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DEPARTMENT OF ENERGY, MINES AND RESOURCES

BULLETIN 174

GEOCHEMISTRY OF IRON, MANGANESE, LEAD, COPPER, ZINC, ARSENIC, ANTIMONY, SILVER, TIN, AND CADMIUM IN THE SOILS OF THE BATHURST AREA, NEW BRUNSWICK

E. W. Presant

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By
E. W. Presant

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PREFACE

This report on the soils of the Bathurst area completes part of an extensive geological and geochemical survey of the Bathurst–Newcastle mineral district carried out by the Geological Survey.

The author has given a detailed account of the occurrence of a suite of major and trace elements in the normal soils of the Bathurst area and in the soils and tills that overlie the sulphide deposits. His data, in addition to being a fundamental contribution to soil science, will be found useful by those interested in geochemical prospecting using soil methods.

Y. O. FORTIER,
Director, Geological Survey of Canada

OTTAWA, March 10, 1966

BULLETIN 174 — Geochemie von Eisen, Mangan, Blei, Kupfer, Zink, Arsen, Antimon, Silber, Zinn und Kadmium in den Böden des Bathurst-Gebiets (New Brunswick)

Von E. W. Presant

БЮЛЛЕТЕНЬ 174 — Геохимия железа, марганца, свинца, меди, цинка, мышьяка, сурьмы, серебра, олова и кадмия в почвах района Батерст, Нью-Брансуик.

Э. В. Пресант

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GEOCHEMISTRY OF IRON, MANGANESE, LEAD, COPPER, ZINC, ARSENIC, ANTIMONY, SILVER, TIN, AND CADMIUM IN THE SOILS OF THE BATHURST AREA, NEW BRUNSWICK

Abstract

The purpose of this study was to investigate the amount, distribution, and nature of iron, manganese, lead, copper, zinc, arsenic, antimony, silver, tin, and cadmium in a number of podzol soil profiles from the Bathurst area, northeastern New Brunswick. Total analyses were done on the soils for these elements, as well as determinations for cation exchange capacity, organic carbon, and pH. Statistical correlation studies were also carried out to determine the relationships of the different elements with pH and total iron.

Six soil profiles were selected for detailed chemical and mineralogical studies. These studies included determinations of the amounts of elements associated with the water-soluble, dilute acid-soluble, organic matter, and free iron oxide fractions of the soil. The mineralogical studies included mechanical analyses, heavy mineral separations, and microscopic examinations.

The highest contents of lead, silver, and manganese occur in the surface A_0 horizons. Significant amounts of lead, zinc, copper, and arsenic were removed with the organic matter from the A_0 horizons by a hydrogen peroxide treatment, indicating that these elements are probably combined in some form with humus. Relatively large amounts of dilute HCl-soluble zinc were also removed from the surface horizons. Tin is enriched in the A_2 horizons, where it probably is present in a resistant oxide form. Iron, arsenic, antimony, and lead are most enriched in the B horizons, where they appear to be associated with free iron oxides. The content of most elements is higher in the C horizons, because of the absence of strong mineral weathering in this horizon.

The mean trace element contents for all soil horizons overlying sulphide deposits are higher than the mean trace element contents of horizons above unmineralized bedrock.

Résumé

La présente étude visait à déterminer la quantité, la répartition et la nature du fer, du manganèse, du plomb, du cuivre, du zinc, de l'arsenic, de l'antimoine, de l'argent, de l'étain et du cadmium contenus dans des profils de sols du type podzol de la région de Bathurst, dans le nord-est du Nouveau-Brunswick. On a fait l'analyse complète des sols afin d'identifier ces éléments et de déterminer la capacité de substitution des cations, la teneur en carbone organique et le pH. On a également effectué des études de corrélation statistique afin de déterminer la relation des divers éléments avec le pH et le fer total.

Six profils de sols ont subi des examens chimiques et minéralogiques détaillés. Les examens comprenaient la détermination quantitative des divers éléments dans des fractions de sols solubles dans l'eau ou dans un acide dilué ou constituées de

matière organique ou d'oxyde de fer libre. Les examens minéralogiques comportaient des analyses mécaniques, des séparations de minéraux lourds et des examens au microscope.

Les horizons A_0 supérieurs ont la plus forte teneur en plomb, en argent et en manganèse. Des quantités importantes de plomb, de zinc, de cuivre et d'arsenic des horizons A_0 ont été retirées avec la matière organique au moyen d'un traitement au peroxyde d'hydrogène, ce qui indiquerait que ces éléments sont probablement associés d'une certaine façon à l'humus. On a également retiré des couches supérieures des quantités assez importantes de zinc soluble dans l'acide chlorhydrique. L'étain est enrichi dans les horizons A_2, où il s'y trouve probablement sous forme d'oxyde résistant. Le fer, l'arsenic, l'antimoine et le plomb sont le plus enrichis dans les horizons B, probablement en raison de leur association à des oxydes de fer libres. Les horizons C renferment les plus fortes concentrations des divers éléments en raison du faible effet des agents atmosphériques à ce niveau.

La teneur moyenne en oligo-éléments des horizons de sol recouvrant les dépôts de sulfures est plus élevée que celle des horizons situés sur la roche de fond non minéralisée.

Chapter I

INTRODUCTION

Object and Scope of the Investigation

The purpose of the work described in this bulletin was to determine the amount, nature, and location of several trace elements and their compounds in a number of soil horizon samples from the Bathurst area, northeastern New Brunswick (Fig. 1, *in pocket*). About 450 soil samples and 15 bedrock samples were collected from 80 separate soil profile locations in the counties of Restigouche, Gloucester, and Northumberland. Some profiles were chosen directly above known mineralized areas or adjacent to them; others were chosen from areas where there was little or no known bedrock mineralization. The sample locations are shown on Figures 1, 3, and 5.

Analyses were done for pH, organic carbon, copper, lead, zinc, arsenic, antimony, iron, manganese, silver, tin, and cadmium. Detailed studies carried out on six selected profiles included determinations of cation exchange capacity, soil particle composition, mineral composition, water-soluble metal, dilute acid-soluble metal, metal associated with organic matter, and metal associated with free iron oxides. Statistical correlation studies were done to determine the relationship of iron and other elements and the effect of pH on the mobility of the various elements.

Physical Features of the Area

Topography

Most of the samples were taken from the Central Highlands area, an upland belt about 50 miles wide trending north-northeast across the northern part of New Brunswick. Near Bathurst this belt is bounded approximately on its southeast side by the Nepisiguit River. It is a region of ridges and hills developed on strongly folded Paleozoic sedimentary and volcanic rocks intruded by granitic bodies (Skinner, 1956). The Central Highlands area reaches a maximum elevation of 2,150 feet in the west, and slopes gently northeastward to sea level within about 40 miles. The almost flat upland surface between dissecting valleys is thought to represent a peneplain developed during Cretaceous or early Tertiary times (Alcock, 1941). South and east of the Nepisiguit River, the relatively flat-lying Eastern Plain reflects the underlying horizontal Pennsylvanian sedimentary rocks, and has an average elevation of about 400 feet above sea level.

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Glaciation

During Pleistocene time the entire Bathurst area was glaciated by an ice sheet or sheets that moved easterly to northeasterly across the area. Chalmers (1881) and Alcock (1941) believed the ice was of relatively local derivation, and that it originated in the Central Highlands, southwest of the Bathurst area.

There are indications that both the thickness of the ice and its movement were limited in magnitude, especially in the upland regions. Thus, Chalmers (1887) cites examples of apparently residual soil material grading into bedrock and overlain by glacial till in the Bathurst region, and certain gossans overlying mineralized rocks appear to be partly residual in nature. In drift-covered upland areas of northeastern New Brunswick where outcrops are scarce or absent, glacial boulders and till fragments are generally acknowledged to give a reasonably good indication of the underlying bedrock. Exceptions are found in those areas overlain by stratified water-lain material that has obviously been transported considerable distances.

Evidence of glaciation in the Bathurst area includes fluted or drumlinized till plains, eskers, kames, glacial striae, glacial erratics, gorges, and waterfalls (Skinner, 1956). There is a large drumlinized till plain straddling the boundary between the Eastern Plain and the Central Highlands in the Nepisiguit Falls area. This is a depressional area about 10 miles wide, less than 450 feet above sea level, that trends north-northeasterly. The Brunswick No. 6 orebody is overlain by this till plain. Eskers occur in the Nepisiguit Falls region, and kames are present in several places, notably in the Nigadoo mine area. Glacial striae are found in most of the upland areas where rock exposures are present. With the exception of the northeasterly trending striae of the fluted till plain, most of the striae indicate an eastward ice movement. Glacial erratics are widespread. Small, angular rock fragments that grade into larger and more angular fragments with depth are common in upland tills.

According to Young (1911) isostatic uplift following deglaciation probably reached 150 feet. The gorges of such rivers as the Nepisiguit and Tetagouche are thought to have been cut or re-excavated during this time.

Drainage

Most of the streams and rivers near the coast in the Bathurst area are characterized by narrow, steep-walled valleys, rapids, waterfalls, and gorges. Further inland, however, the stream valleys broaden, the streams meander and are swampy, and peat bogs and beaver ponds are common. The two largest rivers in the area are the Nepisiguit and Tetagouche. Near their outlets, both rivers have gorges and waterfalls which have probably resulted from disruption of their previous courses by Pleistocene glaciation.

Vegetation

The humid, maritime New Brunswick climate supports a heavy forest vegetation rather than grasses; coniferous rather than deciduous trees predominate. This is particularly true of the Bathurst region although local variations in vegetation are dependent upon many factors such as topography, drainage, underlying soil and rock types, lumbering practices, and forest fires.

The most common species of tree in the uplands region are hemlock, balsam fir, black spruce, white spruce, white pine, red pine, white birch, and poplar. Beech, maple, mountain ash, and other hardwood varieties are fairly common on well-drained upland ridges. Most of the region has been burned at least once. Some burnt-over areas are almost devoid of trees,

and have a cover of blueberries and other low-growing shrubs. Cedar, tamarack, ash, elm, balsam, and poplar are common in swamps and intervales. Some muskeg-like peat bogs contain scattered stunted tamarack and spruce growing in sphagnum moss.

Climate

The climate of the Bathurst area is temperate and humid like that of the rest of New Brunswick and the other Atlantic Provinces. A maritime climate might be expected, but occurs only near the coast. This is due to the strong influence of air masses moving eastward off the North American continent, a feature that produces a climate chiefly continental in nature.

The following climatic table is compiled from data supplied by the Meteorological Branch of the Department of Transport, Ottawa.

Climatic Data for Bathurst, N.B., 1921–50

Average annual precipitation	34.43 in.
Average monthly precipitation	
highest (June)	3.38 in.
lowest (March)	2.32 in.
Average mean temperature	38.9°F
Average monthly temperature	
highest (July)	66.5°F
lowest (January)	11.0°F
Average length of frost-free period	120 days

General Geology

Early geological descriptions of the Bathurst area are given in the reports by Ells (1881, 1883), Young (1911), Shaw (1936), and Alcock (1935, 1941). More recent descriptions and geological maps have been published by Skinner and McAlary (1952), Skinner (1953, 1955), Smith and McAllister (1956), McAllister and Smith (1956), Jones and Smith (1957), Smith (1957), Davies (1959), Jones (1961), and Boyle and Davies (1964).

Smith and Skinner (1958) recognized three regional geological units in the Bathurst area: the Ordovician folded belt; the Silurian folded belt, now better termed the Silurian–Devonian folded belt; and the Pennsylvanian cover.

The Ordovician folded belt (Fig. 1) underlies the central part of the area and includes highly folded and contorted volcanic and sedimentary rocks that are intruded by gabbro and diorite sills and dykes, and by granitic stocks and masses of Devonian age. The major massive lead-zinc-copper sulphide bodies of the district occur in the Ordovician rocks. These include the Brunswick No. 6, Brunswick No. 12, New Larder U, Heath Steele, Wedge, Caribou (Anaconda), New Jersey Zinc, Middle River, and other deposits. Most of these deposits are localized in intensely sheared and drag-folded zones and were formed partly by replacement. The principal primary minerals are pyrite, pyrrhotite, sphalerite, galena, chalcopyrite, tetrahedrite, and arsenopyrite. Several of the massive sulphide deposits have well-developed gossans, consisting mainly of limonite accompanied by jarosite, anglesite, beudantite, and other secondary minerals. In a few deposits, e.g., Heath Steele and Brunswick No. 6, irregular enriched copper zones containing covellite and chalcocite are developed below the gossans.

The Silurian–Devonian folded belt is separated in part from the Ordovician folded belt by a prominent fault locally termed the "Rocky Brook–Millstream break". The rocks of the Silurian–Devonian belt are mainly volcanics and sediments of Middle and Upper

Silurian age and Lower and Middle Devonian age. The deformation of these rocks is not as intense as that in the Ordovician folded belt. Locally the Silurian strata are intruded by gabbro and diorite sills and dykes, granitic stocks, quartz-feldspar porphyry dykes, sills, and plugs, and aplitic dykes, all of which are thought to be Devonian. The Silurian rocks are hosts to a number of small lead-zinc-copper sulphide lenses and veins in fractures and faults. These include the Nigadoo, Sturgeon River, and other deposits. The principal primary minerals in these deposits are pyrite, arsenopyrite, sphalerite, galena, pyrrhotite, chalcopyrite, tetrahedrite, and marcasite. Most of the deposits have only a thin limonitic gossan, and secondary enriched zones are generally absent.

Flat-lying, Pennsylvanian conglomerates and sandstones underlie the eastern part of the area, and small outliers, suggesting a once continuous cover, occur in several places, particularly near Tetagouche Lakes in the northern part of the area. The Pennsylvanian rocks rest unconformably on the older rocks and were laid down after the lead-zinc-copper sulphide deposits of the district were formed.

Previous Soil Work in the Area

General descriptions of the soils in the Bathurst area are given in early reports by Chalmers (1885, 1887) and Young (1911). Schmidt (1955) investigated the dispersion of copper, lead, and zinc from mineralized zones in northeastern New Brunswick, and Dreimanis (1960) has given an account of the copper, lead, and zinc content of the soils and their parent glacial materials in the vicinity of the Nigadoo deposit, ten miles northwest of Bathurst.

Acknowledgments

The writer wishes to express his sincere appreciation to Dr. R. W. Boyle of the Geological Survey of Canada who suggested the study and methods of procedure, supervised the field work, and made arrangements with the various laboratories for total analyses, water analyses, cation exchange studies, and X-ray studies. Thanks are expressed to all those who were involved with or assisted in analysis of the samples in the laboratories of the Geological Survey; Mines Branch; Soil Research Institute, Department of Agriculture; Carleton University; and the Ontario Agricultural College. In particular the cooperation and advice of Mrs. M. A. Jardine, G. Mihailov, R. Levick, and Dr. R. Wicklund was much appreciated. Sincere thanks are also extended to Dr. J. Riddell and Dr. W. Tupper for their supervision and helpful suggestions and criticisms during the preparation of the thesis on which the present report is based.

Chapter II

MATERIALS AND METHODS

General Description of the Soils[1]

The soils of the Bathurst area and of the Maritime Provinces in general have developed under climatic conditions particularly conducive to the formation of podzol soils. These soils are best developed where the climate gives rise to a coniferous tree cover and the accumulation of organic material on the soil surface. Figure 2 shows a typical podzol profile and its characteristic horizons.

The upper part of the profile is commonly known as the A horizon and is the zone of maximum weathering and maximum removal of weathering products. The A horizon is usually subdivided into the A_0, A_1, and A_2 horizons. In podzol soils the A_0 horizon contains a high proportion of relatively undecomposed organic debris. Since much of the Bathurst area has been burnt over by forest fires in the past, the A_0 horizons locally contain considerable charcoal. As the organic matter decomposes, organic acids are formed which initiate leaching and migration of the soluble bases, sesquioxides, and clay minerals from the surface soil. The grey, leached, silica-rich layer that remains is called the A_2 horizon. The A_1 horizon, a humus-rich zone between the A_0 and A_2 horizons, is usually thin and lacking in places in the podzol soils of the Bathurst area.

Underlying the A horizon is the B horizon which is the zone of maximum concentration of the weathering products that have moved downward from the A horizon. The B horizon is subdivided into the B_1 and B_2 horizons. The B_1 horizon is characteristically reddish brown and somewhat compacted. The underlying B_2 horizon is usually lighter coloured and less compacted than the B_1 horizon.

The C horizon lies beneath the B horizon and consists of parent material only slightly altered by soil-forming processes. In most of the profiles studied in the area the C horizon begins at 1½ to 2 feet below the soil surface.

Imperfect drainage is indicated in podzol profiles by mottling which is usually most prominent in the B horizon. Poorly drained profiles are usually drab in colour and have no apparent horizons of leaching and accumulation. These drab horizons are referred to as gley horizons.

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[1]Under the present system of soil classification in Canada (as outlined in *The System of Soil Classification for Canada*, Can. Dept. of Agriculture, Queen's Printer, 1970) most horizons designated as A_0 horizons in this report would be L, F, or H horizons in well- and imperfectly-drained soils, and O horizons in poorly-drained soils. A_2 horizons in this report would now be classified as Ae or Aeg horizons, depending on drainage conditions.

B_1 and B_2 horizons of this report would mainly be classified as Bf or Bfg horizons under the present system. A few that have high contents of organic matter would be Bh or Bfh horizons.

G horizons of poorly-drained profiles would now be classified as Aeg, Bg, or Cg horizons. Similarly the C, C_1, and C_2 horizons in profiles 19 and 44 would now be classified as Cg, Cg_1, and Cg_2.

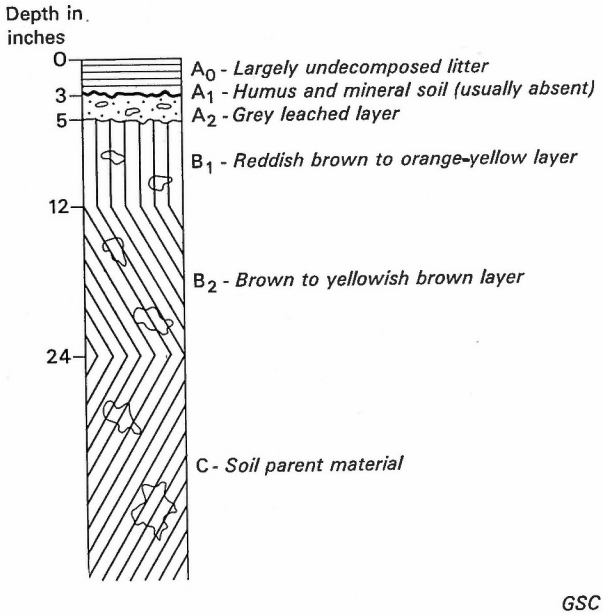


FIGURE 2. Diagram representing a typical well-drained podzol soil in the Bathurst area.

The parent material of the profiles in the Bathurst area is glacial till, fluvial material, lacustrine material, or mixtures of these types. Much of the glacial till appears to be of local derivation as indicated by the similarity of the till pebbles and rock fragments to underlying or nearby bedrock. In some places the soil immediately above bedrock appears to be of a semi-residual nature and to have been affected by glaciation only slightly. Soil profiles developed above sulphide bodies in the Bathurst area may be marked by differences in the number, depth, or colour of horizons as compared to those profiles developed over normal bedrock. This is especially true of the Brunswick No. 6 profiles.

Gossans

Gossans cap many of the sulphide bodies in the Bathurst area which in turn are overlain by till and soil. There, the most spectacular gossan is the one on the No. 6 sulphide deposit which has been described by Rajah (1962) and Boyle and Davies (1964). The description that follows is taken from the latter publication.

"The No. 6 deposit was covered by an extensive gossan whose distribution is shown in Figure 3.[1] The thickness of this gossan was variable, being up to 6 feet in places and only a few inches in others.

"Two distinct types of gossan were developed on the deposit—residual gossan, and transported or pseudogossan. Both were overlain by till and soil.

"The residual gossan had a general erratic distribution, but was well developed on the west-central part of the deposit, where it averaged about 1½ feet in thickness and was composed essentially of limonite and quartz exhibiting a variety of boxwork structures. In some other parts of the deposit an unusual type of residual gossan presently overlies the massive

[1]Also Figure 3 of this report.

sulphides. This is 1 inch to 3 inches thick and is composed essentially of highly leached white quartz sand, in places stained with limonite. Locally the quartz residue contains thin black layers of a very fine-grained mineral, which may be secondary pyrite or marcasite.

"The term transported or pseudo-gossan is used to designate all materials that have been cemented or heavily impregnated by limonite and other iron salts. The distribution of this type of gossan is difficult to outline because of its variable character. It was well developed on the northern, eastern, and central parts of the deposit, where remnants are still available for study. Laterally, the transported gossan grades into and is often interfingered with loosely consolidated limonite-cemented till and highly iron-stained till and soil.

"Characteristically the remnants of transported gossan exhibit two zones—a leached till, and a 'hardcap' or limonite-cemented conglomerate.

"The leached till is poorly consolidated, light brown to buff coloured, and rests on the residual gossan. It rarely exceeds 5 feet in thickness, and consists mainly of highly leached and decomposed till and rock fragments, which are mainly of local derivation. Just above the residual gossan the till is clayey and light buff coloured, and somewhat resembles gumbotil in its physical properties. Locally this clayey section has thin grey to black layers of a fine sooty material, the composition and mineralogy of which is unknown at the present time. Towards the top of the leached till zone, the till is progressively cemented by limonite, yielding a compact material, which is laminated in places.

"The 'hardcap' or limonite-cemented conglomerate rests on the leached till in most places, but in others it is developed directly on the wall rocks. It is hard, reddish brown, from 6 inches to 5 feet thick, and is composed essentially of angular pieces of magnetite, chlorite schist, and chert, with some pebbles, stones, and boulders of granite and other rocks, all of which are cemented by limonitized sandy to silty material. Most of the angular pieces of magnetite, chlorite schist, and chert are of local derivation; the pebbles, stones, and boulders of granite and other rocks are largely exotic.

"The till overlying the 'hardcap' is compact and heavily impregnated and partly cemented by limonite. The upper part is loose, sandy, and highly stained with limonite. Laterally the till grades imperceptibly into the normal till of the area.

"The principal mineral in the various types of gossan is *limonite*, consisting chiefly of goethite with smaller amounts of hematite. It is derived mainly from pyrite, with smaller amounts from magnetite-hematite, chalcopyrite, pyrrhotite, and sphalerite. The limonite occurs in many forms: as pseudomorphous replacements of pyrite, magnetite-hematite, and chlorite; in a variety of boxworks; as clinkery masses; as colloform, ocherous, and earthy masses; as needle-like crystals in vugs and incrustations; as a cementing material in all of the gossans; and as a stain or coating on the constituents of the till.

"*Quartz* is the next most abundant mineral in the gossans, being particularly common in the residual variety. It occurs as small clear prisms arranged in aggregates in the earthy oxidized materials or as cryptocrystalline masses lining druses and cavities. The main varieties of secondary quartz include jasper, opal-jasper, and chalcedony.

"*Anglesite* is the most abundant of the secondary lead minerals and is present only in the residual gossan developed on the rich galena zones of the deposit. Pseudomorphs of anglesite after galena, and cavities lined with minute crystals of anglesite are common. Anglesite also occurs in granular to compact masses and in concentric bands enclosing the galena.

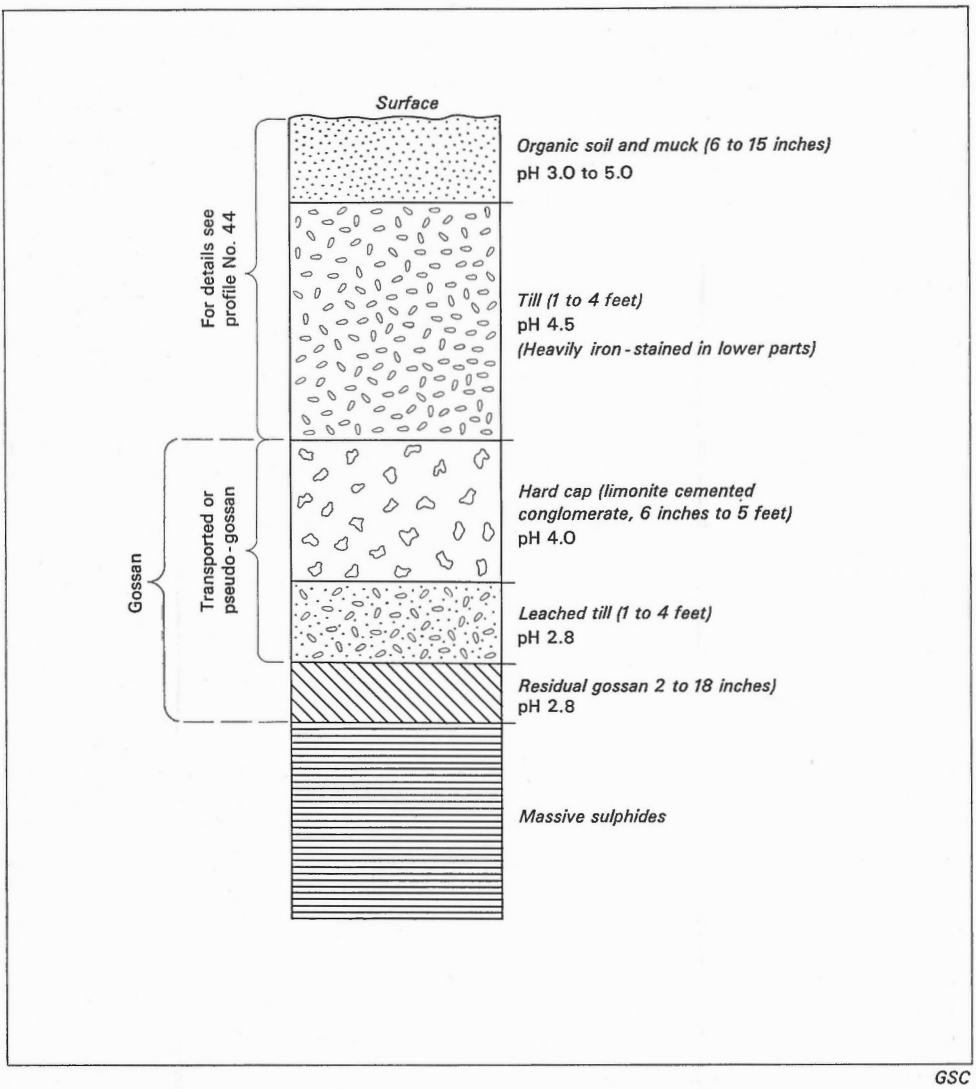
"*Beudantite*, the basic sulphate-arsenate of lead and iron, is relatively abundant as globular aggregates, microcrystalline coatings and crusts, and in boxworks in the residual gossan.

"*Barite* is present in a number of places in the residual gossan as large white to nearly colourless, in places inclining to yellow or light brown, crystals.

"Other less common minerals identified in the various types of gossan include *scorodite*, *jarosite*, *woodhouseite*, various *clay minerals*, and secondary *pyrite*. Several other minerals have not yet been identified.

"Most of the residual gossan, especially that in the central part of the deposit, was probably formed before Pleistocene time. The remainder is of post-Pleistocene age, for glacial boulders and stones of granitic and other composition are cemented by the limonite and other secondary minerals."

A typical, reconstructed section of the gossan overlying the No. 6 deposit prior to stripping is shown on Figure 4. The gossan capping the Middle River deposit has not yet



GSC

FIGURE 4. Idealized section of overburden and gossan, Brunswick No. 6 deposit (after Boyle and Davies, 1964).

been studied in detail. Briefly, it occurs as masses of dark grey, limonitic material with a botryoidal structure. The gossan developed on the Nigadoo deposit is rarely more than a few inches thick, and commonly is little more than a thin crust on the sulphides. Relict galena is present in the poorly developed boxwork structures, together with greenish yellow arsenic-bearing ochres and brownish red iron oxides.

Description of Soil Profiles Studied in Detail

Six soil profiles were selected from representative soil bodies overlying normal bedrock and sulphide bodies for detailed mineralogical and chemical work.

Four profiles were chosen from soils overlying sulphide deposits. Two of these profiles (17 and 19) were from the area of the Nigadoo deposit, and represented well-drained and poorly drained soils. The other two profiles (44 and 79) were from soils overlying the Brunswick No. 6 and Middle River sulphide deposits, respectively.

Two profiles were selected from soils overlying normal bedrock. Profile No. 64 was chosen from an area of relatively shallow soil over granite. Profile No. 51 was chosen from an area of deeper, water-worked soil overlying mixed sedimentary and volcanic rocks.

Nigadoo Profiles

The locations of the two Nigadoo profiles (17 and 19) chosen for detailed study, are shown on Figures 1 and 5. These profiles were taken from a relatively flat-lying area of outwash material and loamy till. Since both profiles were located along trenches from which soil and weathered debris have been excavated, it is probable that their A horizons are somewhat contaminated by this material.

