EVALUATION OF EXTRACTION AND PRETREATMENT

OF SOIL MANGANESE AND ASSOCIATED

ELEMENTS

by

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B.Sc. (Agric.), University of British Columbia, 1973

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

SOIL SCIENCE

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September, 1975

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ABSTRACT

The manganese content of soils from the Lower Fraser Valley

hhas been previously investigated. The studies conducted were con-

flicting in the total amounts of manganese in the soils. Also there

was no attempt in the earlier studies to relate manganese to some of

the other oxides in the soils. This study was undertaken to elucidate

further the chemistry of manganese in the soils of the Lower Fraser

Valley and to evaluate extractants and effects of soil pretreatment on

the amount of manganese extracted. Iron, aluminum and silicon, which

are commonly associated with soil manganese, were also included in

the study.

The total manganese concentrations obtained were higher than

previously reported, even though the soils were derived from the same

area. The distribution of total iron within the soil pedon was closely

related to that of manganese.

Conventional extractants for amorphous inorganic and organic

oxides were evaluated with reducing and chelating agents, for their

ability to extract manganese, together with aluminum, iron and silicon.

The extractants used were sodium pyrophosphate, acid ammonium oxalate,

disodiumEDTA, hydroxylamine hydrochloride and hydroquinone. Hydroquinone

was only effective in extracting manganese, while sodium pyrophosphate,

disodiumEDTA, acid ammonium oxalate and hydroxylamine hydrochloride

extracted larger amounts of manganese, iron and aluminum. Only hydroxyl-

amine hydrochloride and acid ammonium oxalate extracted silicon from

the samples. All extractants, with the exception of sodium pyrophos-
phate, were consistent with each other in showing similar distributions
of the different elements within the soil pedon.

Successive extraction analysis indicated that the elements
extracted by hydroxylamine hydrochloride were those derived from the
organic and inorganic complexed forms. This study also showed that
the preceding extractants may alter the soil system, thus questioning
the reliability of successive extraction analysis.

The effect of soil pretreatments on the extractability of man-
ganese, iron, aluminum and silicon was also investigated. Some dif-
ferences were observed between in-situ extraction and air-drying treat-
ments. Freezing and storing moist, contributed to significantly high
results. There was no consistency for the effect of the pretreatments
on the different soils.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

INTRODUCTION

The chemistry of manganese in soil is still vague. Recently more attention has been directed to the study of manganese in soil. This is partly the result of the realization that manganese plays a greater role than was assumed previously, both as plant nutrient and in soil formation.

The manganese status of the Lower Fraser Valley soils has been studied by Baker (1950) and Safo (1970). Results for the total concentration of manganese obtained by Baker were significantly higher than those obtained by Safo. Instrumentation, experimental procedure, sampling and treatment of samples before extraction, are some of the factors that could contribute to this difference in observations.

The objective of this study was to understand further:

  i) the chemistry of manganese in those Lower Fraser Valley soils which are derived from alluvial and marine parent materials, and

  ii) the effects of various pretreatments on the extraction of manganese from these soils.

Iron, aluminum and silicon were also included in the study because they are associated with manganese. The simultaneous occurrence of manganese, aluminum, iron and silicon in soil has been cited in soils research. They have some common physical and chemical properties which is explained by the respective position of these elements in the periodic table.

1

The compounds and complexes formed by these elements are important in soil genesis. The variable valencies exhibited by manganese and iron offer numerous possibilities for coordination compounds with organic matter in the soil. The formation of these compounds has been cited as one of the important mechanisms for the transport of these elements down the profile, during soil formation.

The conventional extraction procedure for manganese has been based on Leeper's (1947) differentiation:

    i) water soluble form - extracted with distilled water,

   ii) exchangeable form - extracted by neutral normal ammonium acetate,

 iii) easily reducible forms - extracted by 0.2 percent hydroquinone in neutral normal ammonium acetate,

  iv) total amount - perchloric - hydrofluoric acid digestion.

The first three of these differentiations are biased more towards the different oxidation states of manganese, and their reducibility rather than the actual form present in the soil. It was, therefore, deemed necessary to evaluate the manganese by other extractants that are correlated with the forms actually present in the soil. The various forms of manganese in the soil can be categorized as:

1. well-crystallized

2. amorphous inorganic oxides (which include both aged and relatively recent forms), and

3. the organically complexed forms (either with humic or fulvic acids).

Each or a combination of these forms may be extracted by various extractants. In fact, the concentration and pH of each extractant has been evaluated for routine analysis in various literatures. Limitations such as the overlapping of forms extracted should be realized. The well-crystallized form of manganese oxide is known to be relatively inert. In this paper the amorphous as well as the organically-complexed forms will be the highlight of the investigations. The amorphous oxides have not reached an equilibrium state and have a relatively large surface area compared to the crystalline form. They are more reactive and will, therefore, influence soil properties to a greater extent.

Five extractants were used to extract amorphous oxides and the organically complexed forms. These were:

1) 0.2 M acid ammonium oxalate at pH 3.0, which extracts the amorphous organic and inorganic oxides;

2) 0.1 M hydroxylamine hydrochloride ($NH_2OH.HCl$) in 0.01 M nitric acid at pH 2.0. This is a strong reducing agent and is also capable of complexing organically bonded elements;

3) 0.02 M disodiumEDTA at pH 4.5 which extracts the organically complexed forms by chelation as well as dispersion;

4) 0.1 M sodium pyrophosphate at pH 10.0 which peptizes organic matter and extracts the amorphous organic oxides; and

5) 0.2 percent hydroquinone in neutral normal ammonium acetate solution. This is a reducing agent, relatively weaker than hydroxylamine hydrochloride.

Dissolution brought about by these extractants often makes it possible to analyze all four elements simultaneously with the atomic absorption spectrophotometer. This thesis attempts to evaluate the effectiveness of these extractants in extracting manganese, iron, aluminum and silicon. An attempt is also made to determine the correlation among extractants as well as between extractants and soil properties.

The sequential extraction of these elements by hydroxylamine hydrochloride ($NH_2OH.HCl$) followed by one of the other extractants and then again by hydroxylamine hydrochloride was also carried out. A comparison was made between the concentration of the elements extracted by the extractants individually and with the combination of hydroxylamine hydrochloride. The results obtained should allow the evaluation of the significance of using sequential analysis in soil extraction studies.

Moisture content, aeration, temperature and duration of soil sample storage are some of the factors that affect the extractability of a particular element. These factors control the decomposition of organic matter, microbial activity and the oxidation-reduction of the oxides in soils. The effect of different soil treatments on the concentration of water-soluble and exchangeable manganese extracted, has often been mentioned. Studies were conducted to evaluate the effect of soil treatments on the amorphous oxides and organically-complexed manganese, iron, aluminum and silicon. As stressed earlier these are more important, relative to the other forms. The soil treatments

involved were:

A. <u>In-situ</u> extraction,

B. Air-drying for one week,

C. Oven-drying at 50°C for one week,

D. Oven-drying at 100°C for one week,

E. Stored moist in plastic containers for three months,

F. Air-drying for four months,

G. Frozen for one month.

It is hoped that the results obtained will help to explain the differences in values reported by previous workers. These treatments should also make it possible to evaluate the effect of sampling at different seasons of the year on the extractability of manganese, aluminum, iron and silicon.

CHEMISTRY OF MANGANESE, IRON, ALUMINUM AND SILICON

MANGANESE

General properties

Manganese constitutes about 0.085 percent of the earth's crust

(Cotton and Wilkinson, 1972). Theoretically it can exhibit valencies

of 1 to 7 (Remy, 1966), but in the soil only valencies of 2, 3, and 4

are common. The manganous (Mn^{2+}) and manganic (Mn^{3+}) ions are basic,

while tetravalent manganese (Mn^{4+}) is amphoteric. The conversion of

manganese from one oxidation state to another is dependent on the redox

potential and pH, which are indirectly related to microbiological

activity (Mann and Quastel, 1946). The presence of unsatisfied d-

orbitals, which is a characteristic of all transition elements, makes

it possible for manganese to form numerous complex compounds.

Manganese in soil

Manganese is thought to occur as the divalent ion in solution

and on the exchange sites; in transition between crystallized and amor-

phous form such as pyrolusite and manganite (Dion et al., 1947); as a

well-crystallized mineral, e.g. hausmanite and hollandite; in combination

with amorphous hydrous oxides of iron and aluminum; in association

with clay structure (Hemstock and Low, 1953); and complexed with or-

ganic matter. The presence of manganese in the soil can also be

6

categorized according to the different extractable states (Leeper,
1947; Serdobolski, 1950). They postulated that there was a dynamic
equilibrium between these forms:

Water soluble manganese $\rightleftharpoons$ Exchangeable manganese

(Mn^{2+}) (Mn^{2+})

$\updownarrow$

Relatively inert manganese oxides $\rightleftharpoons$ Easily reducible man-
ganese
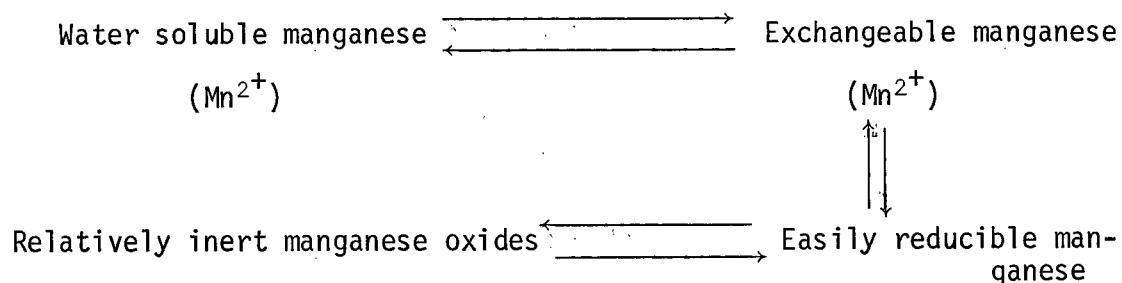
The conventional methods of extracting manganese from soil are based
on these forms.

According to Geering (1969), total divalent manganese in acid
and neutral soil ranges from 10^{-4} to 10^{-6} M and lower in calcareous
soil. He also found that 85 to 99 percent of this divalent manganese
was organically-complexed. The reduction of the higher oxides into
the divalent state depended on microbiological activity and on the
presence of thiols and ferrous ions (Jones, 1957).

The presence of amorphous hydrous oxides of manganese in asso-
ciation with the sesquioxides was first noted by Mitchell et al. (1964).
These oxides provide a good source of cementation in soil. Manganese
concretions in soil are the result of the presence of microcrystalline
structures (Taylor et al., 1964). These microcrystalline forms are
merely "aged" amorphous inorganic oxides and have been analyzed and
found to be:

Birnessite: $M.Mn^{2+}Mn^{4+} (O.OH)_2$,
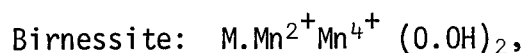
M is an alkaline earth metal;

Lithiophorite: $Li_2Al_8M_4^{4+}O_{35}$ $14H_2O$,

M is Mn^{2+}, Co^{2+} or Ni^{2+};

Hollandite: $Ba(Fe^{3+}Mn^{4+})_8O_{16}$

Pyrolusite: MnO_2

The manganese present ranges from +2 to +4 oxidation states. The first three forms contained 35 to 60 percent manganese, 3 to 9 percent barium, 0.5 to 1.5 percent cobalt and variable amounts of iron, aluminum, silicon and other elements.

Russell (1973) showed that humic acid is able to complex divalent manganese. The strength of these complexes is weaker than other metallic cations such as divalent zinc and copper, and trivalent aluminum and iron. No statement was made with regard to the bond strength between trivalent or tetravalent manganese, and humic polymers. The greater electropositivity and smaller ionic radii would tend to make it stronger. Further studies need to be done on this aspect, considering the relative abundance of these forms in the soil.

IRON

General properties

Iron is the second most abundant metal after aluminum, and is the fourth most abundant element in the earth's crust (Cotton and Wilkinson, 1972). It is the 26th element in the periodic table having the electronic configuration of $[Ar]3d^64S^2$. The partially filled 3 d-

orbital, puts it in the category of a transition element, and also accounts for the various complexes formed.

The oxides FeO, γ-Fe_2O_3 and Fe_3O_4 are closely related structurally, the oxygen atoms having a cubic close packing arrangement. Fe_3O_4 is made up of a combination of FeO and Fe_2O_3, the proportion of which depends on the redox potential. A summary of the various oxides and conditions that lead to their formation, is given in Figure 1. Complexes of iron with organic radicals are known. These complexes account for some of the mechanisms involved in iron removal and deposition in the soil system.

The electronic configuration of iron is very similar to that of manganese ($[Ar]3d^54S^2$), the 25th element. Indeed iron and manganese have many physical and chemical properties in common. The occurrence of ferro-manganese nodules in the soil, often in association with cobalt, nickel, and zinc has been cited in the literature (Taylor et al., 1966).

Iron in soil

In the soil, iron is thought to be present in solution, as primary and secondary minerals, as amorphous oxides and as ions attached on the cation exchange sites of both clay and organic colloids. Iron has also been found associated in clay-organic complexes.

The primary minerals of iron include olivine, pyroxene, amphiboles, micas and the various oxides of iron such as hematite, magnetite, lepidocrite and goethite. Hematite (αFe_2O_3) is often found in the drier and well-oxidized soil. It accounts for the dark-reddish tinge

Fe³⁺ ← — Ox. Red. — → Fe³⁺ | Fe²± ← — Ox. Red. — → Fe²⁺

Al_2O_3
+
SiO_2
Iron-rich
clay minerals

Slow
Pptn.
Low
pH

Pptn.
OH⁻

Pptn.
OH⁻

Slow
Oxidn.

Pptn.
OH⁻

αFeOOH

Aging

High pH,
Temp

Fe(OH)₃

Fe₃O₄

Fe(OH)₂
OH⁻

Slow oxidn. in presence $CO_3{}^{2-}$

Oxidn.
pH
4-8

Instant
oxidn.

Aging
pH
4-7

Dehydration

Oxidn.
at high
temp.

γ-FeOOH

Slow
oxidn.
H_2O_2
at 100°C

Aging in
dilute alkali

Hydrohematite

Aging at
high temp.

Dehydration

αFe₂O₃ ← — High temp. — γFe₂O₃

Fe(OH)₂
Crystalline

Ignition in presence of organic material

Alpha iron oxides or amorphous iron oxides

Oades, 1963

Figure 1. Interrelationships between the iron oxides
and some closely related compounds.

of soils. Goethite (αFeOOH) is commonly found in temperate soils, often in association with relatively wetter soil conditions. Lepidocrite (γ-FeOOH), which is an isomer of goethite, is usually found in poorly-drained soils. The orange brown mottles found in gley soil is said to be lepidocrite (Kamoshita and Iwasa, 1959). Magnetite (Fe_3O_4) is often present as dark sand size minerals. Oxidation of Fe_3O_4 yields the homogeneous Fe_2O_3 (maghemite). These oxides and complex compounds of iron are initially in the amorphous forms before aging gradually to the crystallized form.

The association of clay colloids and iron (either in the ionic or oxide forms), partly accounts for the accumulation of iron in the subsurface horizons of mineral soil, typically the Podzol. Barbier (1937) demonstrated the fixation of ferric hydrate with electronegative clay. A good X-ray analysis of most clay samples can only be achieved by destruction of the associated iron oxides (Mehra and Jackson, 1960). In well-drained soils the distribution of clay-iron oxide complexes, is more even throughout the profile. In soils subjected to the fluctuation of the water table there is a distinct layer of accumulation.

Accumulation of iron can also be observed in soils in the form of concretions. Concretions are often found in the zone of fluctuating water-table signifying a variable oxidizing and reducing condition. Concretions in the tubular form are observed around root channels often related to biological oxidation (Bloomfield, 1952). Most of these concretions are associated with other elements, namely manganese, cobalt, nickel, copper and zinc (Taylor et al., 1966).

The movement of iron down the profile is preceded by reduction of the higher oxidation states to the ferrous forms, which are more soluble in water, or as organically-complexed iron. Leaf leachates have also been reported to solubilize iron (Oades, 1963).

ALUMINUM

General properties

Aluminum is the most abundant metal in the earth's crust. It is the 13th element in the periodic table and has electronic configuration of $[Ne]3S^2 3P'$. Silicon, being adjacent to aluminum in the periodic table, has similar chemical properties. Two kinds of anhydrous alumina are present. Stoichiometrically they are the same. The hydrated form of alumina corresponds to the stoichiometric formula $AlO.OH$ and $Al(OH)_3$. Two polymorphs of $AlO.OH$ occur, namely boehmite and diaspore. Al^{3+} and Si^{4+} have ionic radii of 0.50 A° and 0.43 A°, respectively. The closeness in the size of the radii between these two elements allows the displacement of Si^{4+} by Al^{3+} in silica tetrahedra structures (Heslop and Robinson, 1960). The deficiency of positive charge is made up by associating other cations. This is the basis of the formation of numerous aluminosilicate minerals.

Aluminum in soil

Aluminum mainly occurs as aluminosilicate minerals in temperate soils. This includes the feldspars, pyroxenes, amphiboles and

phyllosilicates. Aluminum exhibits four-fold coordination to oxygen in igneous rocks formed at high temperature, such as feldspars, but as weathering proceeds hydroxyl ions take over the oxygen positions, and aluminum acquires octahedral coordination.

