut

Horizon	Depth	Texture	%C <sub>m</sub>	%N <sub>T</sub> .	C/N	<b>%</b> S		% Fe			% Al			% Si		pl	H	ex	tracted	Ė
	(cm)		1	1			Pyro	Ox	CBD	Pyro	Ox	CBD	Pyro	Оx	CBD	H <sub>2</sub> O	CaCl,	Ch/Cf	Ca/Cf	%Се
LF	33-20	0														_	-			
H	20-00	0	44.64	1.690	26						0.48			0.00		3.27	2.74	4.71	0.25	57
Ae	00-03	SL	1.53	0.080	19											3.51	3.06			
Bh f	03-20	SL	6.01	0.239	25		1.65	1.77	1.96	1.00	1.03	1.00	0.07	0.05	0.11	4.24	3.75			
Bf1	20-42	SL	4.57	0.183	25		0.91	1.40	1.52	1.49	3.02	2.09	0.14	0.82	0.28	4.64	4.25			
Bf2	42-77	SL	3.51	0.116	30		0.48	0.69	0.79	1.55	2.05	1.75	0.17	0.35	0.29	4.61	4.38			
H2	77-80	0	17.98	0.701	26		0.59	0.63	0.61	8.52	8.59	8.00	0.45	0.51	0.46	4.48	4.38			
Cc	80+	SL	0.86	0.022	39		0.16	0.32	0.34	0.41	0.55	0.42	0.05	0.12	0.11	5.22	4.71			
RC1	42-45	0	19.03	0.781	24		2.21	2.21	2.23	4.50	4.60	4.45	0.14	0.15	0.18	4.51	4.14			
RC2	30-35	0	20.75	0.973	21	0.1367	1.75	1.74	1.90	3.74	3.94	3.69	0.07	0.09	0.11	4.41	4.00			

- 1. There were many small root channels in the Bfl and Bf2 but could not separate these from the organic-poor matrix.
- RC1 is 8 cm wide and extends back into the profile. It contains no live roots, has a massive structure and is greasy.
- 3. The RC2 sits over a rock. It contains many fine roots and is granular in appearance (because of broken pieces of fine roots).

Profile 28 - Pit in the forest on the west side of the Burke Mountain road cut

Horizon	Depth	Texture	%C_	%N_	C/N	<b>%</b> S	% Fe Pyro Ox CBD F					% A]	L			% Si		P	H		tracte	
	(cm)		Т	Т	·		ro	Ox	C	BD	Pyro	Οx	СВ	3D	Pyro	Ox	CBD	H <sub>2</sub> O	CaCl <sub>2</sub>	Ch/Cf	Ca/Cf	%Се
LF	20-08																					
Н	08-00	0	43.26	1.679	26			0.11	Ĺ			0.44	1			0.00		3.35	2.86			
Ae	00-03	SL	1.65	0.089	19													3.70	3.17			
Bhf	03-22	SL	6.79	0.261	26	1.	. 24	1.49	) ]	.64	1.89	2.13	3 2.	.08	0.17	0.35	0.33	4.40	4.03			
Bhf2	22-52	SL	5.93	0.256	23	0.	.98	1.04	1	.29	1.51	1.6	11.	. 45	0.13	0.14	0.22	4.38	3.94	0.30	0.73	92
н2	52-55	0	23.32	0.976	24	2.	.26	2.28	3 2	2.16	5.84	5.92	2 5.	.88	0.23	0.22	0.25	4.26	3.95			
Bhf3	55-92	SL	6.47	0.214	30	0.	.59	0.69	0	.84	2.54	3.06	5 2.	.72	0.29	0.37	0.43	4.44	4.07			
Cc	92+	SL																				
RC	36-45	0	24.72	1.360	18	4.	.60	4.32	2		4.87	4.90	4.	.88	0.07	0.07	0.13					

- 1. The root channel is 6 cm wide and sits obliquely.
- 2. The Bhf was very "red" (5 YR 3/3).
- 3. There were abundant medium, plentiful coarse roots to the Bhf2, but very few fine roots.
- 4. There were no roots in the H2 or below.