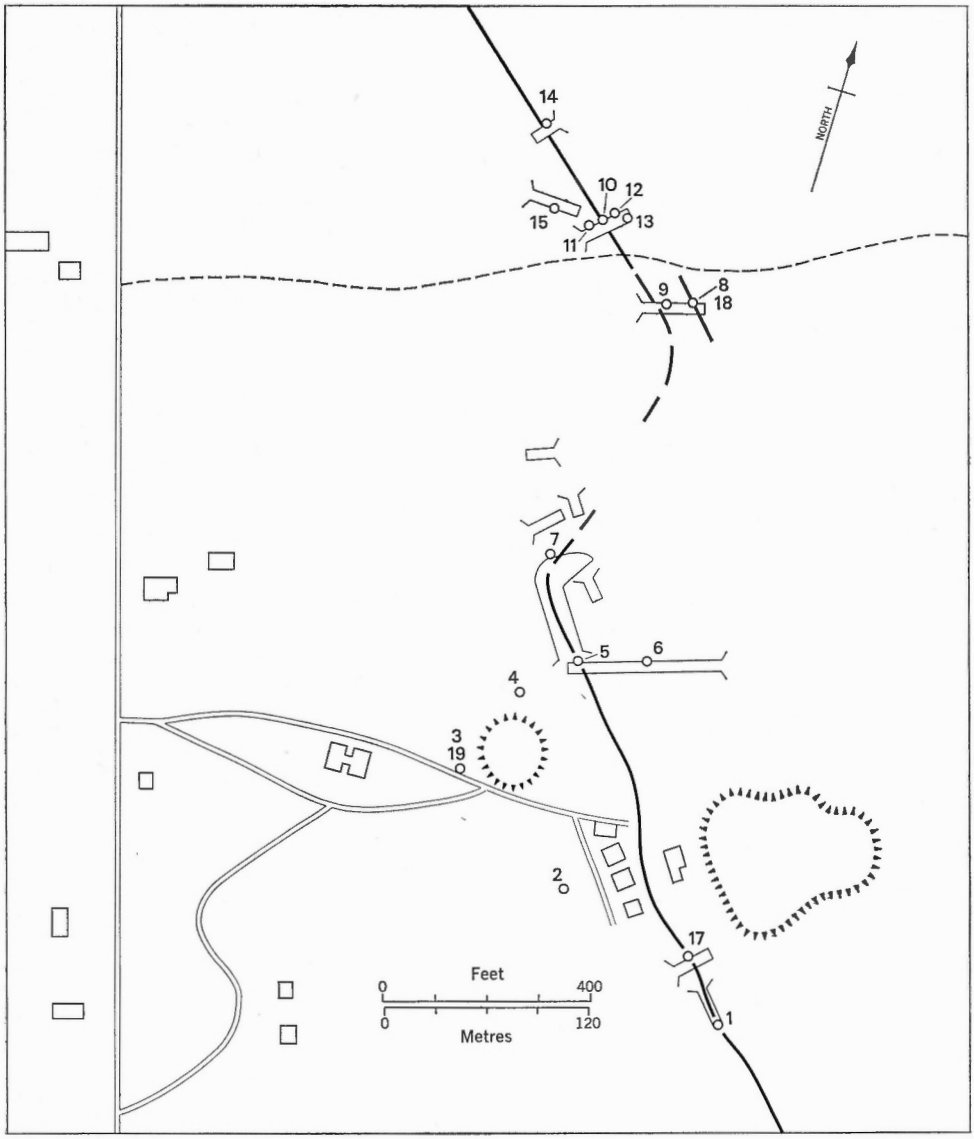
Profile No. 17 is from a relatively well-drained location, about five feet above and near the southern end of the main sulphide vein. Profile No. 19 is in a poorly drained location along a drainage ditch about 100 feet west of the main ore vein, and 50 feet west of a small ore dump. It is characterized by two bluish grey gley horizons that have developed under the influence of excessive moisture.

Profiles 17 and 19 illustrate the details of the horizons of the two Nigadoo profiles[1].

Profile No. 17

Sample No.	*Horizon*	*Depth*	*Description*
17a	A_0	0–7″	Black (5 YR 2/1)[1] organic sandy clay; organic material fairly well decomposed; pH 3.8
17b	A_2	7–11″	Brown (7.5 YR 5/2) silt loam; some rounded, mainly shaly gravel; pH 4.8
17c	B_1	11–16″	Dark brown (7.5 YR 4/4) gravelly loam; subrounded, rusty weathered quartz and argillite pebbles; pH 5.1
17d	B_2	16–21″	Dark brown (10 YR 4/3) gravelly loam; pebbles subrounded, argillitic, and larger than in B_1 horizon; pH 6.0
17e	C	21″ +	Yellowish brown (10 YR 5/4) gravelly loam; slight mottling extends sometimes into B_2 horizon; sub-angular, slightly weathered pebbles of argillite and quartz-feldspar porphyry; pH 6.1

[1]In these and other descriptions of soil profiles, the colour, hue, and chroma of the various soil horizons, e.g., black (5 YR 2/1), are given in terms of the Munsell Color Standards (1954).



Soil profile . . . . . o 4
Sulphide vein . . . . . —— ——
Ore dump . . . . . ▲▲▲▲
Trench . . . . . /

Road . . . . . ═══
Trail . . . . . — — —
Building . . . . . □

GSC

FIGURE 5. Nigadoo mine area showing locations of soil profiles.

Profile No. 19

Sample No.	*Horizon*	*Depth*	*Description*
19a	A_0	0–5″	Black (7.5 YR 2/0) organic material; well-decomposed with a few quartz and highly weathered quartz-feldspar porphyry pebbles; pH 5.8
19b	G_1	5–7″	Very dark grey (7.5 YR 3/0) gravelly silt loam; fine gravel and a few larger shaly pebbles; pH 6.6
19c	G_2	7–14″	Dark brown (10 YR 3/3) gravelly sandy loam; slightly mottled; subrounded quartz-feldspar porphyry and chert pebbles; pH 6.9
19d	Cg	14″ +	Dark brown (10 YR 4/3) gravelly loamy sand; mottled; much well-rounded fine gravel along with some larger resistant quartz-rich pebbles; pH 6.9

Brunswick No. 6 Profile

A glacial till plain of relatively flat relief overlies the Brunswick No. 6 deposit. Much of the surface till overlying the deposit rests upon a limonite-cemented hard cap, which is thought to mark the upper limit of a fluctuating water-table. Below this hard cap is a leached zone, overlying a mottled zone which usually overlies the residual gossan that caps the orebody (Fig. 4). In profile No. 44, which was chosen for detailed study, the lower leached zone is clearly discernible, but the overlying hard cap is present only as an iron and clay-rich horizon with angular, blocky structure. The profile is three and a half feet deep, and rests upon two to three inches of gossan developed on pyritized wall-rock adjacent to the massive sulphide body.

Profile No. 44

44a	A_0	0–4″	Black (10 YR 2/1) organic clay loam, well-decomposed plant material with a few well-weathered augen schist pebbles and some resistant quartz pebbles; pH 3.8
44b	A_2	4–5″	Dark brown (10 YR 4/3) gravelly loam; subrounded pebbles mainly of quartz, but some augen schist and rhyolite pebbles are also present; pH 4.1
44c	B_1	5–10″	Yellowish brown (10 YR 5/6) gravelly loam, mainly flat, subrounded shaly pebbles; pH 3.9
44d	B_2	10–16″	Brownish yellow (10 YR 6/6) gravelly loam; subrounded quartz and gossan pebbles are present; pH 4.0
44e	B_3	16–25″	Strong brown (7.5 YR 5/6) gravelly loam but higher in clay than overlying horizons; angular blocky structure; rounded quartz pebbles predominate; pH 4.0
44f	Cg_1	25–30″	Light grey (2.5 YR 7/2) sandy loam; sub-angular, bleached gossan, quartz and barite pebbles are sparingly present, plus a few larger fragments of gossan; pH 3.8
44g	Cg_2	30–41″	Brownish yellow (10 YR 6/6) gravelly sandy loam; well-leached, angular quartz, shale and gossan pebbles; pH 3.2

Middle River Profile

The Middle River sulphide deposit is in an area of fairly high relief where the tops of the hills have only a thin soil cover. Profile No. 79 overlying the Middle River deposit, is at the top of one of these hills. This profile is shallow, and overlies a peculiar dark grey, botryoidal gossan that is developed on the Middle River sulphide deposit. The area has recently been ravaged by forest fires and is devoid of trees. The location of the Middle River deposit and profiles are shown on Figure 1.

Profile No. 79

Sample No.	*Horizon*	*Depth*	*Description*
79a	A_0	0–2″	Black (2.5 YR 2/0) organic clay loam; fine, well decomposed organic material contains many charcoal fragments; pH 4.0
79b	A_2	2–5″	Greyish brown (10 YR 5/2) gravelly silt loam; subangular, flat yellowish and reddish schistose fragments occur with rounded quartz pebbles; pH 4.2
79c	B_1	5–12″	Dark brown (7.5 YR 4/4) gravelly loam; subangular, schistose pebbles are present; pH 4.9
79d	B_2	12″ +	Yellowish brown (10 YR 5/8) gravelly loam; subangular quartz-rich, schistose pebbles, along with some small pebbles of the underlying gossan; pH 6.2

Granite Profile

Profile No. 64 was selected from the area underlain by the Bathurst granite (Fig. 1). Granite boulders are commonly found throughout the soil, and a thick, bleached A_2 horizon is present under the humus in most of the area.

Profile No. 64

64a	A_0	0–2″	Very dark brown (10 YR 2/2) organic sandy clay loam; loose organic layer containing many reddish, decaying wood fragments; pH 3.4
64b	A_2	2–8″	Greyish brown (10 YR 5/2) loam; pebbles almost absent; pH 3.7
64c	B_1	8–11″	Dark reddish brown (5 YR 3/4) sandy loam; cemented in places; a few subrounded quartz and granite pebbles; pH 4.5
64d	B_2	11–17″	Dark brown (7.5 YR 4/4) gravelly sandy loam containing subangular quartz and granite pebbles; pH 4.7
64e	C	17″ +	Dark yellowish brown (10 YR 4/4) gravelly loam; angular unweathered granite fragments, increasing in size with depth; pH 4.4

Sand Profile

Profile No. 51 was taken about two miles east of the Brunswick No. 6 deposit from an area covered by sandy till and lenses of outwash or deltaic sand typical of much of the alluvial material found in the area. The area is underlain by basic volcanic rocks.

Profile No. 51

Sample No.	*Horizon*	*Depth*	*Description*
51a	A_0	0–2″	Black (10 YR 2/1) organic sandy clay loam; partly decomposed organic material consisting mainly of leaves; pH 4.3
51b	A_2	2–4″	Dark grey (10 YR 4/1) sandy loam; pH 3.8
51c	B_1	4–16″	Dark brown (7.5 YR 4/4) sandy loam; pH 4.2
51d	B_2	16–26″	Dark yellowish brown (10 YR 4/4) sandy loam; occasional schistose fragments; pH 5.1
51e	C	26″ +	Olive-brown (2.5 YR 4/4) loamy sand; pH 4.9

Analytical Procedures

The soil samples were collected during the field seasons of 1960 and 1961. Sieving, grinding, and other preparatory work were done partly in the field and partly in the laboratories of the Geological Survey in Ottawa. Determinations of total lead, zinc, copper, arsenic, antimony, manganese, iron, silver, tin, cadmium, sulphur, carbon dioxide, and organic carbon were carried out by the various chemical and spectrographic laboratories of the Geological Survey. X-ray diffraction determinations of the complex minerals in the soils were done by the mineralogical staff of the Survey. Analyses of the soil leachates were done by the Industrial Waters Division, Mines Branch, under the supervision of J. F. Thomas. Dr. E. Coffin of the Soil Research Institute, Department of Agriculture, Ottawa, determined the cation exchange capacities of a number of samples. The pH determinations, mechanical analyses, optical mineralogical work, determinations of acid soluble metal, and the determination of the content of metals in the free iron and humus fractions of the soils were carried out by the writer in the laboratories of Carleton University, in the field and office laboratories of the Geological Survey, and in the Soil Classification Laboratory of the Ontario Agricultural College, Guelph, Ontario.

Treatment of the Samples

Total copper, lead, zinc, and the pH were determined on all samples collected. Analyses for total amounts of iron, manganese, arsenic, antimony, silver, tin, and cadmium were done on a quarter to a third of all samples. For the more time-consuming leachate and mineralogical studies, a limited number of samples was chosen from profiles overlying the Nigadoo, Brunswick No. 6, and Middle River sulphide bodies, as well as from two normal bedrock areas.

After the soil samples were air-dried, they were crushed and the material was passed through a 10-mesh stainless steel sieve. The minus 10-mesh material was then thoroughly mixed and quartered. Samples of the minus 10-mesh material were used for cation exchange, pH, leachate, and mineralogical studies. For the total element analyses, the minus 10-mesh material was ground to minus 80-mesh size. Extreme precautions were taken throughout all crushing, sieving, and grinding operations to minimize contamination. During the actual analytical procedures, contamination was reduced to a minimum by the careful cleaning of all glassware, corks, etc., and by the use of Pyrex glassware and reagent-grade chemicals, and of metal-free water.

Preliminary Chemical and Physical Analyses

The cation-exchange capacity was determined by the ammonium acetate leaching method as described by Atkinson, *et al.* (1958). The pH was determined from a 1:1 soil-water suspension, using a Beckman Model N pH meter, as outlined by Atkinson, *et al.* (1958). Organic carbon was determined from the CO_2 evolved by ignition of the sample in a furnace. The inorganic carbon was first removed by leaching with dilute acid.

The standard pipette method described by Kilmer and Alexander (1949) and others, was used, with slight modifications, to determine the mechanical analyses. The sand fraction obtained from the mechanical analyses, and a 20 to 50 micron coarse silt fraction obtained by sedimentation procedures, were used for microscope studies.

Trace Element Analyses

Total iron and manganese were determined as Fe_2O_3 and MnO, respectively, by the "rapid" methods outlined by Brannock and Shapiro (1956). Iron was determined by measuring the light transmitted at 560 mμ through a solution containing the orange ferrous orthophenanthroline complex. Manganese was determined by measuring the light transmitted at 525 mμ through a solution in which the manganese was oxidized to permanganate with KIO_4. Total zinc, copper, and lead were determined according to the methods described by Gilbert (1959). Antimony was determined by the rhodamine B method described by Jardine (1963). Arsenic was determined by a modified version of the Gutzeit method as described by Lynch and Mihailov (1963), where the arsenic in gaseous form is passed through lead acetate onto mercuric chloride paper. Tin, silver, and cadmium were determined by emission spectrography, by a D.C. arc method that employs partial volatilization of a 40 mg sample plus an appropriate buffer mixture with an external standard exposed on the same plate.

Other Analyses

Soluble salts were extracted from the soils by shaking fifty grams of soil with metal-free water for two hours and then by filtering the suspension (Jackson, 1958). The filtrate was then analyzed for calcium, magnesium, sodium, potassium, silica, manganese, copper, lead, zinc, carbonate, bicarbonate, sulphate, and chloride. The pH and conductance were determined on the same filtrate.

The method outlined by Tucker and Kurtz (1955) was used to determine the metals soluble in 0.1 N HCl. The soil was shaken for 45 minutes in the dilute acid, and the liquid was then analyzed for zinc and copper. The residue was analyzed for zinc, copper, lead, arsenic, and antimony.

Free iron oxides were removed by the sodium hydrosulphite leaching treatment of Aguilera and Jackson (1953), and determined colorimetrically by a photometer. The residues were analyzed for zinc, copper, lead, arsenic, and antimony.

Determination of the elements associated with the organic fraction was attempted, by following the H_2O_2 - dilute HCl method of Tucker and Kurtz (1955). The residues were analyzed for zinc, copper, lead, arsenic, and antimony, however, and the amounts of metal were determined by subtraction of these values from the dilute acid residue values.

In addition to visual examinations of the pebbles and rock fragments that were larger than 1 mm, microscope examinations were made of both light and heavy mineral separations of the sand and coarse silt fractions. Heavy minerals were separated by a bromoform method, and the grains from the light and heavy mineral separates were mounted on gelatin slides and examined with a petrographic microscope.

Chapter III

CHEMICAL AND MINERALOGICAL RESULTS

Total Analyses

This section contains the mean values of all the analyses carried out on the soil samples for cation exchange capacity, pH, organic carbon, iron, manganese, lead, copper, zinc, arsenic, antimony, silver, and tin. The detailed analyses for each of the soil and rock samples are given in Tables 35 to 38 in the Appendix.

Tables 1 to 12 give the results for each test or element and show the range of values and the mean values for each soil horizon. In addition to the mean values for all profiles, mean values for the horizons of the normal, Brunswick No. 6, Nigadoo, and Middle River profiles have been determined separately in order to observe any significant differences. Means were also determined for all profiles overlying sulphide deposits, but were not included in the final tables because they were always strongly influenced by the numerically greater Nigadoo group.

The number of profiles from which the means were determined is shown in brackets at the top of each group. The following abbreviations have been used above the columns in Tables 1 to 12.

C.E.C.	—Cation exchange capacity	Br. 6	—Means of Brunswick No. 6 horizons
m.e.	—Milli-equivalent weight	Nig.	—Means of Nigadoo horizons
Range	—Range of values	M.R.	—Means of Middle River horizons
All	—Means of all profile horizons		
Nor.	—Means of normal horizons		

Cation Exchange Capacity

Cation exchange capacity determinations were done on five profiles, and the ranges and mean values obtained for their horizons are shown in Table 1. This table also gives the mean values for the organic carbon and clay content of the profiles. The high organic content of the A_0 horizon is probably responsible for this horizon's high exchange capacity. The drop in exchange capacity of the A_2 horizon roughly parallels that of organic carbon, whereas the 200 to 500 per cent increase in exchange capacity of the B_1 horizon over the A_2 horizon is only matched by a 40 per cent increase in organic carbon. The means for the clay content of three profiles indicate an increase in clay per cent in the B_1 horizon, which may account for part of the increased exchange capacity. The low humus content of the B_2 and C horizons probably indicates that most of the exchange capacity is associated here with the inorganic clay-size fraction.

TABLE 1 *Range and mean cation exchange capacity values compared with mean organic carbon and clay values for five profiles*

Horizon	C.E.C. range (m.e./100g.)	C.E.C. means (m.e./100g.)	Organic carbon means (%)	Clay means (%)
A_0	91–143	106	36.3	29.4
A_2	5–17	12	0.9	9.0
B_1	25–37	33	1.3	18.0
B_2	6–30	14	0.3	17.7
C	5–15	10	0.1	12.1

Organic Carbon

The per cent error of the analytical method used to determine organic carbon was estimated to be ± 2 to 5 per cent. Determinations were done on sixteen profiles and the ranges and mean values are shown in Table 2. Although the normal profiles show a gradual decrease in organic carbon down the profile after an initial high A_0 value, the three groups over the sulphide deposits show a greater accumulation of organic carbon in the B_1 than in the contiguous A_2 or B_2 horizons.

TABLE 2 *Range and mean distribution of total organic carbon in podzol profiles (in per cent)*

Horizon	Range	All (16)	Nor. (9)	Br. 6 (2)	Nig. (3)	M.R. (2)
A_0	22.90–43.43	33.52	31.37	31.79	37.31	34.48
A_2	0.27–2.34	1.15	1.23	0.91	1.10	1.03
B_1	0.17–1.71	1.07	0.95	1.16	1.65	1.16
B_2	0.06–1.78	0.44	0.29	0.25	1.17	0.26
C	0.05–0.62	0.23	0.12	0.25	0.30	—[1]

[1]No C horizon present

Hydrogen-ion Concentration (pH)

The pH was determined for the horizons of eighty-four profiles. The range of values indicates a high variability for all horizons and a general tendency for decreasing acidity with depth (Table 3). The means of the various groups also emphasize this tendency.

The influence of the limy rocks of the Nigadoo area is reflected in the higher alkalinities of the Nigadoo group. A check of the means of the normal profiles from north of the "Rocky Brook–Millstream break" and overlying the same general country rocks as the Nigadoo deposit showed that they too are more alkaline than normal profiles south of the "break". These soils, like the Nigadoo group, have probably been influenced by the higher carbonate content of the underlying Silurian rocks. The failure of the alkalinity to increase in the C horizon of the Brunswick No. 6 profile is probably due to the highly acid conditions resulting from the oxidation of the massive sulphides.

TABLE 3 *Range and mean distribution of pH in podzol profiles*

Horizon	Range	All (84)	Nor. (56)	Br. 6 (4)	Nig. (17)	M.R. (3)
A_0	2.2–6.5	4.2	4.2	2.9	4.9	4.0
A_2	2.9–5.8	4.2	4.1	3.4	5.2	4.0
B_1	3.4–6.6	4.6	4.5	3.6	5.2	4.6
B_2	3.8–6.8	4.9	4.8	4.2	5.6	5.2
C	3.2–6.9	5.1	4.9	4.2	6.1	—[1]

[1]No C horizon present

Iron

The per cent error of the method used was estimated at 1 to 2% of the actual iron present. Although Table 4 shows that the range is variable for each horizon, the B horizons of all but the Nigadoo group contain the highest mean iron values. The highest mean iron values occur in the B_1 horizon of all groups except the Brunswick No. 6 and Nigadoo. In the Brunswick group, slightly more iron occurs in the B_2 than in the B_1 horizon. In the Nigadoo group there is a progressive increase in iron from the B_1 to the C horizon which may be partly due to the higher alkalinity of these profiles.

TABLE 4 *Range and mean distribution of total iron in podzol profiles (in per cent)*

Horizon	Range	All (26)	Nor. (13)	Br. 6 (2)	Nig. (5)	M.R. (2)
A_0	0.09–4.67	1.34	1.52	0.83	1.02	2.15
A_2	0.79–6.20	3.05	2.54	1.26	1.55	2.84
B_1	2.67–10.30	6.05	5.07	9.08	4.74	7.89
B_2	3.23–13.40	5.91	4.55	10.04	5.16	7.58
C	0.79–11.68	5.27	4.53	4.99	6.50	—[1]

[1]No C horizon present

Manganese

The per cent error of the method used was estimated at 5 to 10% of the actual manganese present, and the lower analytical limit of the method was 100 ppm manganese. Table 5 indicates that the highest values are present in the Nigadoo group and the lowest in the Brunswick No. 6 group. The ranges and means of all but the Brunswick group indicate high values in the A_0 horizon followed by marked decreases in the A_2 horizon, then a gradual increase downwards to the C horizon. In all three profile groups overlying sulphide bodies, the lowest values occur in the A_2 horizon. In the Brunswick group, the only manganese that was detected by the method used was in the B_1 and B_2 horizons of one profile.

TABLE 5 *Range and mean distribution of total manganese in podzol profiles (in ppm)*

Horizon	Range	All (26)	Nor. (13)	Br. 6 (2)	Nig. (5)	M.R. (2)
A_0	<100–5,740	800	680	<100	2,280	470
A_2	<100–4,600	500	350	<100	160	275
B_1	<100–1,200	460	570	115	380	350
B_2	<100–1,160	570	610	80	1,020	540
C	<100–2,780	740	800	<100	1,730	—[1]

[1]No C horizon present

Lead

The estimated error of the method used to determine lead is ±25% of the actual amount present. Table 6 shows the extreme range of values that are present for lead in all horizons. The highest values are from the Brunswick No. 6 profiles, although the Nigadoo group has more horizons with values greater than 5,000 ppm lead than any of the other groups.

TABLE 6 *Range and mean distribution of total lead in podzol profiles (in ppm)*

Horizon	Range	All (84)	Nor. (56)	Br. 6 (4)	Nig. (17)	M.R. (3)
A_0	0–55,000	989	73	14,320	754	1,020
A_2	0–3,200	189	13	931	519	288
B_1	0–5,600	384	36	2,100	1,180	402
B_2	0–46,000	1,235	28	18,000	671	1,368
C	0–31,000	1,060	65	11,000	2,044	—[1]

[1]No C horizon present

The normal and Nigadoo groups show enrichments of lead in three horizons, namely the A_0, B_1, and C horizons, with the maximum amounts occurring in the A_0 horizon. This immediately suggests a relationship of lead with organic matter in the A_0 horizon, an association of lead with the products of accumulation in the B_1 horizon, and an affiliation with relatively unweathered material in the C horizon. The Brunswick group exhibits an enrichment of lead in the B_2 rather than in the B_1 horizon. The Nigadoo and Middle River groups have basal enrichments just above the ore zones.

Copper

The per cent error of the method used is estimated at ±25% of the actual copper present. Table 7 shows that the highest mean values of copper occur in the basal horizons of all groups. There is a general similarity to the pattern of the mean values in all groups. The mean values in the A_2 horizons are less than the mean values in the A_0 horizons, and they

increase gradually towards the basal horizons. The only major break in this pattern occurs in the Nigadoo group where the mean copper value in the A_2 horizon is higher than the mean value in the underlying B_1 horizon.

TABLE 7 *Range and mean distribution of total copper in podzol profiles (in ppm)*

Horizon	Range	All (84)	Nor. (56)	Br. 6 (4)	Nig. (17)	M.R. (3)
A_0	5–310	29	11	50	68	67
A_2	5–250	19	7	19	52	33
B_1	5–150	24	10	88	33	95
B_2	5–920	61	16	386	58	267
C	5–2,200	92	26	720	94	—[1]

[1]No C horizon present

Zinc

The per cent error of the method used is estimated at ±25% of the actual zinc present. Table 8 indicates that the lowest mean values occur in the normal group, and the highest in the Nigadoo group. The highest zinc values are found in the surface and basal horizons.

TABLE 8 *Range and mean distribution of total zinc in podzol profiles (in ppm)*

Horizon	Range	All (84)	Nor. (56)	Br. 6 (4)	Nig. (17)	M.R. (3)
A_0	20–4,400	295	87	130	919	117
A_2	10–2,200	112	59	15	586	40
B_1	20–3,300	251	90	57	1,087	120
B_2	30–4,600	416	98	104	1,621	147
C	20–5,100	448	98	173	1,780	—[1]

[1]No C horizon present

All groups show some tendency for zinc accumulation in the A_0 horizons, and the element shows a general trend to reach a minimum value in the A_2 horizon, then to increase in the B_1 horizon to a value similar to that of the A_0 horizon. This is followed by a general increase downwards to a maximum value in the C horizon. An interesting feature of the normal group is that all horizons except the A_2 have similar mean values of about 90 ppm zinc.

Arsenic

The error of the analytical method is estimated at ±25% of the actual arsenic present. It is apparent from Table 9 that the greatest ranges and highest arsenic values are present in the lower horizons of most of the profiles. The highest mean values occur in the Middle River and Nigadoo profiles.

TABLE 9 *Range and mean distribution of total arsenic in podzol profiles (in ppm)*

Horizon	Range	All (26)	Nor. (13)	Br. 6 (2)	Nig. (5)	M.R. (2)
A_0	0–1,100	121	2	20	141	1,035
A_2	0–1,900	180	5	38	28	590
B_1	0–2,900	352	22	190	343	1,240
B_2	0–3,500	341	14	193	448	2,400
C	0–4,200	445	11	98	1,491	—[1]

[1]No C horizon present

The peak mean value of arsenic in the normal group occurs in the B_1 horizon. In the Brunswick group the peak mean arsenic value is in the B_2 horizon. The mean values for the Nigadoo and Middle River groups show no such concentration of arsenic in the B_1 horizon. Instead, there is a gradual increase from the B_1 horizon downwards to the basal horizons where peak values are attained. The relatively high mean arsenic value in the A_0 horizon of the Middle River profiles could be related to a concentration of arsenic in ash or charcoal, since this area has recently been devastated by forest fires.

Antimony

The error of the analytical method used for antimony is estimated as a maximum of $\pm 25\%$ of the actual amount present. Table 10 indicates that antimony is considerably less abundant than arsenic in these soils. The highest contents of antimony occur in the Brunswick No. 6 profiles.

TABLE 10 *Range and mean distribution of total antimony in podzol profiles (in ppm)*

Horizon	Range	All (26)	Nor. (13)	Br. 6 (2)	Nig. (5)	M.R. (2)
A_0	1–24	4	2.2	14	5	7
A_2	1–75	7	2.3	38	6	4
B_1	1–110	10	2.4	68	2	5
B_2	1–152	11	1.6	91	5	8
C	1–61	10	1.9	36	15	—[1]

[1]No C horizon present

The greatest range of values is found in the B horizon, which is usually the location of the maximum mean values. In the Nigadoo and Middle River groups there are slight concentrations of antimony in the A horizons. Antimony behaves like arsenic by increasing downward to a peak value in the B horizon. The increases of antimony in the basal horizons of the Nigadoo and Middle River groups are probably related to bedrock enrichments.

Silver

The error of the spectrographic method employed is estimated at ±50% of the actual silver present. Silver shows three general sites of concentration in the profiles (Table 11). The most consistent site of enrichment for all groups is in the A_0 horizon. There is also some tendency in the B horizons for enrichment of the profiles overlying sulphide deposits. There is a peak value for silver in the B_2 horizons in the Brunswick group similar to that formed by other elements in this group. Also, like most other elements studied, silver is enriched in the basal horizons of the Nigadoo and Middle River groups.