The crystalline mineral gibbsite [$Al(OH_3$ or $Al_2O_33H_2O$] is the most abundant form of alumina in soil. It occurs primarily in tropical and subtropical soils which have undergone intensive weathering and leaching of silicon. Gibbsite consists of paired sheets of hydroxyl ions, held together dioctahedrally by aluminum ions. The series of paired sheets are held together by H-bonding. Gibbsite forms a very effective cement for soil granules (Desphande, 1968). It has also been shown that $Al(OH)_3$ is more effective than $Fe(OH)_3$ as a cementing agent. Gibbsite also has great affinity for silica and reaction between these constituents lead to crystallization of kaolinite or halloysite (Loughnan, 1969).

Amorphous hydrous oxides of aluminum, such as boehmite and its isomer diaspore, occur frequently with iron oxides. These amorphous oxides of aluminum and iron are often positively charged. They are usually attached to the negatively-charged surface of colloids. This association of amorphous oxides with clay colloids results in a net-positive charge instead of a negative charge in certain soils (Sumner, 1967).

SILICON

General properties

Silicon is the second most abundant element on the earth's crust, and has an atomic number of 14. It is in the same group as carbon and this accounts for many similar physical and chemical properties between these elements. Carbon has an electronic configuration of $2S^2 2P^2$ and silicon $3S^2 3P^2$. The availability of 3 d-orbitals in the case of silicon makes it possible to have variable valencies from 4 up to 40 (Heslop and Robinson, 1960). Practically, only the valency of four has been reported. Silicon also has a lower ionization potential than carbon. Both factors explain the greater reactivity of silicon. A look at the bond strengths of various silica diatomic molecules will give an idea of the relative stability of silicon compounds.

Bond Energies of Silicon at 25°C[*]

Si - Si	76 kcal/mole
Si - Cl	105 kcal/mole
Si - O	188 kcal/mole
Si - H	71 kcal/mole
Si - C	104 kcal/mole

[*]Chemical Rubber Company, Handbook of Physics and Chemistry, 1971/72.

The values indicate the importance of electronegativity in bond strengths. Chlorine, oxygen and carbon are more electronegative than silicon and hydrogen. The Si - C bond strength (104 kcal/mole)

is relatively lower than the C - C bonds. This is due to the greater polarity of the bond, $Si^{\delta+}$ - $C^{\delta-}$, allowing nucleophilic attack on silicon and electrophillic attack on carbon. These values will also be important in studying the various silicates, aluminosilicates and clay-organiccomplexes in soils.

Silicon lies adjacent to aluminum in the periodic table. They have some common physical and chemical properties. Aluminosilicate compounds are important in affecting soil properties.

Silicon in soil

Silicon in soil is present in the form of silica, silicates and aluminosilicates. The soluble form being represented by monosilicic acid $[Si(OH)_4]$. The total amount of silicon ranges from 50 to 70 percent, with sandy soils having the upper limit, and the relative concentration decreases with increasing organic matter content. Intensive weathering such as that prevalent in tropical soils leads to depletion of silicon followed by negative enrichment of the sesquioxides (Bear, 1964).

Silica in soil is present in the form of quartz, tridymite and cristobalite, each having low temperature (α) and high temperature (β) forms. The transformation into different forms takes place slowly, since reforming and transforming of bonds is necessary to bring this about. Silica is also present as opal $SiO_2.nH_2O$, often the decomposition product of organic matter.

The silicates and aluminosilicate forms of silicon are present as amorphous aggregations with the sesquioxides, in minerals such as

micas, feldspars and the phyllosilicates.

The behaviour of silicon in solution does not seem to coincide with that in soil. In solution, solubility of silica is independent of pH from pH 2.0 to 9.0. There is a rapid increase above pH 9.0, because of the dissociation of the monosilicic acid [$Si(OH)_4$] into silicate ions (Mckeague and Cline, 1963). In the soil, Beckwith and Reeve (1963) found that the concentration decreased from 70 ppm to 23 ppm as pH increased from 5.4 to 7.2. The concentration reaches its minimum at pH 9.0 and starts increasing again above pH 9.0. This characteristic behaviour of silicic acid in soil seems to coincide with the adsorption of monosilicic acid on aluminum and iron oxides (Beckwith and Reeve, 1963; McKeague and Cline, 1963). It has been concluded that solubility of monosilicic acid in soil is dependent on the sesquioxides and pH. H-bonding is thought to be responsible for this adsorption - $(OH)_3Si-O-H$ . . . . .$O(Fe_2O_4H_4)$. A summary of the sources of silicic acid is indicated in Figure 2. The figure also shows the sources of aluminum and iron compounds discussed in the preceding sections.

Relationship between the Basic Properties of Manganese, Iron, Aluminum and Silicon

A further look into the basic chemistry of these elements helps to explain the numerous complexes of manganese, iron, aluminum, and silicon which add to the heterogeneity of soil. Manganese and iron, aluminum and silicon exhibit closeness in ionic radii giving them the possibility of displacing each other in crystal lattices. The displacement of Si^{4+} (0.42 A°) by Al^{3+} (0.51 A°) in the silica tetrahedra

Olivine, Augite,
Hypersthene, ⟶ Amorphous
Hornblende   hydrous oxides

$\begin{cases} Ti \\ Fe \\ Al \\ Si \end{cases}$ → Anatase
Goethite,
Hematite
Gibbsite
Bioehmite

Kaolin. ⟶ Silicic acid

Volcanic glass
(basic) ⟶ Amorphous
Zeolites   hydrous oxides

$\begin{cases} Fe \\ Al \\ Si \end{cases}$ ⇄ Gibbsite ⟶ Kaolin. ⟶ Silicic acid
Allophane

Ca^{++}

Biotite ⟶ $\begin{cases} \text{Trioctahedral (illite)} \xrightleftharpoons[K]{H, Ca} \\ K^+ \uparrow\downarrow H^+ \\ \text{Clay vermicullite} \xrightarrow{Ca} \\ H^+ \uparrow\downarrow K^+ \\ \text{Dioctahedral (illite)} \xrightleftharpoons[K]{H, Ca} \end{cases}$ Montmorrillonite

Muscovite

$-SiO_2 \downarrow\uparrow +SiO_2$

Kaolin. ⟶ Silicic acid

Volcanic glass (acid) ⟶ Amorphous hydrous $\begin{cases} Al \\ Si \end{cases}$ ⟶ Gibbsite ⟶ Kaolin.
Feldspars   oxides

Silicic acid

*Modified from Loughnan, 1969

Figure 2.   Silicon in minerals and its reaction products

17

has been mentioned in a previous section. Manganese, iron and aluminum have the same coordination number of six (Table 1). Aluminum also has the coordination number of four, which is the same as that of silicon. Ionization potentials for iron and manganese are almost the same; this adds stability for the association of these two elements in the same compound. The electronic configuration of manganese, iron, aluminum and silicon have one thing in common; that is an incompletely filled d-orbital even though their reactivity varies. This give the chance for these elements to form numerous common complexes with each other, with other cations and organic molecules.

An extractant destined to extract one of these elements often brings into solution the other elements too. The concentration extracted depends on the properties of the extractant and the procedure employed.

TABLE 1

Selected Basic Properties of Manganese,
Iron, Aluminum and Silicon

	Mn	Fe	Al	Si
Atomic Number	25	26	13	14
Atomic Radii (A^o)	1.17	1.16	1.25	1.17
Ionic Radii M^{2+} (A^o)	0.80	0.74	-	-
Ionic Radii M^{3+} (A^o)	0.66	0.64	0.51	-
Ionic Radii M^{4+} (A^o)	0.60	-	-	0.42
Coordination Number with Oxygen	$Mn^{2+} = 6$ $Mn^{3+} = 6$ $Mn^{4+} = 6$	$Fe^{2+} = 6$ $Fe^{3+} = 6$	$Al^{3+} = 4,6$	$Si^{4+} = 4$
Ionization Potential				
1. (eV)	7.43	7.90	5.95	8.15
2. (eV)	15.46	16.16	18.82	16.30
3. (eV)	-	-	28.44	33.50
4. (eV)	-	-	-	45.10
E_h M/M^{2+} (V)	-1.05	-0.44	-	-
M/M^{3+} (V)	-	-	1.67	-
M^{2+}/M^{3+} (V)	1.51	0.77	-	-
Electronic Configuration	$[Ar]3d^54S^2$	$[Ar]3d^64S^2$	$[Ne]3S^23P^1$	$[Ne]3S^23P^2$

LITERATURE CITED

Barbier, G. 1937. Conditions and modalities of the fixation of colloidal ferric hydrate by soil clay. Ann. Agron. 8: 34-43.

Bear, F. E. 1964. Chemistry of the soil. 2nd Edition. A C S Monograph No. 160. Reinhold Publishing Corp.

Beckwith, R. S., and Reeve, R. 1963. Studies on soluble silica in soils. I. The sorption of silicic acid by soils and minerals. Aust. J. Soil Res. 1: 157-68.

Bloomfield, C. 1952. The distribution of iron and aluminum oxides in gley soils. J. Soil Sci. 3: 167-171.

Cotton, F. A., and Wilkinson, G. 1972. Advanced Inorganic Chemistry. Interscience Publishers.

Desphande, T. L., Greenland, D. J., and Quirk, J. P. 1968. Changes in soil properties associated with the removal of iron and aluminum oxides. J. Soil Sci. 19: 108-122.

Dion, H. G., Mann, P.J.G., and Heintze, S. G. 1947. The easily-reducible manganese of soils. J. Agr. Sci. 37: 17-22.

Geering, H. R., Hodgson, J. F., and Sdano, C. 1969. Micronutrient cation complexes in soil solution. IV. The chemical state of manganese in soil solution. Soil Sci. Soc. Amer. Proc. 33: 81-85.

Hemstock, G. G. and Low, P. F. 1953. Mechanism responsible for the retention of manganese in the colloidal fraction of soil. Soil Sci. 76: 331-343.

Heslop, R. B., and Robinson, P. L. 1960. Inorganic Chemistry. A guide to advanced study. Elsevier Publishing Co. Inc.

Jones, L.H.P. 1957. The effect of liming a neutral soil on the cycle of manganese. Pl. and Soil 8: 315-327.

_____, and Handreck, K. A. 1967. Silica in soils, plants and animals. Adv. Agron. 19: 107-149.

Kamoshita, Y. and Iwasa, Y. 1959. On the rusty mottles in paddy field soils. J. Sci. Soil, Tokyo 30: 185-188.

Leeper, G. W. 1947. The forms and reactions of manganese in the soil. Soil Sci. 63: 79-94.

Loughnan, F. C. 1969. Chemical Weathering of the Silicate Minerals. Elsevier Publishing Co. Inc.

McKeague, J. A., and Cline, M. G. 1963. Silica in soils. Adv. Agro. 15: 339-396.

Mehra, O! P. and Jackson, M. L. 1958. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Proc. 7th Nat. Conf. Clay and Clay Minerals 5: 317-327.

Mitchell, B. D., Farmer, V. C., and McHardy, W. J. 1964. Amorphous inorganic materials in soils. Adv. Agron. 16: 327-383.

Oades, J. M. 1963. The nature and distribution of iron compounds in soils. Soils and Fertilizers XXVI: 69-80

Remy, H. 1966. Treatise on inorganic chemistry. Vol. 2. Elsevier Publishing Co., Amsterdam.

Russell, E. W. 1973. Soil conditions and plant growth. 10th Edition. Longman's Publishers.

Serdobolskii, E. P. 1950. The effects of soil conditions on the transformations of manganese compounds in the soil. Trudy Pochv. Inst. Dukuchaev 43: 192-216.

Sumner, E. M. 1963. Effect of iron oxides on positive and negative charges in clays and soils. Clay Minerals 5: 218-238.

Taylor, R. M., McKenzie, R. M., and Norrish, K. 1964. The mineralogy and chemistry of manganese in some Australian soils. Aust. J. Soil Res. 2: 235=248.

_____, and _____. 1966. The association of trace elements with manganese minerals in Australian soils. Aust. J. Soil Res. 4: 29-39.

Weast, R. C. 1971-72. Handbook of Chemistry and Physics. The Chemical Rubber Company.

CHAPTER I

SELECTED PHYSICAL AND CHEMICAL PROPERTIES

OF THE SOILS STUDIED

INTRODUCTION

Robinson (1929) cited the range of 0 to 0.31 percent manganese

in the soils of the United States. Bear (1946) working on Hawaiian

soils reported concentrations of as high as 10.0 percent in highly

leached soils. Leeper (1947) reported a range of 0 to 0.1 percent

of total manganese in Australian soils. The total concentration of

manganese in British Columbia soils ranges from 0.007 to 0.494 percent

(Baker, 1950). He also stressed the relatively high concentration

of manganese in the Lower Fraser Valley compared to other areas in

the province. Further studies by Safo (1970) showed that total man-

ganese in the Lower Fraser Valley soils ranged from 82.0 to 957.5 ppm.

The results were lower than those indicated by Baker. Total analysis

for manganese and other elements are very tedious. Many factors control

the results obtained and total elemental analysis is still in its in-

fancy with regards to manganese. The total manganese concentration

in soil is affected mainly by the climate, relief, parent material and

time. The interaction of these factors control the concentration of

manganese deposited or leached away from a particular area.

The total iron content of soils expressed as Fe_2O_3 ranges from

1 to 6 percent (Byers et al., 1935). There is negative enrichment

22

or iron as the soil weathers. The iron content of some Latosols and Laterites may go as high as 20 to 80 percent (Alexander et al., 1962). The silicon content of many soils, expressed in SiO_2 ranges from 50 to 70 percent (Clarke et al., 1924). The concentration rises in sandy soil and decreases with the relative increase in organic matter content (Feustal et al., 1930). Aluminum content of soil ranges from 2 to 12 percent expressed on the basis of Al_2O_3, and may go as high as 60 percent in highly weathered soils (Alexander et al., 1962).

Leeper (1947) postulated that eight factors influence the distribution of manganese, iron, aluminum, silicon and other elements in the soil profile. They are:

1. the liberation of metal ions from the weathering of minerals, rocks and living organisms;

2. translocation of these ions down the soil profile by percolating water;

3. the dynamic equilibrium between these ions in solution and on the cation exchange sites;

4. uptake of these elements by plant roots, and its return to the soil surface from falling leaves;

5. the oxidation of certain elements by oxygen or by electron-accepting bacteria;

6. aging of the oxides from the highly reactive to the inert forms;

7. reduction of the higher oxides by organic matter and bacteria;

8. utilization of the higher oxides directly, by plants and micro-organisms.

Leeper then predicted the distribution of these elements in the profile of different types of soil. Leeper's statements are as follows:

i) Leached soil. The surface horizon has a high concentration of these elements, originating from decomposed plant material. The concentration in the immediate subsurface horizon is at a minimum, and then a gradual increase with depth. This kind of soil is found in a temperate climatic zone, which has high precipitation.

In some leached soils illuviation does not take place, instead there is a gradual decrease with depth. The soil is highly leached and the parent material is often poor in the element concerned.

ii) Pedocals and unleached soils. There is a steady distribution of the element throughout the profile. In some pedocals, there is an accumulation of the element just above the calcareous layer.

Browman et al. (1969), evaluating eight soil manganese tests found that the soil variables, pH, and total manganese often correlated significantly with the tests.

The objective of this study was to determine the total concentration of manganese together with aluminum and iron in some of the Lower Fraser Valley soils. The relationship between the total concentration of these elements and other inherent chemical properties of the soils was observed. The results obtained will be helpful for characterizing the soils in subsequent investigations. A comparison is also made between the results obtained with those of Safo for soils derived from the same area.

MATERIAL AND METHODS

Soils used in these studies were sampled from the Lower Fraser
Valley of British Columbia. The Blundell, Grevell and Monroe series
are derived from alluvial parent material, and Tsawwassen, Cloverdale
and Sunshine from marine parent material. A more comprehensive de-
scription of these soils is given by Luttmerding and Sprout (1967).
Most of these soils are subjected to a high water table throughout
the year and the Blundell and Tsawwassen series are affected by the tide.
Texture of the soilsvvary from loamy sand to silty clay (Table 1.1).
Sampling was done in late June. Samples from the field were air dried,
and large aggregates were crushed with a wooden roller, and passed
through a 2.0 mm sieve. The less than 2.0 mm samples were stored in
paper containers. Subsamples were taken and ground in an agate mortar
to pass through a 100 mesh sieve.

Soil pH

Soil pH was determined in both field conditions and following
drying in the laboratory. The procedures using the ratio of 1:1 dis-
tilled water and 1:2 0.01 M $CaCl_2$ (Jackson, 1958) were followed.
Corning Model 12 pH meter was used to make the pH measurement.

Cation exchange capacity (CEC)

The CEC of the soils were determined using the < 2.0 mm samples
by saturation of the soil with neutral normal ammonium acetate followed
by displacement of the NH_4^+ ions on the exchange sites with normal

potassium chloride solution. The NH$_4^+$ ions were analysed following

the semi-micro kjeldahl procedure. This procedure was actually an adap-

tation of Chapman's ammonium saturation procedure in C. A. Black's

Methods of Soil Analysis. Instead of using ammonium chloride, potassium

chloride was used.

The exchangeable forms of manganese, iron and aluminum were

determined simultaneously from the extracts, following saturation of

the soil with ammonium ions.

Soil organic matter

The Walkley-Black procedure was followed using less than 40

mesh samples. Potassium dichromate was used to oxidize the organic

matter in concentrated sulphuric acid. Excess potassium dichromate

was titrated with ferrous sulphate solution and ferroin indicator.