Profile 29 - Pit in the forest on the west side of the Burke Mountain road cut

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	%N <sub>T</sub>	C/N	<b>%</b> S	Pyro	% Fe Ox	CBD	Pyro	% Al Ox	CBD	Pyro	% Si Ox		р Н <sub>2</sub> О	H CaCl		tracte Ca/Cf	
LF	37-10	0					•			=			=			2	2			
H	10-00	0	40.53	1.974	21			0.25			1.25			0.00		3.53	3.05			
Ae	00-02	SL	2.43	0.099	24											3.75				
Bhfl	02-30	SĽ	7.21	0.297	24		1.11	1.23	1.27	1.22	1.28	1.20	0.11	0.11	0.13	4.16	3.70	0.36	0.78	86
Bh£2	30-55	SL	6.04	0.237	25		0.79	0.85	0.98	1.72	1.89	1.69	0.10	0.14	0.17	4.48	4.07	0.22	0.74	99
Bhf3	55-69	SL	6.37	0.207	31		0.60	0.65	0.80	2.05	2.19	1.96	0.13	0.17	0.18	4.44	4.12			
H2	69-82	0	23.14	0.777	30	0.1298	1.15	1.32	1.33	6.46	6.74	6.58	0.19	0.20	0.19	4.61	4.16	0.24	0.75	98
BC	82+	SL					0.18	0.32	0.40	1.02	1.44	1.18	0.06	0.30	0.28	4.90	4.31			

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- 1. There were many small root channels in the Bhf1, Bhf2 and Bhf3
- 2. There were abundant coarse and medium roots in the Bhfl, few medium roots in the Bhf2, very few fine roots in the H2.

Profile 30 - Pit in the forest on the west side of the Burke Mountain road cut

Horizon	Depth (cm)	Texture	$C_{\mathrm{T}}$	%N <sub>T</sub>	C/N %S	Pyro	% Fe	CBD	Pyro	% Al Ox CBD	Pyro	% Si Ox			H CaCl <sub>2</sub>		tracted Ca/Cf	
LF	35-14	0				•			•		•			2	2			
H	14-00	0	51.30				0.11			0.21		0.00		3.45	2.96			
Аe	00-01	SL																
Bhf1	01-24	SL	7.97			1.14	1.30	1.41	1.03	1.05 0.97	0.09	0.09	0.14	4.25	3.75			
В£	24-58	SL	4.28			0.87	0.84	1.03	0.91	0.94 0.87	0.11	0.10	0.13	4.49	4.02			
Н2	58-90	0	31.30		0.189	6 3.70	3.70	3.54	5.57	5.67 5.53	0.09	0.10	0.11	4.55	4.01	0.38	0.74	81
Bhf2	90+	SL																
RC	47-53	0	28.73	1.611	0.222	6 5.05	4.63	4.25	5.42	5.56 5.29	0.04	0.02	0.06	4.32	3.96			

- 1. The H2 horizon is very deep and it extends down between 40% cobbles in Bhf2.
- 2. Found three pieces of coarse dead roots at approximately 50-60 cm, lying obliquely in the pit.
- 3. Remnants of good coarse root structure found in the H2.

Profile 31 - Pit in the forest near the beginning of the Burke Mountain road, elevation 320 m

Horizon	Depth (cm)	Texture	%C <sub>T</sub>	T <sup>N\$</sup>	C/N	%S	% Pyro	Fe Ox	CBD		Al Ox	CBD	% Pyro	Si Ox	CBD	рН Н <sub>о</sub> О	CaCl,		tracted Ca/Cf	
LFH	09-00	0														2	2			
Аe	00-05	SL	1.00	0.03	6 28											4.58	4.08			
Bf1	05-26	LS	4.14	0.18	7 22					1.04										
Bf2	26-49	LS	2.60	0.12	7 20					0.59										
Bf3	49-77	LS	2.58	0.13	3 19		0.15	0.85	1.34	0.64	3.12	1.27	0.04	1.23	0.18	5.25	5.00	0.13	0.59	56
Bf4	77-97	SL	3.61	0.17	7 20		0.31	2.07	2.45	0.92	4.44	1.88	0.04	1.41	0.14	5.19	4.82			
Bfg	97+	LS	1.97	0.07	7 26		0.29	1.25	1.52	0.58	2.39	1.06	0.06	0.79	0.13	5.34	4.93			

- 1. Plentiful roots to bottom of Bf3.
- 2. The Bf4 is redder and finer texture than the overlying horizons (5YR 3/3).
- 3. There was seepage water coming in quickly at 97 cm, above uncemented but compact basal till.
- 4. The Bfl was partially cemented.