TABLE 11 *Range and mean distribution of total silver in podzol profiles (in ppm)*

Horizon	Range	All (26)	Nor. (13)	Br. 6 (2)	Nig. (5)	M.R. (2)
A_0	0.2–90.0	5.7	1.6	45.6	5.2	3.4
A_2	.1–36.0	2.4	0.4	18.6	0.4	1.8
B_1	.2–6.7	1.8	0.3	3.9	4.6	4.1
B_2	.1–24.0	3.5	0.3	19.5	4.1	6.1
C	.1–16.0	2.7	0.3	5.3	9.0	—[1]

[1]No C horizon present

Tin

The estimated error of the spectrographic method used to determine tin is ±50% of the actual amount present. Table 12 shows that the Brunswick No. 6 profiles contain the highest tin values, followed by the Nigadoo group. An appraisal of Table 12 also indicates that there is some concentration of tin in the A_2 horizon of all groups, and in the B_2 horizon of the Brunswick and normal groups. The Nigadoo group has its maximum value in the C horizon, where the influence of bedrock mineralization is again manifest. The presence of relatively high tin values in the A_2 horizon may result from residual concentrations of the oxide. In this form the tin would probably exhibit a marked resistance to the intense weathering processes that normally occur in this horizon in podzol soils.

TABLE 12 *Range and mean distribution of total tin in podzol profiles (in ppm)*

Horizon	Range	All (26)	Nor. (13)	Br. 6 (2)	Nig. (5)	M.R. (2)
A_0	0–68.0	7.8	2.3	—	6.5	15.2
A_2	2.0–136.0	19.1	5.5	83.5	32.0	36.2
B_1	1.6–120.0	14.2	3.4	68.0	15.1	24.5
B_2	0.7–127.0	10.7	3.9	125.0	9.0	7.5
C	0.9–126.0	19.2	3.3	38.0	58.5	—[1]

[1]No C horizon present

Summary

In the normal profiles, lead, silver, and manganese are the elements most enriched in the A_0 horizons, and tin shows a moderate concentration in the A_2 horizons. Iron is enriched in the B horizons, arsenic and lead in the B_1 horizons, and tin and zinc in the B_2 horizons. The C horizons of the normal profiles exhibit relatively high concentrations of manganese, lead, copper, and zinc.

In the profiles overlying sulphide deposits, lead and silver have accumulated in the A_0 horizons of all profiles, and manganese and arsenic are enriched in the humic horizons of the Nigadoo and Middle River groups. Zinc, copper, and antimony show local enrichments in the A_0 horizons.

Tin has accumulated in the A_2 horizons of all profiles. The silver content is relatively high in the A_2 horizons of the Brunswick group. Copper is slightly enriched in the A_2 horizons of the Nigadoo group.

Lead is concentrated in the B_1 horizon of the Nigadoo profiles, and manganese and arsenic have accumulated in the B_1 horizons of the Brunswick group.

Iron, lead, arsenic, antimony, silver, and tin are markedly enriched in the B_2 horizons of the Brunswick profiles. These same elements, as well as copper, are enriched in the basal B_2 horizons of the Middle River profiles.

All elements show higher concentrations in the C horizons of the Nigadoo group. Copper and zinc reach their highest concentration in the C horizons of the Brunswick and Nigadoo groups.

Correlation Coefficients

It was thought that two of the most important factors affecting the movement and distribution of elements in the soils of the Bathurst area would be pH and iron content. Hence calculations were made of the correlation of pH and total iron with the various elements under study. The correlations of pH with the different elements are shown in Table 13, and correlations of iron with other trace elements in Table 14. In both tables the "r" values are given for all soil horizons, as well as for the horizons overlying three sulphide bodies. The coefficients of correlation, or "r" values were calculated according to the examples given by Krumbein and Pettijohn (1938).

pH Correlation Coefficients

Table 13 shows that all the elements behave differently with respect to pH, although there are some general similarities. Zinc is apparently affected the most strongly in all soil horizons. Lead is significantly affected in all horizons, although the two A_0 values are somewhat contradictory. Copper and iron are significantly correlated with pH in certain horizons. Manganese, arsenic, and antimony show only occasional significant correlations with pH. Although organic carbon exhibits little relationship to pH in the individual horizons, significant relationships are evident above the orebodies. Silver and tin seem to be the elements least affected by pH.

The response of the elements to changes in pH as indicated by the "r" values is usually significantly different in the B_1 and A_2 horizons. An oxidizing environment supposedly predominates in the B_1 horizons, and since reducing conditions appear to be present for at least part of the time in the A_2 horizons, the "r" value may give a measure of the elemental response to pH under oxidizing (B_1) and reducing (A_2) conditions. Elemental mobility appears to increase as the "r" values increase positively.

TABLE 13 *Correlation coefficients of pH with organic carbon, iron, and other elements*

	Horizons						Sulphide bodies (all horizons)			Nigadoo horizons				
	All	A_0	A_2	B_1	B_2	C	Br. 6	M.R.	Nig.	A_0	A_2	B_1	B_2	C
No. of samples	79–388	14–79	14–69	15–69	16–82	17–75	12–22	8–13	13–80	16–19	10–12	10–11	15–17	13–15
Organic carbon	−.345[2]	−.440	−.137	+.420	+.012	+.118	−.640[2]	−.552	−.541[1]					
Iron	+.343[2]	+.940[2]	+.385[1]	−.640[2]	−.141	+.210	+.567[2]	+.900[2]	+.665[2]					
Manganese	+.363[2]	+.093	+.323	+.091	+.552[2]	+.023		+.390	+.407[1]					
Arsenic	+.178[1]	+.455[2]	+.117	+.152	+.098	+.035	+.430	+.875[2]	+.285					
Antimony	−.124	+.034	−.002	−.480[1]	−.082	−.335	+.306	+.585	+.248					
Silver	−.005	+.212	−.005	+.302	−.101	+.320	+.182	+.278	+.398[1]					
Tin	−.076	−.140	−.085	−.234	−.078	+.161	−.165	−.268	.000					
Lead	−.077	−.055	+.252[2]	−.885[2]	−.210[1]	−.265[2]	+.230	+.546[1]	+.092	+.494[1]	+.054	−.512	−.213	−.087
Copper	+.144[2]	+.387[2]	+.500[2]	−.101	−.080	−.028	+.586[2]	+.790[2]	+.280[2]	+.557[2]	+.338	−.293	−.136	−.159
Zinc	+.498[2]	+.368[2]	+.690[2]	+.433[2]	+.505[2]	+.615[2]	+.156	+.528[1]	+.380[2]	+.190	+.828[2]	+.015	+.142	+.237

[1]Significant at the 5% level
[2]Significant at the 1% level

TABLE 14 *Correlation coefficients of iron with other elements*

	Horizons						Sulphide bodies		
	All	A_0	A_2	B_1	B_2	C	Br. 6	M.R.	Nig.
No. of samples	79–123	14–26	14–20	15–21	16–22	17–22	12–13	8	13–20
Organic carbon	−.493[2]	−.177	−.510[1]	−.014	−.054	−.051	−.413	−.605	−.733[2]
Tin	+.081	−.073	−.103	+.310	+.130	−.110	−.430	−.130	+.510[1]
Silver	−.097	−.430[1]	−.093	+.256	+.425[1]	+.298	−.360	+.365	+.575[2]
Arsenic	+.181[1]	+.069	+.303	+.380[1]	+.364[1]	+.295	+.672[2]	+.685[1]	+.267
Antimony	+.141	+.025	−.031	+.375[1]	+.328	−.022	+.014	+.418	+.558[2]
Manganese	+.044	+.032	+.320	−.272	−.365[1]	+.005		+.061	+.029
pH	+.343[2]	+.940[2]	+.630[2]	−.640[2]	−.141	+.210	+.567[1]	+.900[2]	+.665[2]
Lead	+.045	−.088	+.011	+.340	+.095	−.073	−.254	+.355	+.683[2]
Copper	+.309[2]	−.044	+.560[2]	+.695[2]	+.573[2]	+.708[2]	+.363	+.670[1]	+.174
Zinc	+.072	−.008	+.538[2]	−.245	−.047	+.137	−.064	+.575	+.565[2]

[1]Significant at the 5% level
[2]Significant at the 1% level

Iron Correlation Coefficients

Table 14 indicates that iron correlates best with pH, copper, and arsenic. Sporadically high correlations of iron with silver, antimony, zinc, and manganese also occur in some horizons and above the sulphide bodies. Tin and lead are highly correlated with iron only in the Nigadoo profiles.

Detailed Profile Studies

The six soil profiles chosen for detailed chemical and mineralogical studies are considered to be representative of normal soils and of soils overlying sulphide deposits in the Bathurst district. Four profiles were chosen from above the Nigadoo, Brunswick No. 6, and Middle River sulphide deposits. Two normal profiles were selected, one overlying granite, and the other from an area underlain by basic and intermediate volcanic rocks. These six profiles were described in detail in Chapter II. The results for the cation exchange capacity, pH, total iron, manganese, lead, zinc, copper, arsenic, antimony, silver, tin, and cadmium determinations on samples from these profiles are shown in Table 35 of the Appendix.

Leaching of Water-Soluble Salts

The primary purpose of this part of the project was to determine the presence and amounts of lead and zinc in a water-soluble form. Determinations were also made of the amounts of a number of other common water-soluble cations and anions. Remarkably little information is present in the literature concerning the determination of water-soluble heavy metals in soils. Hibbard (1940) attempted to determine water-soluble zinc, and concluded that pure water has almost no solvent power for loosely bonded zinc in soils except where large amounts of zinc were added to the soil. Jones, *et al.* (1936) found that water-soluble zinc was present immediately after addition of zinc sulphate to the soil, but decreased rapidly as it was leached by rainfall.

In addition to lead and zinc, water-soluble sodium, potassium, and manganese were determined, and water-soluble calcium and magnesium were estimated as total hardness. Water-soluble iron and aluminum were not determined but were undoubtedly present in many of the samples. The water-soluble anions determined were the carbonate, bicarbonate, sulphate, and chloride ions. No carbonate anions were found; if initially present, they were presumably converted to bicarbonates during the mixing and filtering operations. Nitrates were not determined, but they are presumably present in some horizons, especially those rich in organic matter. Other anions such as silicate and phosphate may have been present in certain samples. The presence of silica was determined and it was assumed to be colloidal SiO_2, but in some of the more alkaline horizons this compound may be present partly as the silicate ion. Water-soluble ions were not determined from the A_0 horizons because it was found that the dark colour of the dissolved humic material generally interfered seriously with the ionic determinations.

After the soils were shaken for two hours in water and the mixtures filtered, most filtrates contained fine, brownish suspended matter which could not be removed with conventional filter paper. It was, however, removed by special "millipore" filters. The suspended material probably consisted of iron oxides and hydroxides, together with some aluminum hydroxides and possibly some colloidal silica. It is probable that small amounts of dissolved copper, lead, zinc, and manganese, were "scavenged" by these iron and other oxides and hydroxides as a result of adsorption and coprecipitation processes. As a result the values reported for

the water-soluble ions of these metals are lowered by an amount equal to the small amounts of the adsorbates.

Analyses for water-soluble ions are presented in Tables 15 to 22. For each horizon the ions reported as parts per million (ppm) were converted to equivalents per million (epm), and the total cation equivalents were balanced against the total anion equivalents to determine the accuracy. The per cent error was computed in the following way, as outlined by Thomas (1953).

$$\frac{\text{Sum of cations (epm)} - \text{Sum of anions (epm)}}{\text{Total ions (epm)}} \times 100$$

The per cent error is positive where there is an excess of cation over anion equivalents, and negative where the anion equivalents are in excess. Although calcium and magnesium were not determined as such, the value obtained for total hardness represents the sum of calcium and magnesium expressed as $CaCO_3$ in parts per million. In converting this value to equivalents per million, the reacting weight for calcium carbonate was used. Silica was assumed to be present as colloidal silica (SiO_2); in some samples it was probably also present in the soluble form.

Nigadoo Profile No. 17

An outstanding feature of this profile is the large amount of sulphate ion present relative to the other profiles tested. Most of the sulphate is probably derived from vein material that was thrown on top of the profile during trenching operations. As this material is rich in pyrite, exposure to oxygen and water would result in the following reaction:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

$FeSO_4$ undergoes oxidation to produce $Fe_2(SO_4)_3$ which in turn may again attack the sulphides producing more $FeSO_4$. The resulting large amounts of water-soluble iron sulphates could account for the high sulphate values. Water-soluble lead, copper, and zinc are virtually absent from this profile.

Nigadoo Profile No. 19

The leachates from this poorly drained profile are more alkaline than those of the other profiles examined. The high pH values probably reflect the high bicarbonate contents of these samples (Table 16). It is also possible that some nitrates occur in these leachates, as most groundwaters that saturate poorly drained soils have components high in nitrate.

The small amount of lead reported in the leachate from the G_1 horizon may be present as lead nitrate. This compound is one of the most soluble of the common lead salts (solubility: 56.5g per 100g of water at 20°C). The traces of copper in all horizons may be present in nitrate, chloride, or sulphate form, as all these copper compounds are relatively water soluble.

Brunswick Profile No. 44

This profile produced the most acid leachates of all the profiles examined. Neither carbonate nor bicarbonate ions were detected in the leachates (Table 19). The high negative errors that occur for some horizons could have been caused by the presence of undetermined hydrogen or aluminum ions. Water-soluble lead, copper, and zinc occur in all horizons.

TABLE 15 *Water-soluble ions in Nigadoo profile No. 17 (in ppm)*

Horizon	Pb	Cu	Zn	Mn	Total hardness as $CaCO_3$	Na	K	Cl	SO_4	HCO_3	SiO_2	pH	% Error
A_0	Not determined												
A_2	0	0	0	0.10	35.0	0.6	0.3	1.5	32.4	0.5	2.6	5.7	+0.1
B_1	0	0	0	.02	93.0	1.9	.5	2.2	81.6	10.7	4.8	6.3	+1.3
B_2	0	0	0	.20	47.9	1.0	.8	1.9	33.9	15.8	2.8	6.8	+1.9
C	0	Tr	0	.20	38.6	0.6	.8	2.0	27.5	10.8	2.9	6.9	+3.0

TABLE 16 *Water-soluble ions in Nigadoo profile No. 19 (in ppm)*

Horizon	Pb	Cu	Zn	Mn	Total hardness as $CaCO_3$	Na	K	Cl	SO_4	HCO_3	SiO_2	pH	% Error
A_0	Not determined												
G_1	0.04	0.01	0	0	41.8	1.0	0.5	1.4	4.9	45.5	3.6	7.4	+2.1
G_2	0	.01	0	0.10	14.4	0.4	.3	1.0	2.1	16.7	3.0	7.1	+0.2
Cg	0	Tr	0	0	9.9	.4	.4	0.6	2.8	12.2	3.0	7.0	−9.9

The amounts of water-soluble lead are much higher than those in the leachates of any of the other profiles. However, total lead values are also high in this profile. The proportions of water-soluble lead to total lead are shown in Table 17. It is interesting that the highest concentrations of soluble lead occur in the two bleached horizons, the A_2 and Cg_1 horizons. The soluble lead in this profile may be present in either sulphate or chloride form, even though lead sulphates and chlorides are only slightly soluble in water. The high concentration of total lead present, and the high acidity, however, would favour an increased solubility of these compounds.

TABLE 17 *Water-soluble lead in Brunswick profile No. 44*

Horizon	Total lead (ppm)	Water-soluble lead (ppm)	Water-soluble lead % of total lead
A_0	55,000		
A_2	2,900	7.6	0.26
B_1	6,300	5.6	.09
B_2	33,000	8.0	.02
B_3	46,000	16.8	.04
Cg_1	3,000	19.0	.63
Cg_2	31,000	15.0	.05

This is the only profile in which water-soluble zinc was detected. The proportions of water-soluble zinc to total zinc are shown in Table 18. The highest proportions of water-soluble zinc occur in the bleached A_2 and Cg_1 horizons. Otherwise, the proportions of water-soluble to total zinc in the other horizons are remarkably similar. The solubility of $ZnCl_2$ is 432g per 100g of water solution (25°C) and that of $ZnSO_4$ is 42.0g per 100g of water solution (0°C), so that the amounts of zinc reported may easily be accounted for by either of these very water-soluble compounds.

TABLE 18 *Water-soluble zinc in Brunswick profile No. 44*

Horizon	Total zinc (ppm)	Water-soluble zinc (ppm)	Water-soluble zinc % of total zinc
A_0	60		
A_2	20	0.15	0.75
B_1	60	.08	.13
B_2	70	.10	.14
B_3	220	.25	.11
Cg_1	100	.23	.23
Cg_2	360	.17	.05

Water-soluble copper is present in much smaller amounts than either lead or zinc. Although copper chlorides and sulphates are not as soluble in water as their zinc counterparts, there could easily be sufficient amounts of these compounds in this acid environment, to supply the water-soluble copper detected.

TABLE 19 *Water-soluble ions in Brunswick profile No. 44 (in ppm)*

Horizon	Pb	Cu	Zn	Mn	Total hardness as $CaCO_3$	Na	K	Cl	SO_4	HCO_3	SiO_2	pH	% Error
A_0	Not determined												
A_2	7.6	0.02	0.15	Tr	4.4	0.2	0.3	3.1	9.0	0	3.2	4.1	−20.1
B_1	5.6	Tr	.08	0.01	3.7	.4	.4	2.0	8.2	0	4.8	4.2	−17.9
B_2	8.0	.01	.10	Tr	4.3	.4	.6	3.7	5.6	0	4.9	4.3	− 5.2
B_3	16.8	.01	.25	0.01	10.5	.5	.8	3.7	13.2	0	5.5	4.2	+ 5.4
Cg_1	19.0	.01	.23	0	10.6	.4	.6	0.8	15.7	0	7.9	4.2	+10.9
Cg_2	15.0	.02	.17	Tr	7.8	.6	.7	.5	24.7	0	8.1	3.6	−20.3

TABLE 20 *Water-soluble ions in Middle River profile No. 79 (in ppm)*

Horizon	Pb	Cu	Zn	Mn	Total hardness as $CaCO_3$	Na	K	Cl	SO_4	HCO_3	SiO_2	pH	% Error
A_0	Not determined												
A_2	0.02	0.01	0	0.02	2.3	0.5	0.4	2.4	2.0	0	6.7	4.7	−16.5
B_1	0	Tr	0	.01	1.4	.3	.6	1.7	0.8	0	2.9	5.3	− 6.9
B_2	0	0.01	0	.18	1.0	.4	.1	0.9	1.3	1.0	4.7	6.3	−23.1

The increase in soluble lead and zinc in the bottom three horizons is about the same magnitude as the increase in sulphate. Groundwater has risen into these horizons, and it is probable that both the heavy metal and the sulphate ions have moved upward or laterally from the underlying sulphide body.

Middle River Profile No. 79

This profile is marked by a sharp increase in pH with depth and a consistent negative error. The chief balancing ion could be aluminum which was not determined. Small amounts of water-soluble copper occur in all horizons. The copper is probably in the chloride or sulphate form. Water-soluble lead is reported only from the A_2 horizon. This lead may be present in the soluble nitrate form, since the area has been recently burned over, and there is still much ash and charcoal in the A_0 horizon. Leaching of this material by rainfall could supply both the nitrates and the lead to the A_2 horizon.

Sand Profile No. 51

The cationic excess indicated by the consistent positive error could be balanced by nitrate, which was not determined (Table 21). Ammonium ions may also be present, as a relatively high organic content is found as far down as the B_2 horizon in this well-drained sandy profile (Table 35).

Some water-soluble manganese occurs in the leachates from the B horizons. It is probable that, in such a well-aerated soil as this, the manganese exists as relatively insoluble oxides or hydroxides, but the mild acidities present may cause some dissolution of these compounds. Water-soluble copper is present in small amounts in the lower three horizons, and as there are only 5 to 10 ppm of total copper in this profile, it is probably present as water-soluble chlorides or sulphates. The occurrences of water-soluble lead in the A_2 and B horizons are surprising, in view of the low total values present. According to Hawkes (1957), the pH of hydrolysis of lead from aqueous solution as a hydroxide or basic salt is 6.0. If lead is assumed to be present as $Pb(OH)_2$ in the B horizons, it would have a solubility in water of 0.016g per 100g of water solution (20°C), which could account for the small amounts detected. Water-soluble lead in the A_2 horizon could be present as water-soluble nitrates or as the slightly soluble chlorides.

Granite Profile No. 64

It is possible that the unbalanced excess of anions indicated by the large negative per cent error in the B_1, B_2, and C horizons could be balanced by aluminum which was not determined. The high silica contents reflect the high quartz content of the parent soil material and granite bedrock. Soluble copper, lead, and zinc are virtually absent. There is a little water-soluble copper in the two lower horizons, possibly in chloride or sulphate form.

Summary

Water-soluble lead was detected in four of the six profiles. It is most abundant in the Brunswick profile, where it is presumably sulphate. Water-soluble copper is present in small amounts in all six profiles. It is probably present as the soluble sulphate or chloride. Water-soluble zinc was detected only in the Brunswick profile, where it may be present as the sulphate or chloride. Soluble manganese is present in all six profiles. The lowest amounts occur in the acid Brunswick profile, and the highest in the sand profile. Soluble calcium and magnesium (total hardness as calcium carbonate) were most abundant in the Nigadoo

TABLE 21 *Water-soluble ions in sand profile No. 51 (in ppm)*

Horizon	Pb	Cu	Zn	Mn	Total hardness as $CaCO_3$	Na	K	Cl	SO_4	HCO_3	SiO_2	pH	% Error
A_0	Not determined												
A_2	0.08	0	0	0.05	7.7	0.5	0.9	2.4	4.0	1.2	3.7	5.2	+13.8
B_1	.08	0.01	0	.40	4.5	.4	.8	0.8	3.7	2.3	6.3	6.1	+3.7
B_2	.20	.01	0	.10	3.1	.3	.8	.8	1.8	2.3	4.2	6.3	+1.8
C	0	.01	0	.05	1.2	.3	.4	.7	1.0	0	1.9	5.7	+8.0

TABLE 22 *Water-soluble ions in granite profile No. 64 (in ppm)*

Horizon	Pb	Cu	Zn	Mn	Total hardness as $CaCO_3$	Na	K	Cl	SO_4	HCO_3	SiO_2	pH	% Error
A_0	Not determined												
A_2	0	0	0	0.01	5.8	0.4	1.1	3.0	3.2	0.0	7.0	4.4	+3.3
B_1	0	0	0	.10	7.0	.5	0.9	2.5	5.8	1.7	15.0	5.3	−10.8
B_2	0	0.01	0	.10	3.5	.5	1.5	4.6	2.2	1.2	7.5	6.1	−22.4
C	0	.01	0	.10	1.6	.4	0.8	2.2	1.5	1.2	6.8	5.8	−20.0

profiles. Water-soluble sodium and potassium were detected in every horizon of the six profiles. Soluble sodium is most abundant in the well-drained Nigadoo profile. Soluble potassium reaches its highest value in the granite profile.

Water-soluble chloride and sulphate anions are present in every horizon. Soluble chloride is most common in the Brunswick and granite profiles, and the soluble sulphate content is highest in the Brunswick and well-drained Nigadoo profiles. No soluble carbonate was found, mainly because it had apparently all been converted to bicarbonate. Bicarbonate ions were detected in all but the Brunswick profile and are most common in the Nigadoo profiles.

Silica was detected in all samples. It may be present as dissolved ions and in a colloidal form. The pH of the leachate samples ranged from 3.6 in the basal Brunswick horizon to 7.4 in the upper gley horizon of the poorly drained Nigadoo profile.

In most samples the high negative errors in the reported analyses reflect the presence of one or more cationic constituents that were not determined, e.g., iron, aluminum, and in the case of acid water, hydrogen ions. Conversely the high positive errors reflect the presence of undetermined anionic constituents such as nitrates.

Determination of Dilute Acid-Soluble Trace Elements

Dilute acid-extractable metal was removed by the method outlined by Tucker and Kurtz (1955) in which the soil sample is mechanically shaken with 0.1 N HCl for 45 minutes then centrifuged and the clear supernatant liquid removed for analysis. Zinc and copper in the supernatant liquid were determined by dithizone methods. The soil residue that was left after decantation of the supernatant liquid was dried, weighed, and later analyzed for zinc, copper, lead, arsenic, and antimony. The removal of zinc by leaching with 0.1 N HCl has also been investigated by Wear and Sommer (1948), Nelson and Melsted (1955), Boawn, *et al.* (1957), and Nair and Mehta (1959). Agreement is fairly general among these workers that dilute acid-soluble zinc represents zinc available to plants. There is some disagreement as to the nature of this acid-soluble zinc. Nelson and Melsted (1955) believe this acid-soluble zinc differs from exchangeable zinc. Tucker and Kurtz (1955) claim that zinc removed by 0.1 N HCl in non-calcareous soils is the sum of water-soluble, exchangeable, and similar easily extracted forms plus an amount that apparently is released slowly from the inner part of the soil particles as they decompose in the acid. Nair and Mehta (1959) found a significant positive correlation between zinc soluble in 0.1 N HCl and organic matter.

Because of certain physicochemical similarities between zinc and copper, the nature, occurrence, mode of binding, and other properties of dilute acid-soluble copper should be somewhat similar to those of zinc. Jackson (1958) mentions cases where dilute acids have been used to measure available copper.

Nothing was found in the literature on the nature, occurrence, etc., of lead, arsenic, or antimony leached from soils by dilute acids. Table 23 shows the amounts of the various elements removed by the dilute acid treatment. Zinc and copper were determined in the leachates by colorimetric methods. Lead, arsenic, and antimony were determined by subtracting the contents in the leached residues from the total contents in the samples.

Zinc and Copper

In the well-drained profiles, the largest amounts of dilute acid-soluble zinc are in the A_0 horizons. The excessively high zinc value obtained for the A_0 horizon of profile 17 is probably due to the presence of mineralized material from the trench. In general, there is a sharp decrease in acid-soluble zinc from the A_0 to the A_2 horizon, followed by a gentle decrease downwards that is interrupted in some profiles by slight increases in the B_1 horizon,

and in profile 17 by an increase in the C horizon. In the poorly drained No. 19 profile the peak amount of acid-soluble zinc underlies the A_0 horizon in the uppermost gley horizon, and the contents decrease downwards from this gley horizon.

The trends for dilute acid-soluble copper are somewhat similar to those for zinc. In most profiles, the amount of acid-soluble copper in the A_0 horizon is equal to or slightly greater than the amounts in other horizons. In profile 44, however, acid-soluble copper like zinc, is considerably enriched in the A_0 horizon. Acid-soluble copper increases in the lower horizons of profiles 17 and 79 near the mineralized bedrock. In the poorly drained No. 19 profile, the concentration of copper is similar to zinc, highest in the G_1 horizon, and decreasing downwards.

Lead, Arsenic, and Antimony

Because of inherent sources of error in the method of analysis, higher values were obtained in a number of instances from the leached residues than from the unleached samples. In Table 23 these occurrences are indicated with plus signs. Blank spaces indicate simply that

TABLE 23 *Metal removed by 0.1 N HCl leaching solution (in ppm)*

Location	Sample No.	Horizon	Zn	Cu	Pb	As	Sb
Nigadoo area	17a	A_0	1,000	2	+	+	+
	17b	A_2	28	1	12	+	+
	17c	B_1	22	1	26	8	+
	17d	B_2	37	2	180	55	3
	17e	C	60	10	10,850	+	6
Nigadoo area	19a	A_0	50	1	20	127	+
	19b	G_1	200	33	360	20	2
	19c	G_2	77	18	+	+	2
	19d	Cg	45	4	85	+	+
Brunswick No. 6 area	44a	A_0	40	17	53,580	14	7
	44b	A_2	4	2	1,930	11	32
	44c	B_1	3	2		60	31
	44d	B_2	1	1	30,410	+	32
	44e	B_3	1	1		+	22
	44f	Cg_1	2	0	+	10	15
	44g	Cg_2	2	0		22	+
Overlying volcanic rocks, etc.	51a	A_0	40	1	0	<1	0
	51b	A_2	6	0	+		1
	51c	B_1	8	0	10	+	<1
	51d	B_2	5	0	+	+	<1
	51e	C	3	0	+	4	0
Overlying Bathurst granite	64a	A_0	43	0	+	<1	<1
	64b	A_2	3	1	+	+	0
	64c	B_1	2	1	5	7	2
	64d	B_2	0	0	6	+	<1
	64e	C	0	0	13	+	1
Middle River sulphide body	79a	A_0	33	1	600	+	1
	79b	A_2	1	0	+	+	+
	79c	B_1	3	1	+	+	+
	79d	B_2	1	3	1,500	730	3

+Indicates that the metal contents in the leached samples were higher than those in the unleached samples.

one or both values were above or below the detection limits of the method, and no calculations could be made.

A few tentative statements can be made about the values that lend themselves to calculation and correlation. Dilute acid-soluble lead, arsenic, and antimony have a tendency to increase with depth in profiles 17 and 79 as mineralized bedrock is approached. Certain profiles have higher contents of dilute acid-soluble lead and arsenic in their A_0 horizons, and there may also be a tendency for greater amounts of the acid-soluble form of these metals to occur in the B_1 horizons of some profiles. Remarkable similarities are present in the amounts of antimony removed from the central horizons of profile 44 by dilute HCl. Accumulations of dilute acid-soluble lead in poorly drained profile 19 roughly parallel those of zinc and copper, but differ from those of arsenic and antimony. Arsenic appears to be the only one of the elements investigated that has a maximum amount of acid-soluble metal in the A_0 horizon of profile 19.