Total manganese, iron and aluminum

The mixed perchloric, hydrofluoric acid procedure adapted from

Pratt's (1965) procedure for total potassium and sodium was used.

About 1.00 gm of air-dried 100 mesh soil in a porcelain crucible was

dried at 105°C for 16 hours, followed by ashing at 900°C. 5 N hydro-

chloric acid was added to the ash and centrifuged. The supernatant

solution was decanted and this contained the major portion of the alka-

line earth metals. The residue was then dissolved with concentrated

hydrofluoric-hydrochloric acid mixture in a Teflon beaker and evaporated

to dryness. This procedure was repeated using a hydrofluoric-hydrochloric

perchloric acid mixture. The residue which remained was again dissolved in 1.0 N hydrochloric acid, and diluted for atomic absorption analysis. The procedure is outlined in greater detail in Methods of Soil Analysis by Prof. L. M. Lavkulich, Department of Soil Science, University of British Columbia. This digestion procedure is relatively accurate for the three elements--manganese, iron, and aluminum. Silicon can also be determined by difference; however, considering the large error involved, the total amount of silicon was not recorded.

All the determinations for manganese, iron, aluminum and silicon were carried out using a Perkin Elmer 306 atomic absorption spectrophotometer. An air-acetylene flame was used for manganese and iron, and nitrous oxide flame, for aluminum and silicon.

RESULTS AND DISCUSSIONS

The pH of the samples varied from 4.0 to 8.0 (Table 1.2). No significant difference was observed when the pH was determined in the field moisture condition or following drying of the samples, for the surface horizon. A difference of around one pH unit was observed for the lower horizons. Similar trends were shown by the procedure using 0.01 M calcium chloride. The pH determined by the latter procedure was lower than by using distilled water.

Cation exchange capacity of the samples varied from 3.4 m.e./ 100 gm for the Grevell C and IIC horizons to 62.2 m.e./100 gm for the Cloverdale Ahl horizon (Table 1.1). Results of the latter concurred with the high organic matter present (Table 1.1).

The Blundell samples showed the lowest concentration of total manganese (Table 1.2). The concentration of manganese remained steady in both Ap and Bg horizons, and increased slightly in the Cg horizon. The Ap and Bg horizons have acid pH while the Cg horizon had an alkaline pH. Manganese appears therefore to be mobilized from the upper horizons of the Cg horizon. The high organic matter present accounts for the retention of a relatively high quantity of manganese in the surface horizon. The low concentration of manganese relative to the other soils is more of a genetic factor rather than due to leaching.

The manganese concentration in the Tsawwassen samples also remained constant for the Ah and C horizon (Table 1.2). There was a slight decrease in IIC horizon. The trend is again related to the pH of the horizons. The surface horizon has an acid pH and therefore

Table 1.1

Selected Physical and Chemical Properties of the Soils

Order	Sub-Group	Series Texture	Parent Material	Horizons	Depth (inches)	C E C me/100 g	% Organic Matter
Gleysols	Saline-Rego	Blundell (Silty Clay)	Alluvial	Ap Bg Cg	0-7 7-20 20+	55.5 23.8 17.6	17.7 4.3 4.4
Regosol	Orthic	Tsawwassen (Loamy Sand)	Marine	Ah C IIC	0-12 12-30 30+	8.1 11.8 22.2	3.0 0.2 0.1
Regosol	Orthic	Grevell (Loamy Sand)	Alluvial	Ah C IIC	0-2 2-12 12+	22.4 3.4 3.4	8.6 0.1 0.1
Gleysol	Humic Eluviated	Cloverdale (Silty Clay Loam)	Marine	Ah1 Ah2 Bg Cg	0-14 14-22 22-33 33+	62.2 50.5 33.9 31.7	19.0 7.9 0.9 0.4
Brunisol	Degraded Eutric	Monroe (Sandy Loam)	Alluvial	Ap Btj IICg	0-7 7-14 21+	24.2 18.9 10.3	4.0 1.7 0.4
Podzol	Mini-Humo Ferric	Sunshine (Sandy Loam)	Marine	Ah Bf1 Bf2 BC C	0-5 8-15 15-29 29-36 36+	51.9 32.7 22.8 16.3 15.1	17.8 4.5 2.7 1.3 0.9

Table 1.2

Total Manganese, Iron and Aluminum in Relation to pH of the Soil

| Soils | pH - Wet | | pH - Dry | | Total Concentration | | |
	H$_2$O Ratio 1:1	0.01 M CaCl$_2$ Ratio 1:2	H$_2$O Ratio 1:1	0.01 M CaCl$_2$ Ratio 1:2	Mn (ppm)	Fe (ppm)	Al (ppm)
Blundell							
AP	4.90	4.4	5.0	4.6	297.0	28,410	55,540
Bg	4.1	3.9	4.1	3.8	302.1	44,430	62,210
Cg	7.4	6.8	4.9	4.8	411.9	45,490	75,810
Tsawwassen							
Ah	5.9	4.9	5.9	5.0	663.6	30,050	62,600
C	7.4	6.6	7.3	5.8	665.8	31,290	66,330
IIC	8.6	7.5	8.0	7.4	593.2	28,790	63,830
Grevell							
Ah	6.0	5.4	5.9	5.3	633.5	26,610	34,210
C	6.9	5.6	6.0	5.0	575.0	26,370	48,970
IIC	7.1	5.9	6.3	5.2	706.0	33,820	57,620
Cloverdale							
Ah 1	5.2	4.4	5.1	4.5	1,366.0	44,910	56,800
Ah2	5.9	4.9	5.9	5.1	566.6	49,610	37,860
Bg	6.2	5.5	5.8	5.5	517.8	62,140	64,290
Cg	6.5	5.8	6.0	5.7	994.2	60,840	81,550
Monroe							
AP	5.9	5.2	5.7	5.2	895.7	43,010	58,190
Btj	6.0	5.4	5.9	5.3	1,230.0	47,470	44,910
IICg	6.2	5.2	5.8	5.2	750.2	40,140	55,200
Sunshine							
Ah	4.3	3.9	5.3	3.9	573.6	28,810	43,210
Bf1	5.5	4.9	5.2	4.6	756.9	38,880	68,690
Bf2	6.1	4.9	5.1	4.5	634.9	34,840	46,460
BC	6.1	4.8	5.1	4.7	642.1	34,400	77,710
C	6.3	4.8	5.3	4.7	626.3	33,100	61,100

Table 1.3

Exchangeable Manganese, Aluminum, and Iron
and Organic Matter Content of the Soil

| Soil | Horizons | Exchangeable Forms | | | Percent Organic Matter |
		Mn (ppm)	Fe (ppm)	Al (ppm)	
Blundell	Ap	3.8	10.0	35.0	17.7
	Bg	1.5	6.3	17.5	4.3
	Cg	7.5	2.5	5.0	4.4
Tsawwassen	Ah	12.3	3.8	2.5	3.0
	C	3.5	2.5	-	0.2
	IIC	2.0	2.5	-	0.1
Grevell	Ah	59.0	5.0	2.5	8.6
	C	9.5	7.5	5.0	0.1
	IIC	7.0	2.5	2.5	0.1
Cloverdale	Ah1	22.8	5.0	25.0	19.0
	Ah2	0.8	2.5	30.0	7.9
	Bg	5.3	2.5	-	0.9
	Cg	19.8	2.5	-	0.4
Monroe	Ap	24.8	3.8	-	4.0
	Btj	4.3	2.5	-	1.7
	IIC	5.0	2.5	-	0.4
Sunshine	Ah	8.8	32.5	82.5	17.8
	Bf1	7.3	5.0	40.0	4.5
	Bf2	0.8	5.0	17.5	2.7
	BC	0.5	5.0	15.0	1.3
	C	0.5	5.0	-	0.9

probably the manganese has been mobilized to the C and IIC horizons which have alkaline pH. This observation also indicates that most of the manganese in the Tsawwassen soils are from surface accumulation rather than from the parent material.

The trend exhibited by Grevell and Cloverdale series were the same (Table 1.2). There was an initial decrease in the subsurface horizon followed by an increase in the lower horizons. Leeper (1947) cited this observation as the characteristic of leached soils. (The Lower Fraser Valley area has a high annual precipitation.)

Monroe and Sunshine series showed an increase in the subsurface horizon followed by a decrease of manganese in the lower horizon. The middle horizons are zones of illuviation. The Monroe soil has some clay in the B horizon and this would help to fix manganese. The acid pH of the Sunshine Ah horizon probably mobilized the manganese allowing its movement to the Bf horizon, where there is an abrupt increase in pH.

Iron results showed a similar trend as manganese, except for Cloverdale samples. In this case, there was a significant increase from the Ah to Bg horizon followed by a decrease in the Cg horizon (Table 1.2).

Aluminum showed the same trend as manganese for Blundell and Tsawwassen horizons (Table 1.2). There was a gradual increase in aluminum with depth for Grevell. Cloverdale samples indicated a decrease in aluminum from the surface Ah1 to Ah2 horizon. This was followed by a significant increase in Bg and Cg horizons which are the zones of illuviation for the sesquioxides. This may also indicate the

contribution of both parent material and organic matter to the total
content of elements in the soil.

Safo (1970) reported the total concentration of manganese of
the Sunshine soil to be in the range of 80 to 300 ppm; Grevell in the
range of 250 to 550 ppm; and Monroe ranging from 350 to 700 ppm. Table
1.2 shows that the total manganese extracted in this study was signi-
ficantly higher. Further modification of total elemental analysis
is necessary for precise comparison.

Exchangeable manganese decreased with depth for the Tsawwassen,
Grevell and Sunshine series. For Blundell, Cloverdale and Monroe series
there seemed to be a decrease in the subsurface horizons, followed by
an increase again in the parent material. This observation correlated
well with soil texture.

Exchangeable iron decreased with depth in all cases. The highest
amount was related to the highest organic matter content which corres-
ponds with the surface horizons of Sunshine, Grevell, and Blundell
series (Table 1.3).

Exchangeable aluminum was highest in the Sunshine Ah horizon.
The concentration decreased with depth. The association with other
oxides might account for this. Some of the horizons showed undetectable
amounts of exchangeable aluminum.

CONCLUSION

No definite trend was observed between the concentration of manganese, iron and aluminum and the type of parent material. Iron results were closely related to manganese but not for aluminum. This further stressed the similarity in chemical properties of iron and manganese in the soil. The total concentration of manganese reported in this study was significantly higher than that reported by Safo (1970), even though the soils were from the same area. Further studies are necessary for total element analysis.

The results for exchangeable manganese were also higher than Safo's results for certain horizons. The exchangeable manganese concentration has been known to vary with the treatment of samples prior to extraction. Generally, the exchangeable concentration of manganese, iron and aluminum correlate well with the organic matter content of the soil.

LITERATURE CITED

Alexander, L. T., and Cady, J. G. 1962. U.S.D.A. Tech. Bull. 1282.

Bear, F. E. 1946. Soils and Fertilizers. New York, John Wiley and Sons, Inc., p. 51.

_____. 1964. Chemistry of the Soil. 2nd Edition. ACS Monograph No. 160, Reinhold Publishing Corp.

Black, C. A. 1965. Methods of Soil Analysis. Part 2. Agron. No. 9, American Society of Agronomy Inc., Publisher.

Browman, M. G., Chesters, G., and Pionke, H. B. 1969. Evaluation of tests for predicting the availability of soil manganese to plants. Agric. Sci. Camb. 72: 335-340.

Byers, H. G., Alexander, L. T., and Holmes, R. S. 1935. U.S.D.A. Tech. Bull. 484.

Clarke, F. W., and Washington, H. S. 1924. "U.S. Geol. Survey Prof. paper 127."

Feustal, I. C., and Byers, H. G. 1930. U.S.D.A. Techn. Bull. 214.

Lavkulich, L. M. 1974. Methods of Soil Analysis. Pedology Laboratory, Dept. of Soil Science, University of British Columbia.

Leeper, G. W. 1947. The forms and reactions of manganese in the soil. Soil Sci. 63: 79-94.

Luttmerding, H. A. and Sprout, P. N. 1967. Preliminary report of the Lower Fraser Valley Soil Survey. British Columbia Dept. of Agric., Kelowna, B.C.

Robinson, W. O. 1929. Detection and significance of permanganate (MnO_4) in soil. Soil Sci. 27: 335-350.

Safo, E. Y. 1970. Manganese status of some Lower Fraser Valley soils developed from alluvial and marine deposits. M.Sc. thesis, Dept. of Soil Science, University of British Columbia.

CHAPTER 2

EVALUATION OF FIVE EXTRACTANTS FOR THE EXTRACTION

OF MANGANESE, IRON, ALUMINUM AND SILICON

INTRODUCTION

The conventional procedure for extracting manganese from the

soil is biased towards its availability to plants. Not many literature

described the extraction of manganese in relation to the other oxides,

even though manganese is commonly associated with these oxides in the

soil. This study will evaluate some of the common extractants for

organically and inorganically complexed oxides in the soil.

Acid ammonium oxalate presumably extracts the amorphous organic

and inorganic forms, and very little of the crystalline forms of iron

and aluminum in soils (McKeague, 1967). Acid ammonium oxalate has been

found to be useful in characterizing the accumulation products of podzols

and other soils. Oxalate-extractable aluminum and iron also gives

useful indication of the development of Bf horizons, even though the

parent material is rich in iron oxides (McKeague and Day, 1966). The

acidity of the extractant renders the sesquioxides soluble. The NH_4^+

ions displace the iron and aluminum adsorbed or attached to the soil.

The oxalate ion ($C_2O_4^=$) is both a strong chelating agent as well as

a reducing agent. All these properties account for its usefulness.

Sodium pyrophosphate extracts the amorphous organic forms of iron and aluminum at pH 10.0 (McKeague et al., 1971). Results obtained allow distinction between amorphous organic and amorphous inorganic forms of iron and aluminum in the soil. At pH 7.0, sodium pyrophosphate dissolved the ferrous silicate minerals (Titova, 1962; Kononova et al., 1964). Bascomb (1968) tried to differentiate the different forms of iron and aluminum oxides in soil and showed which extractant was useful for which forms as indicated in Figure 2.1. Bascomb concluded that 0.1 M sodium pyrophosphate at pH 10.0 extracts:

1. colloidal organic matter,

2. organic complexes of iron and aluminum,

3. active amorphous inorganic forms of iron oxides,

and poorly extracts aged "inactive" inorganic oxides and well crystallized oxides.

Bascomb's classification thus includes part of the inorganic amorphous oxides contradictory to McKeague's breakdown. Schnitzer (1962) showed that the organic material involved in the complexes with iron and aluminum was fulvic acid, therefore any differences in result between sodium pyrophosphate and acid ammonium oxalate extraction would be due to the amorphous "aged" hydrous oxides portion (Refer to Figure 2.1).

Dion et al. (1946) indicated that sodium pyrophosphate was useful in extracting the trivalent form of manganese. They did not give the concentration and pH of the extractant. They postulated that a stable complex $Na_3(Mn H_2 P_2 O_7)$ was formed between the trivalent manganese and sodium pyrophosphate.

	Inorganic Iron Compounds			Silicates +	Organic Compounds	
Silicates	Well-Crystallized Oxides	Amorphous "Aged" Hydrous Oxides	Amorphous "Gel" Hydrous Oxides		Acid Soluble "Fulvate'	Acid Insoluble "Humate"

(pH 3.8) Dithionite

(pH 3.0) Acid Oxalate

(pH 7.0) Pyrophosphate

(pH 10.0) Pyrophosphate

Modified from Bascomb, 1968.

Figure 2.1. Extractability of different compounds of iron by different extractants.

DisodiumEDTA has been used as a chelating agent in soil studies by many workers. The stability of a metal ion with a chelating agent is dependent on the ionic radius, charge, and the presence of electrons on the d-orbitals. The stability constant is directly proportional to the charge and inversely proportional to the radius. For the transition elements the stability constant increases with increasing atomic number. Thus iron has a higher stability constant with chelating agents than manganese. Irregularities in the trend are due to the ligand field stabilization energy (Murmann, 1964).

Mortvedt et al. (1970) tried to calculate stability constant diagrams for iron and aluminum with EDTA at different pH values. It was found that EDTA complexes with Fe^{3+} almost exclusively below pH 6.3. Complexation of Al^{3+} by EDTA was only minor, between pH 4.0 to 9.0. The above observations were obtained from studies in aqueous solutions. The heterogeneity of the soil has to be realized when dealing with the chemical effects of the different extractants. The interactions between cations as well as with the organic chelating agents present in the soil would contribute large irregularities in the trend (Schnitzer and Skinner, 1966, 1967).

Beckwith (1955) and Heintze (1957) indicated that disodiumEDTA is specific for extracting organically bonded manganese. This is not exactly true. A chelating agent will extract any form of the element. Browman et al. (1969) evaluated the availability of manganese to plants using eight extractants, namely ammonium acetate, magnesium nitrate, H_3PO_4, hydroquinone, 3.0 M $NH_4H_2PO_4$, 1.5 M $NH_4H_2PO_4$ and EDTA. They

found that EDTA and H_3PO_4 extractable manganese were more superior in predicting manganese uptake.

Safo (1970) tried to show that "active manganese" (the forms of manganese that are available to plants and extracted by distilled water, ammonium acetate, and hydroquinone) is analogous to EDTA manganese. However, he found that EDTA extracted more manganese after the extraction of "active manganese." Dispersion of the soil aggregates by EDTA might account for the extra manganese released.