Profile 32 - Pit in the forest near the beginning of the Burke Mountain road, elevation 320 m

Horizon	Depth	Texture	%C <sub>m</sub>	%N <sub></sub>	C/N	%S		% Fe			% A1			% Si		р		extracted
	(cm)		1	1			Pyro	Оx	CBD	Pyro	Ox	CBD	Pyro	Оx	CBD	H <sub>2</sub> O	CaCl <sub>2</sub>	Ch/Cf Ca/Cf %Ce
LFH	10-00	0					-			=						2	2	
Ae	00-03	SL	0.93	0.049	19											4.13		
Bf1	03-15	LS	3.48	0.119	29		0.38	0.89	1.27	1.04	2.82	1.59	0.12	0.78	0.24	4.83	4.42	
Bf2	15-40	LS	1.88	0.069	27		0.10	0.48	0.86	0.54	2.46	0.98	0.07	0.86	0.16	4.97	4.97	
Bm	40-82	LS	1.20	0.046	26		0.03	0.39	0.52	0.34	1.77	0.58	0.03	0.66	0.11	5.21	5.16	
Bfg	82-99	LS	1.57	0.074	21		0.17	0.60	0.70	0.57	1.66	0.77	0.04	0.51	0.13	5.26	4.91	
C	99+	LS																

- 1. Some cementation of structure throughout Bfl to Bm.
- 2. The Hl is very thin.
- 3. Water was seeping along basal till.

Profile 33 - Pit in the forest half way up the Burke Mountain road, elevation 520 m

Horizon	Depth	Texture	%C <sub>T</sub>	%N <sub>™</sub>	C/N	%S		% Fe			% A1			% Si		р	Н	extracted
	(cm)		1	1			Pyro	Οx	CBD	Pyro	Ox	CBD	Pyro	Оx	CBD	H <sub>2</sub> O	CaCl	Ch/Cf Ca/Cf %Ce
LFH	03-00	0														2	Z	•
Bfl	00-17	SL	2.46	0.126	20 ء		0.14	0.53	1.11	0.68	2.08	1.23	0.04	0.64	0.20	5.18	4.94	
Bm	17-48	SL	1.22	0.064	19		0.02	0.60	1.13	0.37	2.37	0.92	0.03	0.87	0.08	5.44	5.33	
Bm 2	48-76	SL	1.92	0.095	20		0.05	0.76	1.34	0.43	3.06	1.24	0.02	1.22	0.16	5.23	5.24	
Bf2	76-93	LS	2.90	0.154	19		0.28	0.76	1.11	0.73	2.93	1.32	0.06	0.97	0.22	5.18	4.71	
Cg	93+	LS	0.29	0.011	26		0.00	0.57	0.41	0.16	0.62	0.22	0.00	0.27	0.07	5.74	5.32	

- The Cg is compact basal till of fine sand and stones with no cementation.
   There is seepage along the Cg.
   There are plentiful medium and few fine roots throughout.

Profile 34 - Pit in the forest half way up the Burke Mountain road, elevation 520 m

Horizon	Depth	Texture	%C <sub>T</sub>	%N <sub>m</sub>	C/N	%S	_	% Fe			% A1			% Si		р	H	еx	tracted	ì
	(cm)		1	1			Pyro	Ox	CBD	Pyro	Оx	CBD	Pyro	Οx	CBD	H <sub>2</sub> O	CaCl <sub>2</sub>	Ch/Cf	Ca/Cf	%Сe
LFH	10-00	0					_			-			-			2	2		-	
Ae	00-03	SL	2.74																	
В£	03-26	SL	4.31	0.170	25		0.49	0.50	0.75	1.07	1.27	1.08	0.09	0.21	0.20	4.77	4.30	0.35	0.70	79
Bfq	26-66	SL	2.34	0.100	23		0.34	0.50	0.88	0.68	2.14	0.98	0.04	0.72	0.15	5.31	4.78			
Cg¯	66+	SL	0.76	0.024	31					0.27										

- Water seeped into bottom of the pit.
   Medium mottles were common in the Bfg.
   Abundant medium and coarse live roots throughout pit.