Summary

Dilute HCl-soluble zinc is most abundant in the surface horizons of all profiles. There are small amounts of acid-soluble zinc in the B_1 horizons of two profiles. The Nigadoo profiles have the highest content of acid-soluble zinc.

Dilute acid-soluble copper is relatively abundant in the Brunswick A_0 horizon, in the gley horizons of Nigadoo profile 19, and in the basal horizon of Nigadoo profile 17. Acid-soluble copper is virtually absent in all other horizons.

Large amounts of dilute acid-soluble lead are present in the surface horizons of the Brunswick and Middle River profiles, in the basal horizons of the Middle River and Nigadoo No. 17 profiles, and in the B horizon of the Brunswick profile.

Dilute HCl-soluble arsenic is most common in the Brunswick profile. Other accumulations occur in the basal horizon of the Middle River profile and in the Nigadoo profiles.

Dilute acid-soluble antimony is highest in the Brunswick profile, and is present in large amounts in all but the basal horizon of this profile. Small, local concentrations occur in the basal horizons of the Middle River and well-drained Nigadoo profiles.

Determination of Trace Elements Removed by Hydrogen Peroxide

The procedure for determining the amounts of metal removed by the hydrogen peroxide treatment was modified after the one described by Tucker and Kurtz (1955). After treatment with hydrogen peroxide until reaction with organic matter appeared complete, the mixture was dried and 0.1 N HCl was added to extract the heavy metals as described in the previous section. After the supernatant liquid was poured off, the residue was thoroughly washed, dried, weighed, and analyzed for zinc, copper, lead, arsenic, and antimony. The amount of metal removed by the peroxide treatment was determined by subtracting the content remaining in the residue after this treatment (leaching with $H_2O_2 + 0.1$ N HCl) from that remaining in the residue after leaching with 0.1 N HCl only.

Most of the metal removed by the peroxide treatment is assumed to be associated with the organic matter which is oxidized and broken down by the peroxide. However, hydrogen peroxide is known to oxidize certain inorganic compounds including carbonates; this may release some metal, but the amounts are probably small.

There are a number of references in the literature on the association of zinc with the organic fraction of soils. Baughman (1956) found that one-half to two-thirds of the total zinc in the surface layers of two poorly drained Indiana soils was associated with the organic fraction. Hibbard (1940a) obtained increasing amounts of zinc from the surface layers of California soils as the organic matter was progressively decomposed. Schmidt (1955), Wright,

et al. (1955), and Dreimanis (1960) found enrichments of zinc in the surface humus layers of Maritime podzol soils.

Enrichments of copper in the surface humic horizon have been noted by Pack, *et al.* (1953), Wright, *et al.* (1955), and Dreimanis (1960).

Goldschmidt (1937) was one of the first investigators to notice a concentration of lead in the surface humic layer of forested soils, and to suggest its precipitation as metal-organic complexes. Wright, *et al.* (1955) found notable concentrations of lead in the A_0 horizons of podzol and brown podzol soils in eastern Canada. Schmidt (1955) and Dreimanis (1960) both reported enrichments of lead in the humic layers of New Brunswick soils.

Few references are extant regarding the association of arsenic and antimony with the organic fraction of soils. Rankama and Sahama (1950) state that according to the Goldschmidt enrichment principle arsenic is one of the elements known to be enriched in humic soils. Sainsbury (1957) noted a concentration of antimony at the base of the humic layer of Alaska soils. Both elements have been reported to be concentrated in organic-rich black shale, coal, and coal ashes.

Table 24 gives the amounts of elements removed from the samples by the peroxide treatment. Plus signs indicate that values from the samples treated with peroxide and dilute HCl were greater than those treated only with dilute HCl. Blank spaces indicate values that were less than the limits of detection.

Zinc and Copper

Relatively large amounts of zinc and copper were removed by peroxide in the A_0 horizons of practically all well-drained profiles, and were no doubt mainly derived from the organic fraction. The smaller amounts of zinc and copper removed by the peroxide treatment in most A_2 and B_1 horizons probably reflect a decrease in organic matter and a lower total content of the two metals in these horizons. The increase in peroxide-soluble zinc and copper in the lower B and C horizons of profiles 17 and 44 can hardly all be derived from the traces of organic matter present, and must, therefore, represent metal that has been partly leached from the inorganic fraction. High amounts of peroxide-soluble zinc and copper occur in nearly all horizons of the poorly drained profile. The main difference between the two metals in these profiles is that the maximum zinc concentration does not appear to be in the A_0 horizon like copper, but farther down in the lower gley layer.

Lead, Arsenic, and Antimony

The maximum amounts of peroxide-released lead are in the A_0 horizons except for profile 79 where the A_2 horizon has the greatest amount. The occurrences and amounts of lead released by peroxide in the B and C horizons are variable.

Maximum amounts of arsenic are released by peroxide from the surface horizons of the Nigadoo and Middle River profiles. The upper gley horizon of Nigadoo profile No. 19 also has a high content of arsenic liberated by peroxide. In the organic-rich horizons much of this arsenic is probably organically bound. The arsenic removed from the lower B horizon of profile No. 79 is probably derived chiefly from inorganic sources.

The peroxide treatment removed only small amounts of antimony from the A horizons of the Nigadoo and Middle River profiles. The relatively large amount of antimony removed by peroxide from the C horizon of profile 17 was probably of inorganic derivation.

TABLE 24 *Metal removed by hydrogen peroxide treatment (in ppm)*

Location	Sample No.	Horizon	Zn	Cu	Pb	As	Sb
Nigadoo area	17a	A_0		13	143	239	2
	17b	A_2	10	2	+	0	1
	17c	B_1	+	1	20	2	0
	17d	B_2	8	+	58	40	+
	17e	C	300	13	+	+	11
Nigadoo area	19a	A_0	768	331	584	55	4
	19b	G_1	+	95	+	60	+
	19c	G_2	1,985	15	+	+	+
	19d	Cg	95	8	37	9	1
Brunswick No. 6 area	44a	A_0	32	117	840	+	+
	44b	A_2	+	3	0	0	+
	44c	B_1	+	+		+	+
	44d	B_2	+	+		+	+
	44e	B_3	180	+		+	+
	44f	Cg_1	70	+	+	+	+
	44g	Cg_2	200	0		+	+
Overlying volcanic rocks, etc.	51a	A_0	38	5	16	+	0
	51b	A_1	30	0	13	5	<1
	51c	B_1	+	2	1	+	+
	51d	B_2	+	2	8	2	+
	51e	C	+	+	4	+	0
Overlying Bathurst granite	64a	A_0	31	2	21	0	<1
	64b	A_2	0	+	0	+	<1
	64c	B_1	4	11	+	+	+
	64d	B_2	+	0	+	2	<1
	64e	C	+	+	3	+	<1
Middle River sulphide body	79a	A_0	15	11	920	1,215	1
	79b	A_2	0	38	1,770	530	6
	79c	B_1	+	2	300	470	2
	79d	B_2	+	+		1,070	+

+Peroxide-HCl-treated sample values greater than HCl-treated sample values.
Blank spaces indicate values that were less than the limits of detection.

Summary

Relatively large amounts of zinc were released from the surface horizons of most profiles by the hydrogen peroxide treatment; large amounts of zinc were also released by peroxide from the basal horizons of the Nigadoo and Brunswick profiles. Copper was also released in relatively large quantities from the surface horizons of most profiles by peroxide. There was some local liberation of copper by peroxide from the A_2, B_1, C, and gley horizons. The poorly drained Nigadoo profile has the greatest amount of copper released by peroxide. High amounts of lead were released by peroxide from the A_0 horizons of all profiles as well as from the A_2 and B_1 horizons of the Middle River profile. Smaller amounts of lead were

released by peroxide from some of the lower Nigadoo horizons. Relatively large amounts of arsenic were released by peroxide from the Middle River and Nigadoo profiles, particularly from the surface and basal horizons of these profiles. Measurable amounts of antimony were released by peroxide from the Nigadoo and Middle River profiles; the largest amounts came from the surface and basal horizons.

Determination of Trace Elements Removed with Free Iron Oxides

The procedure followed for removing and determining free iron oxides was the one described by Aguilera and Jackson (1953). The soils were treated with a hot solution of sodium hydrosulphite, sodium citrate, and versene, so that the iron, in the form of iron oxides, was reduced by the hydrosulphite and removed by complexing with the citrate and versene. After the soil mixtures were centrifuged, the supernatant liquid was analyzed for iron by colorimetric methods; potassium thiocyanate and a Lumetron photoelectric colorimeter were used. The residues from this treatment were dried, weighed, and later analyzed for zinc, copper, lead, arsenic, and antimony.

To determine the zinc and copper removed with the free iron oxides, the contents of these metals in the residues were subtracted from the total values that were previously obtained from the dilute HCl leachates and residues. For lead, arsenic, and antimony, the amount of element removed with the free iron oxides was determined by subtracting the content of the elements in the residue from the original total content of the sample.

References to these trace elements with respect to their degree of association with free iron oxides are scarce and usually not quantitative. An exception was White (1957) who determined zinc in subsurface soils from Tennessee, and estimated that 29 to 60 per cent and an average of 45 per cent of the total zinc in these soils was associated with free iron oxides.

In lateritic soils of Northern Rhodesia, Govett (1960) found that copper showed maximum values in the sesquioxide-rich B horizon. It is probably safe to assume that a good proportion of the sesquioxides were free iron oxides. In lateritic soils of Southern Rhodesia, James (1957) observed that the retention of arsenic and antimony was highest in iron-rich soils. Mason (1958) notes that the adsorptive power of precipitated ferric hydroxide is very great and that arsenic and antimony have been reported in sedimentary iron ores in larger amounts than their average abundance in the earth's crust.

Table 25 gives the amounts of zinc, copper, lead, arsenic, and antimony that were removed by the free iron oxide treatment. Also shown are the amounts of free iron in each horizon. In Table 25, except for free iron, a plus sign indicates that the contents of Zn, Cu, Pb, As, and Sb in the residue were higher than the total amounts in the sample. Blank spaces in the table indicate that the contents of metal in the samples were lower than the limits of detection of the method employed. Missing values in the free iron column indicate that the analyses were unreliable because of the dark colour imparted to the A_0 horizon samples by organic matter.

Free Iron

Free iron oxides are expressed as ppm of free iron in Table 25. The most noticeable feature of the free iron is its enrichment in the B_1 horizons of all well-drained profiles. Other enrichments are present in the C horizon of profile 17, in some of the lower horizons of profile 44, and in the A_0 horizons of profiles 44 and 79. The leached A_2 horizons and the bleached Cg_1 horizon of profile 44 are the most impoverished in free iron. In poorly drained profile 19, there is a decrease in free iron from the top gley horizon downwards.

TABLE 25 *Free iron and other trace elements removed with free iron oxides (in ppm)*

Location	Sample No.	Horizon	Free Fe	Zn	Cu	Pb	As	Sb
Nigadoo area	17a	A_0		1,654	26	+	+	+
	17b	A_2	95	38	3	+	0	+
	17c	B_1	161	32	0	+	31	<1
	17d	B_2	128	47	+	+	209	4
	17e	C	363	810	25	10,230	2,535	18
Nigadoo area	19a	A_0		904	304	374	208	3
	19b	G_1	130	+	163	+	392	3
	19c	G_2	100	2,277	78	+	65	1
	19d	Cg	60	195	8	+	52	2
Brunswick No. 6 area	44a	A_0	105	61	83		13	10
	44b	A_2	88	4	2	1,640	55	28
	44c	B_1	260	39	18	4,015	233	76
	44d	B_2	162	23	+		136	90
	44e	B_3	199	+	+	44,160	203	24
	44f	Cg_1	28	12	1	805	28	39
	44g	Cg_2	195	+	1	29,190	69	29
Overlying volcanic rocks, etc.	51a	A_0	30	67	5	+	<1	0
	51b	A_2	35	40	0	+		1
	51c	B_1	213	14	0	+	9	0
	51d	B_2	70	15	4	+	6	0
	51e	C	83	13	2	+	14	1
Overlying Bathurst granite	64a	A_0		61	2	+	<1	0
	64b	A_2	50	3	1	+	<1	<1
	64c	B_1	303	10	10	+	14	2
	64d	B_2	123	0	6	+	3	<1
	64e	C	100	10	+	+	4	1
Middle River sulphide body	79a	A_0	73	60	48	2,670	690	3
	79b	A_2	56	0	37	+	465	3
	79c	B_1	179	2	+	+	430	4
	79d	B_2	143	+	+	2,355	1,760	4

+Hydrosulphite-treated sample values higher than non-treated sample values.

Zinc and Copper

The maximum removal of zinc by the leaching of free iron oxides apparently occurs in the A_0 horizons of all well-drained profiles, and in the lower gley horizon of the poorly drained profile. Correlation of zinc with free iron is only fair. Increases in zinc corresponding to increases in free iron occur in three B_1 horizons and in the C horizon of profile 17. Like zinc, maximum copper values from the leaching treatment are found in the A_0 horizons of all profiles but one. Also, like zinc, enrichments of copper occur in some B_1 horizons and in the C horizon of profile 17.

Lead, Arsenic, and Antimony

Many of the lead values in the residues were higher than the total values, which was due probably to errors inherent in the method of analysis. Profile 44, however, appears to be representative and shows three peak values that correspond with peak free iron values for the same horizons. Other horizons where the free iron treatment removed significant amounts of lead were the basal horizons of profiles 17 and 79, and the A_0 horizons of profiles 19 and 79.

Arsenic exhibits a fair correlation with free iron in most profiles and shows more of a tendency to be enriched in the A_2 or G_1 horizons underlying the A_0 horizons than does zinc or copper.

Antimony, although often present in amounts too small to indicate trends, nevertheless shows an increased amount at the base of profile 17 corresponding to that shown by free iron and all the other elements. In profile 44 its main area of concentration is in the upper B horizons. In profile 64 a slight concentration in the B_1 horizon parallels similar concentrations of other elements in this horizon. Like arsenic and copper, there is a tendency for increased amounts of antimony to be removed with the free iron from the upper horizons of the poorly drained profile.

Summary

The range of free iron in the six profiles is 30 to 363 ppm. Minimum free iron values usually occur in the A_2 horizons and maximum values in the B_1 horizons of the profiles. Other concentrations of free iron are present in the basal horizons of the Nigadoo No. 17 and Brunswick profiles.

The hydrosulphite treatment removed large quantities of zinc from all the A horizons. Much of this zinc is probably not associated with the free iron, since the A horizons contain minimum amounts of free iron. Other zinc accumulations, probably associated with free iron, were removed from the B_1 horizons of the Brunswick and granite profiles and from the lower horizons of the Nigadoo profiles.

Large amounts of copper were removed by the hydrosulphite treatment from the A horizons of profiles overlying sulphide deposits. Probably only a little of this copper is associated with free iron. Most of the copper removed from the B_1 horizons of the Brunswick and granite profiles, from the gley horizons of Nigadoo profile 19, and from the basal horizon of Nigadoo profile 17 is probably associated with free iron.

The low precision of the analytical method prevented the determinations of lead removed with free iron in many horizons. Large amounts of lead were removed by the hydrosulphite treatment from most horizons of the Brunswick profile and from the basal horizons of the Nigadoo 17 and Middle River profiles.

The amounts of arsenic removed by the hydrosulphite treatment from the Brunswick and the two normal profiles parallel fairly closely the amounts of free iron removed from these profiles. The large arsenic contents removed by the treatment from the basal horizons of the Middle River and Nigadoo 17 profiles are probably related to the free iron oxides.

The largest quantities of antimony were removed with the free iron oxides from all horizons of the Brunswick profile, and from the basal horizon of Nigadoo profile 17.

Mineralogical Investigations

Mechanical Analyses

The mechanical analyses were slightly modified from the standard pipette method outlined by Kilmer and Alexander (1949). Duplicate 10 gram samples were treated with hydrogen peroxide to destroy organic matter. One sample was dried and weighed to determine per

cent loss of weight. The other was dispersed with 10 per cent Calgon solution and passed through a 300-mesh sieve to separate the sand fraction that is greater than 50 microns from the clay and silt.

The clay fraction was determined from a 10 ml aliquot drawn off from the clay and silt in solution by pipette at a depth and time calculated from Stokes law. The percentage of silt was determined by subtracting the combined percentages of sand and clay from 100. There was an insufficient amount of sample 19a to complete its mechanical analysis.

The percentage loss in weight from the peroxide treatment is a fair approximation of the organic matter content for most horizons. Table 26 shows predictably that the organic-rich A_0 horizons have the highest weight losses. The B_1 horizon, usually second highest in organic content in these profiles, shows correspondingly high weight losses in four profiles.

TABLE 26 *Results of mechanical analyses*

Location	Sample No.	Horizon	Loss %	Sand %	Silt %	Clay %	Clay Wt.	Texture
Nigadoo area	17a	A_0	72.5	50.1	13.6	36.3	0.010	sandy clay
	17b	A_2	3.6	37.1	52.5	10.4	.010	silt loam
	17c	B_1	8.4	39.4	38.8	21.8	.020	loam
	17d	B_2	3.3	39.7	38.3	22.0	.021	loam
	17e	C	2.8	42.6	35.6	21.8	.021	loam
Nigadoo area	19a	A_0	72.1					
	19b	G_1	12.6	17.0	56.6	26.4	0.023	silt loam
	19c	G_2	2.2	56.3	28.3	15.4	.015	sandy loam
	19d	Cg	1.0	78.3	12.6	9.1	.009	loamy sand
Brunswick No. 6 area	44a	A_0	42.1	44.4	26.1	29.5	0.017	clay loam
	44b	A_2	2.2	48.7	42.1	9.2	.009	loam
	44c	B_1	1.6	41.6	43.2	15.2	.015	loam
	44d	B_2	0.5	51.3	28.7	20.0	.020	loam
	44e	B_3	0.5	38.0	36.9	25.1	.025	loam
	44f	Cg_1	0.4	58.6	34.3	7.1	.007	sandy loam
	44g	Cg_2	0.5	58.1	28.9	13.0	.013	sandy loam
Overlying volcanic rocks, etc.	51a	A_0	55.7	56.3	14.3	29.4	0.013	sandy clay loam
	51b	A_2	4.4	60.4	27.0	12.6	.012	sandy loam
	51c	B_1	4.7	65.0	23.5	11.5	.011	sandy loam
	51d	B_2	1.6	74.3	20.4	5.3	.005	sandy loam
	51e	C	0.6	88.6	6.4	5.0	.005	loamy sand
Overlying Bathurst granite	64a	A_0	67.9	62.4	12.7	24.9	0.008	sandy clay loam
	64b	A_2	3.3	48.0	41.6	10.4	.010	loam
	64c	B_1	14.3	60.0	24.8	15.2	.013	sandy loam
	64d	B_2	4.8	65.8	25.8	8.4	.008	sandy loam
	64e	C	2.1	57.2	34.6	8.2	.008	sandy loam
Middle River sulphide body	79a	A_0	57.5	43.0	28.7	28.3	0.012	clay loam
	79b	A_2	3.0	36.6	54.1	9.3	.009	silt loam
	79c	B_1	9.1	50.0	35.7	14.3	.013	loam
	79d	B_2	5.7	44.1	44.2	11.7	.011	loam

The percentage of sand increases near the base of most profiles as witnessed by the predominance of loam and sandy loam textures. The minimum percentages of sand are usually in the A horizon. The highest percentages of silt in all the well-drained profiles but one are in the leached A_2 horizons.

The highest percentages of clay are found in the A_0 horizons of the well-drained profiles. These do not usually correspond with the greatest amounts of clay as shown by comparison of the clay percentage and weight columns in Table 26. Although the clay concentrations show no strong trends, there is a tendency for the clay contents to decrease in the A_2 horizons. This suggests a possible downward translocation of clay from the A horizon into the B_1 horizon.

The increase in the percentage of sand towards the base of most of the profiles usually results in a loam texture. Glacial till often has a loam or clay loam texture, and a glacial till origin for these soils is also indicated by the increase in number, size, and angularity of pebbles with depth. The percentage increase of sand with depth is probably the result of decreased weathering with depth coupled with an increase in sorting and sedimentation by water and wind towards the surface.

The high percentage of silt in the leached A_2 horizons is possibly the result of weathering and removal of clay. It is also possible that some of the less resistant sand fraction is weathered down to silt-sized particles. The high percentage of clay in the A_0 horizons may be partly due to wind and water action on surface soil, as a result of blowing, splashing, and absorption of clay particles on the humus. The lower content of clay in the A_2 horizons compared with the higher content in the B_1 horizons is possibly due to the movement of clay out of the A_2 horizon into the B_1.

X-ray Diffraction Studies of Mineral Coatings

X-ray diffraction determinations were made on the powdery coatings of the soil particles in the horizons of profile 44. The minus 10-mesh material was examined with a 50X binocular microscope, and the yellow powder was taken up on glass fibre spindles with vaseline as a binding medium. The material was examined with a Philips x-ray diffractometer using both copper and iron-filtered radiation. Several runs were made to be certain that all minerals were identified. A similar procedure was followed in the examination of the soil particles of profiles 17, 44, and 79 after free iron oxides had been removed.

Profile 44 was chosen for the x-ray study of the particle coating, because these coatings give a peculiar yellowish colour to the soil. The results are shown in Table 27 together with the soil colours of each horizon as determined from the Munsell Soil Color Charts. A surprising feature of profile 44 is that no limonite or goethite were found in the coatings although these minerals are usually common associates of the jarosite minerals, are present as particles in the various horizons, and are found abundantly in the residual gossan underlying the soil profile. The reason for the absence of these two iron oxides may be the relatively low pH in this profile. In other words the minerals are probably not stable under such acid conditions.

Microcrystalline quartz is ubiquitous in the powdery coatings of the soil particles of profile 44. Feldspar is almost as common, although it is missing from the B_2 and C_2 horizons. The extreme acidity (pH 3.2) of the Cg_2 horizon may account for the presence only of quartz in this horizon.

The basic salt jarosite, $KFe_3(SO_4)_2(OH)_6$, was found throughout the B horizon, and the basic salt beudantite, $Pb,Fe_3(AsO_4)(SO_4)(OH)_6$, was determined in the two upper B horizons.

Both these minerals are also present in the gossans and result from complex oxidation reactions involving the various sulphides. In the soil a small amount of these basic salts may be derived from sulphides caught up in the till, but the greater amounts are probably precipitated from solutions (groundwater) that migrated upward and laterally from the orebody through the till.

After the treatment to remove the free iron oxides, the x-ray analyses of the soils indicated that jarosite and beudantite had been leached and the yellow colour had disappeared. Only quartz, feldspar, and hydromica remained in the residue. Thus, jarosite and beudantite are mainly responsible for the peculiar yellow colours in the soil of profile 44.

X-ray analyses of samples from profiles 17 and 79, after the removal of free iron oxides, showed major quartz with minor feldspar and hydromuscovite. These results are similar to those obtained on samples 44b and 44c (Table 27). Later microscopic studies showed that other minerals are present in the samples but generally in amounts too small to detect effectively by x-ray methods.

TABLE 27 *Mineralogy of soil coatings in Brunswick profile No. 44 as determined by x-ray*

Sample No.	Horizon	Minerals	Soil colour of coatings
44b	A_2	Quartz, feldspar	Dark brown (10 YR 4/3)
44c	B_1	Quartz, feldspar jarosite, beudantite	Yellowish brown (10 YR 5/6)
44d	B_2	Quartz, jarosite, beudantite	Brownish yellow (10 YR 6/6)
44e	B_3	Quartz, feldspar jarosite	Yellow (2.5 Y 7/6)
44f	Cg_1	Quartz, feldspar	Light grey (2.5 Y 7/2)
44g	Cg_2	Quartz	Brownish yellow (10 YR 6/6)

Visual and Microscopic Examinations

The pebbles and rock fragments greater than 1 mm in size, separated by sieving during initial sample preparation, were weighed and examined with a hand lens. The approximate per cent weights of these fractions of the total soil are shown in Table 28. Results of the mineralogical examinations on this material are shown in the mineralogical tables that follow. The 1 mm to 50 micron sand fractions used for microscope study were obtained from sieve separations carried out during the mechanical analyses. The 50- to 20-micron coarse silt fractions were obtained by repeated sedimentations to remove the material of less than 20 microns, and by sieving the remaining sediment to remove the sand fraction greater than 50 microns.

Organic matter and free iron oxides were removed from all the samples before microscope study. Organic matter was removed by treatment with 30 per cent H_2O_2. Free iron oxides were removed by the method outlined by Mackenzie (1954) wherein the soil is leached with hot solutions of sodium hydrosulphite dissolved in water.

TABLE 28 *Per cent weights of pebbles greater than 1 mm, sand heavies, and coarse silt heavies*

Location	Sample No.	Horizon	Material >1 mm Wt. % of total soil	Heavies Wt. % of sand	Heavies Wt. % of coarse silt
Nigadoo area	17a	A_0		88.2	
	17b	A_2	20	2.2	0.5
	17c	B_1	40	4.4	2.9
	17d	B_2	50	2.3	2.3
	17e	C	60	14.1	8.4
Nigadoo area	19a	A_0		0.0	
	19b	G_1	50	34.6	0.2
	19c	G_2	50	3.2	0.9
	19d	Cg	60	2.9	2.2
Brunswick No. 6 area	44a	A_0		2.8	2.1
	44b	A_2	35	1.7	0.2
	44c	B_1	40	2.2	2.3
	44d	B_2	40	2.7	2.7
	44e	B_3	25	1.8	1.7
	44f	Cg_1	15	0.9	1.3
	44g	Cg_2	10	5.5	6.1
Overlying volcanic rocks, etc.	51a	A_0		3.5	3.2
	51b	A_2	0–5	3.7	1.1
	51c	B_1	0–5	6.7	1.9
	51d	B_2	10	5.1	3.0
	51e	C	5	9.1	14.4
Overlying Bathurst granite	64a	A_0		0.6	0.9
	64b	A_2	5–10	2.3	0.1
	64c	B_1	20	8.0	7.6
	64d	B_2	25	9.2	3.2
	64e	C	30	4.4	2.9
Middle River sulphide body	79a	A_0		18.5	6.1
	79b	A_2	45	15.4	0.0
	79c	B_1	35	19.6	1.3
	79d	B_2	35	26.5	1.3

Heavy minerals were separated from the sand and coarse silt fractions by a simple bromoform procedure with two glass funnels as described by Krumbein and Pettijohn (1938). The heavy mineral fractions were weighed and their weight proportions calculated and recorded in Table 28.

Table 28 shows that the material greater than 1 mm in size increases in amount with depth in all profiles but two. A particularly high value is reached in the C horizons of profiles 17 and 19. The material greater than 1 mm in size in profile 17 consists principally of large, angular, weathered bedrock fragments, whereas in profile 19 it is mainly smaller, rounded gravelly material. The amount of the material greater than 1 mm in size decreases from the B_3

horizon downwards in profile 44 as this is the upper limit of the acidified water which probably has decomposed the larger pebbles and fragments.

It is interesting to note that the proportions of heavy minerals in both sand and coarse silt fractions are approximately similar in most profiles, especially in profile 44. Both heavy mineral fractions are featured by a decrease in the A_2 horizon followed by an increase in the B_1 horizon. A peak value is usually reached in the B_1 or B_2 horizons, often followed by a decrease and then a sharp rise in the C horizon. An outstanding feature of the poorly drained profile is the high proportion of heavy minerals present only in the G_1 horizon of the sand fraction.

The fraction greater than 1 mm in size was identified with the aid of a hand lens. The minerals in the sand and coarse silt fractions were identified with a petrographic microscope, and rough quantitative estimates were made by careful scanning of slides of the fractions.

In Tables 29 to 34 the minerals and rocks identified in the particles of sand and coarse silt fractions greater than 1 mm in size are presented in approximate order of their relative amounts.

Mineralogical Features of Nigadoo Profile No. 17 (Table 29)

Weathering of the fraction greater than 1 mm in size decreases with depth in this profile. The porphyry pebbles and fragments are severely weathered near the surface, but relatively unweathered in the C horizon.

TABLE 29 *Mineralogy of profile No. 17 overlying Nigadoo deposit*

Sample No.	Horizon	>1 mm	Sand	Coarse silt
17a	A_0		Rock fragments, quartz, magnetite, sphalerite, pyrite, malachite	
17b	A_2	Shale, quartz-feldspar porphyry	Quartz, feldspar, muscovite, magnetite, hematite, pyroxene, rutile	Quartz, muscovite, feldspar, magnetite, goethite, hematite, ilmenite, zircon, pyroxene, rutile
17c	B_1	Shale, quartz-feldspar porphyry	Rock fragments, quartz, feldspar, muscovite, biotite, hornblende, pyroxene, ilmenite	Rock fragments, feldspar, quartz, muscovite, biotite, hematite, magnetite, hornblende, ilmenite, zircon
17d	B_2	Shale, quartz-feldspar porphyry, diorite	Quartz, rock fragments, feldspar, hornblende, pyroxene, biotite, muscovite, hematite, sphalerite, chalcopyrite	Quartz, rock grains, feldspar, muscovite, biotite, magnetite, hornblende
17e	C	Shale, quartz-feldspar porphyry	Quartz, rock fragments, feldspar, mica, hornblende, hematite, goethite, magnetite, sphalerite	Rock grains, quartz, feldspar, mica, hornblende, hematite, goethite

The quantity of rock grains in both sand and silt fractions also increases with depth and they appear to be more plentiful than quartz in some of the lower coarse silt fractions. Red and brown rock fragments, coloured by hematite, limonite, and jasper, are the most common type, but green and yellow grains, containing olivine, pyroxene, chlorite, etc., are also fairly abundant. Some reddish purple to purplish black grains and small particles in the lower two horizons may owe some of their colour to manganese. The rock grains in the C horizon have irregular, pitted surfaces and a partial coating of iron oxides. Weathering appears to have penetrated deeply into these grains. Some rock grains of a similar nature are present in the A_0 horizon and may have come partly from material excavated from nearby trenches.