Hydroquinone is a good reducing agent. It has been used in both soil and plant analysis. It prevents unwanted autooxidation and polymerization of organic compounds (Noller, 1968). The potential involves in oxidizing hydroquinone to quinone is approximately 0.6994 V.

$$\text{[Hydroquinone]} \rightleftharpoons \text{[Quinone]} + 2H^+ + 2e^- \qquad E^\circ = 0.6994 \text{ V}$$
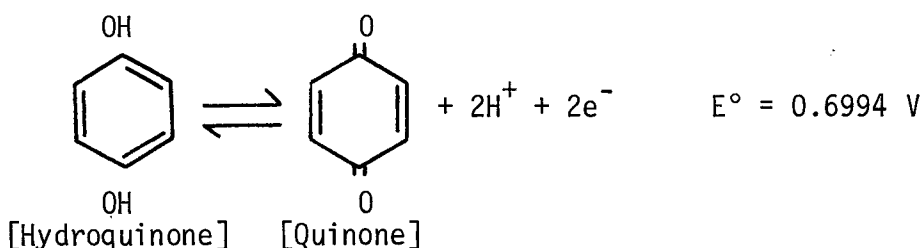
In soil science hydroquinone in neutral ammonium acetate has been used to extract the easily reducible form of manganese. The pH of the extractant is important in determining its effectiveness. Hydroquinone is also sensitive to exposure to light. Therefore, the time interval between preparing the extractant and extracting the soil is critical. Chao (1972) found that hydroquinone not only reduced manganese but also iron, and the latter always interfered with manganese

analysis. Mn^{3+} and Mn^{4+} have oxidation potentials of 1.51 V and 0.77 V, respectively. Theoretically hydroquinone would bring iron into solution more easily than manganese. The forms of iron present in the soil are important in studying the magnitude of the extraction.

Hydroxylamine hydrochloride has been used in soil and plant analysis. 0.1 M hydroxylamine hydrochloride in 0.01 M nitric acid was used by Chao (1970) to extract manganese from soils. He found that there was selective dissolution of manganese by hydroxylamine hydrochloride. This was found to be untrue for the Lower Fraser Valley soils (Zulkifli, 1973). Hydroxylamine hydrochloride did solubilize a large portion of iron, in fact comparatively higher than that of hydroquinone.

Hydroxylamine hydrochloride is a stronger reducing agent than hydroquinone. They have oxidation potentials of 0.496 V and 0.699 V, respectively (Latimer, 1938). It was this factor and the acid pH that lead to hydroxylamine hydrochloride being used in this study as it was felt it would bring into solution greater amounts of manganese, iron, aluminum and silicon than hydroquinone.

Some biases can be seen in selecting the extractants to be used in this study. The extractants are those that extract the amorphous oxides and the organically-complexed forms. Extractants that dissolve the crystalline forms such as sodium bicarbonate-citrate dithionite were not included because relatively speaking these forms are not as active in affecting immediate properties of the soil.

MacKenzie and Meldau (1959) stressed that the amorphous oxides have a relatively large surface area and consequently affect the properties of the soil significantly. Oades (1965) cited that amorphous forms of oxides were the active forms of oxide in the soil. Mitchell (1964) differentiated the "active" and "inactive" oxides in soil. "Active" oxides are those readily extractable by common extracting agent and "inactive" oxides being those not readily extractable. Dixon (1958) stated that changing from amorphous to crystalline forms involved reduction in surface area. Amorphous iron and aluminum oxides were found to adsorp 109 to 137 times as much $PO_4^=$ than the crystalline forms (Gorbunov, et al., 1961).

As indicated in the periodic table iron and manganese are adjacent to each other. The different oxidation states of iron and manganese have the following ionic radii:

$$Mn^{2+} \quad = \quad 0.80 \ A°$$
$$Mn^{3+} \quad = \quad 0.66 \ A°$$
$$Fe^{2+} \quad = \quad 0.74 \ A°$$
$$Fe^{3+} \quad = \quad 0.64 \ A°$$

Resemblances in the ionic radii account for the occurrence of iron as well as manganese in the same complex. They can coordinate the same way, even though their stability may vary. Aluminum and silicon are the 13th and 14th elements respectively in the periodic table. Al^{3+} has an ionic radius of 0.50 A° and Si^{4+}, 0.43 A°. This closeness of ionic radii accounts for the possibility of aluminum displacing silicon in the silica tetrahedra (Heslop and Robinson, 1960).

Aluminum also forms many compounds with silica. Loughnan (1960)
cited that alumina in the amorphous form has great affinity for silica
to form aluminosilicate compounds.

The association of iron and manganese with aluminosilicate
compounds has been mentioned repeatedly in the literature. Fripiat
and Gastuche (1952) accounted for the accumulation of iron down the
profile as being the result of fixation on the aluminosilicate com-
pounds. Hemstock and Low (1953) showed the possibility of manganese
in associating itself with aluminosilicate compounds. Taylor et al.
(1964) studying concretions and black coatings on soil crumbs, con-
cluded that they were "micro crystalline" aggregates of manganese,
iron, aluminum and silicon with minute admixture of lithium, barium
and other alkaline earth metals.

All these findings indicate that dissolution of a component
of a soil would bring into solution the other components associated
with it. In fact, this procedure is more natural, since the elements
in the soil are not present as separate entities but interact with
one another.

The purpose of this study was to evaluate the extractability
of manganese, iron, aluminum and silicon by five extractants. They
were:

    1. 0.2 M acid ammonium oxalate -   pH 3.0

    2. 0.1 M sodium pyrophosphate -   pH 10.0

    3. 0.02 M disodiumEDTA   -   pH 4.5

    4. 0.1 M hydroxylamine hydro-
       chloride in 0.01 nitric acid   pH 2.0

5. 0.2 percent hydroquinone in
   neutral normal ammonium
   acetate   -   pH 7.0

Emphasis will be given to the distribution of manganese in the dif-

ferent soil profiles. Characterization of the different forms of these

elements is carried out to differentiate the different forms of man-

ganese, iron, aluminum and silicon extracted by these extractants in

reference to hydroxylamine hydrochloride.

MATERIAL AND METHODS

Six soils of varying texture and parent material were used
in this study. A more detailed description of the soils was outlined
in Chapter 1. One hundred mesh soil samples were used in each case.
The general procedure included shaking, centrifuging and filtering
the supernatant liquid. Aliquots of the supernatant solution were
analyzed for manganese, iron, aluminum and silicon using the atomic
absorption spectrophotometer. Dilution was done where necessary.
A soil extractant ratio of 1:50 was maintained in all cases. Different
shaking methods and speeds of centrifugation were used for the dif-
ferent extractants to coincide with conventional procedure. These
were:

i)   0.2 M acid ammonium oxalate - pH 3.0

These samples were shaken in 100 ml centrifuge tubes in the
dark for 4 hours. The mixture was then centrifuged at 2,500 rpm for
10 minutes.

ii)   0.1 M sodium pyrophosphate - pH 10.0

The shaking was done overnight in a temperature regulated box.
The samples were then centrifuged at 8,200 rpm for 10 minutes.

iii) 0.1 M hydroxylamine hydrochloride in 0.01 M nitric acid - pH 2.0

0.2 percent hydroquinone in neutral normal ammonium acetate,
and 0.02 M disodiumEDTA   -   pH 4.5

For these extractants the samples were shaken for 1 hour fol-
lowed by centrifugation at 2,500 rpm.

In all these procedures only a clear supernatant solution was analyzed with the atomic absorption spectrophotometer. Centrifugation was repeated if this was not achieved. The time interval between the sample extraction and processing through the atomic absorption spectrophotometer was also critical. Prolonged storage did lower the results. Samples were stored in the refrigerator, since this should reduce this effect.

Statistical analysis

Correlation studies between extractants and between soil properties and extractants were done using the IBM 360/7 computer. The INMSDC of the Triangular Regression Package (TRIP) program was used. This program can be obtained from the University of British Columbia Computing Centre's library.

RESULTS AND DISCUSSIONS

The total manganese present in the Tsawwassen horizons were
uniform for the Ah and C horozons, and decreased slightly in the IIC
horizon (Table 1.2). The portion of the total manganese extracted
by acid ammonium oxalate decreased almost linearly with depth (Figure
2.2). Greater amounts of the total manganese is in the crystalline
form with depth. The trend showed by the other extractants, excepting
sodium pyrophosphate, was almost the same. Hydroquinone extracted
3.8 percent of the total manganese in the Ah horizon but decreased to
0.9 percent in the C horizon. It remained at 0.9 percent for the IIC
horizon. There was a wide difference between the amount of manganese
in Ah and C horizons extracted by hydroxylamine hydrochloride and hydro-
quinone. The results became closer together in the IIC horizon. There
must be some differences in the forms of manganese extracted by these
two extractants, in the Ah and C horizons. The amounts extracted by
disodiumEDTA, sodium pyrophosphate and hydroxylamine hydrochloride in
the Ah horizon were very close together, however. Disparity in results
increased with depth. DisodiumEDTA and hydroxylamine hydrochloride
showed a decrease with depth, but sodium pyrophosphate showed an in-
crease from the C to IIC horizon (Figure 2.2). A few things can be
derived from these observations. The form of manganese extracted by
sodium pyrophosphate, disodiumEDTA, and hydroxylamine hydrochloride
appeared to be the same in the Ah horizon. This form decreased signi-
ficantly in the C horizon. The relatively higher result shown by

MANGANESE

Figure 2.2: Relative concentration of manganese extracted by the extractants in Tsawwassen, Blundell and Cloverale series.

disodiumEDTA and hydroxylamine hydrochloride in the C horizon could be due to their specific extracting ability. The high amount of sodium pyrophosphate manganese in the IIC horizon is perhaps from the trivalent form.

Manganese extracted from the Blundell by disodiumEDTA, hydroxylamine hydrochloride, hydroquinone, and acid ammonium oxalate showed the same trends in all horizons. Sodium pyrophosphate manganese increased significantly from an undetectable amount in the Ap horizon to the relatively high amount in the Bg and Cg horizons (Figure 2.2). The high concentration could be derived from the acid-insoluble humate portion (Figure 2.1). The pH of sodium pyrophosphate was more alkaline than any of the other extractants. The extra manganese could also be from the trivalent form (Dion et al., 1946).

There were great differences in results for the five extractants with the Cloverdale's Ah1 horizon (Figure 2.2). Hydroquinone extracted higher amounts of manganese than disodiumEDTA. No significant difference was observed between disodiumEDTA and sodium pyrophosphate extractions in Ah2 and Bg horizons.

The manganese extracted by sodium pyrophosphate, disodiumEDTA, hydroxylamine hydrochloride was again closely related in Grevell's Ah horizon and differed significantly in the C horizon (Figure 2.3). DisodiumEDTA showed almost the same result as hydroxylamine hydrochloride in the IIC horizon. Surprisingly sodium pyrophosphate manganese was lowest among the five extractants in C and IIC horizons (Figure 2.3). The manganese extracted by hydroquinone, disodiumEDTA, hydroxylamine

MANGANESE
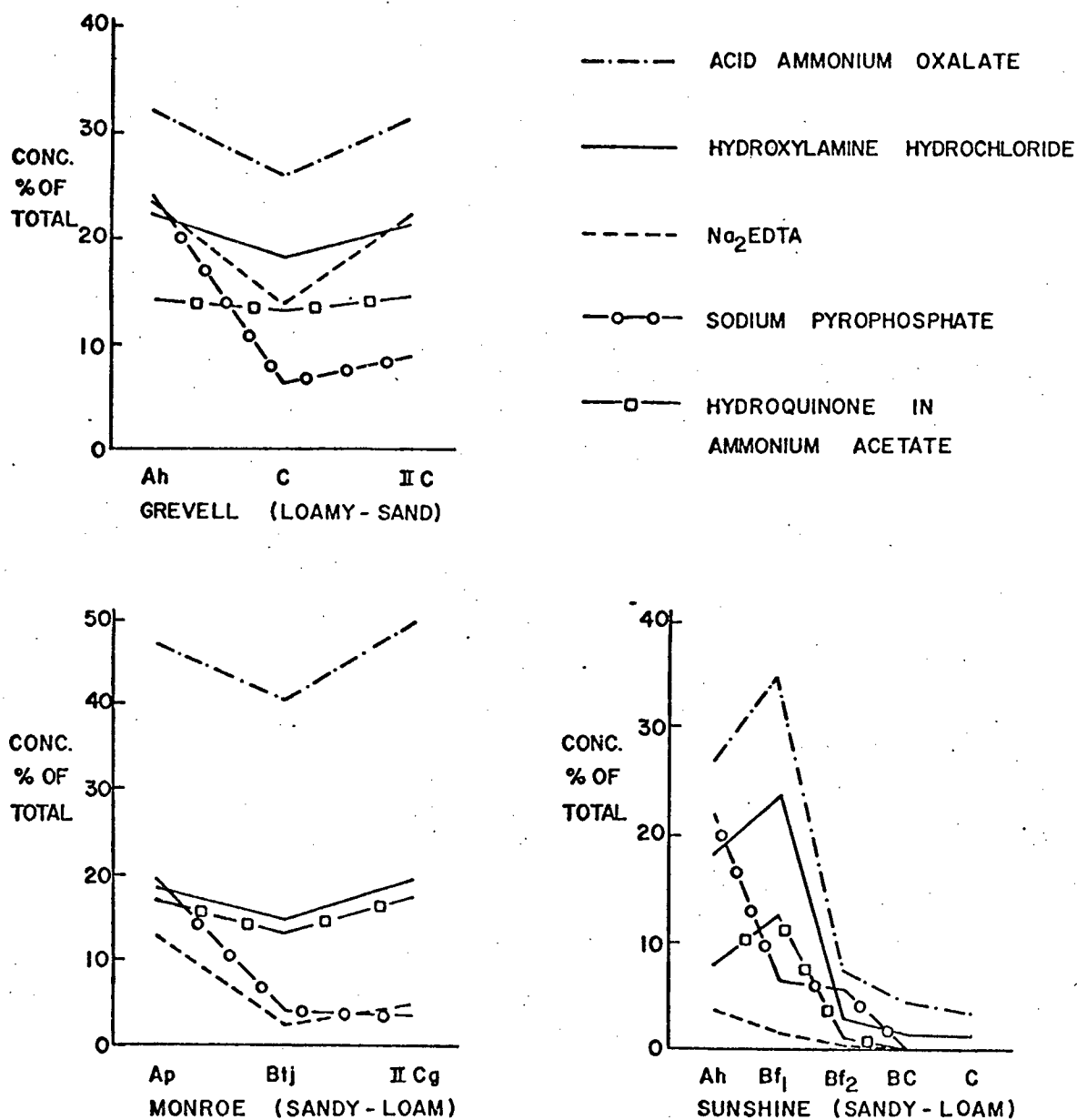
Figure 2.3: Relative concentration of manganese,
extracted by the extractants in Grevell,
Monroe and Sunshine series.

hydrochloride and acid ammonium oxalate is perhaps from the well-aged amorphous oxides.

Sunshine's acid ammonium oxalate, hydroxylamine hydrochloride, hydroquinone results showed similar trends for all horizons (Figure 2.3). Acid ammonium oxalate extracted the highest concentration of manganese followed by hydroxylamine hydrochloride and hydroquinone, respectively. Sodium pyrophosphate extracted relatively high amounts of manganese in the Ah horizon, but decreased significantly in the Bf1 horizon. Conversely the other three extractants showed an increase from the Ah to Bf1 horizon. DisodiumEDTA results were again lower than hydroquinone results in the Ah and Bf1 horizon. This observation further signifies that manganese is extracted in greater amounts by a reducing agent than just a chelating agent, especially in the lower horizons. The same distribution of manganese was shown by acid ammonium oxalate, hydroxylamine hydrochloride, disodiumEDTA and hydroquinone in the Monroe soil (Figure 2.3). Sodium pyrophosphate results indicate a distinct form of manganese is present.

Undetectable amounts of iron were extracted by hydroquinone for all samples. Acid ammonium oxalate extracted the greatest portion of iron in all Tsawwassen horizons (Figure 2.4). There was an increase in iron content from the Ah to the C horizon. The trend was the same for the other three extractants. Sodium pyrophosphate extracted higher amounts of iron than disodiumEDTA and hydroxylamine hydrochloride in the upper horizons but lower amounts in the IIC horizon. The organic matter content of the IIC horizon was very low. To assume that

IRON

Figure 2.4: Relative concentration of iron
extracted by the extractants in
Tsawwassen, Blundell and Cloverdale
series.

disodiumEDTA only extracts organically-bonded iron is not exactly valid. Sodium pyrophosphate presumably extracts the organically-complexed and the recent amorphous inorganic forms of iron. The observations therefore indicate that disodiumEDTA and hydroxylamine hydrochloride also extract iron from the aged amorphous inorganic portion, as well as from the organically complexed form.

There was a decrease in percentage of sodium pyrophosphate and acid ammonium oxalate iron with depth for Cloverdale samples (Figure 2.4). This result could be the result of the relatively increase in total concentration of iron from Ah2 to Cg horizon. DisodiumEDTA and hydroxylamine hydrochloride results were close together and almost uniform with depth. One significant difference between the Cloverdale and the coarse-textured samples (Tsawwassen and Grevell) was the relatively greater amount of iron extracted by sodium pyrophosphate in comparison to disodiumEDTA and hydroxylamine hydrochloride. One possible reason for this is the presence of greater concentration of organic and recent amorphous inorganic oxides in the Cloverdale soil. The fine texture of the Cloverdale samples reduced the rate of decomposition of the organic complex, and aging of the amorphous oxides.