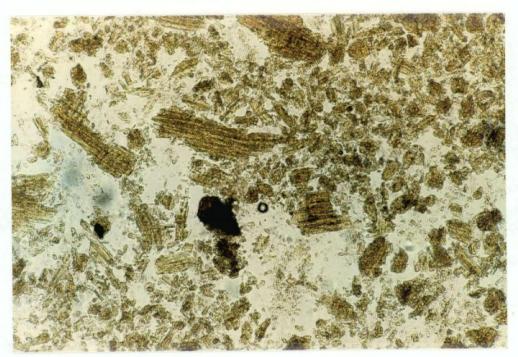


Root Mat of Profile 2 situated at a depth of 70 cm, immediately over a duric horizon

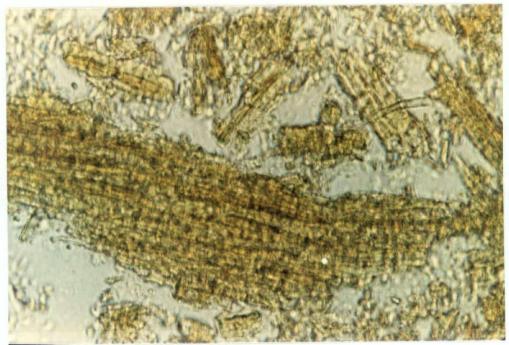


Profile 1 - Root Channels

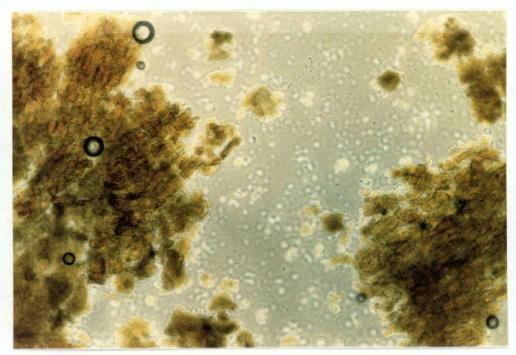
Appendix C: The organic-rich material filling the mats and channels as seen with a Wilde-Lietz Dialux 2, phase microscope



Profile 30 - The cellular nature of the root channel material, seen at 125 X magnification



Profile 30 - Root Channel material at 500 X magnification



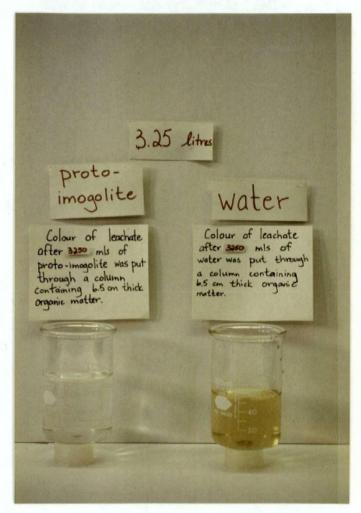
Profile 25 - cellular nature of the H2 horizon, 125 X magnification



Profile 25 - pollen grains found at approximately 78 cm within the H2 horizon



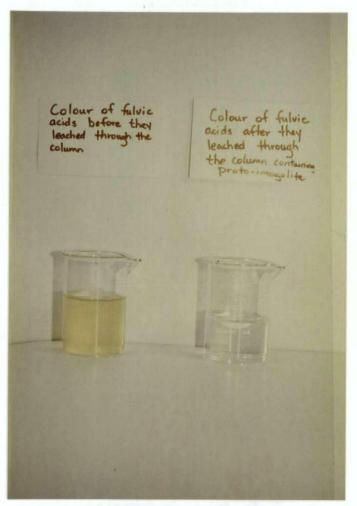
After a total of 750 ml eluent has leached through the column the proto-imogolite leachate is as clear as distilled water. The leachate from the organic control column is the yellow brown of fulvic acids



Even after 3.25 1 of eluent has leached through the organic control, the leachate is still coloured yellow-brown



Set Up of Columns - Note the yellow brown of the leachate of the 3 organic control columns on the left



Fulvic acids leached through a column previously leached with proto-imogolite