Sphalerite, pyrite, and malachite were all found in the sand fraction of the A_0 horizon and may also have been derived from material excavated from the trenches. Sulphides were not observed in the A_2 or B_1 horizons, but sphalerite is present in both the B_2 and C horizons, and chalcopyrite occurs in the B_2 horizon. The amount of greenish hornblende and biotite increases from the B_1 horizon downwards.

Mineralogical Features of Nigadoo Profile No. 19 (Table 30)

In this profile rock grains of material greater than 1 mm in size are apparently derived from both local and distant sources. This assumption, along with relatively good rounding and sorting of this and some of the finer fractions, implies a glacio-fluvial origin. In general, a more resistant suite of rocks and minerals occurs throughout this profile than in profile 17. Quartz is more plentiful and dominant in nearly all fractions and horizons. Zircon appears frequently. Brownish black and bluish black rock fragments and nodules are common in

TABLE 30 *Mineralogy of profile No. 19 overlying Nigadoo deposit*

Sample No.	Horizon	>1 mm	Sand	Coarse silt
19a	A_0	Shale	Quartz, rock grains	
19b	G_1	Shale, gravel pebbles	Rock fragments, quartz, limonite, feldspar biotite, muscovite, hematite, ilmenite, magnetite, amphibole, pyroxene, chlorite	Quartz, rock fragments, feldspar, mica, limonite, hematite, magnetite, zircon, epidote
19c	G_2	Shale, quartz-feldspar porphyry, varied assortment of igneous and volcanic pebbles	Quartz, feldspar, rock fragments, mica, zircon, pyroxene, tremolite, epidote, magnetite, sphene	Quartz, feldspar, rock fragments, mica, pyroxene, amphibole, zircon, epidote, magnetite, rutile
19d	Cg	Quartz and rock pebbles of igneous, metamorphic, and volcanic origin	Quartz, feldspar, rock fragments, biotite, muscovite, zircon, pyroxene, epidote, magnetite	Quartz, mica, feldspar, rock grains, zircon, pyroxene, hematite, magnetite

horizon G_1, fairly common in G_2, and present in the A_0 horizon, although all grains are obscured by organic matter in the latter horizon. Some of these grains may be magnetite or ilmenite; most of them, however, are of a colour that is usually associated with manganese minerals. Mica is relatively common in all horizons, especially in the coarse silt fraction.

Mineralogical Features of Brunswick Profile No. 44 (Table 31)

The fraction greater than 1 mm consists predominantly of quartz and quartz-rich pebbles in this profile. These minerals constitute a large proportion of this fraction in the lower three horizons. The proportion of quartz to non-quartz minerals is high in both sand and silt

TABLE 31 *Mineralogy of profile No. 44, Brunswick No. 6 deposit*

Sample No.	Horizon	>1 mm	Sand	Coarse silt
44a	A_0	Quartz, quartz-feldspar porphyry	Quartz, rock fragments, muscovite, feldspar, goethite, hematite, magnetite	Quartz, muscovite, feldspar, rock grains, goethite, hematite, biotite, magnetite, epidote, zircon
44b	A_2	Quartz, quartz-feldspar porphyry, mixed igneous and metamorphic pebbles	Quartz, rock fragments, muscovite, biotite, zircon, goethite, magnetite, hematite, pyroxene	Quartz, feldspar, mica, rock fragments, zircon, goethite, magnetite
44c	B_1	Slate, quartz-feldspar porphyry	Quartz, rock grains, feldspar, mica, zircon, hematite, goethite, magnetite, pyroxene	Quartz, rock fragments, feldspar, mica, magnetite, goethite, hematite, zircon, rutile, epidote
44d	B_2	Quartz, quartz-rich pebbles	Quartz, rock fragments, feldspar, mica, magnetite, goethite, zircon, hematite, barite, pyroxene, staurolite	Quartz, feldspar, rock fragments, mica, magnetite, zircon, rutile, epidote, goethite
44e	B_3	Quartz	Quartz, feldspar, rock fragments, mica, zircon, magnetite, barite	Quartz, feldspar, rock fragments, mica, zircon, rutile, magnetite, hematite, epidote, chalcopyrite
44f	Cg_1	Quartz, quartz-rich grains, barite pebbles	Quartz, feldspar, rock fragments, barite, zircon, magnetite, epidote	Quartz, feldspar, rock fragments, mica, zircon, magnetite
44g	Cg_2	Slate, quartz, quartz-rich pebbles	Quartz, feldspar, rock fragments, mica, zircon, barite, magnetite, ilmenite	Quartz, feldspar, rock fragments, mica, goethite, zircon, rutile, pyrite, chalcopyrite

fractions, increasing in the three lower horizons and in the A_2 horizon. An increase in the non-quartz fraction is usually reflected by increased amounts of less resistant minerals, such as feldspar, pyroxenes, and mica. In all horizons where these minerals are recognizable, they are highly weathered.

Although many of the grains in the A_0 horizon are obscured by organic matter, there are some sand grains with iron oxide coatings, not dissimilar in appearance from the iron-rich grains in the B and C horizons. It is possible that these grains were derived from nearby trenching operations, although care was taken to select a profile that was not contaminated.

The proportion of quartz to non-quartz minerals and the degree of weathering increase in the A_2 horizon and in the lower three horizons. In the A_2 horizon most of the weathering is probably due to the leaching action of acidic solutions. According to Rajah (1962), the leached zone above the residual gossan, which corresponds to the Cg_1 horizon in this profile, is caused by fluctuations in the strongly acidic water table. The pH measurements of groundwater in a nearby pit gave readings of 2.1 to 2.5. Evidence for acid solution of this leached zone include the low pH of the Cg_1 and Cg_2 horizons, increased proportions of quartz, increased incidence of resistant non-quartz minerals such as barite and zircon, and the etching, pitting, and rounding of mineral grains.

It seems probable that the B_3 horizon of this profile corresponds with the "hard cap" layer (Fig. 4) which Rajah believes is caused by precipitation of dissolved iron in the groundwater by hydrolysis and oxidation at the groundwater-soil-air interface. Although concentration is not marked in the B_3 horizon, there is an increase in both free and total iron, and the mineral grains show more evidence of acid solution than the overlying B horizons.

The Cg_2 horizon at the base of the profile possesses many of the acid solution characteristics of the overlying Cg_1 and B_3 horizons. However, it differs in having poorer sorting, more limonitic grains, more heavy minerals including sulphides, and more nodular quartz than any of the overlying horizons. These distinctive characteristics probably result partly from the mechanical uptake of material from the underlying residual gossan by the till, and partly from the pervasive leaching of the acid solutions derived from the nearby oxidizing orebody.

The presence of nodular secondary quartz, barite, and sulphides throughout most of the profiles, and their increase downwards through the profile, lends support to the idea that residual gossan and possibly even unoxidized ore were taken up by the till during glaciation and are an important source of many of the trace elements in the profile.

Mineralogical Features of Sand Profile No. 51 (Table 32)

This profile consists predominantly of medium- to coarse-grained, moderately well sorted and rounded sand. The only material greater than 1 mm is a little fine gravel and a few slaty fragments. There are many greenish and brownish rock fragments in the sand fraction showing some schistosity or slaty cleavage. These are similar to the metamorphosed volcanic and sedimentary rocks that are present in the vicinity.

The high incidence of relatively unweathered rock fragments, pyroxene, amphibole, biotite, etc., along with only fair sorting and rounding of the rock and mineral grains, indicates that much of the material comprising the profile has probably not moved far from its source. Magnetite and dark hornblende make up a significant part of the sand fraction in the C horizon.

TABLE 32 *Mineralogy of sand profile No. 51 overlying sand deposits*

Sample No.	Horizon	>1 mm	Sand	Coarse silt
51a	A_0		Quartz, feldspar, rock fragments, pyroxene, amphibole, garnet, mica, magnetite	Quartz, feldspar, rock fragments, mica, amphibole, pyroxene, magnetite, epidote, zircon, rutile, sphene, andalusite
51b	A_2		Quartz, feldspar, rock fragments, muscovite, amphibole, pyroxene, biotite, goethite, zircon, magnetite	Quartz, feldspar, rock fragments, mica, zircon, rutile, magnetite, goethite, pyroxene
51c	B_1		Quartz, rock fragments, feldspar, muscovite, biotite, chlorite, pyroxene, magnetite, amphibole, zircon, garnet	Quartz, rock fragments, feldspar, mica, hematite, pyroxene, amphibole, zircon, epidote, rutile, magnetite, garnet
51d	B_2	Grey slate	Quartz, rock fragments, feldspar, muscovite, biotite, amphibole, pyroxene, magnetite, chlorite, garnet, zircon, ilmenite	Quartz, rock fragments, feldspar, mica, pyroxene, amphibole, zircon, hematite, epidote, rutile, magnetite, garnet
51e	C		Quartz, rock fragments, feldspar, amphibole, pyroxene, magnetite, ilmenite (?)	Quartz, rock fragments, feldspar, mica, pyroxene, amphibole, goethite, hematite, garnet, zircon, epidote, magnetite, rutile

Mineralogical Features of Granite Profile No. 64 (Table 33)

The fraction greater than 1 mm is composed mainly of quartz and granite pebbles that increase in size, angularity, and lack of weathering with depth. These and other features suggest that the till on which the soil profile was developed is of relatively local derivation. The sand and coarse silt fractions contain a wide assortment of minerals, most of which are typical of soils derived from acid igneous rocks. Mica, zircon, epidote, hematite, apatite, and sphene are relatively more common in profile 64 than in the other profiles examined.

Leaching appears to have been more extreme in the A_2 horizon of profile 64 than in the A_2 horizons of the other profiles. This is indicated by the high proportion of quartz to non-quartz minerals in the sand and coarse silt fractions. The effect of strong weathering is also apparent in the B_1 and B_2 horizons where most of the grain surfaces of the non-quartz fraction are clouded or covered with a thin film of iron oxides. In the C horizon, however, nearly all grains have fresh-looking, unweathered surfaces.

TABLE 33 *Mineralogy of profile No. 64 overlying granite*

Sample No.	Horizon	>1 mm	Sand	Coarse silt
64a	A_0		Quartz, feldspar, rock fragments, muscovite, biotite, zircon, magnetite, topaz, andalusite	Quartz, feldspar, rock fragments, mica, zircon, magnetite, epidote, pyroxene, apatite
64b	A_2		Quartz, feldspar, rock fragments, mica, amphibole, pyroxene, zircon, magnetite, hematite, apatite, rutile, ilmenite	Quartz, feldspar, rock fragments, muscovite, magnetite, zircon, rutile, garnet
64c	B_1	Quartz, granite, green schistose fragments	Quartz, feldspar, rock fragments, mica, amphibole, pyroxene, zircon, epidote, magnetite	Quartz, feldspar, rock fragments, mica, amphibole, pyroxene, zircon, epidote, magnetite
64d	B_2	Quartz, granite, schist	Quartz, feldspar, rock fragments, mica, zircon, epidote, amphibole, sphene, andalusite, magnetite, apatite	Quartz, mica, feldspar, rock fragments, amphibole, hematite, pyroxene, magnetite, zircon, epidote, apatite
64e	C	Granite	Quartz, feldspar, rock fragments, muscovite, biotite, amphibole, pyroxene, zircon, epidote, hematite, magnetite, andalusite, apatite, sphene	Quartz, feldspar, rock fragments, mica, pyroxene, amphibole, zircon, epidote, magnetite, hematite, sphene

Mineralogical Features of Middle River Profile No. 79 (Table 34)

This twelve-inch-deep soil profile grades into gossan and judging from its pebble content, is of restricted local derivation. The fraction greater than 1 mm consists chiefly of metamorphic volcanic rocks found in the immediate vicinity. In the B_2 horizon (the transition zone between soil and gossan), about 25% of the material greater than 1 mm in size consists of irregular, rusty-weathering gossan fragments. When broken, these fragments show plates and needles of a resinous, black mineral filling the interstices between limonitic masses.

Rock fragments rich in black, dark brown, and dark red minerals, rock fragments coated with iron oxides, and grains of iron and titanium oxides are relatively common in the sand and silt fractions of all horizons. The numbers of these grains increase in the B horizons and account partly for the higher than normal heavy metal content of this profile.

Pyroxenes and amphiboles are relatively common in all horizons. They may be present in larger amounts than indicated in the B horizons, but identification is difficult because of oxide coatings on the grains that render many of them opaque under the microscope. Rutile is an ubiquitous mineral in this profile, and is more common in all horizons of this profile than in any of the others examined.

TABLE 34 *Mineralogy of profile No. 79 overlying Middle River deposit*

Sample No.	Horizon	> 1 mm	Sand	Coarse silt
79a	A_0		Quartz, rock fragments, mica, goethite, hematite, magnetite, rutile	Quartz, feldspar, rock fragments, mica, goethite, zircon, rutile, epidote, magnetite
79b	A_2	Quartz-sericite schist, quartz, reddish schistose pebbles	Quartz, rock fragments, feldspar, mica, pyroxene, hematite, magnetite rutile, chalcopyrite	Quartz, feldspar, rock fragments, mica, rutile, magnetite, zircon, hematite, staurolite
79c	B_1	Quartz-sericite schist, chlorite schist, slate, quartz	Quartz, rock fragments, feldspar, mica, hematite, goethite, amphibole, pyroxene, magnetite, zircon, rutile, garnet	Quartz, feldspar, rock fragments, mica, goethite, amphibole, pyroxene, zircon, rutile, magnetite, ilmenite
79d	B_2	Quartz-sericite schist, gossan fragments, chlorite schist, quartz	Quartz, rock fragments, feldspar, mica, amphibole, pyroxene, goethite, hematite, rutile, magnetite, zircon, ilmenite, garnet, pyrite	Quartz, rock fragments, feldspar, mica, goethite, hematite, amphibole, rutile, magnetite, ilmenite, garnet, tourmaline

Chapter IV

DISCUSSION OF RESULTS

In this chapter the data obtained on each element by the various chemical, physical, and statistical methods is summarized and correlated, and its mode of binding and migration characteristics in the soils are discussed.

Iron

In all profiles, the A_0 horizons have the lowest iron contents (Table 4). The A_2 horizons average as much as 2 per cent more iron than the A_0 horizons. Although most of the profiles overlying sulphide bodies have lower contents of iron in the A_2 horizons than the normal profiles, they usually contain more iron in their B horizons. In about half the profiles in which iron was determined, the B_1 horizons contain the most iron. The iron contents of the B_2 and C horizons are variable. The highest average iron content in the C horizon (6.5%) was found in the Nigadoo group.

Iron is positively correlated with pH in the A_0, A_2, and C horizons (Table 13). Positive iron-pH correlations are significantly high in both the A_0 and A_2 horizons, and there is an extremely high r value of +.940 in the A_0 horizon. Correlation of iron with pH in the C horizons is only fair (r = +.210). Negative iron-pH correlations occur in the B horizons, and in the B_1 horizons there is a highly significant r value of −.640. A weak iron-pH correlation of r = −.141 is present in the B_2 horizons. Highly significant correlation coefficients were calculated for iron and pH in the profiles overlying the Nigadoo, Brunswick No. 6, and Middle River sulphide bodies.

The content of free iron is highest in the B_1 horizons of the well-drained profiles (Table 25). The horizon with the lowest free iron content is the leached Cg_1 horizon of the Brunswick profile containing only 28 ppm. Otherwise, the A_2 horizons have the lowest free iron contents. The highest free iron content is in the C horizon of the well-drained Nigadoo profile, where 363 ppm were detected. The highest free iron per cent of the total iron is in the Brunswick A_0 horizon where 105 ppm of free iron represent 1.46 per cent of the total iron. In the poorly-drained Nigadoo profile, the free iron decreases consistently down the profile, from a high of 130 ppm in the G_1 horizon, through 100 ppm in the G_2, to a low of 60 ppm in the Cg horizon. The drab grey and brown colours of the poorly drained Nigadoo profile suggest that most of the free iron in the profile is in the ferrous state. The low content in the Cg horizon may be due to the solution of ferrous iron in the groundwater and its removal from the horizon. In the Brunswick No. 6 profile, the yellowish colours of the soil in the B horizons are due mainly to the minerals jarosite and beudantite which coat the soil particles (Table 27). These minerals can be removed with the free iron or by leaching either with dilute acid or metal-free water.

Iron oxides and hydroxides were observed in every fraction of every horizon (Tables 29-34). Goethite and limonite are present usually as coatings and as grains and nodules. Hematite occurs as crusts and grains, and magnetite and ilmenite are present as grains and particles. All these oxides were also detected as constituents of the rock fragments in practically every horizon. Goethite and hematite are usually most common in the B and C horizons where free iron is highest. In a few profiles these minerals appear to be more common in the A_0 than in the underlying A_2 horizons.

Magnetite and ilmenite are relatively important as iron minerals in the A_0 and A_2 horizons, where goethite and hematite are usually less common. There is generally an absolute increase in magnetite and ilmenite in the lower B and C horizons together with an increase of the other resistant silicates and oxides. Pyrite and other iron-rich sulphides were observed in the profiles above sulphide bodies, generally in the basal horizons.

Mode of Binding of Iron

With respect to iron, the results of the investigations suggest that the element is bound in a variety of ways: in humic substances, as water-soluble sulphates, in an exchangeable form, probably in iron carbonates, as various iron oxides, and in a variety of iron-bearing minerals. In the A_0 and other near surface horizons some of the iron is bound by the various humic substances. The value of 0.09 per cent iron obtained from the dry, undecomposed surface humus of profile 52 (Table 36) probably represents a minimum value for iron bound in the undecomposed plant material. With increasing decomposition of the humus the iron content increases, mainly because absorption is greater as a result of the presence of more broken bonds and exchange sites. Iron is also more available from the disintegrated humic and inorganic materials.

In some profiles a part of the iron is probably present in a variety of soluble sulphates. This is suggested by the presence in some profiles of large anionic excesses of sulphate. In the well-drained Nigadoo profile (Table 15) much of the water-soluble iron is probably present as soluble iron sulphates resulting from the oxidation of sulphide-rich material scattered about on the surface. In the Brunswick profile (Table 19), some of the soluble iron may have come from a variety of amorphous sulphates and sulphate-arsenates.

Iron carbonates, although not specifically identified, may be present in the lower horizons of the Nigadoo and Middle River profiles where the water-soluble leachates contained significant amounts of bicarbonates.

The free iron oxides removed during the treatment of samples from the well-drained profiles are probably present as hydrated ferric oxides with the approximate formula FeO(OH) and as the simple oxide Fe_2O_3, as suggested by Russell (1961). The hydrated ferric oxides probably consist of mixtures of amorphous limonite, ferric hydroxide, and microcrystalline goethite and lepidocrocite. The simple oxides are probably mainly hematite and maghemite. All these oxides are present in the soil horizons above the sulphide bodies and are probably derived from the oxidation of the underlying iron sulphides. In the B horizons of the Brunswick profiles, most of the free iron oxide removed during the treatment of the samples probably came from sulphates and sulphate-arsenates such as jarosite and beudantite.

According to Ignatieff (1941), much of the ferrous iron present in gley horizons exists in an exchangeable form. Thus, much of the free iron removed by the sodium hydrosulphide treatment from the gley horizons of Nigadoo profile No. 19 may be associated with humus and clay in an exchangeable form. Similarly, a small part of the iron in the well-drained horizons of all the profiles may be associated with clay minerals in an exchangeable form. Some may also be tightly bonded to the clay minerals (non-exchangeable).

Much iron is bound in goethite, hematite, magnetite, and ilmenite, which are present in nearly every horizon, either as discrete minerals, mineral coatings, or as constituents of rock fragments. Pyrite, chalcopyrite, sphalerite, and other iron-bearing sulphides are generally restricted to basal profiles overlying the sulphide bodies. The remainder of the iron in the soils is bound in minerals such as amphiboles, pyroxenes, biotite, epidote, and rutile. Where these minerals appear abundantly in the horizons of the soil profiles, the total and free iron contents are generally high.

Summary

Both the total and free iron contents are generally lowest in the A horizon and highest in the B_1 horizon. Variations in this distribution trend are most pronounced in profiles above sulphide bodies. Correlation of iron with pH indicates that the pH has a strong influence on the amounts of total iron present in the A_0, A_2, and B_1 horizons. Water-soluble iron is thought to be present in the sulphate form in the well-drained profiles overlying sulphide bodies. Most of the free iron oxides coating the soil particles of the well-drained profiles probably consists of limonite, goethite, and hematite. Jarosite and beudantite probably contribute free iron in the profiles overlying the Brunswick No. 6 deposit.

Goethite, hematite, and magnetite are present in every horizon of the six profiles studied in detail. Ilmenite is present in most horizons, and iron-rich sulphides are present in the basal horizons of the profiles above sulphide deposits.

Manganese

Most profiles have a concentration of manganese in the A_0 horizon. The Nigadoo group has the highest (2,280 ppm) and the Brunswick No. 6 group the lowest (80 ppm) manganese concentrations in this horizon. Manganese is generally lowest in amount in the A_2 horizon of the profiles. The content of manganese in the B_1 horizon is often higher than that of the A_2 horizon. Progressive increases in the content of the element usually occur in the B_2 and C horizons, often attaining maximum values in the C horizon (Table 5).

In some of the acid soils of the profiles above sulphide bodies, maximum manganese contents occur in the B_1 horizons. In the poorly drained Nigadoo profile, the manganese contents decrease progressively downwards from a high of 5,740 ppm in the A_0 horizon to a low of 470 ppm in the Cg horizon. High concentrations of manganese in the bedrock are not generally reflected by correspondingly high concentrations of the element in the C horizons of the overlying profiles (Table 37). Profiles overlying manganese-rich rocks, however, tend to have higher than normal concentrations of manganese in their A_0 or B_1 horizons.

Manganese shows positive correlations with pH in all horizons of the normal profiles and in those overlying the Nigadoo and Middle River sulphide bodies (Table 13). The highest r value is for the B_2 horizons ($r = +.552$) and is significant at the 1 per cent level. Correlation between manganese and pH in the A_2 horizons is fairly high ($r = +.323$), but not significant. Low manganese-pH correlations occur in the A_0, B_1, and C horizons. Correlation of manganese with pH in samples from the Nigadoo area is significant at the 5 per cent level ($r = +.407$).

Manganese and iron show positive correlations in the A_0, A_2, and C horizons (Table 14). The only significant r value for the B_2 horizon is the negative one ($r = -.365$), which is significant at the 5 per cent level. The highest positive correlation for manganese and iron is in the A_2 horizon ($r = +.320$) ,but it is not quite significant at the 5 per cent level. Correla-

tion between manganese and iron is very low in the A_0 and C horizons and over the Nigadoo and Middle River sulphide bodies.

Small amounts of water-soluble manganese were detected in all six of the profiles studied (Tables 15-22). In the well-drained Nigadoo profile No. 17, soluble manganese values decrease from the A_2 horizon (0.10 ppm) to the B_1 (0.02 ppm), then reach a peak value of 0.2 ppm in the B_2 and C horizons. The poorly drained Nigadoo profile No. 19 contains a small amount of water-soluble manganese (0.10 ppm) only in the lower gley horizon. The Brunswick profile contains only slight concentrations of soluble manganese in the B_1 and B_3 horizons. The Middle River profile contains minute amounts of dissolved manganese, the largest being 0.08 ppm in the basal B_2 horizon. Soluble manganese was detected in all horizons of the sand profile, with a relatively high peak value of 0.4 ppm in the B_1 horizon. The granite profile contains manganese ten times more soluble in its B and C horizons (0.10 ppm) than in its A_2 horizon (0.01 ppm).

Manganese oxides were identified visually in both Nigadoo profiles (Tables 29 and 30). In the well-drained No. 17 profile they occur as purplish and brownish colorations and crusts on the pebbles and sand fractions. They were also observed in the A_0, G_1 and G_2 horizons of the poorly drained No. 19 profile, with the highest concentrations in the G_1 horizon, where they are present as crusts, grains, and nodules.

Mode of Binding of Manganese

The relatively high concentration of manganese in the A_0 horizons of all but the more acid profiles indicates that the element is probably associated with organic matter. Wright, *et al.* (1955) found noticeable accumulations of manganese in the A_0 horizons of two podzol soils. Others, including Goldschmidt (1937), have found concentrations of manganese in the surface humus of forested soils. Humus is known to hold manganese firmly. Hemstock and Low (1953) present evidence indicating that the element is held as a chelate complex, and Russell (1961) mentions that certain types of readily soluble soil organic matter form insoluble manganese coordination compounds that are unavailable to plants. These investigations and the data obtained in this investigation suggest that much of the manganese in the A_0 horizons is probably bound in the humic substances as chelated complexes. Some of the soil manganese is probably also associated with the base exchange complex. Goldschmidt (1954) maintained that the large, easily soluble divalent manganese ions should react like those of calcium and magnesium and take part in the base exchange processes in soils. Hemstock and Low (1953) found, however, that in the presence of sufficient oxygen, the manganese in the clay fractions formed insoluble oxides more readily than it would react with clay. It follows, therefore, that exchangeable manganese would be more common in the deeper, more poorly aerated horizons.

According to numerous investigations, the most common forms of manganese in well-oxidized horizons of neutral and alkaline soils are the very insoluble hydroxides and oxides of trivalent and quadrivalent manganese. Pyrolusite (MnO_2) is the most common of these compounds. In reducing or acid environments, manganese is present as the soluble, divalent manganous ion.

The presence of manganese oxides and the lack of water-soluble manganese in the surface horizons of profile 19 indicate that near-surface oxidation and neutral pH are conducive to the formation of insoluble manganese oxides. The downward depletion of manganese in this profile may be due to increasing anaerobic conditions with depth, causing manganese to be present in the soluble Mn^{2+} form, possibly as $Mn(HCO_3)_2$. Any soluble manganous ions that moved upward would then tend to be oxidized and precipitated as

insoluble oxides at or near the surface of the groundwater table. In this way, the surface has become enriched in manganese at the expense of the lower horizons.

In the well-drained profiles, there is no correlation between manganese and pH in the B_1 horizons (Table 13), perhaps because the manganese is in the form of insoluble oxides or humic compounds or both, which are relatively unaffected by pH changes. In the less well-oxygenated, lower organic B_2 layer, however, the pH may be the most important factor in determining the amount of manganese present. High pH would favour oxidation and accumulation in insoluble forms; low pH would favour solubility and removal. This is indicated by the highly significant coefficient of correlation for pH and manganese in the B_2 horizons.

The high acidities present in profiles such as those overlying the Brunswick No. 6 sulphide deposit have undoubtedly been the main factor in causing the reduction, solubility, and removal of manganese from these profiles. The abundance of sulphate ions in the water-soluble leachates from the profiles above sulphide deposits indicates that manganese may have been removed as manganous sulphate. There is sufficient sulphate and bicarbonate present in the horizons of all profiles to account for the small amounts of water-soluble manganese that were found.

Manganese is commonly a constituent of a number of minerals present in the profiles. The iron oxide minerals such as goethite, hematite, etc., often contain manganese as intimately associated manganese oxides, or as manganese ions that have been scavenged by the iron oxide during its formation. Negative correlations of manganese and iron in the B and C horizons could be interpreted as indicating that manganese has little relation with iron oxides in those horizons where high free iron oxide contents prevail. However, these negative manganese-iron correlations probably reflect the greater disruptive effect of pH and eH on the lattice manganese than on the more tightly-bound iron in the lattice of the oxides and silicates.

Mn^{2+} commonly replaces Fe^{2+} in magnetite, ilmenite, and the ferromagnesian silicates. As much as 400 ppm of manganese have been reported in plagioclases. The relatively high positive correlation between iron and manganese in the A_2 horizons ($r = +.320$) may indicate that much of the manganese is present in the more resistant silicates and oxides. If the element is present in the iron sites of the minerals, it may react like iron to pH changes.

Mn^{2+} can also substitute for Ca^{2+} in such minerals as apatite, garnet, and calcite. Some of the soluble manganese present in the lower horizons of the Nigadoo profiles may be present in carbonates. Some of the manganese in these profiles may also be bound in sphalerite, in which Mn^{2+} is known to substitute for Zn^{2+}.

Summary

The surface and basal horizons are the ones most commonly enriched in manganese. With increasing acidity, the amounts of manganese decrease in all horizons. A combination of relatively high pH and increased available oxygen may be responsible for the high contents of manganese oxides in the surface horizons of the poorly drained Nigadoo profile. Manganese is positively correlated with pH in all soil horizons. It is suggested that the highly significant manganese-pH correlation in the B_2 horizons is due to the higher mobility of the element in these horizons compared with the others.