Sodium pyrophosphate extracted higher amounts of iron in the Blundell Ap horizon than did acid ammonium oxalate (Figure 2.4). The acid-soluble humate portion may account for the extra iron extracted. Percentage of acid ammonium oxalate iron increased significantly from Ap to Bg horizons. The other extractants showed a decrease with depth. DisodiumEDTA, hydroxylamine hydrochloride and sodium pyrophosphate gave the same trend as in the Cloverdale samples.

The distribution of iron in the Grevell soil was the same for all extractants except sodium pyrophosphate (Figure 2.5). Sodium pyrophosphate extracted lower concentrations of iron in C and IIC horizons, in comparison with disodiumEDTA and hydroxylamine hydrochloride.

Hydroxylamine hydrochloride extracted higher amounts of iron than sodium pyrophosphate in the Monroe Ap horizon (Figure 2.5). The hydroxylamine hydrochloride result was significantly different from disodiumEDTA. This was contradictory to the other two fine-textured samples (Figure 2.4). In the latter, results for both extractants were very close. The concentration of the easily-reducible form of iron must be high in the Ap horizon. This coupled with hydroxylamine hydrochloride acid pH, brought into solution more iron than the other two mild extractants.

Figure 2.5 acid ammonium oxalate results for iron further showed that it is superior to any other extractant in detecting zones of iron accumulation in a Podzol.

Hydroquinone did not extract a detectable concentration of aluminum in the samples studied. The percentage of total aluminum extracted by sodium pyrophosphate decreased with depth in the Tsawwassen soil (Figure 2.6). The other extractants showed an initial increase from Ah to C horizons and then decreased in the IIC horizon. This observation corresponded to that of iron (Figure 2.4), another indication of the close association between the sesquioxides. The percentage of aluminum extracted by both sodium pyrophosphate and acid ammonium oxalate were very similar in the Cloverdale Ah1 and Ah2 horizons

IRON
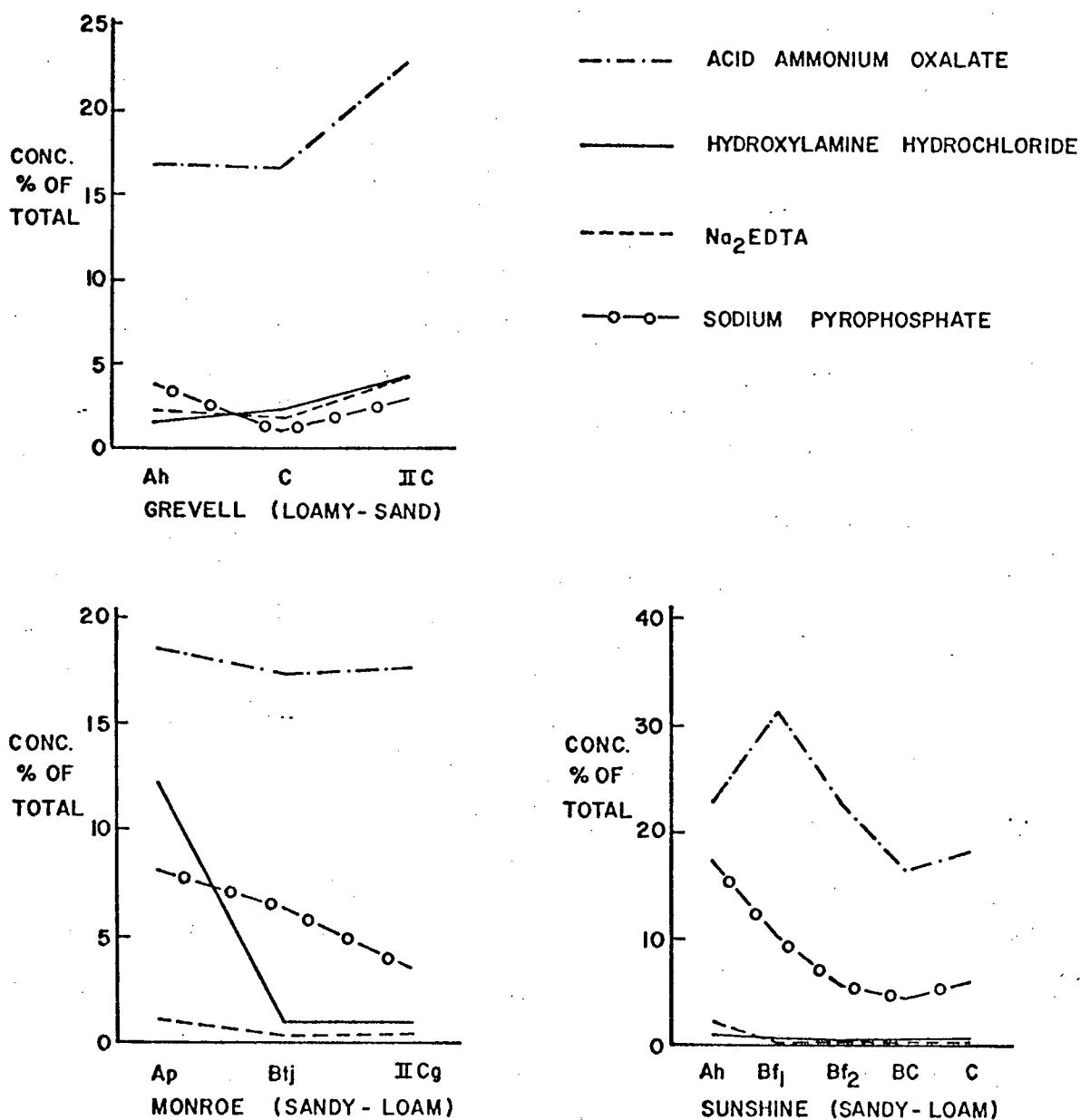
Figure 2.5: Relative concentration of iron
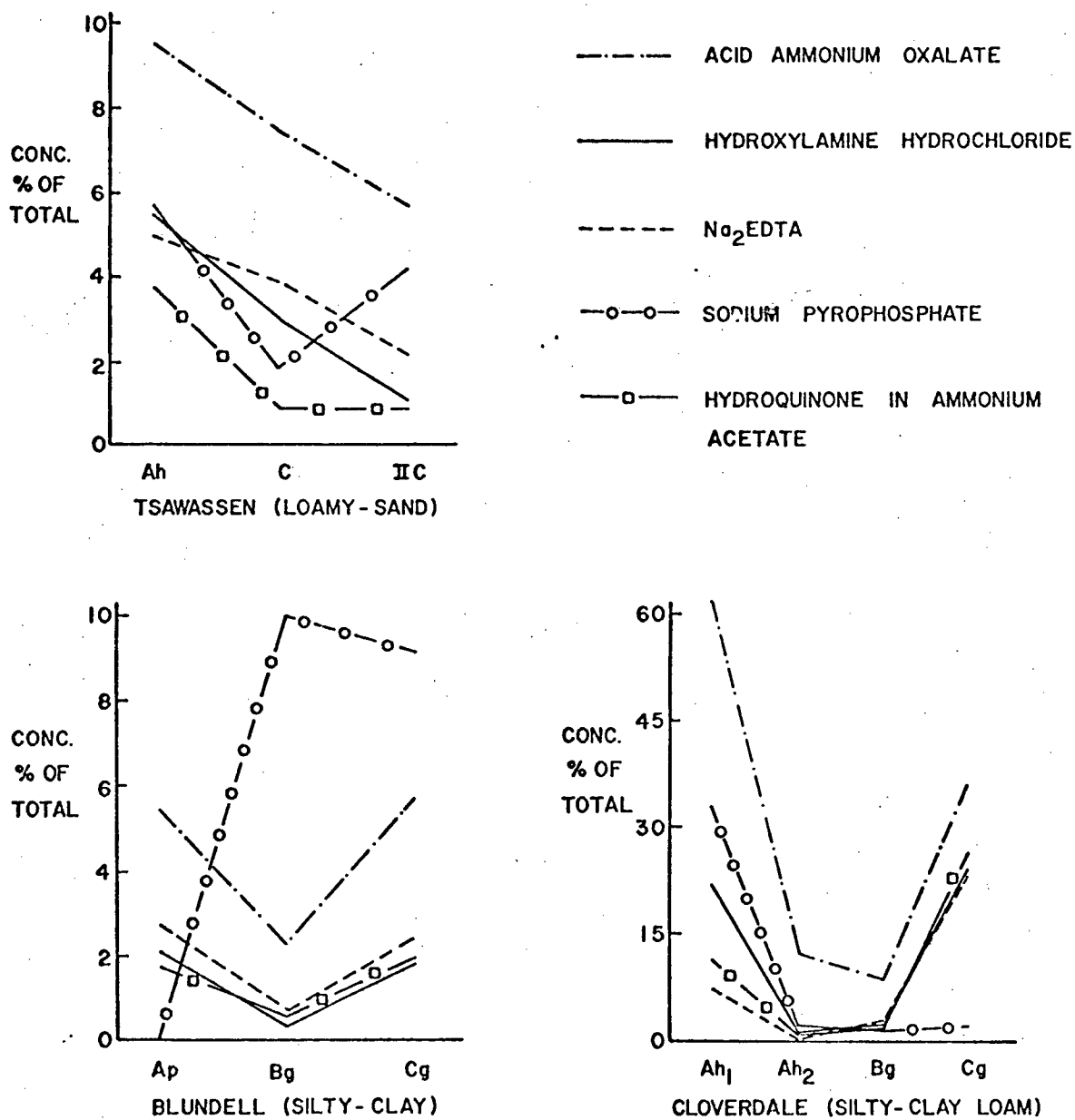extracted by the extractants in
Grevell, Monroe and Sunshine series.

ALUMINUM
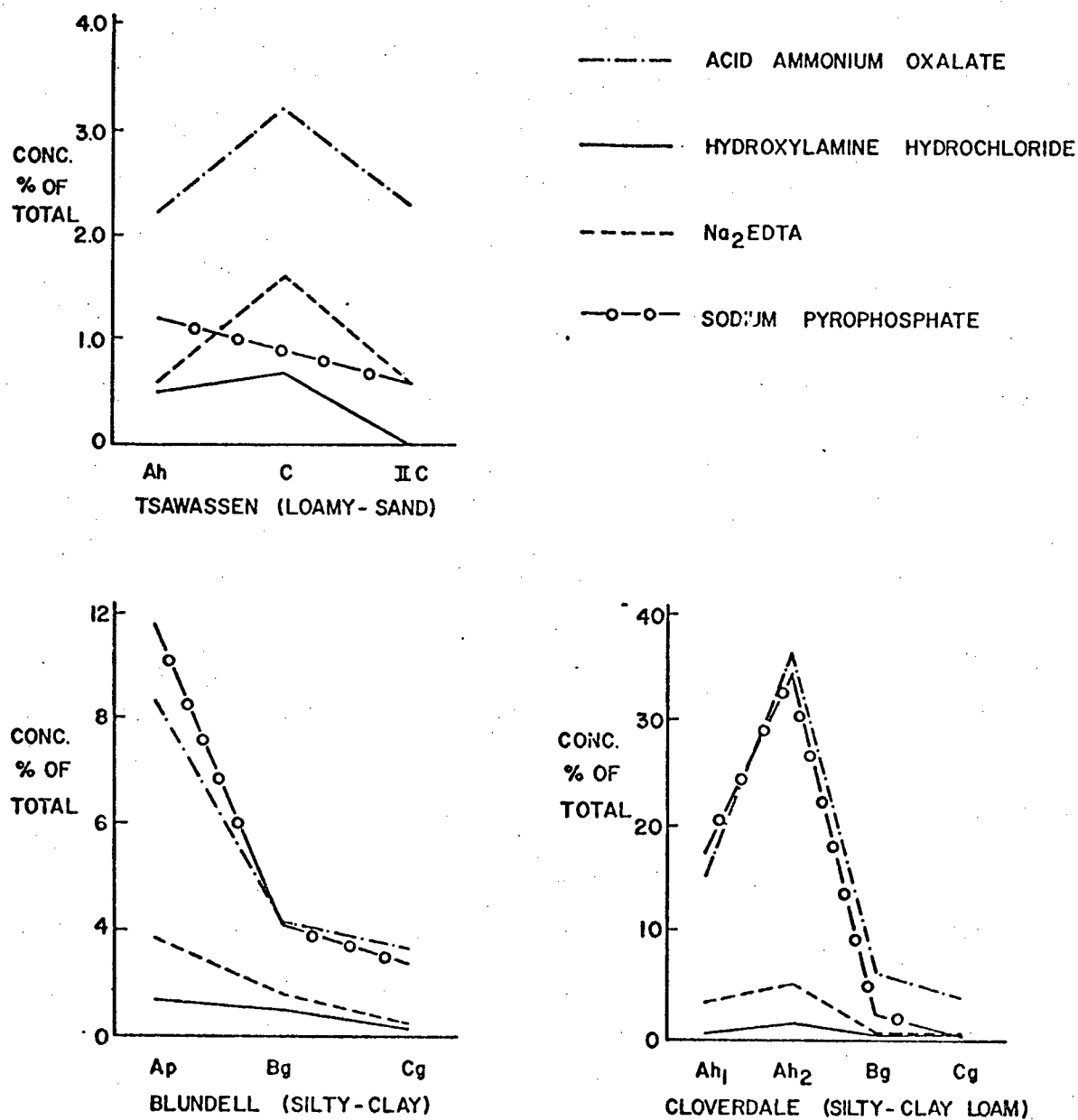
Figure 2.6: Relative concentration of aluminum extracted by the extractants in Tsawwassen, Blundell and Cloverdale series.

(Figure 2.6). Disparity increased in the Bg and Cg horizons. This
may be due to the variability in the aging process for the amorphous
oxides. The trend exhibited by the other two extractants was the same
except that the amount extracted was lower.

A higher percentage of aluminum was extracted by sodium pyro-
phosphate than acid ammonium oxalate in the Blundell Ap horizon (Figure
2.6), but the results remained close together in Bg and Cg horizons.
The Blundell soil has a high organic matter content. Most of the alu-
minum was organically complexed, as indicated by the higher amount of
aluminum extracted by disodiumEDTA, compared to hydroxylamine hydro-
chloride. The iron and aluminum results did not show similar trends
in the fine-textured soils as it did in the coarse-textured soils.
Iron assumes a more complex chemistry with the organic matter and col-
loidal material in the fine-textured soils.

Aluminum and iron results from the Grevell soil are shown in
Figures 2.7 and 2.5, and sodium pyrophosphate was again inconsistent
with the other extractants. The distribution of aluminum and iron in
the Sunshine series was consistent (Figure 2.7). Acid ammonium oxalate
extracted the highest percentage of aluminum for all Monroe's horizons
(Figure 2.7). This was followed by sodium pyrophosphate, disodiumEDTA
and hydroxylamine hydrochloride, consecutively.

Results reported for silicon are in concentration ppm rather
than percent of the total concentration. Only acid ammonium oxalate
and hydroxylamine hydrochloride were effective in extracting silicon.
Hydroxylamine hydrochloride extracted the lower amount of silicon.

ALUMINUM
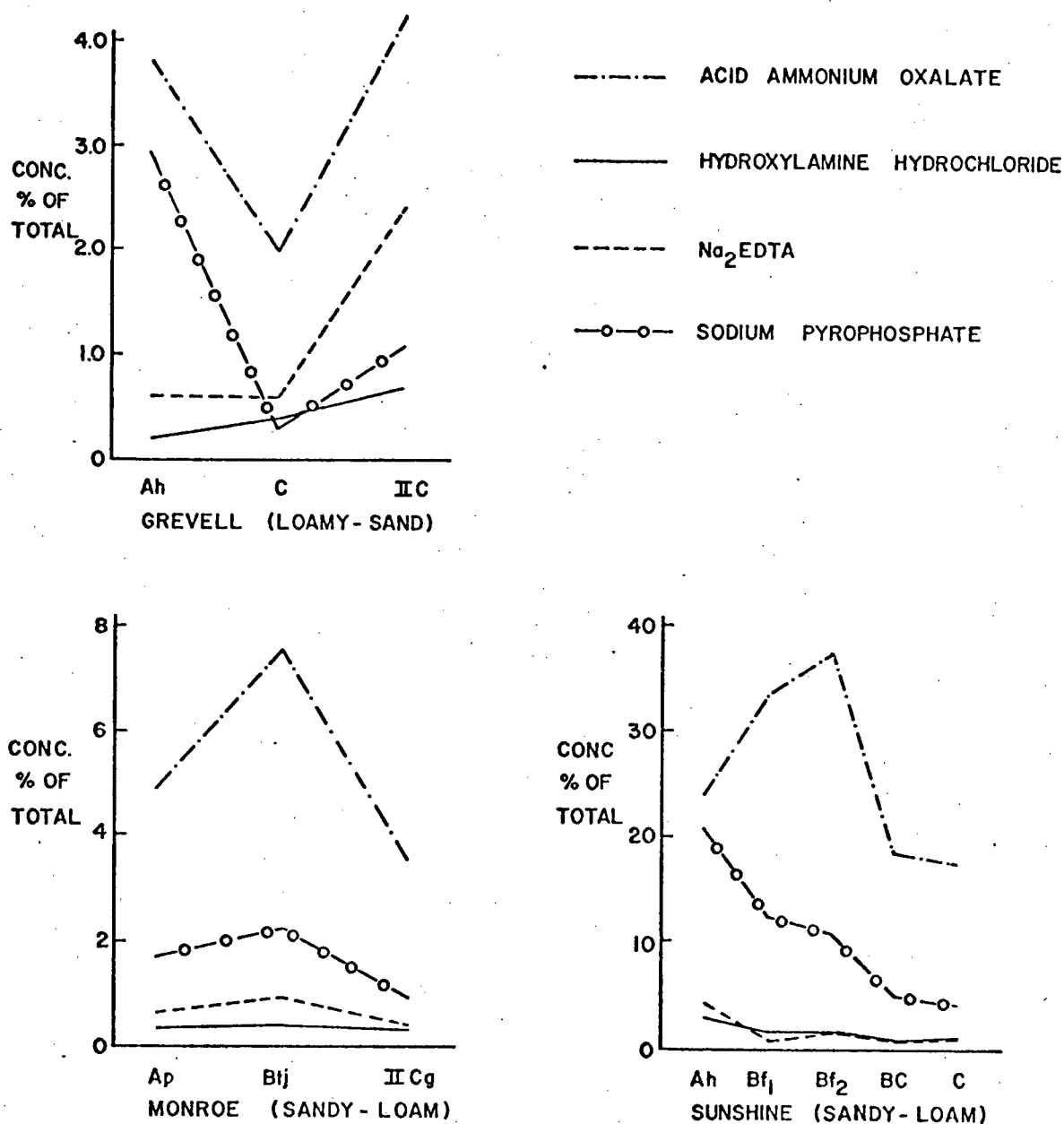
Figure 2.7: Relative concentration of aluminum
extracted by the extractants in
Grevell, Monroe and Sunshine series.