Manganese and iron are positively correlated in the A and C horizons and negatively correlated in the B horizon. The negative manganese-iron correlation in the B_1 horizons is significant at the 5 per cent level.

Water-soluble manganese is present in all six profiles studied in detail. It is probably present in a soluble sulphate or bicarbonate form where these anions are available. Manganese oxides and stains were observed in the Nigadoo profiles. Manganese is probably also present as a constituent of many of the other common minerals in the soils.

Lead

In nearly all profiles, lead exhibits a definite enrichment in the A_0 horizons and a depletion in the A_2 horizons (Table 6). In the normal and Nigadoo profiles lead shows higher mean values also in the B_1 and C horizons. The Brunswick and Middle River profiles have the greatest lead concentrations in the A_0 and B_2 horizons. In the poorly drained Nigadoo profile, the highest lead content is in the upper gley horizon where 2 to 5 times more lead is present than in the other horizons (Table 35). High contents of lead in the bedrock are usually paralleled by relatively high lead contents in the basal horizons of the overlying profiles (Table 37).

In the correlation studies of all profiles, lead exhibits a negative correlation with pH in all horizons with the exception of the A_2, where a highly significant positive correlation of $r = +.252$ occurs (Table 13). Lead and pH show a weak negative correlation in the A_0 horizons, but significant negative correlations in the B_1, B_2, and C horizons. The r value of $-.885$ for lead and pH in the B_1 horizon is exceptionally high.

A somewhat different correlation pattern for lead and pH is present in the Nigadoo profiles (Table 13) where a weak positive lead-pH correlation occurs in the A_2 horizons. Negative correlation between lead and pH is present in the B_1, B_2, and C horizons, with the B_1 horizon having the highest r value of $-.512$. In none of these horizons, however, is the correlation significant. Instead of a negative correlation in the A_0 horizons, such as occurs in the lead-pH correlation of all horizons, the Nigadoo profiles show a positive correlation ($r = +.494$), significant at the 5 per cent level.

Lead and pH show a positive correlation in the profiles overlying the sulphide bodies, ranging from a low r value of $+.092$ in the Nigadoo samples to a significant r value of $+.546$ in the Middle River samples.

A positive correlation of lead with iron occurs in the A_2 and B horizons. The highest correlation of lead with iron is in the B_1 horizons where an r value of $+.340$ is attained (Table 14). The A_0 and C horizons have weak, negative lead-iron correlations. Soil samples from the Nigadoo profiles show a highly significant lead-iron correlation of $r = +.683$ (Table 14).

Water-soluble lead was detected in four of the six profiles studied (Tables 15 to 22). The largest amounts are present in Brunswick profile No. 44 where water-soluble lead is present in all horizons tested and ranges in amount from 5.6 to 10.0 ppm. The sand profile contains 0.08 ppm of soluble lead in the A_2, and B_1 horizons, increasing to 0.2 ppm in the B_2 horizon. The poorly drained Nigadoo profile has soluble lead in only one horizon, the G_1 (0.04 ppm), where the highest total lead (1,600 ppm) in the profile occurs.

Dilute acid-soluble lead is present in all horizons except the surface horizon of the well-drained Nigadoo profile No. 17. The amounts increase with depth to the C horizon where 75 per cent of the total lead value of 13,000 ppm is dilute acid-soluble lead (Table 23). In the poorly drained Nigadoo profile (No. 19) the G_1 horizon contains the most acid-soluble lead. The Brunswick profile has high contents of dilute acid-soluble lead in the A_0, A_2, and B_2 horizons; in the other horizons the contents of acid-soluble lead were too low to be determined. Relatively high concentrations of acid-soluble lead are present in the surface and basal horizons of the Middle River profile. Both normal profiles have small amounts

of acid-soluble lead in their B_1 horizons; in the granite profile acid-soluble lead increases with depth.

The lead released by the hydrogen peroxide treatment (Table 24) represents a high proportion of the total lead in all surface humic horizons that were treated, except the Brunswick A_0 horizon where it represents only 1 to 2 per cent of the total lead. Lead was released by peroxide in the A_2 horizons of only two profiles, the sand and the Middle River. In both these horizons the acid-soluble lead constitutes a considerable percentage of the total lead present. The peroxide treatment removed 30 to 40 per cent of the total lead in the B_1 horizons of the Nigadoo and Middle River profiles, and some acid-soluble lead was removed from the B_2 horizons of the two profiles. About 10 per cent of the total lead in the C horizons of the poorly drained Nigadoo and the two normal profiles was removed by the peroxide treatment.

Removal of the free iron oxides was accompanied by the greatest lead losses from the Brunswick No. 44 profile (Table 25). Large amounts of lead were removed by this treatment from all horizons of this profile except perhaps the A_0 and B_1 which could not be measured because of interference. The largest amount (44,160 ppm) was removed from the B_3 horizon, the level of the groundwater-soil interface. In the well-drained Nigadoo profile, the only removal of lead with free iron was in the C horizon where about 75 per cent of the total lead was removed. In the poorly drained Nigadoo profile, the only horizon from which lead was removed was the A_0 where there was 50 per cent loss. In the Middle River profile, nearly all the lead from the surface horizon and about 60 per cent of the lead from the basal horizon were removed during the free iron treatment.

Mode of Binding of Lead

Lead accumulations in the surface horizon of podzol soils, similar to those found in this study, have been reported by several investigators. The lead is thought to have been absorbed from the soil by plants, and then to have accumulated in an insoluble form in the humus derived from the dead plant material. There is much speculation as to the nature of the insoluble compounds in the humus. Hawkes (1957) states that lead is known to be immobilized by precipitation in the cell walls and roots of some plants. Perhaps lead remains in this state after decomposition of its plant host, or, if released, it may form compounds with the decomposing humus that are equally immobile. This study shows that in the normal and Nigadoo profiles, most of the lead in the surface horizons was released by the peroxide treatment and is hence probably combined with the organic humic substances. Accumulations of lead in the B horizons may also be partly due to organic immobilization of lead.

Some lead may be associated with the exchange complex in the soils. Goldschmidt (1954) states that divalent lead would be more firmly bound to clay minerals than univalent potassium which has the same ionic size. Mitchell (1955) is of the opinion that heavy metal cations such as Pb^{2+} are readily adsorbed by exchange-active clay minerals, perhaps forming basic salts with the clay, which would be difficult to displace. This may partly explain the enrichments of lead in horizons such as the B_1 where clay contents are often high (Table 26).

Some of the lead appears to be bound in the iron oxides. Table 14 shows that the correlation coefficient of lead and iron in the B_1 horizons is relatively high ($r = +.340$), but not quite significant at the 5 per cent level. This is the horizon in which the maximum amounts of free iron occur in all the five well-drained profiles studied in detail. Table 25 also indicates that there is a trend for lead to be removed with the free iron from the B and C horizons of these profiles. In the Brunswick profile No. 44, lead was removed from the B_1 and B_2 horizons by the free iron treatment probably from the sulphate-arsenate, beudantite, and probably

also from jarosite in which the lead may replace some of the potassium in the lattice of the mineral.

Lead may be present in a more mobile form in some of the poorly drained and reduced horizons since Swaine and Mitchell (1960) among others, have noted an increased mobility of lead in poorly drained soils. In the poorly drained Nigadoo profile, an increased solubility of lead due to reducing conditions has probably facilitated its movement in the groundwater and its precipitation at the groundwater table or near it. Similar reducing conditions are probably present in the three basal horizons of the Brunswick profile. Sharp increases in total and water-soluble lead occur in these horizons (Table 17). Their maximum lead values are in the B_3 horizon which probably represents the upper limit of the groundwater table.

The highly significant positive r value in the A_2 horizons for lead and pH indicates that lead is likely to be removed from this horizon as the acidity increases. If reducing conditions increase as the acidity increases, lead should be more mobile and more readily removed. The extremely high negative r value in the B_1 horizon indicates that lead builds up in this horizon as the acidity increases. This is to be expected, as lead is more mobile and moves from the A_2 horizon downwards eventually into the B_1 horizon as the acidity increases. At the same time, the increased acidity would permit the movement of more free iron, clay, and humic substances downwards into the oxidizing B_1 horizon. These materials would react with the lead and immobilize it. A continuation of this process with lessening intensity downwards could explain the significant negative r values obtained for lead and pH in the B_2 and C horizons.

Anglesite ($PbSO_4$) is a common oxidation product of galena in the gossans and, although not identified in the soils over the sulphide deposits, it may be present in a finely divided form. The relatively high amounts of water-soluble lead and sulphate in the Brunswick profile suggest the presence of anglesite. While $PbSO_4$ is only slightly soluble in water, its solubility would be increased under the acid conditions prevailing in the soils overlying the Brunswick No. 6 deposit. Jarosite and beudantite may also have contributed some soluble lead and sulphate in this profile.

Cerussite ($PbCO_3$) occurs as an oxidation product in some of the gossans and may have contributed some soluble lead from the profiles overlying the sulphide deposits. The mineral may also be present in the sand profile and in the poorly drained Nigadoo profiles from which both water-soluble lead and bicarbonate were extracted. Cerussite most probably occurs in a finely divided form in the upper gley horizon of Nigadoo profile No. 19 (Table 16), where large amounts of both lead and carbonate occur. The slight solubility of cerussite could produce the trace amounts of water-soluble lead extracted from samples of this horizon.

The relatively high amounts of water-soluble lead present in sand profile No. 51 (Table 21) are probably present as the very soluble $Pb(NO_3)_2$ as conditions are conducive to the presence of nitrates in this profile.

Some lead in the C horizons above the sulphide bodies may be present in small particles of galena as this mineral is very common in the ores. Small amounts of lead are probably bound in the various potassium minerals in the soils because of the similar radii of divalent lead and monovalent potassium. Various other minerals such as augite and apatite found in the profiles may contain some lead. It seems probable that some of the lead removed by dilute HCl from granite profile No. 64 is present in potash feldspar, as the granite fragments are larger and less weathered at depth, and more lead was removed in the deeper parts of the profile (Table 23).

Summary

The lead contents are highest in the surface horizons of all profiles, and in the B_1 and C horizons of the normal and Nigadoo profiles. Lead has accumulated in some of the B_2 horizons of profiles overlying sulphide deposits. In poorly drained soil the lead appears to be concentrated at or near the groundwater table. Negative correlations of lead and pH are present in all horizons except the A_2. Lead and pH exhibit a significant correlation in all horizons except the A_0.

Lead and iron are not significantly correlated in any of the soil horizons. The best correlation between the two elements is in the B horizons where $r = +.340$. This may reflect a relationship of lead with free iron.

Water-soluble lead was detected in four profiles and is most abundant in Brunswick profile No. 44, where it is probably derived from lead sulphates and arsenates.

Dilute acid-soluble lead was removed in greatest amounts from surface and basal horizons. The dilute acid-soluble lead from the surface horizon is probably associated with the clay-organic complex. Acid-soluble lead from the lower horizons is probably derived mainly from galena, lead arsenates, and orthoclase. The hydrogen peroxide destruction of organic matter in the surface horizons releases lead, which indicates that much of the lead in these horizons is bound with the organic matter.

Considerable amounts of lead were removed with the free iron from Brunswick profile No. 44 and from the basal horizons of the Nigadoo 17 and Middle River profiles. In the Brunswick profile this lead is probably contained in beudantite and jarosite. Beudantite was the only lead mineral identified in the soil fractions. Galena, anglesite, and cerussite are present in the sulphide deposits and gossans and possibly in the profiles overlying these bodies. Other minerals such as jarosite, limonite, orthoclase, and augite, which generally carry traces of lead, are present in the soil profiles.

Copper

The only horizon where copper shows a definite tendency for enrichment is the C horizon (Table 7). Any tendency for enrichment in the A_0 horizons is slight, except for the Nigadoo group where the mean copper value for the surface horizons (68 ppm) is surpassed only by the mean value for the C horizons (94 ppm). The mean copper value for the A_2 horizons of the Nigadoo group is also relatively high (52 ppm) in comparison with other profile groups where the decrease in copper from the A_0 to the A_2 horizons is as high as 60 per cent. In general, there are no marked increases or enrichments of copper in the B horizons, although a few profiles have peak copper values in their B_2 horizons. The copper contents of the C horizons are variable, but are always higher in profiles above sulphide bodies. Like lead, copper is greatly enriched in the upper gley horizon of the poorly drained Nigadoo profile (Table 35).

Copper shows a strong positive correlation with pH in both the A_0 and A_2 horizons (Table 13). Correlations of copper with pH in the B and C horizons are negative and non-significant. The highest correlation is in the B_1 horizons where $r = -.101$; the lowest correlation occurs in the C horizons ($r = -.028$). Correlation coefficients for copper and pH are all highly significant in each of the profiles above sulphide bodies. There is a marked high positive correlation between copper and iron in the A_2, B, and C horizons, with r values ranging from $+.560$ to $+.708$ (Table 14). A low negative r value of $-.088$ is present for the two elements in the A_0 horizons. Copper and iron are positively correlated in the profiles above the three sulphide bodies, but significance at the 5 per cent level is achieved only in the Nigadoo profiles.

Water-soluble copper ranging from traces to 0.02 ppm was detected from the leachates of the six profiles chosen for detailed work (Tables 15-22). The highest amounts were present in the Brunswick profile, where water-soluble copper was detected in all horizons. In the other well-drained profiles water-soluble copper has a slight tendency to be most abundant in the lower horizons.

Dilute HCl leached the most copper from the gley horizons of the poorly drained Nigadoo profile (18 to 33 ppm), the C horizon of the well-drained Nigadoo profile (10 ppm), and the surface A_0 horizon of the Brunswick No. 6 profile (17 ppm). The amounts of copper leached from other horizons were small, ranging from nil to 4 ppm (Table 23).

Hydrogen peroxide released copper from all six A_0 horizons in amounts ranging from 2 to 330 ppm (Table 24). Significant amounts of copper released by the peroxide treatment were obtained from all horizons of the poorly drained Nigadoo profile (8 to 331 ppm), from the A_2 horizon of the Middle River profile (38 ppm), from the B_1 horizon of the granite profile (11 ppm), and from the surface and basal horizons of the well-drained Nigadoo profile (13 ppm).

The sodium hydrosulphite treatment removed relatively large amounts of copper with the free iron oxides from the A_0 horizons of the four profiles overlying sulphide deposits (Table 25). This treatment also removed substantial amounts of copper from all horizons of the poorly drained Nigadoo profile (8 to 304 ppm), the A_2 horizon of the Middle River profile (37 ppm), the B_1 horizons of the Brunswick and granite profiles (10 to 18 ppm), and the C horizon of the well-drained Nigadoo profile (25 ppm).

The only copper minerals identified in the soil fractions were from Nigadoo profile No. 17 and Brunswick profile No. 44 (Tables 29 and 31). Malachite was observed in the sand fraction of the Nigadoo A_0 horizon. Chalcopyrite was identified in the B_2 horizon of the Nigadoo profile and in the B_3 and Cg_2 horizons of the Brunswick profile.

Mode of Binding of Copper

Copper, unlike lead, shows less tendency to accumulate in the A_0 horizons of podzol profiles, although it is known to form compounds with many organic substances including humic and fulvic acids, fungi, coal ashes, plankton, etc. Many investigators think that copper forms chelate compounds with humus; others maintain that some other type of complex coordination compound joins the two substances. The results of the peroxide treatment shown in Table 24 indicate that relatively large amounts of copper are usually released from the A_0 horizon by the oxidation of organic matter. Some of this may be in an exchangeable form. Manskaya, *et al.* (1958) determined that the largest amounts of copper combined with humic acids at pH 2.5 to 3.5, and with fulvic acids at pH 6.0. These were the approximate pH values at which Schlichting (1955) found that the copper adsorbed to humic acids is most available. Lundblad, *et al.* (1949) determined that copper in Swedish soils was not fixed as strongly by organic as by inorganic matter. He noted further that copper deficiencies in peat did not necessarily mean fixation of copper in an unavailable form, but simply a lack of the element.

The highly significant r values obtained for copper and pH in the A horizons indicate a sensitivity of copper to pH changes. Furthermore, as removal of copper is facilitated by increasing acidity, it provides an answer to the question of why there are no marked accumulations of copper in the relatively acid A horizons of most profiles in the Bunswick No. 6 area.

As mentioned above, some copper may be combined with the organic matter in exchangeable form. There is also evidence to show that exchangeable copper is combined with the clay fraction, but like other heavy metals it is attracted strongly and displaced with

difficulty from clay, suggesting possible formation of a basic salt with the clay rather than a simple base-exchange relationship.

If available copper is indicated by dilute HCl-soluble copper as suggested by Steenbjerg and Boken (1950), then the data in Table 23 indicates that the largest amounts of available copper are present in the gley horizons of the poorly drained profile. Swaine and Mitchell (1960) also found an increase in the amount of available copper in soils with impeded drainage. Presumably, much of this copper is present in an exchangeable form.

The highly significant positive correlation of $r = +.500$ between copper and pH in the A_2 horizons of all profiles indicates a removal of copper with increasing acidity. However, in the Nigadoo A_2 horizons the copper-pH correlation is considerably less ($r = +.338$) and not significant. Coupled with the relatively high mean copper value of the Nigadoo A_2 horizons (52 ppm), this suggests that the element is removed with more difficulty from the Nigadoo A_2 horizons than from the A_2 horizons of other profiles. This could be the result of increased precipitation of copper as the relatively insoluble hydroxide, since the mean pH of the Nigadoo A_2 horizons is 5.2, and the pH of hydrolysis of Cu^{2+} ion from aqueous solution is 5.3.

Hawkes (1957) mentions copper enrichments in limonites from soils and rocks. Table 25 indicates that in some of the B, C, and gley horizons, relatively large amounts of copper were removed with the free iron. This suggests that copper and free iron are combined in some way in these horizons.

Although the high correlation between copper and iron in the A_2, B, and C horizons (Table 14) may be partly due to a relationship between copper and free iron, this relationship should have little effect on the correlations because of the small ($<1\%$) proportion of the total iron that the free iron represents. It seems more likely that this correlation signifies similarity in the response of iron and copper to pH, eH, humus, and the presence of other elements. Copper accompanies iron in most iron-containing minerals, with Cu^{2+} substituting in small amounts for Fe^{2+}. Thus, in the B horizons, enrichments of copper could be associated with increases in oxidation, humus, free iron, or clay content that occur in the A_2, B, and C horizons. The weak negative correlations for copper and pH in the B horizons probably reflect a tendency for fixation of copper in the B horizons. The r values indicate, however, that this tendency is not nearly as strong as the one for fixation of lead or iron in these horizons.

Water-soluble copper, which was detected in minute amounts in all six profiles studied in detail, is most plentiful in the Brunswick profile where it probably is present as soluble copper sulphate. In profiles where the contents of SO_4 are low, water-soluble copper may be present as the slightly soluble hydroxycarbonate or chloride, or as the very soluble hydrous copper nitrate.

Small amounts of copper are probably bound in the various ferromagnesian minerals present in the soils, especially in the C horizons. Some copper is probably also present in the small amounts of pyrite in the C horizons of some profiles, and in the chalcopyrite observed in the lower horizons of the Brunswick profile and Nigadoo profile No. 17. Malachite was identified in the A_0 horizons of the Nigadoo profile, but this may be due to contamination from the trenches.

Summary

Most profiles show an increase in copper content from the surface horizon downwards to the C horizon, interrupted only by a sharp decrease in copper in the A_2 horizon. Copper has a slight tendency to accumulate in the surface horizons, especially in the Nigadoo profiles.

In the copper-pH correlation studies of all profiles, copper shows a highly significant positive correlation with pH in the A horizons, but weak negative correlations with pH in the B and C horizons. This correlation pattern reflects the strong effect of pH on the enrichment of copper in the A horizons and its lack of effect on copper enrichment in the B horizons.

The correlation of copper with iron is positive and highly significant in all horizons except the surface A_0 horizon where it is negative. These significant copper-iron correlations indicate some similarity in reaction or origin of the two elements. It is possible that Cu^{2+} substitutes for Fe^{2+} in many of the iron minerals in the soils.

Water-soluble copper is present in minute amounts in all profiles studied in detail. It is most plentiful in Brunswick profile No. 44 where it is probably present as soluble copper sulphate.

The hydrogen peroxide treatment released significant amounts of copper from the A_0 horizon of all six profiles. Most of this copper is probably organically combined.

Moderately large amounts of copper were removed with the free iron from some of the B and C horizons in well-drained profiles. This copper may be associated with the iron in some form. The free iron treatment also removed large amounts of copper from the surface A_0 horizons, but it seems improbable that this copper is associated with the free iron.

Larger amounts of copper were released from the poorly drained Nigadoo profile by the dilute acid, hydrogen peroxide, and sodium hydrosulphite treatments than from the well-drained profiles. This suggests that the copper in the poorly drained profile is present in a more reactive and mobile form.

Some copper is present in small particles of chalcopyrite and malachite, the only copper minerals identified in the soil fractions.

Zinc

In most profiles the content of zinc shows a gradual increase from the A_0 to the C horizon interrupted only by a lower value in the A_2 horizon (Table 8). The decrease in zinc in the A_2 horizon is most pronounced in highly acid profiles such as those overlying the Brunswick No. 6 and Middle River sulphide bodies. There are no general tendencies for enrichment of zinc in any horizon, although local enrichments occur. The Brunswick and Middle River profiles show some zinc enrichment in their A_0 horizons. The content of zinc in the poorly drained Nigadoo profile is distributed in a manner similar to that of copper, with a peak value of 4,000 ppm Zn in the G_1 horizon decreasing to 1,000 ppm in the Cg horizons. Of all the profiles, those in the vicinity of the Nigadoo deposit have the highest contents of zinc.

Zinc is similar to copper in having highly significant positive correlations with pH in the A_0 and A_2 horizons (Table 13), but unlike copper, in having significant positive correlations with pH in the B and C horizons. The correlation increases down the profile from the B_1 to the C horizon. There is a high positive correlation of zinc with pH in the A_2 horizons of the Nigadoo profiles ($r = +.828$) but only low positive correlations in the other Nigadoo horizons (Table 13). The r values for the zinc-pH relationships at the Nigadoo and Middle River locations are significant.

In zinc-iron correlation studies (Table 14), zinc is significantly correlated with iron only in the A_2 horizons ($r = +.538$). Correlations of zinc and iron in the A_0 and B horizons are negative and low; the highest r value in these horizons is $-.245$ in the B_1 horizons. In the C horizons, zinc and iron have a low, positive correlation of $r = +.137$. Zinc and iron show little correlation in the Brunswick No. 6 samples ($r = -.064$), fairly high correlation

in the Middle River samples (r = +.575), and a highly significant correlation in the Nigadoo samples (+.565).

Water-soluble zinc was detected only in the Brunswick profile, where it occurs in greatest concentrations in the three basal horizons and in the A_2 horizon (Tables 18 and 19).

The largest amounts of dilute acid-soluble zinc were removed from the A_0 horizons of the six profiles chosen for study (Table 23). The largest amount (1,000 ppm) was obtained from the contaminated A_0 horizon of Nigadoo profile 17. Much lower amounts of zinc were removed from the other A_0 horizons (33 to 50 ppm). In addition to the high content in the A_0 horizon, the No. 17 Nigadoo profile contained 28 to 60 ppm of acid-soluble zinc in its other horizons. There were slight accumulations (3 to 8 ppm) of acid-soluble zinc in the B_1 horizons of the sand and Middle River profiles. High contents of acid-soluble zinc were removed from the poorly drained Nigadoo profile (45 to 200 ppm).

Relatively high amounts of zinc (15 to 770 ppm) were released by the hydrogen peroxide treatment from the A_0 horizons of all profiles except No. 17 where calculation was impossible (Table 24). Significant amounts of zinc were released by peroxide from the poorly drained horizons of Nigadoo profile No. 19 and from the three basal horizons of the No. 44 Brunswick profile.

Table 25 shows that the amounts of zinc removed with the free iron oxides usually do not correlate well with the amounts of free iron. Large amounts of zinc were also removed by sodium hydrosulphite from the A_0 horizons of these profiles. The hydrosulphite treatment also released large amounts of zinc from the basal horizons of the two Nigadoo profiles.

The only zinc mineral identified was sphalerite, and this was observed only in the sand fractions of the two basal horizons of the well-drained Nigadoo profile.

Mode of Binding of Zinc

There is little evidence of zinc enrichment in the A_0 horizons of the podzol soils, other than in those profiles overlying the Brunswick No. 6 deposit. However, evidence shows that part of the zinc is associated with the organic matter, as 15 to 50 per cent of the total zinc content was released when the organic matter was destroyed by hydrogen peroxide.

Although the association of zinc with organic matter is fairly well-known, the mechanism of the bonding involved is still not clear. Baughman (1956) in an extensive investigation of the association of zinc with organic matter, determined that 50 to 66 per cent of the zinc in the surface horizons of two soils he studied was associated with organic matter. He concluded that the zinc was bonded to the humus in a chelated form. Increase in available zinc with increased organic matter has been noted by Nair and Mehta (1959), Bear (1954), and others. There are few comments upon the nature of this available zinc; Bear thinks that it is supplied by the decaying organic material, or made more available by it.

Leaching soil with 0.1 N HCl is a practice commonly used to extract acid-soluble "available" zinc, but opinions are divided as to whether this acid-soluble zinc is a separate form of zinc or whether it includes exchangeable zinc as well. Table 23 indicates that this "available" zinc is definitely more abundant in the humus-rich horizons, a feature that correlates satisfactorily with the organic carbon content in all profiles except the two at Nigadoo.

The relationship of exchangeable zinc to inorganic colloidal material has been extensively discussed in the literature. Mitchell (1955) notes that zinc differs from the other heavy metal cations in being one of the least readily absorbed of the cations. Although its exchange relationship is closer to the alkaline earths than to the other heavy metals, it is thought to form basic salts with clay and to contribute only part of its valency to the exchange complex.

The r values for the correlation of zinc and pH (Table 13) indicate an increase of mobility of zinc in response to increasing acidity, and show that zinc is much less readily absorbed than elements such as copper or lead. Highly significant r values occur for every horizon and range from +.368 to +.690. Correlations of zinc with pH are much lower for the Nigadoo profiles, except in the A_2 horizons where r = +.828. This can perhaps be explained from the higher mean pH values (5.2 to 6.1), which would be increasingly favourable to hydrolysis of the zinc. Reducing conditions in the Nigadoo A_2 horizons may discourage hydrolysis and account for the high zinc-pH correlation.

Zinc is one of the elements that shows increased availability and mobility with impeded drainage, according to Swaine and Mitchell (1960). This probably explains the high amounts of available zinc obtained from the poorly drained Nigadoo profile by dilute acid leaching.

Zinc has been found to be associated with free iron oxides. White (1957) determined that 30 to 60 per cent of the total zinc in some Tennessee subsoils is held with the free iron oxides. In Table 25, which shows the free iron and amounts of various elements calculated to have been removed with it, the association of zinc and free iron could be postulated in only a few horizons. The large amount of zinc removed from the humus horizons by sodium hydrosulphite is almost certainly associated with humus rather than with free iron.

If zinc is associated with free iron, one might expect it to show a positive correlation with iron in the B_1 horizon but the correlation is negative and weak in this horizon (r = −.245). There is, however, a good zinc-iron correlation in the A_2 (r = +.538) horizon which probably indicates the close similarity in the response of the two elements to the acid, leaching conditions present.

The excess of sulphate ions and the high acidity of Brunswick profile No. 44 suggest that zinc would be quite mobile in this profile, and is probably present as water-soluble $ZnSO_4$. The very high zinc values obtained from dilute acid leaching of the A_0 horizon of Nigadoo profile No. 17 are probably also derived from weakly bonded, soluble zinc salts such as $ZnSO_4$ that are weathered products of sphalerite in the trench material overlying this profile.

Sphalerite (ZnS) contributes to the zinc content of the two basal horizons in Nigadoo profile No. 17 (Table 29). The increase in acid-soluble zinc in these horizons may be mainly due to the acid-soluble sulphide, although zinc carbonate, which was not detected, is also acid-soluble and could be present.

Goldschmidt (1954) observed that the geochemistry of zinc is mainly determined by the similarity in radii between divalent zinc and the metals of the magnesium-iron group which include Mg^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, and Mn^{2+}. Mutual replacement of these elements, especially of Zn^{2+} and Fe^{2+}, is extremely common in the ferromagnesian silicates, and much of the zinc content of the C horizons, where the ferromagnesian silicates are least weathered, is probably derived from these minerals. Zinc is commonly found in magnetite and ilmenite, and in some of the more highly weathered A and B horizons these fairly resistant oxides may be significant zinc carriers. Zn^{2+} can substitute for Mg^{2+} in some 2:1 trioctahedral-type clay minerals, resulting in the mineral species sauconite, which may be present in some of the zinc and clay-rich horizons.

Summary

Most profiles show an increase, except for the A_2 horizon which has a decrease, in the zinc content from the surface to the C horizon. In the acid profiles overlying the Brunswick No. 6 and Middle River profiles the A_0 and A_2 horizons tend towards greater zinc accumulation and depletion, respectively.

Correlation of zinc with pH is positive and highly significant in all horizons in the correlation study involving all profiles. In the correlation study involving only the Nigadoo profiles, zinc is positively correlated with pH in all horizons but significantly so only in the A_0 horizon. This is interpreted as indicating a lower mobility and greater fixation of zinc in the Nigadoo profiles. There is little correlation between zinc and iron except in the A_2 horizons where correlation is positive and highly significant.

Water-soluble zinc was detected only in Brunswick No. 44 profile, where it is thought to be present mainly as zinc sulphate. Zinc soluble in 0.1 N HCl supposedly represents zinc "available" to plants. The largest amounts of "available" zinc are in the surface horizons of all profiles and in the poorly drained Nigadoo profile. This zinc is probably associated mainly with the humus exchange complex. Some zinc in the poorly drained profile is probably also associated with the inorganic exchange complex.

The hydrogen peroxide oxidation of organic matter in the A_0 horizons of six profiles releases 15 to 50 per cent of the total zinc of these horizons.

There are no obvious relationships of zinc with free iron in the six profiles that were studied. Sphalerite was the only zinc mineral identified in the soil fractions, and was present only in the two basal horizons of Nigadoo profile No. 17.

Arsenic

Arsenic is abundant in all profiles overlying sulphide deposits (Table 9), with the largest amounts in the Middle River profiles. In the normal profiles the highest mean value comes from the B horizons (20 ppm). The lowest mean value of arsenic in the normal profiles comes from the A_0 horizons (3 ppm), with the A_2 horizons having a slightly higher mean value of 5 ppm. Arsenic distribution in the Brunswick profiles is similar to that in the normal ones, except that both the B_1 and B_2 horizons are enriched in the former. The Nigadoo and Middle River profiles are enriched in arsenic in their A_0 horizons and show a greater tendency to release arsenic from their A_2 horizons than do the other profile groups. Arsenic increases downwards in these profiles to reach peak values in the basal horizons (1,490 to 2,400 ppm). A comparison of the analyses of seventeen bedrock samples with the soil profiles overlying them shows that bedrocks having contents greater than 35 ppm arsenic are almost invariably accompanied by high arsenic contents in the profiles, which generally attain peak amounts in the basal horizons. Where bedrock values of less than 35 ppm are present, the arsenic values in the profiles are also low, with maximum values usually in the B_1 horizons (Table 37).

Arsenic exhibits a highly significant positive correlation ($r = +.455$) with pH in the A_0 horizon (Table 13). In the other horizons, the arsenic-pH correlations remain positive, but the r values are much lower ($r = +.152$ to $+.035$). Arsenic and pH are positively correlated in the samples from the three mineralized areas, significantly so at the Middle River location.

Arsenic is significantly correlated with iron at the 5 per cent level in both the B_1 and B_2 horizons (Table 14). There is also a fair positive correlation between the two elements in the A_2 and C horizons. Iron and arsenic are positively correlated in the profiles in the vicinity of the three sulphide bodies and are correlated at the 1 per cent level of significance at the Brunswick No. 6 and Middle River localities.

The only arsenic removed by dilute acid from the two normal profiles (Table 23) was in small amounts from the B_1 horizon of the granite profile (7 ppm) and the C horizon of the sand profile (4 ppm). A large amount of arsenic (1,500 ppm), representing 20 per cent of the total amount of arsenic in the horizon, was leached from the basal horizon of the Middle

River profile. In the Brunswick profile, relatively large amounts of arsenic (10 to 60 ppm) were leached from all horizons except the lower B ones. The B_2 horizon yielded the most arsenic (55 ppm) to dilute acid in the well-drained Nigadoo profile. The surface horizons contained the most acid-soluble arsenic in the poorly drained Nigadoo profile (20 to 127 ppm).

The hydrogen peroxide treatment released practically no arsenic from the normal profiles, but considerable amounts from some horizons of the profiles overlying sulphide bodies (Table 24). Large amounts of arsenic were released from all horizons of the Middle River profiles (470 to 1,215 ppm), from the B_2 horizon of the well-drained Nigadoo profile (40 ppm), and from the surface horizons of both Nigadoo profiles (55 to 239 ppm).

Arsenic was removed with free iron from almost every horizon. Table 25 shows that the arsenic contents correlate well with the free iron contents in most profiles. The most arsenic removed with free iron was found in the basal horizons of the Middle River and well-drained Nigadoo profiles, just above the arsenic-rich veins.

Beudantite, the sulphate-arsenate coating the soil particles in the upper B horizons of the Brunswick profile, was the only arsenic mineral identified. Rajah (1962), however, identified small amounts of scorodite, $Fe(AsO_4).2H_2O$, in the residual gossan of the Brunswick No. 6 deposit, and arsenopyrite occurs in the Nigadoo and Brunswick sulphide bodies.

Mode of Binding of Arsenic

Two references to the association of arsenic with organic-rich rocks and soils are those by Mason (1958), who cites examples of arsenic concentrations in black and bituminous shales, and Goldschmidt (1954), who found concentrations of as much as 8,000 ppm in coal ashes, and as much as 320 ppm in the ash from the uppermost humus layer of a beech forest. Total analyses and peroxide treatments indicate that arsenic is associated with organic matter in some of the A_0 horizons of the New Brunswick samples. The large amount of arsenic released by hydrogen peroxide in the A_0 horizon of the Middle River profile No. 79 (1,215 ppm) may occur in some manner in the ashes and charcoal left from a recent forest fire.

The high r value (+.455) for the arsenic-pH correlation in the A_0 horizons indicates that increasing alkalinity favours retention of arsenic by the humus. This may explain the relatively high concentrations of arsenic in the humus horizons of the Nigadoo profiles.

The distribution of total arsenic in the poorly drained Nigadoo profile is similar to that of the other heavy metals, suggesting that the element may be present in a soluble and mobile state, a feature that is supported by the relatively high amounts removed by dilute HCl (Table 23).

Hawkes (1957) asserts that the mobility of arsenic is dominated by the extreme stability and insolubility of the iron arsenates that form as secondary minerals, and Goldschmidt (1954) cites ferric iron hydroxide as being a very effective precipitant of soluble arsenic. Both authors mention known occurrences of arsenic in limonite, bauxite, and sedimentary iron ores.

There are strong indications that much of the arsenic in these podzols is associated with the free iron oxides. In Table 25, arsenic removed with the free iron correlates well with it in most of the horizons. In the correlation studies of horizons, arsenic is significantly correlated with iron in the B_1 and B_2 horizons. These horizons also contain the most free iron. Arsenic is also known from x-ray studies to occur in beudantite in the free iron oxides of the upper B horizons of the Brunswick profile.

Small amounts of arsenic may be present in scorodite and other arsenates in the lower horizons of the profiles overlying sulphide bodies as well as in residuals of arsenopyrite, tetrahedrite, and other sulphides.

Summary

Concentrations of arsenic occur in the B horizons of the normal and Brunswick No. 6 profiles. Soils overlying the Nigadoo and Middle River sulphide deposits contain large amounts of arsenic in all horizons, and show accumulations of the element in their surface and basal horizons. Large amounts of arsenic in the bedrock are usually accompanied by concentrations of arsenic in the C horizons of the overlying soil profiles.

The only significant correlation of arsenic with pH is a positive correlation in the A_0 horizons. This may indicate an increased retention of arsenic by humus as the alkalinity increases.

There are significant positive correlations of arsenic with iron in the B_1 and B_2 horizons. These correlations probably reflect the association of arsenic with free iron oxides that are usually most common in the B horizons.

Arsenic was removed with free iron by sodium hydrosulphite in amounts that appear to correlate well with the free iron contents. Most of this arsenic is probably associated with the iron oxides as iron arsenates.

Arsenic leached by dilute HCl from the basal horizons of the profiles overlying sulphide deposits may be partly derived from acid-soluble sulphides that contain arsenic. Some arsenic may also be derived from acid-soluble arsenates such as beudantite and scorodite which have been identified in the soils and gossan above the Brunswick No. 6 deposit.

The large amount of arsenic released by hydrogen peroxide in the surface horizons of the Nigadoo and Middle River profiles is probably largely combined with the humus.

Antimony

The contents of antimony in the normal profiles are uniformly low (Table 10), averaging about 2 ppm in all horizons. All the profiles overlying sulphide deposits contain more antimony than the normal profiles, especially the Brunswick No. 6 profiles which have the highest antimony values (14 to 91 ppm). The A horizons and basal horizons of the Middle River and Nigadoo profiles are enriched in antimony. The B_2 horizons of the Brunswick No. 6 profiles contain the most antimony in the Brunswick profiles (91 ppm). High antimony contents in the bedrock are usually matched by higher than average antimony contents in the profiles overlying it. The highest contents are generally in the C horizons, but also in the A and B horizons (Table 37).

In its correlation with pH, antimony differs from arsenic in having negative r values for all horizons except the A_0 (Table 13). The positive r value for the A_0 horizons is much lower for antimony ($r = +.034$) than for arsenic ($r = +.455$). The only significant r value for antimony and pH is in the B_1 horizon ($r = -.480$), although the value for the C horizon ($r = -.335$) is almost significant at the 5 per cent level.

The positive correlation of antimony with iron (Table 14) is significant at the 5 per cent level in the B_1 horizons ($r = +.375$), and almost significant in the B_2 horizons ($r = +.328$). Correlation between the two elements is very low in other horizons. There is a positive correlation between antimony and iron in the profiles overlying the three mineralized localities. A significant r value of $+.558$ occurs in the Nigadoo profiles.

Dilute HCl removed antimony from every horizon but the basal one in Brunswick profile No. 44 (Table 23). The largest amounts of antimony were leached from the lower A_2

and upper B horizons of this profile (31 and 32 ppm). Smaller amounts of antimony were leached by dilute HCl from the basal horizons of the Middle River (3 ppm) and well-drained Nigadoo profiles (6 ppm). The only antimony released by the hydrogen peroxide treatment (Table 24) from the surface horizons was found in the A_0 and A_2 horizons of the Nigadoo and Middle River profiles (1 to 6 ppm). The largest amount of antimony released by peroxide was 11 ppm from the C horizon of the well-drained Nigadoo profile.

The amounts of antimony removed with free iron by the hydrosulphite treatment show some relationship to free iron although they do not correspond as well as do the amounts of arsenic (Table 25). Antimony is associated with the free iron oxides in all horizons of the Brunswick profile.

Maximum amounts of 76 and 90 ppm were removed with the free iron from the B_1 and B_2 horizons of the Brunswick profile, and 18 ppm antimony was removed with the free iron from the basal horizon of the well-drained Nigadoo profile. Small amounts of antimony are associated with the free iron oxides throughout the Middle River profile (3 to 4 ppm), and in the surface horizons of the poorly drained Nigadoo profile (3 ppm). No antimony minerals were identified in the mineralogical study of the soils.

Mode of Binding of Antimony

There are few references in the literature concerning the association of antimony with organic-rich rocks and soils. Antimony is known to be concentrated in black and bituminous shales and in the ashes of certain coals. Sainsbury (1957) and Boyle (1962) have noted slight enrichments in the humus layers of poorly developed Alaskan and Yukon soils. In the New Brunswick soils, the Middle River and Nigadoo profiles were the only ones where both total analyses and peroxide treatment indicated an association of antimony with humus. Antimony, like arsenic, may have concentrated in ashes and charcoal in the A_0 horizon of the Middle River profile. The higher pH of the profiles at the Nigadoo site may be a factor facilitating surface concentration of the element, although correlation studies indicate pH has little effect on enrichment of antimony in the A_0 horizon (Table 13).

There are a few tentative indications from this study that suggest that antimony may be somewhat more mobile under impeded drainage conditions. Its proportional distribution in the poorly drained Nigadoo profile is similar to that of other heavy metals which are known to be more mobile under reducing conditions (Table 35). Larger than average amounts of antimony were removed by dilute acid with the free iron both from Nigadoo profile No. 19 and from the base of Brunswick profile No. 44 where reducing conditions are present.

On the basis of antimony concentrations in ferruginous bauxites, Goldschmidt (1954) suggested that antimony in soils may be associated with concentrations of ferric hydroxide. The removal of free iron oxides from the New Brunswick soils was accompanied in nearly all horizons by removal of antimony, presumably associated with the free iron, although the correlations between antimony and the free iron contents were not as good as those for arsenic and free iron (Table 25). Another indication that antimony is associated with the free iron oxides arises from the statistical correlation study where antimony shows complete lack of correlation with iron in all horizons except the free iron-rich B_1 and B_2 horizons. The correlation is significant at the 5 per cent level in the B_1 horizon, and almost so in the B_2 horizon (Table 14). Antimony may be associated with free iron oxides as admixed antimony oxides or as scavenged antimony ions. In the Brunswick profile, where considerable amounts of antimony were removed with the iron oxides, some may be present in beudantite.

In the statistical correlation of antimony and pH, antimony, like iron and lead, is negatively correlated with pH to a significant level in the B_1 horizon (Table 13). This may be due to the formation of very insoluble, immobile oxides of antimony with decreasing pH,

although unlike iron and lead there is no strong positive correlation of antimony with pH in the A_2 horizon to indicate retention of the metal with increased alkalinity.

Goldschmidt (1954) mentions situations where antimony has accumulated with manganese dioxide deposits; he attributes this to the formation of Sb_2O_3 or Sb_2O_5 resulting from the high oxidation potential of the surrounding manganese dioxide. In Nova Scotia, Boyle (1962) noted enrichments of antimony in manganese nodules and stains. Part of the concentration of antimony in the basal horizons of Nigadoo profile No. 17 may be due to the manganese coatings noted there. Similarly the manganese nodules at the top of Nigadoo profile No. 19 may contain some admixed antimony oxides.

The most common primary source of antimony in these profiles is probably from sulphides and sulphosalts. Tetrahedrite, containing antimony, is present in the Brunswick deposits. Antimony is often a minor constituent of galena, and has been found in pyrite, sphalerite, arsenopyrite, and chalcopyrite, all of which are present in the sulphide deposits of the Bathurst district. Pyrite, sphalerite, and chalcopyrite, which were identified in the basal horizons of the mineralized profiles, probably contribute some antimony; much of the dilute acid-soluble antimony from these horizons probably originated from sulphides.

Antimony may be present with iron and manganese oxides as admixed antimony oxides or adsorbed on the iron or manganese oxides. Antimony may also be present in arsenates, where it substitutes for arsenic. The element is also present in trace amounts in barite, anglesite, siderite, tourmaline, and apatite. Small amounts of these minerals are present in certain horizons of the soil profiles in Bathurst area.

Summary

The mean antimony values are low ($\sim$ 2 ppm) in all horizons of the normal profiles, but considerably higher (2 to 91 ppm) in the profiles above sulphide deposits. Soils above the Brunswick No. 6 deposit contain the most antimony. Soils above the Nigadoo and Middle River deposits contain antimony accumulations in their surface and basal horizons.

The highest correlations of antimony with pH are negative and are in the B_1 and C horizons. The only positive antimony-pH correlation is in the A_0 horizons. Antimony-iron correlations are featured by a good positive correlation in the B horizons, and a general lack of correlation in the other horizons. This may result from an association between antimony and the free iron oxides which are most common in the B horizons.

Antimony was removed by sodium hydrosulphite with the free iron in the profiles above sulphide deposits. The contents of antimony and free iron correspond most closely in Brunswick profile No. 44.

Small amounts of antimony were released by the hydrogen peroxide treatment from the A horizons of the Nigadoo and Middle River profiles. The largest amount of antimony released by peroxide was from the basal horizon of Nigadoo profile No. 17. Dilute HCl removed considerably more antimony from all horizons except the basal one of Brunswick profile No. 44 than from the horizons of the other profiles. Small amounts of antimony were removed from the lower horizons of the Nigadoo and Middle River profiles.

No antimony minerals were identified in the soil fractions. However, in the B horizons antimony is probably present as oxides or adsorbed to iron oxides. In the profiles above the sulphide deposits the element is probably also present in the B and C horizons in arsenates and sulphides.

Silver

Silver shows a marked enrichment in the A_0 horizon of all profiles, a tendency that is most striking in the normal profiles where the enrichment is 3 to 5 times higher in the A_0 than in other horizons (Table 11). All the A_2 horizons are depleted of silver, especially in the Nigadoo group, and least of all in the Brunswick and Middle River groups. High mean values for the element occur in the B_1 horizon of the Nigadoo profiles (4.6 ppm), and the B_2 horizons of the Brunswick No. 6 profiles (19.5 ppm). Silver increases in the basal horizons of the Nigadoo and Middle River groups. In the poorly drained Nigadoo profile, the silver contents are highest in the upper two horizons. Increases in the content of silver in the bedrocks are almost invariably matched by corresponding increases in silver in the A_0 horizons of the overlying profiles, and usually but not always, by smaller increases in the C horizon (Table 37).

The positive correlation of silver with pH is relatively good in the A_0, B_1, and C horizons ($r = +.212$ to $+.320$) but does not attain significance at the 5 per cent level in any of these horizons (Table 13). A low negative correlation of silver and pH occurs in the B_2 horizon; in the A_2 horizon the correlation is virtually absent. The correlation of silver and pH is positive in the soils above the three orebodies, significantly so in the Nigadoo profiles.

Silver is significantly correlated with iron at the 5 per cent level (Table 14), negatively in the A_0 horizons ($r = -.430$), and positively in the B_2 horizons ($r = +.425$). In the B_1 and C horizons, fair positive correlations exist between the two elements ($r = +.256$ and $+.298$). In the A_2 horizons, their correlation coefficient is relatively low and negative ($r = -.093$). Silver and iron are significantly correlated at the 5 per cent level in the Nigadoo samples. Correlation is fair at the other two orebodies.

No silver minerals were identified in the mineralogical studies of the soils.

Mode of Binding of Silver

Silver is one of the elements that are concentrated in black shales, bituminous shales, and coal, and is known to be enriched in the organic-rich horizons of some soils. In the Bathurst district the element is definitely associated with the high organic A_0 horizons. As silver is known to form chelate compounds with many of the organic compounds postulated to exist in the soil, it is probably present in this form in the surface horizons. The distribution of silver in the poorly drained Nigadoo profile is similar to that of the other heavy elements and suggestive of increased mobility and availability under restricted drainage conditions (Table 35). According to Hawkes (1957) silver is also mobile under normal oxidizing conditions.

There are reasons to suspect that some silver may be associated with the free iron oxides, especially in the Nigadoo group where a higher content of silver is apparent from the mean value for the B_1 horizon (Table 11). There is also a fair positive correlation between silver and iron, and a good positive correlation between silver and pH in the B_1 horizon. All this suggests that some silver moves with or behaves in a manner similar to a part of the iron in this horizon, and that silver tends to concentrate in the B_1 horizon as alkalinity increases. The enrichment of the element in the Nigadoo B_1 horizons verifies the latter suggestion.

The significant positive correlation of silver and iron in the B_2 horizon may be the result of two factors. First, the high mobility of silver may tend to move it farther down the profile than most other heavy metals before it is effectively precipitated. Secondly, its affinity for humus may cause more of it to be immobilized by organic matter in the higher organic B_1 horizon than in the B_2 horizon, thus preventing it from reacting with iron. Silver concen-

trations in the B horizons of the Brunswick profiles are probably due to substitution of Ag^+ for K^+ in jarosite[1].

In addition to native silver and silver-rich tetrahedrite in the Brunswick orebodies, other sulphides and sulphosalts in this and the other orebodies contain silver, and are probably the original source of much of the silver in the soil profiles. The fairly high positive r value for the correlation of silver and iron in the C horizon suggests a sensitivity to acidity that might occur if much of the silver were still associated with sulphides. Large amounts of silver have been found in galena; smaller amounts occur in sphalerite, chalcopyrite, and pyrite which were all detected in the mineralogical studies of the profiles above the sulphide bodies.

Silver apparently substitutes very little or not at all in the common silicates and oxides that were identified in the mineralogical studies. Chlorargyrite (AgCl), a secondary silver mineral often found in the oxidized zones of silver-rich orebodies, may be present with the jarosite, barite, etc., in the profiles above the Brunswick deposits.

Summary

Silver has a distinct tendency to accumulate in the surface A_0 horizon, which suggests that it is combined with organic matter; this tendency is especially marked in the normal profiles. In the profiles overlying sulphide deposits, other horizon concentrations are apparent. Large amounts of silver in the bedrock are usually matched by higher than normal concentrations of silver in the surface horizons of the overlying soils.

The good positive correlations between silver and pH in the A_0, B_1, and C horizons suggest that increasing acidity facilitates the removal of silver from these horizons. In the A_0 horizon this silver is probably associated with humus, in the B_1 horizon it may be partly associated with iron and manganese oxides, and in the C horizon silver is probably present mostly in the lattice of sulphides and other minerals.

Silver shows a relatively good positive correlation with iron in the B and C horizons, correlation is relatively low and negative in the A_2 horizons, and there is a significant negative correlation with iron in the A_0 horizons.

No silver minerals were identified in the soil fractions. Silver is present in tetrahedrite and other sulphide minerals in the sulphide deposits, and small amounts of these minerals may be present in the basal horizons of the soils overlying the deposits. In the soils above the Brunswick No. 6 deposit, silver is present in jarosite and may also be bound in chlorargyrite.

Tin

In nearly all profiles tin tends to be enriched in the A horizons (Table 12). In the normal and Brunswick No. 6 profiles the only other horizon exhibiting enrichments of tin is the B_2. The well-drained Nigadoo profiles are featured by a sharp mean increase in tin content from the B_2 to the C horizons (9.0 to 58.5 ppm). The poorly drained Nigadoo profile has its maximum tin concentration (6.2 ppm) in the upper gley horizon (Table 35). The highest tin values occur in the soils above the Brunswick No. 6 deposit. The tin contents of the bedrock are generally reflected closely by the tin contents in the C horizons of overlying profiles, and the closer the sample to the bedrock, the more nearly it corresponds to the bedrock value (Table 37).

[1]Recent work by Boyle (personal communication) indicates that the jarosite in these horizons is silver-bearing.

Correlation of tin with pH is low in all horizons and at the three orebodies (Table 13). Correlation is negative in all except the C horizon. Negative r values range from −.234 in the B_1 horizons to −.078 in the B_2 horizons. There is no correlation of tin with pH over the Nigadoo vein, and only weak negative r values at the other two mineralized localities.

Tin shows little correlation with iron in horizons other than the B_1. Tin-iron correlations are negative in the A and C horizons and positive in the B horizons. The highest correlation of tin and iron is in the B_1 horizon where r = +.310. Above the orebodies, tin shows significant correlation with iron only in the Nigadoo samples where r = +.510. In the Brunswick No. 6 and Middle River profiles, tin and iron are negatively correlated, with the highest r value (−.430) in the Brunswick profiles.

In the mineralogical studies, no tin minerals were identified. Cassiterite and stannite are known to be present in the Brunswick deposits.

Mode of Binding of Tin

Goldschmidt (1954) found concentrations of tin in the surface humus of both deciduous and coniferous forests, and enrichments of as much as 500 ppm in certain coal ashes. Accumulation of tin in the A_0 horizons of some of the profiles in the present investigation suggests that tin may be combined with the humus in some manner. Concentrations of tin appear in the A_2 horizons of nearly all profiles, but the pH does not appear to have much influence on the element. Much of the tin is probably in the form of the relatively stable dioxide, cassiterite.

The mobility of tin in poorly drained or reducing environments is not well known. The studies of Swaine and Mitchell (1960) indicate a small increase in acetic-acid extractable tin from the near surface horizons of Scottish soils. There is a slight enrichment of total tin in the upper gley horizon of the poorly drained Nigadoo profile (Table 35).

Although tin and iron show a relatively high positive correlation in the B_1 horizon, this may mean only that the two elements have a similar response to a higher oxygen level in this horizon, or that the free iron oxides supply oxygen to precipitate SnO_2, and not that the iron oxides absorb or incorporate tin in their lattices. Goldschmidt (1954) reports that tin is enriched in some bauxite deposits in dioxide form and proposes that it may have precipitated from colloidal stannic hydroxide. Tin has been identified in the Brunswick deposits as the oxide cassiterite, and in the sulphide form as stannite, and may be present in these forms in the other deposits as well. Furthermore, tin is probably present in all the deposits in sulphides such as sphalerite, galena, and chalcopyrite. The positive correlation between tin and pH in the C horizon suggests that increasing acidity encourages removal of tin. This may mean that much of the tin is present in acid-soluble minerals such as sulphides and that other acid-susceptible minerals such as olivine, sphene, and rutile may contain tin.

Summary

Tin is enriched in the A_2 horizons of all profiles, probably as the resistant dioxide form, cassiterite. Other local enrichments of tin occur in the B and C horizons. High contents of tin in the bedrock are generally accompanied by high contents in the C horizons of the overlying soils.

The correlation of tin with pH is low and negative in the A and B horizons. This suggests that the element in these horizons is in a form that is relatively resistant to pH changes, e.g., cassiterite. The tin-pH correlation in the C horizon is positive, although the r value is low, which suggests that the tin in this horizon may be in a more mobile form and more susceptible to pH changes than the tin in the A and B horizons.

Tin shows a low negative correlation with iron in the A and C horizons. The tin-iron correlation is positive in the B_1 horizons. The good correlation in the B_1 horizons may result from the oxidation effect of the iron oxides on tin.

No tin minerals were identified in the soil fractions, but finely divided cassiterite may be present in some profiles. Sulphides containing tin are probably present in all the basal layers of the soils above sulphide deposits.

Cadmium

Cadmium was determined by emission spectrographic methods with a minimum detection limit of 3 ppm. Only a few values exceeding this limit were obtained from some "high" profiles. Lack of data prevents a meaningful summary of the distribution or nature of the element in these soils, but some tentative inferences may perhaps be drawn from the few high contents detected.

The three profiles that contained amounts greater than 3 ppm were either above or close to the Nigadoo sulphide vein, and the only two cadmium values reported for bedrock were from samples taken of rock underlying two of the high cadmium soil profiles. The high content of cadmium in the basal horizons of two of these profiles is proof that the element was derived from these rocks.

As cadmium possesses a strong chalcophile nature, it is probably present in sulphide form in these sulphide-rich rocks. The element is nearly always present in sphalerite, and has been found in galena and other sulphides. Since sphalerite was identified in the B_2 and C horizons of profile 17, and is probably present in the basal horizons of the other profiles, this mineral is probably one of the main carriers of cadmium in these horizons.

Values of 23 and 18 ppm were found in the surface A horizons of two of these profiles. Although there are no references to its enrichment in soil humus, it is one of the elements that are enriched in black and bituminous shales and coal ashes. Hence there is a possibility that cadmium is associated with organic matter. It is also possible that contamination from trench material produced the high values found in the surface samples.

Chapter V

SUMMARY AND CONCLUSIONS

The chemical and mineralogical studies of the soils of the Bathurst area are summarized below.

1. The normal soils are represented by fifty-six profiles chosen at random from the Bathurst area. These soils are not associated with known sulphide deposits, and were derived from glacial till, and glacio-fluviatile and alluvial materials. The two normal profiles chosen for detailed study were developed from glacial till and glacio-fluviatile materials.

2. The Nigadoo soils are represented by seventeen profiles selected from above the Nigadoo sulphide deposit, and adjacent to it. The soils were derived from glacial till and glacio-fluviatile materials. The two Nigadoo soils chosen for detailed study are representative of well-drained and poorly drained soils.

3. Soils above the Brunswick No. 6 deposit are represented by four profiles from above the deposit. These soils were developed from glacial tills. The basal section of one of the profiles chosen for detailed study consists partly of "transported gossan" which overlies most of the deposit.

4. The Middle River soils are represented by three profiles taken from above the Middle River sulphide deposit. These shallow soils are developed on glacial tills which lie upon a gossan that caps the deposit. One profile from this location was chosen for detailed study.

5. The detailed chemical studies, carried out on six representative soil profiles, give some indication of the amounts of certain elements that are associated with the water-soluble, dilute acid-soluble, humus, and free iron oxide fractions. Information on the amounts of elements in exchangeable form or in the lattices of the soil minerals cannot be directly obtained from any studies carried out mainly because of the very fine grained nature of the minerals. Hence, it is only possible to make inferences about the presence of elements in exchangeable positions and in the lattices of the minerals from results of the detailed chemical and mineralogical studies, total analyses, and correlation studies.

6. Chemical studies and observations on the distributions of elements in poorly drained reducing horizons indicate that most elements are more chemically reactive in these horizons than in oxidizing horizons, and that they tend to concentrate and precipitate out at the groundwater surface.

7. If one assumes that the A_2 and B_1 horizons are the most reducing and most oxidizing environments, respectively, in normal well-drained podzol soils, it is possible to obtain an idea of the mobility of the elements in reducing (A_2) and oxidizing (B_1) environments. This can be done if one assumes that elements in the B_1 horizons with the highest positive r values of pH correlation (Table 13) represent the most mobile elements present and those in the A_2 horizons with the lowest negative values represent the least mobile.

8. The highest total metal contents for all elements except iron and manganese occur in the profiles overlying sulphide deposits. Total amounts of iron, lead, copper, antimony, silver, and tin are highest in profiles above the Nigadoo deposit. Arsenic contents are highest in soils above the Middle River deposit.

9. A comparison of the analyses of seventeen bedrock samples with analyses of the overlying soils indicates that the high contents of tin, lead, and arsenic in the bedrock are usually matched by high contents of these elements in the C horizons of the overlying soils. Soils overlying rocks with a high silver content usually have good silver values for their A_0 horizons.