The concentration of silicon extracted by acid ammonium oxalate in Tsawwassen samples increased significantly from Ah to C horizon, and decreased again in IIC horizon. Similar trends were observed for hydroxylamine hydrochloride (Figure 2.8). No definite trends were observed in the other samples (Figure 2.8 and 2.9).

Correlation studies

Correlation among extractants and some of the properties of the soil are tabulated in Table 2.1. Manganese extracted by hydroxylamine hydrochloride showed very high correlation with acid ammonium oxalate and hydroquinone, being 0.9243 and 0.9250, respectively. This indicates that the manganese extracted by hydroxylamine hydrochloride and acid ammonium oxalate included the major portion extractable by hydroquinone. Of all the elements, iron and silicon showed the lowest correlation for all extractants. This is rather surprising since manganese should be the lowest, considering its greater variability in oxidation states. Aluminum results for all extractants, except sodium pyrophosphate, correlate very well. This might indicate a more homogeneous form of aluminum in the soil compared to the other elements.

The aluminum and iron extracted by sodium pyrophosphate were significantly related to the percent organic matter in the soil. This shows that only a minor portion of the sodium pyrophosphate, iron and aluminum are derived from the amorphous inorganic hydrous oxide gel. Aluminum extracted by hydroxylamine hydrochloride, disodiumEDTA and sodium pyrophosphate correlated well with the exchangeable aluminum
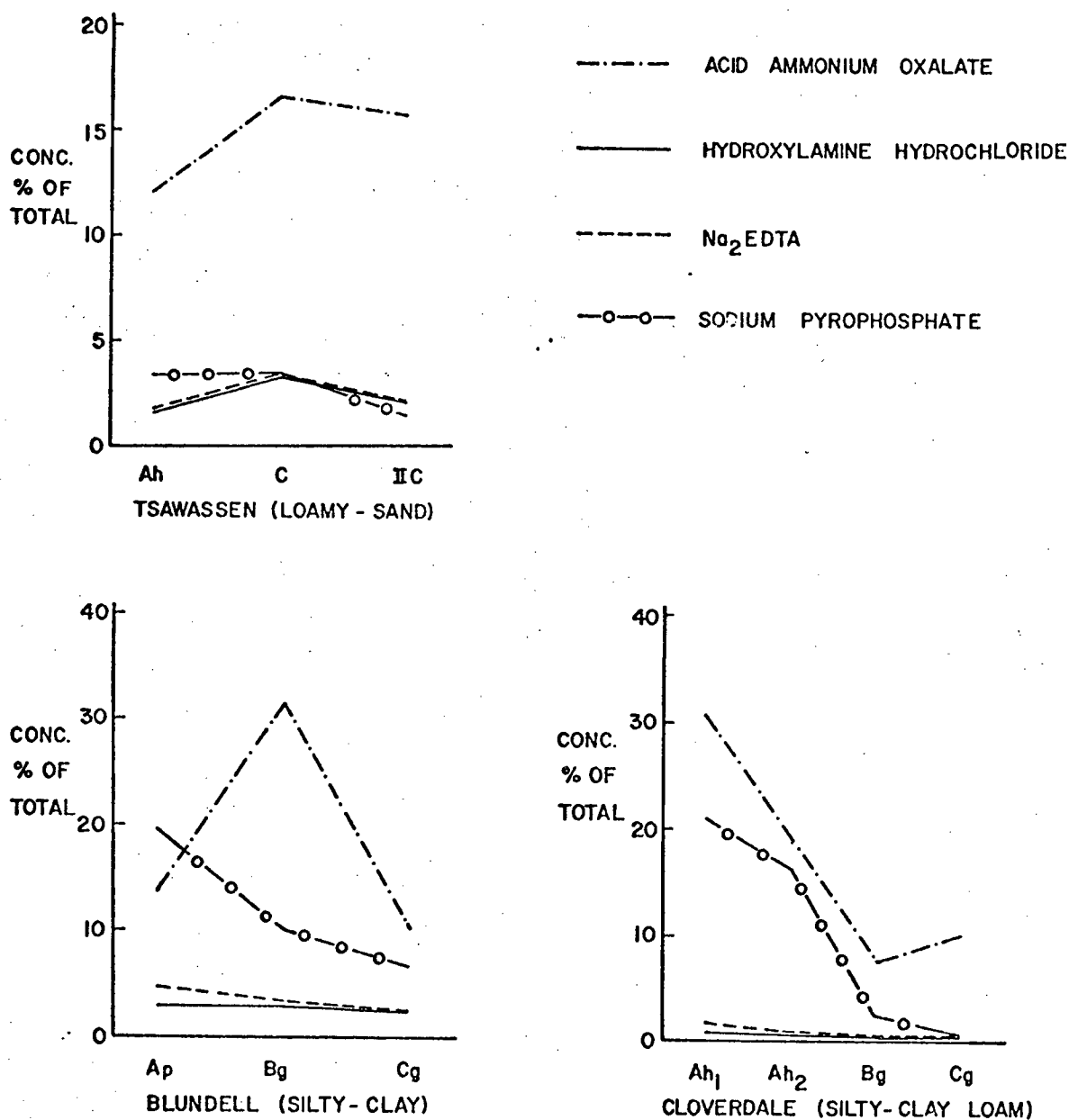
SILICON
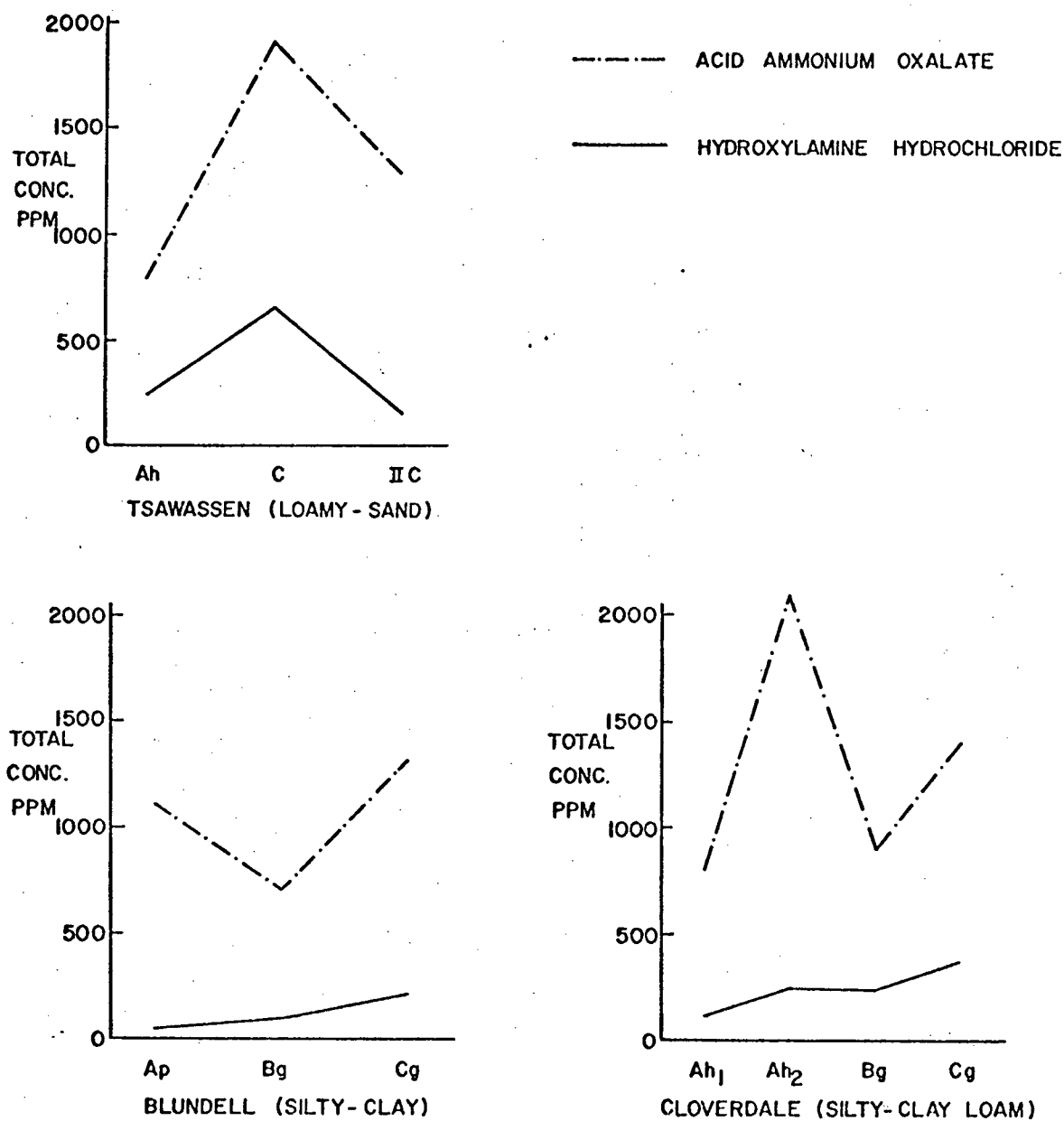
Figure 2.8: Relative concentration of silicon extracted by the extractants in Tsawwassen, Blundell and Cloverdale series.

SILICON
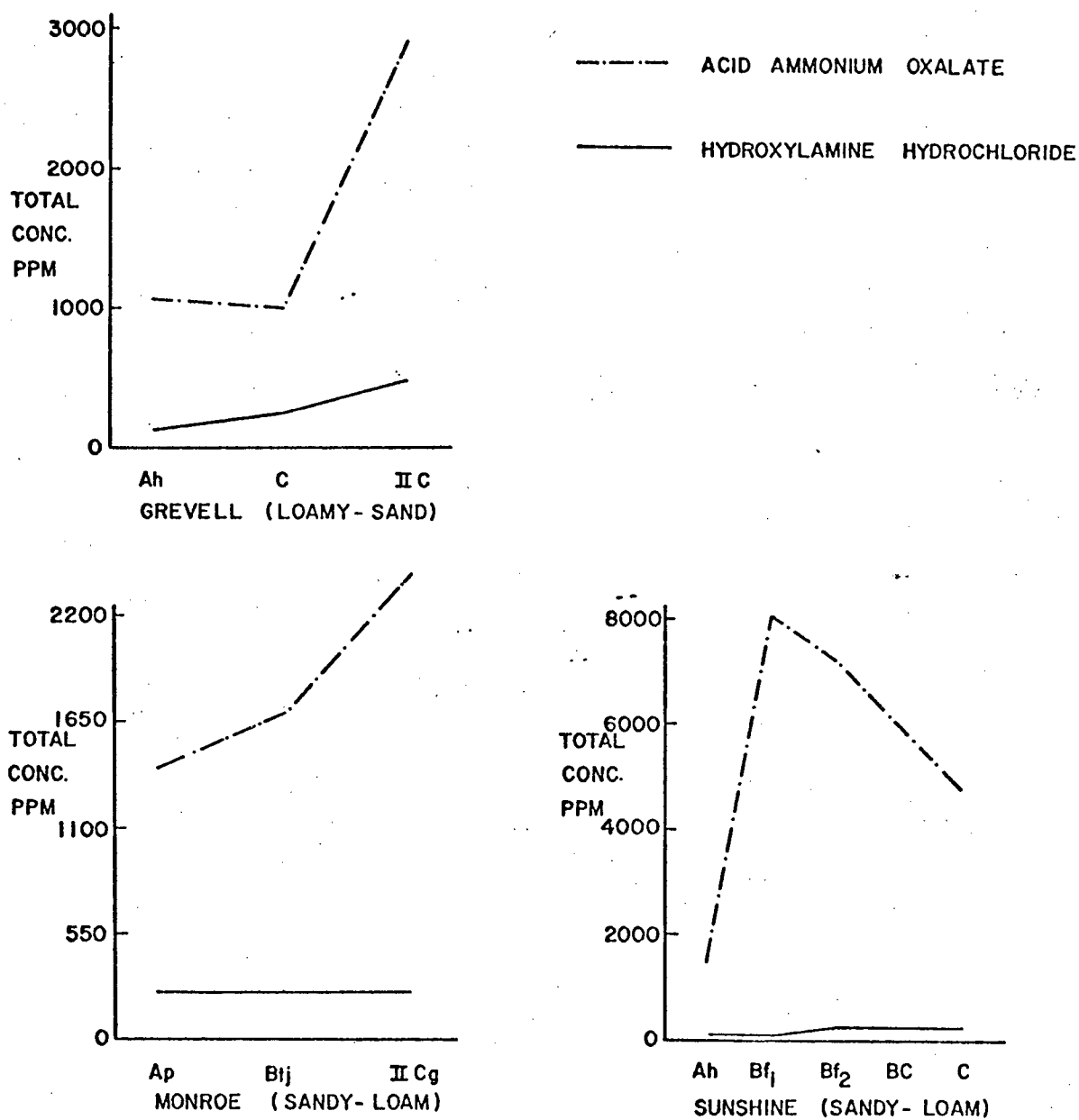
Figure 2.9: Relative concentration of silicon extracted by the extractants in Grevell, Monroe and Sunshine series.

Table 2.1

Correlation Matrix Among Extractants and Soil Properties

	AAO Mn	AAO Fe	AAO Al	AAO Si	HH Mn	HH Fe	HH Al	HH Si	EDTA Mn	EDTA Fe	EDTA Al	EDTA Si	SP Mn	SP Fe	SP Al	SP Si	pH (Dry)	pH (Wet)	Percent O.M.	Percent Moisture	C E C	Exch Mn	Exch Fe	Exch Al
Hydroquinone Mn	0.8107				0.9250				0.7995				0.4422				0.1062	-0.0558	-0.0016	0.1267	0.3160	0.4821		
Fe																								
Al																								
Si																								
Sodium Pyrophosphate Mn	0.7897				0.8585				0.8300								-0.442	-0.5199	0.7006	0.6019	0.8100	0.7781		
Fe		0.6774				0.7050				0.1359							-0.4593	-0.5865	0.7552	0.6681	0.8162		0.2487	
Al			0.7193				0.0881				0.3387						-0.2229	-0.2835	0.5937	0.2911	0.4591			0.5226
Si																								
Disodium EDTA Mn	0.4686				0.8855												0.2997	0.5140	-0.3591	-0.6402	-0.5134	0.7876		
Fe		0.2278				0.7233											-0.2500	-0.3012	0.6172	0.2314	0.6926		0.4147	
Al			0.7886				0.6631										-0.3355	-0.1635	0.2682	-0.0742	-0.0200			0.4167
Si				0.3845													0.0547	0.0652	-0.0658	-0.0205	-0.0086			0.6256
Hydroxylamine Hydrochloride Mn	0.9243																0.2586	0.4852	-0.5293	-0.4791	-0.4696	0.759		
Fe		0.2290															-0.6516	-0.4991	0.3940	0.2539	0.3927		0.0587	
Al			0.8059														-0.3181	-0.1668	0.1711	0.0471	-0.0090			0.5085
Si				0.0176													-0.0520	-0.1649	0.2150	0.1709	0.2567			
Acid Ammonium Oxalate Mn																	-0.2528	-0.0050	-0.2292	0.0767	-0.0870	0.5485		
Fe																	-0.4236	-0.3168	0.2029	0.4156	0.4077		-0.0197	
Al																	-0.4705	-0.5107	0.2535	0.4972	0.3982			0.3939
Si																	-0.0527	-0.1874	0.2891	0.2167	0.3190			

(AAO = Acid Ammonium Oxalate; HH = Hydroxylamine Hydrochloride; EDTA = Disodium EDTA; SP = Sodium Pyrophosphate)

results. Acid ammonium oxalate, however, showed a lower value. The importance of exchangeable aluminum has been stressed; indeed this was one of the bas.es for choosing hydroxylamine hydroxhloride as the extractant for the soil treatment studies.