10. The iron contents are lowest in the A horizons and highest in the B horizons of most profiles. The free iron oxide contents are usually highest in the B_1 horizons. Goethite, hematite, magnetite, and ilmenite are present in nearly all horizons. Iron is also bound in jarosite, beudantite, pyrite, and sulphides in the lower horizons of some profiles above sulphide deposits.

11. The manganese contents are usually highest in the surface and basal horizons. Manganese is probably associated in some form with humus. The element is also present in a water-soluble form, and occurs as oxides in the soils above the Nigadoo deposit.

12. The lead contents are highest in the A_0, B_1, and basal horizons of all profiles. In the surface horizons the element is combined with organic matter in some form. Lead is present in a water-soluble form and as a component of the free iron oxides, iron arsenates, and iron sulphates. Lead is probably also bound in the various sulphides and sulphates in some of the soils overlying sulphide deposits.

13. The copper contents are higher than average in some surface and basal horizons. The element is probably combined in humus in the surface horizons and associated with free iron oxides in some of the B horizons. Some copper is present in a water-soluble form in all profiles, and some occurs in soils above sulphide deposits as sulphides and hydroxy-carbonates.

14. Zinc is slightly enriched in the surface and basal horizons of the profiles above sulphide bodies. "Available" zinc is plentiful in the organic and poorly drained horizons. Water-soluble zinc occurs in one profile. Zinc is bound in sulphides in some basal horizons.

15. Concentrations of arsenic occur in the B_1 horizons of the normal profiles, and in the A_0, B, and basal horizons of the soils above sulphide deposits. Arsenic appears to be combined with humus in the surface horizons, associated with free iron oxides and arsenates in the B horizons, and possibly present in sulphides in some basal horizons over sulphide deposits.

16. Antimony shows slightly higher values in the A horizons of some profiles, but the highest values are usually in the B horizons. It may be associated with humus and free iron oxides. Antimony is almost certainly associated with arsenates and may be present as oxides in the B horizons.

17. Silver is concentrated in the humus horizons of all profiles and in the B horizons of some profiles above sulphide deposits. It is bound is some form with humus in the surface horizons, probably as a chelate complex. Above some sulphide deposits silver is present in jarosite and probably in chlorargyrite in the B horizons, and in sulphides in the basal horizons.

18. Tin is concentrated in the A_2 horizons of all profiles. Some profiles also have tin accumulations in the B and C horizons. The element is probably present chiefly in the A and B horizons in the dioxide form as finely divided cassiterite. In some basal horizons, tin may be present in sulphides.

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APPENDIX

Tables 35 and 36 give the results of analyses done on the soil samples collected in bulk amounts. Table 35 contains analyses of the six profiles that were also used for other detailed chemical and mineralogical studies.

Table 37 contains results of analyses carried out on seventeen rock samples. Table 38 gives results of analyses for those soil profiles from which only small amounts of soil were collected (small bag samples).

TABLE 35 *Total analyses: Bulk soil samples used for detailed studies*
(nd = not detected)

Sample	Horizon	C.E.C. m.e./100 g	Organic carbon (%)	pH	Pb	Cu	Zn	As	Sb	Fe (%)	Mn	Ag	Sn	Cd
					(ppm)						(ppm)			
17a	A_0	98.0	43.43	3.8	100	15	640	75	1	0.15	160	2.9	—	nd
17b	A_2	14.8	1.10	4.8	15	8	50	5	1	1.48	160	0.3	3.1	"
17c	B_1	37.2	1.68	5.1	50	10	490	50	1	5.90	470	3.4	3.2	"
17d	B_2	14.3	0.55	6.0	310	20	1,150	240	5	4.50	1,010	4.5	9.9	3.0
17e	C	11.4	0.15	6.1	1.30%	270	2,500	4,200	33	8.92	2,780	16.0	126.0	11.0
19a	A_0		31.19	5.8	640	230	1,700	210	6	0.46	5,740	7.2	nd	nd
19b	G_1		6.76	6.6	1,600	560	4,000	500	8	3.60	4,880	9.0	6.2	"
19c	G_2		0.57	6.9	260	100	1,700	200	4	4.40	1,160	2.6	2.8	"
19d	Cg		0.15	6.9	360	25	1,000	95	3	4.54	470	1.1	3.2	"
44a	A_0		22.90	3.8	5.50%	120	60	15	24	0.72	<80	90.0	68.0	nd
44b	A_2		0.85	4.1	2,900	15	20	65	75	1.72	"	36.0	136.0	"
44c	B_1		0.17	3.9	6,300	100	60	250	110	7.85	"	6.5	120.0	nd
44d	B_2		0.09	4.0	3.30%	260	70	160	152	5.94	"	15.0	127.0	"
44e	B_3		0.06	4.0	4.60%	360	220	280	94	7.40	"	24.0	123.0	"
44f	Cg_1		0.62	3.8	3,000	10	100	30	61	0.79	"	6.5	117.0	"
44g	Cg_2		0.06	3.2	3.10%	15	360	80	43	2.49	"	7.7	15.0	"
51a	A_0		24.45	4.3	35	15	80	nd	1	1.04	780	7.8	0.9	nd
51b	A_2		2.34	3.8	25	<5	20	<5	2	1.28	<80	0.2	2.5	nd
51c	B_1		1.05	4.2	30	<5	120	10	1	4.31	1,160	0.2	1.6	"
51d	B_2		0.20	5.1	15	10	110	10	1	3.54	700	0.2	1.7	"
51e	C		0.05	4.9	25	15	70	15	2	3.40	930	0.1	1.8	"
64a	A_0	107.0	35.11	3.4	20	10	60	nd	1	0.28	230	0.5	9.1	"
64b	A_2	12.5	0.62	3.7	5	5	15	nd	1	0.83	80	1.7	4.6	"
64c	B_1	36.5	1.16	4.5	25	5	70	20	3	4.70	390	0.5	5.6	"
64d	B_2	11.3	0.20	4.7	35	15	70	5	1	3.53	390	0.4	11.0	"
64e	C	5.1	0.10	4.7	40	15	70	5	2	1.05	540	0.2	7.8	"
79a	A_0		36.96	4.0	2,800	90	110	1,100	9	2.24	470	3.4	27.0	nd
79b	A_2		0.75	4.2	770	60	60	940	6	3.45	390	2.7	57.0	"
79c	B_1		0.60	4.9	1,000	130	120	880	6	8.74	390	6.4	23.0	"
79d	B_2		0.35	6.2	3,900	300	170	3,500	13	9.53	540	10.0	10.0	"

TABLE 36 *Total analyses: Bulk soil samples*
(nd = not detected)

Sample No.	Horizon	C.E.C. m.e./100 g	Organic carbon (%)	pH	Pb	Cu	Zn	As	Sb	Fe (%)	Mn	Ag	Sn	Cd
					(ppm)						(ppm)			
7a	A_0			5.2	730	140	2,000	310	8	1.97	3,100	9.3	2.6	18.0
7b	B_1			5.1	480	8	1,200	540	2	3.68	200	3.7	30.0	nd
7c	B_2			6.2	460	25	2,100	440	4	4.91	900	4.6	7.2	5.7
7d	C			6.4	370	30	3,300	510	4	3.84	1,200	2.7	4.6	22.0
15a	A_0			3.9	95	8	160	95	10	2.29	200	3.3	17.0	nd
15b	A_1			3.6	35	<5	110	14	1	0.24	<80	3.2	—	"
15c	A_2			4.1	15	8	70	50	10	1.70	150	0.4	61.0	"
15d	B			4.5	70	5	210	190	5	—	460	0.7	14.0	"
18a	A		3.21	5.2	1,500	25	1,800	580	6	4.43	620	5.8	43.0	23.0
18b	B_1		1.62	5.4	1,100	40	3,300	440	4	4.65	470	6.7	12.0	<5.0
18c	B_2		1.78	5.6	1,600	50	4,600	920	4	6.08	1,160	6.7	4.7	nd
18d	C		0.59	6.6	2,300	140	5,100	1,160	21	5.93	2,480	16.0	100.0	"
21a	A_0			5.0	20	8	110	5	2	4.67	800	0.6	4.7	nd
21b	A_2			4.8	15	<5	40	nd	2	2.72	850	0.3	2.6	"
21c	B			4.9	10	15	150	5	1	5.06	460	0.2	1.6	"
30b	A_0			4.2	110	8	270	200	1	2.60	1,200	1.0	1.4	nd
30c	A_2			4.3	2,100	8	120	1,900	5	3.84	4,600	1.6	10.0	"
30d	B_1			4.6	2,600	25	330	2,900	5	7.97	1,200	2.0	10.0	"
30e	C			5.1	920	40	670	3,400	3	8.25	900	1.3	5.4	"
38a	A			4.9	30	8	90	30	2	3.72	400	0.5	2.5	nd
38b	B_1			4.9	25	10	130	35	3	5.52	460	0.6	2.2	"
38c	B_2			5.1	25	35	130	40	3	4.56	850	0.7	0.7	"
38d	C			5.5	20	25	120	30	3	7.31	460	0.7	2.5	"
40a	A_{00}			4.5	10	15	60	15	<1	0.29	<80	0.2	nd	nd
40b	A_0			3.7	15	10	70	5	1	0.69	80	1.3	0.8	"
40c	A_1			3.7	15	<5	50	5	2	1.39	<80	0.6	3.1	"
40d	A_2			3.8	10	8	30	5	3	1.86	150	0.2	4.7	"
40e	B_1			4.3	10	<5	50	25	3	4.64	200	0.3	5.2	"
40f	B_2			4.7	15	8	70	15	3	5.08	150	0.4	3.9	"

TABLE 36 (cont.)

Total analyses: Bulk soil samples
(nd = not detected)

Sample No.	Horizon	C.E.C. m.e./100 g	Organic carbon (%)	pH	Pb	Cu	Zn	As	Sb	Fe (%)	Mn	Ag	Sn	Cd
					(ppm)						(ppm)			
40g	C			4.9	10	25	110	15	1	5.51	500	0.9	2.6	"
43a	A_0	143.0	40.68	2.4	360	10	70	25	3	0.94	<80	1.2	—	nd
43b	A_2	5.4	0.97	3.2	65	10	10	10	1	0.79	<80	1.2	31.0	"
43c	B_1	33.3	1.15	3.4	80	80	30	130	26	10.30	230	1.3	16.0	"
43d	B_2	30.4	0.55	4.2	410	110	60	140	26	13.40	230	>10.0	14.0	"
43e	C_1	7.3	0.23	4.6	740	130	90	120	15	9.90	<80	5.0	5.9	"
43f	C_2	10.7	0.10	4.1	2,100	80	90	160	23	13.45	<80	1.8	14.0	"
52a	A_{00}			3.0	20	<5	60	nd	2	0.09	1,000	0.9	nd	nd
52b	A_0			2.7	40	<5	20	"	4	0.64	<80	0.9	1.3	"
52c	A_1			2.8	10	5	20	"	3	0.88	<80	0.4	7.8	"
53a	A_0		34.10	3.3	350	40	80	70	4	1.74	310	1.9	1.0	nd
53b	A_2		2.22	3.6	70	20	20	30	6	1.52	<80	0.6	5.5	"
53c	B_1		0.58	4.0	370	80	70	120	14	7.04	390	0.9	4.0	"
53d	B_2		0.57	4.3	950	210	120	430	28	11.10	310	2.4	4.7	"
55a	A_0			4.1	35	8	100	5	2	1.76	600	1.4	1.1	nd
55b	A_2			4.9	105	25	150	40	4	6.20	900	0.7	6.2	"
55c	B_1			5.0	190	45	210	70	4	7.92	300	0.4	5.4	"
55d	B_2			5.3	300	45	260	35	<1	6.66	400	0.7	5.3	"
60a	A_0		39.20	3.0	30	15	70	22	2	0.69	<80	2.1	—	nd
60b	A_2		0.27	3.6	95	120	30	300	11	6.05	<80	0.3	2.6	"
60c	B_1		0.91	4.1	180	150	30	250	8	7.38	<80	1.2	17.0	"
60d	B_2		0.49	4.4	270	110	70	150	6	8.65	390	4.0	5.9	"
60e	C		0.24	4.8	370	210	100	340	11	11.27	310	0.9	7.4	"
62a	A_0		30.77	4.1	25	<5	70	nd	3	0.96	390	1.4	—	nd
62b	A_2		1.79	3.7	10	<5	10	nd	2	0.98	80	0.2	7.8	"
62c	B_1		1.34	4.2	30	<5	70	15	2	5.30	540	.3	2.7	"
62d,e	B_2		0.41	4.5	25	10	60	5	2	3.23	470	.2	7.8	"
62f	C		0.16	4.4	25	<5	70	nd	2	3.04	470	.2	4.6	"
72a	A_0			5.4	25	10	170	10	3	3.76	1,600	.1	2.9	nd

72b	B			4.4	15	10	110	10	1	4.94	1,000	.3	5.8	"
72c	C			4.9	15	65	120	10	3	7.26	700	.4	3.3	"
73a	A_0		37.35	4.1	25	10	50	nd	1	0.41	310	2.1	—	nd
73b	A_2		0.27	4.3	15	8	15	10	3	6.15	540	0.2	9.6	"
73c	B_1		.70	4.5	20	20	60	15	3	2.67	470	.2	4.6	"
73d	B_2		.26	4.9	25	20	70	10	1	5.02	1,080	.3	4.1	"
73e	C_1		.21	4.9	60	25	70	15	3	4.57	780	.2	8.6	"
73f	C_2		.13	5.3	20	50	100	20	2	4.66	1,160	.1	0.9	"
76a	A_2		0.80	4.1	20	8	20	nd	2	0.86	230	0.3	1.3	nd
76b	B_1		1.69	4.4	45	<5	130	10	1	5.77	1,160	.6	0.4	"
76c	B_2		0.74	3.8	35	15	160	15	2	4.12	390	.3	0.3	"
76d	C_1		0.13	4.7	45	15	150	15	1	4.20	700	.2	0.2	"
76e	C_2		0.10	4.9	50	15	150	5	1	4.16	160	.1	0.1	"
77a	A_0		30.82	3.6	40	5	80	nd	1	0.25	160	1.3	—	nd
77b	A_2		2.09	4.2	25	5	30	"	2	2.08	310	0.4	2.0	"
77c	B_1		0.82	4.4	30	<5	110	"	<1	4.12	540	.3	1.7	"
77d	B_2		0.17	4.7	45	10	120	5	1	4.23	470	.2	1.0	"
77e	C		0.08	5.0	45	5	130	5	<1	4.65	850	.1	1.7	"
78a	A_0			4.3	50	25	170	nd	2	0.67	2,900	.4	6.6	nd
78b	A_2			4.0	20	<5	20	"	2	1.75	400	.1	7.2	"
78c	B_1			4.6	20	15	140	"	2	5.98	1,200	.2	2.3	"
78d	B_2			4.7	15	25	100	"	1	4.80	850	.1	1.3	"
78e	C			4.8	25	40	70	"	1	5.10	1,600	.1	1.1	"
80a	A_0	91.4	32.00	3.9	220	65	120	970	4	2.06	470	3.4	3.4	nd
80b	A_2	16.8	1.30	4.1	70	15	30	240	2	2.22	160	0.8	16.0	"
80c	B_1	31.2	1.71	4.7	130	65	100	1,600	3	7.03	310	1.7	26.0	"
80d	B_2	6.2	0.16	4.9	140	290	150	1,300	3	5.63	700	2.2	5.0	"
85a	A_0	91.3	30.30	4.9	30	10	70	nd	<1	3.16	230	1.3	0.7	nd
85b	A_2	13.5	0.72	4.1	10	<5	20	"	2	1.55	80	0.2	5.6	"
85c	B_1	25.2	.92	5.0	10	10	120	25	2	5.50	470	.3	2.4	"
85d	B_2	10.3	.07	5.4	10	25	70	15	2	4.80	700	.2	1.9	"
85e	C	8.0	.09	5.2	nd	20	70	10	2	3.38	1,010	.2	2.4	"

TABLE 37 *Total analyses: Rock samples*
(nd=not detected)

Sample No.	Pb	Cu	Zn	As	Sb	Fe	Mn	Ag	Sn	Cd	S	CO_2
	(ppm)					(%)	(ppm)					(%)
7e	50	10	440	85	4	4.41	6,120	0.9	9.0	3.9	<200	0.49
15e	400	20	570	70	35	4.62	1,240	1.0	<0.5	nd	<200	1.54
19e	560	45	170	85	3	1.12	620	13.0	62.0	24.0	<200	3.72
21d	40	35	120	5	1	4.97	465	0.2	<0.5	nd	1,400	<.01
30f	75	45	190	80	3	3.64	1,320	1.1	<0.5	"	1,500	<.01
38e	15	20	30	<5	<1	1.40	<80	0.2	0.7	"	2,100	6.00
40h	5	40	100	15	1	3.71	80	0.8	2.8	"	<200	0.10
44h	>10%	150	220	1,500	280	32.13	390	67.0	14.0	"	>3%	0.05
52d	15	5	30	nd	1	4.34	390	0.1	11.0	"	200	<.01
53e	240	75	50	105	6	3.50	2,320	4.6	4.4	"	600	0.02
55e	30	15	60	25	2	3.99	775	0.3	15.0	"	2,900	0.06
62g	25	10	30	20	1	1.75	<80	0.2	4.3	"	<200	<.01
64f	15	<5	20	10	<1	0.63	700	0.1	19.0	"	<200	<.01
72d	5	5	60	35	<1	2.87	775	0.2	9.1	"	<200	<.01
73g	<5	<5	30	20	<1	6.44	540	0.2	0.7	"	600	0.01
78f	<5	30	110	nd	2	10.22	1.20%	0.2	2.6	"	<200	0.24
80e	1.10%	2,100	220	>1%	90	40.15	230	31.0	47.0	"		

TABLE 38 *Total analyses: Small bag samples*

Sample No.	Horizon	pH	Cu (ppm)	Pb (ppm)	Zn (ppm)
1a		4.5	65	360	1,400
1b	A_0	4.3	65	140	3,400
1c	A_2	5.8	250	2,000	>5,000
1d	B_2	6.0	35	70	3,200
1e	C_1	6.2	35	40	2,600
1f	C_2	6.1	50	200	3,000
2a		5.6	<5	10	90
2b	A_0	5.9	10	35	70
2c	A_1	6.2	10	125	220
2d	A_2	6.2	<5	95	480
2e	B_1	6.6	<5	25	100
2f	B_2	6.4	<5	25	110
2g	C	6.6	5	35	170
3a	A_0	5.8	230	520	440
3b	A_2	6.5	85	300	2,200
3c	B	6.6	20	260	510
3d	C	6.7	25	50	570
4a	A_0	6.5	25	340	960
4b	A_2	6.5	70	200	1,700
4c	B	6.8	15	35	280
4d	C	6.9	15	20	140
5a		4.3	<5	50	80
5b		4.2	<5	15	50
5c	A_0	4.5	<5	15	90
5d	A_2	4.9	<5	80	60
5e	B_1	5.5	15	490	1,080
5f	B_2	6.1	30	620	1,600
5g	C	6.1	65	930	2,100
6a	A_0	3.6	<5	30	70
6b	A_2	4.1	<5	15	15
6c	B_1	4.6	<5	180	270
6d	B_2	4.7	20	180	580
6e	C	4.7	25	160	570
8a	A	5.2	50	1,600	1,700
8b	B_1	5.3	20	1,060	2,100
8c	B_2	5.7	30	1,000	2,800
8d	C	6.4	45	1,300	2,700
9c	A_0	6.2	310	>5,000	4,400
9d	B	6.6	65	1,400	3,000
10a	A_0	4.8	100	>5,000	880
10b	A_2	4.7	120	"	720
10c	B	4.6	200	"	1,000
10d	C	4.6	210	"	670
11a	A_0	4.6	15	450	470
11b	A_2	4.6	10	65	140
11c	B_1	4.6	15	220	260
11d	B_2	4.4	20	480	520
12a	A_0	4.6	45	2,400	450
12b	A_2	4.5	50	2,200	420
12c	B_1	4.8	110	>5,000	1,160
12d	B_2	4.8	150	2,800	2,900
13a	A	4.6	15	680	560
13b	B_1	4.8	25	550	960
13c	B_2	4.7	40	760	1,000
13d	C	4.7	85	1,900	1,080
14a	A	5.1	130	>5,000	1,120
14b	B_1	5.9	110	"	1,040
14c	B_2	6.2	250	"	2,000
14d	C	6.4	390	"	1,600
16a	A_0	4.9	25	35	130
16b	A_2	4.9	8	15	30
16c	B_1	4.8	5	30	210
16d	B_2	4.6	15	35	160
16e	C_1	4.6	35	40	120
16f	C_2	5.0	25	35	110
20a	A_0	3.8	15	20	60
20b	A_2	3.9	8	15	25
20c	B_1	4.6	<5	25	130
20d	B_2	4.8	8	25	90
20e	C	5.0	10	25	100
22a	A_0	4.7	40	15	120
22b	A_2	4.5	15	15	40
22c	B_1	4.5	25	10	160
22d	B_2	4.7	60	15	120
22e	C	4.8	35	20	60
23a	A_0	4.7	10	20	40
23b	A_2	4.5	<5	25	15
23c	B_1	4.7	8	10	70
23d	B_2	4.7	<5	20	70
23e	C	5.0	15	10	60
24a	A_0	3.8	5	10	20
24b	A_2	3.9	5	15	10
24c	B_1	4.2	5	nd	30
24d	B_2	4.9	20	15	60
24e	C	4.8	15	20	70
25a	A	4.7	10	20	110
25b	B_1	4.7	8	15	110
25c	B_2	4.6	20	10	100
25d	C	4.6	10	20	60
26a	A_0	3.9	8	40	100
26b	A_2	3.8	<5	20	20

TABLE 38 (cont.) *Total analyses: Small bag samples*

Sample No.	Horizon	pH	Cu (ppm)	Pb (ppm)	Zn (ppm)
26c	B_1	4.7	<5	15	120
26d	B_2	4.6	<5	20	70
27a	A	4.5	5	25	60
27b	B_1	4.7	8	15	60
27c	B_2	4.6	8	15	70
27d	C	4.7	10	15	70
28a	A_0	4.0	5	25	90
28b	A_2	3.9	5	20	30
28c	B_1	4.2	<5	20	70
28d	B_2	4.4	40	25	160
28e	C	4.6	25	30	110
29a	A_0	5.6	15	45	330
29b	A_2	5.1	5	10	20
29c	B_1	5.1	8	10	60
29d	B_2	5.2	10	15	70
29e	C	5.4	15	25	110
31a	A_0	5.2	5	20	80
31b	A_2	4.4	<5	5	30
31c	B_1	4.4	8	nd	60
31d	B_2	5.1	10	15	70
31e	C	5.1	25	10	60
32a	A_2	5.0	<5	20	30
32b	B_1	4.6	<5	45	70
32c	B_2	4.7	15	35	130
32d	C	4.8	10	35	130
33a	A	5.4	5	55	120
33b	B_1	5.6	8	15	120
33c	B_2	5.0	20	20	110
33d	C	5.1	30	10	110
34a	A	4.4	8	10	40
34b	B_1	4.7	<5	nd	20
34c	B_2	4.5	<5	10	70
34d	C	4.8	20	15	70
35a	A_0	4.1	8	15	60
35b	A_2	4.5	10	10	30
35c	B_1	4.6	15	25	60
35d	B_2	5.0	20	10	100
35e	C	5.3	30	20	100
36a	A_0	4.8	15	20	70
36b	A_2	4.8	5	10	20
36c	B_1	4.6	15	15	100
36d	B_2	5.0	30	20	120
36e	C	5.4	30	20	70
37a	A_0	4.4	15	20	70
37b	A_1	4.1	10	10	20
37c	A_2	4.0	<5	nd	10
37d	B_1	4.5	<5	10	50
37e	B_2	4.9	15	15	80
37f	C	5.0	25	20	60
39a	A_2	4.2	10	5	50
39b	B_1	4.7	25	10	110
39c	B_2	5.2	35	15	120
39d	C	5.2	50	10	110
41a	Muck 2″	6.4	10	25	160
41b	Muck 6″	5.2	8	5	30
41c	Muck 24″	4.4	15	5	110
41d	Cg	5.7	15	10	90
42a	A_0	3.6	8	20	30
42b	A_2	3.9	15	5	20
42c	B_1	4.3	<5	20	50
42d	B_2	4.6	30	15	80
42e	C	4.6	35	70	70
45a	A_0	3.3	65	1,900	370
45b	A_2	3.5	25	430	20
45c	B	4.6	920	>5,000	120
45d	C_1	4.8	1,360	"	170
45e	C_2	4.7	2,200	"	230
46a	A_0	4.3	<5	100	120
46b	A_2	3.9	8	30	30
46c	B_1	4.5	10	60	80
46d	B_2	4.6	10	10	90
47a	A_0	2.2	5	10	20
47b	A_2	2.9	25	30	10
47c	B_1	3.4	85	560	50
47d	B_2	4.2	280	>5,000	70
48a	A_0	4.7	30	50	80
48b	A_2	4.7	8	25	30
48c	B_1	4.7	15	20	70
48d	B_2	4.5	20	nd	60
48e	C	4.9	20	15	60
49a	A_0	3.6	10	80	70
49b	A_2	3.5	<5	25	10
49c	B_1	4.4	<5	420	60
49d	B_2	4.7	15	85	60
49e	C	4.7	20	120	70
50a	A_0	3.9	5	40	120
50b	A_2	3.7	10	15	20

TABLE 38
(conc.)

Sample No.	Horizon	pH	Cu	Pb	Zn
			(ppm)		
50c	B_1	4.3	10	20	50
50d	B_2	4.5	8	20	60
50e	C	4.5	10	20	50
54a	A_0	3.0	8	15	60
54b	A_2	3.4	5	5	10
54c	B_1	4.4	<5	25	60
54d	B_2	5.2	25	25	60
56a	B	4.9	<5	20	140
56b	C	4.9	25	20	70
57a	A_0	3.7	5	20	30
57b	A_2	4.2	5	10	10
57c	B_1	4.4	<5	10	60
57d	C	4.8	15	20	70
58a	A_0	5.0	10	25	60
58b	A_2	4.3	5	5	20
58c	B_1	4.6	<5	15	70
58d	B_2	5.3	20	15	70
58e	C	5.1	25	5	60
59a	A_2	4.1	15	100	20
59b	B_1	4.4	20	160	80
59c	B_2	4.9	10	100	100
59d	C	5.0	25	210	100
61a	A_0	3.4	5	25	50
61b	A_2	3.6	5	10	20
61c	B_1	4.2	<5	20	90
61d	B_2	4.6	8	20	100
61e	C	4.7	25	20	90
63a	A_0	3.7	10	20	60
63b	A_2	3.5	8	25	20
63c	B_1	4.1	20	110	110
63d	B_2	5.0	30	90	150
63e	C	5.0	55	105	150
65a	A_0	3.8	15	35	60
65b	A_2	3.8	<5	5	10
65c	B_1	4.8	<5	15	80
65d	B_2	4.7	20	20	50
65e	C	4.5			
66a	A_0	4.1	5	25	120
66b	A_2	4.0	5	15	50
66c	B_1	4.2	<5	25	130
66d	B_2	4.5	10	25	140
66e	C	4.6	15	20	140
67a	A_0	3.2	<5	10	60
67b	A_2	3.7	5	5	20
67c	B_{11}	4.2	<5	25	60
67d	B_{12}	4.6	<5	25	70
67e	B_2	4.5	<5	20	80
67f	C	4.4	<5	25	60
68a	A_0	3.1	<5	nd	20
68b	A_2	3.5	5	10	20
68c	B_1	3.8	<5	20	50
68d	B_2	4.5	<5	20	30
68e	C	4.6	<5	10	20
69a	A_0	4.4	5	25	210
69b	A_2	4.0	<5	15	60
69c	B_1	4.8	<5	20	90
69d	B_2	4.5	8	25	160
69e	C	4.6	8	25	60
70a	A_0	4.8	5	25	100
70b	A_2	4.7	8	15	70
70c	B	4.8	10	15	60
70d	C	4.9	20	20	70
71a	A_0	4.9	15	20	70
71b	A_2	4.1	<5	5	20
71c	B_1	5.0	<5	20	110
71d	B_2	5.4	15	20	60
71e	C	5.2	20	nd	60
74a	A_0	4.9	15	25	200
74b	A_2	4.7	8	nd	10
74c	B_1	4.8	10	20	80
74d	B_2	5.4	<5	15	120
74e	C	4.9	15	15	60
75a	A_0	4.1	20	30	60
75b	A_2	4.4	<5	5	30
75c	B	4.6	<5	nd	30
81a	A_0	4.2	45	40	120
81b	A_2	3.7	25	25	30
81c	B_1	4.3	90	75	130
81d	B_2	4.6	210	65	120
81e	C	4.8	230	65	110
82a	A_0	4.0	10	20	100
82b	A_2	3.6	10	15	30
82c	B_{11}	4.5	10	20	160
82d	B_{12}	4.9	8	15	130
82e	B_2	4.8	20	10	120
82f	C	4.7	25	nd	120
83a	A_0	3.0	8	15	70
83b	A_2	3.4	15	nd	20
83c	B_1	4.5	15	nd	70
83d	B_2	5.0	15	nd	120
83e	C	4.8	25	10	260

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