CONCLUSION

Generally the trend exhibited by hydroxylamine hydrochloride, acid ammonium oxalate, disodiumEDTA and hydroquinone, for the distribution of each element through each soil was the same. Hydroquinone was only effective in extracting manganese as only trace amounts of the other elements were detected by atomic absorption analysis. This observation is contradictory to Chao's findings (1972). Hydroquinone does not have a strong complexing ability in addition to its reducing ability, whereas the other extractants all have strong complexing abilities.

Hydroxylamine hydrochloride, acid ammonium oxalate, disodiumEDTA and sodium pryophosphate were effective in extracting manganese, iron and aluminum. Only acid ammonium oxalate and hydroxylamine hydrochloride extracted silica in detectable amounts. These two extractants have a relatively low pH.

Sodium pyrophosphate manganese results were not consistent with the other extractants. For example, in the Blundell series, in contrast with the other extractants, sodium pyrophosphate manganese increased significantly from trace amounts in the Ap horizon, to larger amounts in the Bg horizon, and decreased again to a relatively low value in the Cg horizon (Figure 2.2). The other extractants showed a decrease in the Bg horizon followed by an increase in the Cg horizon. This inconsistency was also shown in the Cloverdale, Grevell, Monroe and Sunshine soils. The observation did not coincide with McKeague's conclusions (1967) that acid ammonium oxalate extracted both organic and

inorganic amorphous oxides while sodium pyrophosphate merely extracted the organic amorphous oxides. If one agrees with Bascomb's differentiations (Figure 2.1), then the extra manganese must be associated with the acid insoluble humate portion. Further investigations are necessary to explain this phenomenon.

The graphs also indicate the wide differences in disodiumEDTA and sodium pyrophosphate results for manganese, iron and aluminum. Both extractants are known for their chelating abilities. In all cases, except extractable manganese from the Blundell soil, sodium pyrophosphate extracted higher amounts than disodiumEDTA, for the surface horizons. The disparity in results in the lower horizons depended on the type and texture of the soil. These two factors controlled the types of oxides present in the soil. The higher results shown by sodium pyrophosphate could be due to inorganic amorphous hydrous oxide gels, and the acid insoluble humate portion. Sodium pyrophosphate is significantly more alkaline than disodiumEDTA. The superiority of disodiumEDTA as a chelating agent was shown in the lower horizons.

Hydroxylamine hydrochloride and disodiumEDTA results were in close agreement except for iron in the Monroe Ap horizon. This raised the question whether the form of manganese, iron and aluminum extracted by both extractants was the same.

Hydroxylamine hydrochloride being a stronger reducing agent than hydroquinone imparted this property to all manganese results, except for the Blundell Bg and Cg, and Cloverdale Cg horizons. The latter observation may be experimental error. Hydroxylamine hydrochloride is also known for its strong complexing ability. Therefore

to conclude that all the manganese extracted was that reduced from the higher oxides, is not justified.

Relatively hydroxylamine hydrochloride extracted all four elements with a fair degree of consistency. Hydroxylamine hydrochloride results also correlated well with the other extractants as well as with the exchangeable forms of manganese, iron and aluminum.

LITERATURE CITED

Bascomb, C. L. 1968. Distribution of pyrophosphate extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19: 251-268.

Beckwith, R. S. 1955. The use of CaNa2EDTA for the extraction of divalent manganese from soils. Aust. J. Agr. Res. 6: 685-691.

Chao, T. T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified $NH_2OH.HCl$. Soil Sci. Soc. Amer. Proc. 36: 764-8.

Dion, H. G., and Mann, P.J.G. 1946. Occurrences of trivalent manganese. q   J. Agr. Sci. 36: 239-245.

Fripiat, J. J. and Gastuche, M. C. 1952. Physico-chemical studies of clay surfaces. Combination of kaolinite with trivalent iron oxides. Inst. Nat. et Agron. Congo belge Pub. Ser. Sci. No. 54, 59.

Gorbunov, N. I., Dzyaevich, G. S., and Tunik, B. M. 1961. Methods of determining non-silicate amorphous and crystalline sesquioxides in soils and clays. Soviet Soil Sci. 11: 1252-59.

Heintze, S. G. 1957. Studies on soil manganese cycle. Soil Sci. 8: 287-300.

Hemstock, G. G. and Low, P. F. 1953. Mechanism responsible for the retention of manganese in the colloidal fraction of soil. Soil Sci. 96: 331-343.

Heslop, R. B. and Robinson, P. L. 1960. Inorganic chemistry. A guide to advanced study. Elsevier Publishing Co. Inc.

Kononova, M. M., Alexandrova, I. V., and Titova, N. A. 1964. Decomposition of silicates by organic substances in the soil. Soviet Soil Sci. 1005-14.

Latimer, W. M. 1938. The oxidation states of the elements and their potential in aqueous solutions. Prentice Hall Inc., New York, pp. 104 and 138.

Loughnan, F. C. 1969. Chemical weathering of the silicate minerals. Elsevier Publishing Co. Inc.

Mackenzie, R. C. and Meldau, R. 1959. The aging of sesquioxide gels. I. Iron oxide gels. Miner. Mag. 32: 153-165.

67

McKeague, J. A. and Day, J. H. 1966. Dithionite and oxalate extrac-
table iron and aluminum as aids in differentiating various classes
of soils. Can. J. Soil Sci. 46: 13-22.

_____. 1967. An evaluation of 0.1 M sodium pyrophosphate and pyro-
phosphate dithionite in comparison with oxalate as extractants
of the accumulation products in podzols and some other soils.
Can. J. Soil Sci. 47:95-99.

_____, Brydon, J. E., and Miles, N. M. 1971. Differentiation of
forms of extractable iron and aluminum in soils. Soil Sci. Soc.
Amer. Proc. 35:33-37.

Mitchell, B. D., Farmer, V. C. and McHardy, W. J. 1964. Amorphous
inorganic materials in soils. Adv. Agron. 16: 327-383.

Mortvedt, J. J., Giordano, P. M., and Lindsay, W. L. 1972. Micro-
nutrients in agriculture. Soil Sci. Soc. Amer. Publisher.

Murmann, R. K. 1964. Inorganic complex compounds. Reinhold Pub-
lishing Corp., New York.

Noller, C. R. 1968. Textbook of Organic Chemistry. 3rd Edition.
W. B. Saunders Co.

Oades, J. M. 1963. The nature and distribution of iron compounds
in soils. Soils and Fertilizers, XXVI: 69-80.

Safoq, E. Y. 1970. Manganese states of some Lower Fraser Valley soils
developed from alluvial and marine deposits. M.Sc. (Agric.) thesis,
Dept. of Soil Science, University of British Columbia.

Schnitzer, M. and Desjardin, J. G. 1962. Molecular and equivalent
weight of the organic matter of a podzol. Soil Sci. Soc. Amer.
Proc. 26: 362-365.

_____ and Skinner, S.I.M. 1966. Organo-metallic interactions in
soils: 5. Stability constants of Cu^{2+}-, Fe^{2+}-, and Zn^{2+}-fulvic
acid complexes. Soil Sci. 102: 361-5.

_____ and _____. 1967. Organo-metallic interactions in soils:
7. Stability constants of Pb^{2+}-, Ni^{2+}-, Mn^{2+}-, Co^{2+}-, Ca^{2+}-, and
Mg^{2+}-fulvic acid complexes. Soil Sci. 103: 247-52.

Taylor, R. M., McKenzie, R. M., and Norrish, K. 1964. The mineralogy
and chemistry of manganese in some Australian soils. Aust. J.
Soil Res. 2: 235-248.

Zulkifli, M. A. 1973. The extraction of soil manganese using $NH_2OH.HCl$.
B.Sc. (Agric.) thesis, Dept. of Soil Science, University of British
Columbia.

CHAPTER 3

SUCCESSIVE EXTRACTION OF MANGANESE, IRON, ALUMINUM
AND SILICON

INTRODUCTION

The previous chapter has established the effectiveness of
hydroxylamine hydrochloride in 0.01 M nitric acid, as an extracting
agent for manganese, iron, aluminum and silicon. Even though the mag-
nitude of the concentration extracted was lower than that of acid ammo-
nium oxalate, in terms of correlation with other extractants and pro-
perties of the soil, hydroxylamine hydrochloride was favoured. The
forms of manganese, iron, aluminum and silicon extracted by sodium
pyrophosphate and acid ammonium oxalate has been established by Bascomb
(1968). DisodiumEDTA as a strong chelating agent has been intensively
studied by Mortvedt et al. (1972). Safo (1970) investigated whether
"active" manganese (i.e. the sum of water-soluble, exchangeable and
easily-reducible manganese) was the same as EDTA extractable manganese.
He found that EDTA extracted more manganese after extraction of "active"
manganese. The dispersive action of EDTA should be taken into consi-
deration when analyzing these results. A reasonable assumption could
be made that disodiumEDTA extracts both the organically and inorganically
complexed elements, as well as those remaining free in solution and

69

on exchange sites. The magnitude of disodiumEDTA chelation varies according to the stability constants of the different elements with EDTA and with other components of the soil.

This part of the study investigated the relationship of manganese, iron, aluminum, and silicon extracted by hydroxylamine hydrochloride to the different categories of compounds (Figure 2.1). Results of this study will also give an idea of the reducibility of the different compounds in soil. Sequential analysis in which the soil was extracted with hydroxylamine hydrochloride followed by one of the other extractants, followed by hydroxylamine hydrochloride again were carried out. Comparison was made between the concentration extracted by the extractants and the concentration when sequential analysis was carried out. Comparisons were also made between manganese, iron, aluminum, and silicon extracted by hydroxylamine hydrochloride preceding the extractants and after the extractants.

The validity of the successive extraction procedure was also investigated in this study. Successive extraction of soils had been used in soil studies for a long time. The conventional exchangeable cations and cation exchange capacity determinations made use of successive extraction procedure. Safo (1970) did successive extraction for water soluble, exchangeable and easily-reducible manganese. In this case, distilled water, neutral ammonium acetate, and 0.2% hydroquinone in neutral normal ammonium acetate were used successively. The effect of the preceding extractant on the soil properties, cautioned against undertaking this procedure. Distilled water solubilizes many

compounds, disperses the soil aggregates to a minor extent and also affects the ionic equilibrium on the cation exchange sites. Neutral ammonium acetate also has the above mentioned effects on the soil but at a greater magnitude. Therefore, the extraction of easily-reducible manganese following water soluble and exchangeable extractions was on a modified soil system.

Visentin (1973) introduced a new procedure for the successive extraction of iron, aluminum and silicon from amorphous organic and inorganic oxides, and well crystallized oxides in soils. Sodium carbonate, sodium pyrophosphate, acid-ammonium oxalate and citrate di-thionite-bicarbonate extractions were carried out on the samples successively. A sodium acetate and sodium chloride mixture was used to bring the pH back to 5.0 between extractions. Changes brought about by the preceding extractant on the soil system depended on the strength and other properties of the extractant.

It is also hoped that these studies will unravel some of the modifications brought about by the different extractants. The results also give the chance for researchers to make a choice, whether to carry out successive extraction analysis or follow the arduous conventional procedures using fresh samples each time.

MATERIAL AND METHODS

Soils used in the study were derived from the Lower Fraser
Valley. (Chapter 1 of this thesis gives further details on the pro-
perties of the soil.) One gram of air-dried, 100 mesh samples were
used. A soil:extractant ratio of 1:50 was maintained at all times.
The general procedures involved shaking and centrifuging. Centrigu-
gation was repeated until a clear supernatant solution was obtained.
Different shaking and centrifuging procedures were carried out for
different extractants. (Chapter 2, page 45 for a more complete dis-
cussion.) The supernatant solutions were analyzed for manganese, iron,
aluminum and silicon using Atomic Absorption Spectrophotometry.

The following extractants were used in this study:

1. 0.2 M acid ammonium oxalate   pH 3.0

2. 0.1 M sodium pyrophosphate   pH 10.0

3. 0.02 M disodiumEDTA   pH 4.5

4. 0.1 M hydroxylamine hydrochloride in
    0.01 M nitric acid   pH 2.0

5. 0.2% hydroquinone in neutral normal ammonium
    acetate.

The following analysis was carried out:

i) Extraction, using fresh samples each time for acid ammonium
oxalate, sodium pyrophosphate, disodiumEDTA, hydroxylamine hydrochloride
and hydroquinone extractable manganese, iron, aluminum and silicon.

ii) Successive extraction of soil using hydroxylamine hydrochloride
then acid ammonium oxalate followed by hydroxylamine hydrochloride

again.   The samples were washed three times with isopropanol between extractions.

iii) Procedure ii) was repeated for sodium pyrophosphate, disodiumEDTA and hydroquinone.

RESULTS AND DISCUSSIONS

Comparison between sodium pyrophosphate and hydroxylamine hydrochloride followed by sodium pyrophosphate extractions

Hydroxylamine hydrochloride followed by sodium pyrophosphate brought more manganese into solution in all samples except the Blundell Bg and Cg horizons (Table 3.1). The same results could be seen for aluminum in all horizons. Sodium pyrophosphate by itself did not bring into solution significant amounts of silicon, but sodium pyrophosphate preceded by hydroxylamine hydrochloride extracted large amounts of silicon. In some cases the results were higher than shown by acid ammonium oxalate extraction (Table 3.3). Iron results showed that hydroxylamine hydrochloride followed by sodium pyrophosphate did not bring more into into solution for some of the surface horizons, i.e. Blundell Ap and Bg, Tsawwassen Ah, and Cloverdale Ah and Bf. These observations indicate that the forms of manganese, iron, aluminum and silicon extracted by hydroxylamine hydrochloride and sodium pyrophosphate were partially the same. Table 3.2 shows that for most soils the amount of sodium pyrophosphate manganese, extracted after hydroxylamine hydrochloride extraction, was lower except for the Blundell Ap; Cloverdale Bf, Cg1 and Cg2; and Monroe Btj and IICg horizons. The results were again lower for iron except for the Cloverdale Cg1 and Cg2 horizons. Aluminum results showed a subsequent increase for most of the fine-textured subsurface horizons. Silicon results for sodium pyrophosphate after hydroxylamine hydrochloride increased significantly from undetectable amounts. The increases might be due to the dispersion or

Table 3.1

Comparison Between Sodium Pyrophosphate Extraction
and a Combination of Hydroxylamine Hydrochloride
and Sodium Pyrophosphate Extractions

Soils	Sod. Pyro.				Hydroxy. Hydroch. and Sod. Pyro.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	-	4,500	6,500	-	30	3,320	7,158	3,699
Bg	30	4,500	2,000	-	19	4,384	3,891	5,931
Cg	38	3,000	1,500	-	31	3,150	2,733	4,238
Tsawwassen								
Ah	38	1,000	750	-	64	979	1,151	1,083
C	13	1,000	630	-	46	1,252	1,298	1,987
IIC	25	430	380	-	35	791	913	1,117
Grevell								
Ah	150	1,000	1,000	-	193	1,170	1,113	1,385
C	38	300	130	-	144	893	898	1,602
IIC	63	1,000	630	-	194	1,945	1,787	3,041
Cloverdale								
Ah	450	9,500	10,000	-	632	7,826	11,367	3,354
Bf	13	8,000	13,000	-	41	6,134	17,890	6,518
Cg1	8	1,500	1,500	-	37	1,805	3,438	2,571
Cg2	23	330	500	-	367	1,368	2,678	2,697
Monroe								
Ap	175	3,500	1,000	-	313	8,050	2,613	2,576
Btj	50	3,000	1,000	-	355	3,227	3,000	2,593
IICg	25	1,500	500	-	252	1,816	1,727	2,046

Table 3.2

Comparison Between Sodium Pyrophosphate Extraction
and Sodium Pyrophosphate after Hydroxylamine
Hydrochloride Extraction

Soils	Sod. Pyro.				Sod. Pyro. after Hydroxy. Hydroch.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	-	4,500	6,500	-	17	2,522	5,332	3,603
Bg	30	4,500	2,000	-	14	3,125	3,125	5,930
Cg	38	3,000	1,500	-	17	2,119	2,143	4,047
Tsawwassen								
Ah	38	1,000	750	-	18	519	519	902
C	13	1,000	630	-	14	209	162	1,156
IIC	25	430	380	-	12	170	194	728
Grevell								
Ah	150	1,000	1,000	-	26	740	645	1,194
C	38	300	130	-	24	291	316	1,214
IIC	63	1,000	630	-	27	479	479	1,875
Cloverdale								
Ah	450	9,500	10,000	-	212	7,155	9,123	2,314
Bf	13	8,000	13,000	-	32	5,764	15,130	6,323
Cg1	28	1,500	1,500	-	14	1,595	2,762	2,381
Cg2	23	330	500	-	48	1,011	2,071	2,408
Monroe								
Ap	175	3,500	1,000	-	90	2,806	1,886	2,300
Btj	50	3,000	1,000	-	102	2,755	2,130	2,315
IICg	25	1,500	500	-	72	1,397	1,148	1,746

Table 3.3

Comparison Between Acid Ammonium Oxalate Extraction
and a Combination of Hydroxylamine Hydrochloride
and Acid Ammonium Oxalate Extractions

	Acid Ammon. Ox.				Hydroxy. Hydroch. and Acid. Amm. Ox.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	16	3,900	5,300	1,100	15	3,450	4,800	875
Bg	7	13,950	2,050	700	?2	12,213	1,863	375
Cg	23	4,700	1,900	1,300	14	3,963	1,375	875
Tsawwassen								
Ah	63	3,600	1,350	800	50	2,488	1,125	750
C	50	5,150	2,100	1,900	44	3,925	1,750	1,625
IIC	34	4,550	1,450	1,300	24	2,950	1,275	1,125
Grevell								
Ah	203	4,500	1,300	1,100	202	3,650	1,013	875
C	149	4,400	1,000	1,000	139	2,613	662	750
IIC	222	7,700	2,400	2,900	208	4,600	1,775	1,625
Cloverdale								
Ah	846	13,750	8,750	800	732	11,075	8,025	625
Bf	69	9,250	13,750	2,100	40	6,288	10,763	1,625
Cg1	45	4,800	4,000	900	34	2,463	2,638	750
Cg2	355	6,100	3,300	1,400	249	762	575	725
Monroe								
Ap	419	8,000	2,800	1,400	390	5,750	2,413	1,250
Btj	490	8,200	3,400	1,700	403	5,425	2,275	1,125
IICg	367	7,050	1,950	2,200	338	5,525	1,488	1,125

breakdown of complexes brought about by hydroxylamine hydrochloride. This extractant, having a pH of 2.0, might also have attacked some of the semi-crystalline forms, exposing these forms to the subsequent treatment of sodium pyrophosphate. This greater exposure, as well as the alkaline pH of sodium pyrophosphate may account for the higher solubility of silicon in the samples.

The low pH of hydroxylamine hydrochloride may also weaken the soil aggregates (prevalent mostly in the subsurface horizons of fine-textured soils) and make it easy for the following sodium pyrophosphate dispersive action. The pH of both extractants, being at two extremes may have brought into solution both the acid soluble fulvic portion and the acid insoluble humate portion.

The reducing effect of hydroxylamine hydrochloride also destabilized some of the higher oxidation state complexes (generally the higher oxidation state has a higher stability constant). Lower stability constants of the complexes rendered them more susceptible to attack by sodium pyrophosphate.

Comparison between acid ammonium oxalate and hydroxylamine hydrochloride followed by acid ammonium oxalate

The combined effects of hydroxylamine hydrochloride and acid ammonium oxalate were expected to bring into solution greater amounts of manganese, iron, aluminum and silicon. Instead lower concentrations of these elements were extracted in comparison with extraction by acid ammonium oxalate alone (Table 3.3). The forms of manganese, iron, aluminum and silicon extracted by hydroxylamine hydrochloride may be

included in the acid ammonium oxalate extraction. This was further shown by the lower amounts of all the elements extracted by acid ammonium oxalate following hydroxylamine hydrochloride extraction (Table 3.4). The preceding hydroxylamine hydrochloride treatment could have reduced the higher oxides, not easily complexed by the oxalate ions. Theoretically, the ferric and manganic forms have higher stability constants with oxalate ions than the ferrous and manganous forms. The corresponding results for aluminum and silicon further signify the close association of these four elements in the soil. Further studies have to be done on this aspect, to explain more fully what was happening in the system.

Comparison between disodiumEDTA and hydroxylamine hydrochloride followed by disodiumEDTA

DisodiumEDTA extracted detectable amounts of silicon from the parent material of the coarse-textured samples only (Table 3.5). But disodiumEDTA preceded by hydroxylamine hydrochloride extracted a significant amount of silicon in all horizons (Table 3.6), despite the fact that the pH of disodiumEDTA was still in the acid range. The effect of pH of the extractant on the solubility of silicon could be seen by comparing the hydroxylamine hydrochloride and sodium pyrophosphate results (Table 3.1) with hydroxylamine hydrochloride and disodiumEDTA results (Table 3.5). The former showed higher results.

As mentioned earlier, hydroxylamine hydrochloride probably weakened the soil aggregates while at the same time reducing the higher oxides, which indirectly weakened the complexes in the soil. The

Table 3.4

Comparison Between Acid Ammonium Oxalate Extraction
and Acid Ammonium Oxalate after Hydroxylamine
Hydrochloride Extraction

Soils	Acid Ammon. Ox.				Acid Ammon. Ox. after Hydroxy. Hydroch.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	16	3,900	5,300	1,100	9	2,938	4,225	750
Bg	7	13,950	2,050	700	1	11,375	1,413	250
Cg	23	4,700	1,900	1,300	6	3,288	1,125	625
Tsawwassen								
Ah	63	3,600	1,350	800	14	2,188	788	500
C	50	5,150	2,100	1,900	24	3,388	1,288	1,000
IIC	34	4,550	1,450	1,300	18	2,825	1,263	1,000
Grevell								
Ah	203	4,500	1,300	1,100	61	3,525	938	750
C	149	4,400	1,000	1,000	34	2,450	450	500
IIC	222	7,700	2,400	2,900	58	3,950	1,388	1,125
Cloverdale								
Ah	846	13,750	8,750	800	431	10,750	7,563	500
Bf	69	9,250	13,750	2,100	33	6,063	10,125	1,375
Cg1	45	4,800	4,000	900	20	2,350	2,538	500
Cg2	355	6,100	3,300	1,400	16	588	425	250
Monroe								
Ap	419	8,000	2,800	1,400	225	5,563	2,250	1,000
Btj	490	8,200	3,400	1,700	224	5,275	2,088	875
IICg	367	7,050	1,950	2,200	195	5,363	1,325	875

Table 3.5

Comparison Between DisodiumEDTA Extraction
and a Combination of Hydroxylamine
Hydrochloride and DisodiumEDTA Extractions

Soils	Disod.EDTA				Hydroxy. Hydroch. and Disod.EDTA			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	8	1,300	1,500	-	12	2,000	2,188	224
Bg	2	1,500	750	-	3	2,783	1,487	804
Cg	10	1,000	300	-	13	2,053	901	949
Tsawwassen								
Ah	23	450	350	-	46	766	633	421
C	26	1,050	1,050	1,200	30	1,097	1,035	1,377
IIC	13	600	400	500	19	736	712	853
Grevell								
Ah	148	600	200	-	209	1,426	486	459
C	80	500	300	200	127	1,004	572	795
IIC	156	1,450	1,400	1,500	179	1,734	1,222	1,464
Cloverdale								
Ah	101	750	1,850	-	281	2,224	2,402	124
Bf	1	350	1,900	-	14	661	591	309
Cg1	14	200	550	-	28	451	1,143	358
Cg2	232	250	450	-	95	457	527	482
Monroe								
AP	114	500	350	-	194	780	783	336
Btj	27	200	400	-	322	739	1,010	447
IICg	34	200	200	-	233	808	684	504

dispersive action of disodiumEDTA further exposed a greater surface

area of soil for chelation. This was shown by the iron and aluminum

results (Table 3.6), when the extraction was preceded by hydroxylamine

hydrochloride. The results for manganese further showed that the active

manganese and disodiumEDTA extractable manganese were not from the

same forms in the soil.

Comparison between hydroquinone and hydroxylamine hydrochloride followed by hydroquinone

Hydroquinone merely extracted manganese and minute amounts of

aluminum (Table 3.7) in the Blundell Ap horizon and all the Cloverdale

horizons. Hydroquinone preceded by hydroxylamine hydrochloride removed

more manganese (Table 3.8). This further indicates that hydroxylamine

hydrochloride breaks down the soil aggregates and exposes the inner

surfaces to reduction by hydroquinone. Hydroquinone was not expected

to reduce more manganese since hydroxylamine hydrochloride is a stronger

reducing agent. Iron and aluminum results (Table 3.8) further stress

that hydroquinone is not a good extractant for iron and aluminum.

Astonishingly, hydroquinone preceded by hydroxylamine hydrochloride

brought considerable amounts of silicon into solution. The neutral

pH of hydroquinone could account for this observation. Solubility of

silica does increase above pH 7.0.

Hydroxylamine hydrochloride extraction after hydroxylamine hydrochloride and sodium pyrophosphate extractions

Hydroxylamine hydrochloride did not extract any further man-

ganese in the Blundell soil and the Cloverdale Bf and Cg1 horizons

Table 3.6

Comparison Between DisodiumEDTA Extraction
and DisodiumEDTA after Hydroxylamine
Hydrochloride Extraction

Soils	Disod.EDTA				Disod.EDTA after Hydroxy. Hydroch.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	8	1,300	1,500	-	2	1,473	1,709	174
Bg	2	1,500	750	-	1	1,981	1,083	705
Cg	10	1,000	300	-	3	1,371	703	740
Tsawwassen								
Ah	33	450	350	-	6	409	277	173
C	26	1,050	1,050	1,200	7	496	643	918
IIC	13	600	400	500	9	594	707	742
Grevell								
Ah	148	600	200	-	55	1,214	395	273
C	80	500	300	200	20	597	315	484
IIC	156	1,450	1,400	1,500	27	1,009	983	1,058
Cloverdale								
Ah	101	750	1,850	-	14	1,697	1,946	74
Bf	1	350	1,900	-	6	419	165	161
Cg1	14	200	550	-	12	330	1,034	135
Cg2	232	250	450	-	72	235	449	148
Monroe								
Ap	114	500	350	-	100	621	779	224
Btj	27	200	400	-	137	522	838	248
IICg	34	200	200	-	86	578	515	258

Table 3.7

Comparison Between Hydroquinone Extraction and
a Combination of Hydroxylamine Hydrochloride
and Hydroquinone Extractions

Soils	Hydroq.				Hydroxy. Hydroch. and Hydroq.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	5	-	13	-	10	659	988	42
Bg	2	-	-	-	1	1,096	600	87
Cg	8	-	-	-	10	821	433	319
Tsawwassen								
Ah	25	-	≤	-	44	386	512	294
C	6	-	-	-	27	853	956	933
IIC	5	-	-	-	12	179	35	134
Grevell								
Ah	100	-	≙	≙	159	271	225	250
C	75	-	-	-	119	528	437	476
IIC	103	-	-	-	172	1,026	842	983
Cloverdale								
Ah	156	-	4	-	429	595	1,117	-
Bf	3	-	9	-	8	278	1,256	130
Cg1	12	-	4	-	23	147	358	230
Cg2	261	-	5	-	348	281	267	415
Monroe								
Ap	152	-	-	-	233	360	286	339
Btj	159	-	-	-	276	347	569	386
IICg	127	-	-	-	197	231	275	280

Table 3.8

Comparison Between Hydroquinone Extraction and
Hydroquinone after Hydroxylamine
Hydrochloride Extraction

Soils	Hydroq.				Hydroq. after Hydroxy. Hydroch.			
	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)	Mn (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
Blundell								
Ap	5	-	13	-	1	25	13	-
Bg	2	-	-	-	-	13	-	44
Cg	8	-	-	-	-	5	-	91
Tsawwassen								
Ah	25	-	-	-	2	-	-	84
C	6	-	-	-	1	-	-	89
IIC	5	-	-	-	-	9	-	-
Grevell								
Ah	100	-	-	-	-	-	-	83
C	75	-	-	-	20	-	-	87
IIC	103	-	-	-	4	-	-	86
Cloverdale								
Ah	156	-	4	-	9	21	21	-
Bf	3	-	9	-	37	9	17	-
Cgl	12	-	4	-	-	-	-	46
Cg2	261	-	5	-	4	-	5	46
Monroe								
Ap	152	-	-	-	49	-	4	85
Btj	150	-	-	-	24	-	5	48
IICg	127	-	-	-	42	-	-	40

(Table 3.9). Very small amounts of manganese were extracted in the other samples. These results were surprising, considering the peptizing effect of sodium pyrophosphate which might have exposed greater surfaces of soil to attack by hydroxylamine hydrochloride. These low results might just be characteristic of manganese. Sodium pyrophosphate had been used to extract the trivalent form of manganese. Probably the major form of manganese extracted by hydroxylamine hydrochloride is the trivalent form.

Hydroxylamine hydrochloride extracted more iron, aluminum and silicon after sodium pyrophosphate extraction (Tables 3.10, 3.11, and 3.12). In the case of aluminum and silicon, hydroxylamine hydrochloride extracted a greater amount than hydroxylamine hydrochloride prior to sodium pyrophosphate extraction. These results showed the relative involvement of the different elements in soil aggregation - Aluminum and silicon > iron > manganese. Sodium pyrophosphate dispersive action was probably responsible for breaking the soil aggregates.

Hydroxylamine hydrochloride extraction after hydroxylamine hydrochloride and acid ammonium oxalate extractions

Greater amounts of aluminum and silicon were again extracted by hydroxylamine hydrochloride after hydroxylamine hydrochloride and acid ammonium oxalate extractions. These observations indicate that modifications were brought about by the acid ammonium oxalate treatment. The high amount of iron and manganese recorded were probably the residual of oxalate complexing. As mentioned earlier, oxalate does not complex with manganous and ferrous as strongly as it does with ferric and manganic ions.

Table 3.9

Comparison Between Hydroxylamine Hydrochloride
Extraction and Hydroxylamine Hydrochloride
Preceded by Hydroxylamine Hydrochloride
and the Different Extractants

Element: Manganese

Soils	Hydroxy. Hydroch.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Sod. Pyro.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Acid Amm. Ox.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Disod. EDTA	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Hydroq.
	Mn (ppm)	Mn (ppm)	Mn (ppm)	Mn (ppm)	Mn (ppm)
Blundell					
Ap	14	-	2	1	-
Bg	6	-	4	-	-
Cg	14	-	4	2	-
Tsawwassen					
Ah	46	3	6	6	-
C	32	8	9	7	1
IIC	23	4	9	5	1
Grevell					
Ah	166	7	18	14	8
C	120	8	14	10	4
IIC	167	17	19	14	6
Cloverdale					
Ah	419	13	105	51	30
Bf	10	-	9	2	2
Cg1	23	-	11	2	1
Cg2	319	9	93	10	18
Monroe					
Ap	224	27	24	42	15
Btj	253	32	38	43	28
IICg	179	38	21	34	20

Table 3.10

Comparison Between Hydroxylamine Hydrochloride
Extraction and Hydroxylamine Hydrochloride
Preceded by Hydroxylamine Hydrochloride
and the Different Extractants

Element: Iron

Soils	Hydroxy. Hydroch.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Sod. Pyro.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Acid Amm. Ox.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Disod. EDTA	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Hydroq.
	Fe (ppm)	Fe (ppm)	Fe (ppm)	Fe (ppm)	Fe (ppm)
Blundell					
Ap	798	144	500	631	106
Bg	1,259	137	1,588	956	283
Cg	1,028	552	625	843	151
Tsawwassen	461	190	875	501	
Ah	461	190	875	501	59
C	1,044	638	1,088	538	102
IIC	621	456	1,138	461	102
Grevell					
Ah	430	430	1,063	794	46
C	602	515	1,113	595	78
IIC	1,466	1,108	1,088	637	180
Cloverdale					
Ah	671	215	1,338	1,034	73
Bf	370	107	675	500	61
Cg1	209	114	1,300	312	41
Cg2	356	260	1,450	306	46
Monroe					
Ap	524	414	1,050	881	76
Btj	472	435	113	813	92
IICg	419	588	1,050	709	84

Table 3.11

Comparison Between Hydroxylamine Hydrochloride
Extraction and Hydroxylamine Hydrochloride
Preceded by Hydroxylamine Hydrochloride
and the Different Extractants

Element: Aluminum

Soils	Hydroxy. Hydroch.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Sod. Pyro.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Acid Amm. Ox.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Disod. EDTA	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Hydroq.
	Al (ppm)	Al (ppm)	Al (ppm)	Al (ppm)	Al (ppm)
Blundell					
Ap	479	509	825	338	55
Bg	404	483	350	69	48
Cg	199	771	463	117	105
Tsawwassen					
Ah	356	208	350	187	17
C	392	822	425	384	13
IIC	66	621	350	307	45
Grevell					
Ah	91	210	375	121	46
C	257	476	275	155	9
IIC	239	1,233	413	323	26
Cloverdale					
Ah	456	429	975	337	21
Bf	426	1,226	1,088	615	9
Cg1	109	1,190	913	324	9
Cg2	78	895	1,100	116	9
Monroe					
Ap	4	934	588	142	13
Btj	172	497	500	182	5
IICg	169	648	388	129	4

Table 3.12

Comparison Between Hydroxylamine Hydrochloride
Extraction and Hydroxylamine Hydrochloride
Preceded by Hydroxylamine Hydrochloride
and the Different Extractants

Element: Silicon

Soils	Hydroxy. Hydroch.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Sod. Pyro.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Acid Amm. Ox.	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Disod. EDTA	Hydroxy. Hydroch. after Hydroxy. Hydroch. and Hydroq.
	Si (ppm)	Si (ppm)	Si (ppm)	Si (ppm)	Si (ppm)
Blundell					
Ap	50	192	500	225	127
Bg	100	182	375	111	174
Cg	210	1,142	500	259	365
Tsawwassen					
Ah	248	181	375	124	84
C	459	924	375	285	89
IIC	111	874	375	236	90
Grevell					
Ah	186	191	375	260	125
C	311	680	375	235	43
IIC	406	1,749	500	394	128
Cloverdale					
Ah	50	179	375	75	86
Bf	148	487	375	161	44
Cg1	223	381	500	149	92
Cg2	334	482	750	124	92
Monroe					
Ap	112	276	625	224	85
Btj	199	370	500	274	48
IICg	246	399	500	246	80

Hydroxylamine hydrochloride extraction after hydroxylamine hydrochloride and disodiumEDTA extractions

More manganese, iron, aluminum and silicon were extracted by hydroxylamine hydrochloride following hydroxylamine hydrochloride and disodiumEDTA extractions (Tables 3.9, 3.10, 3.11, and 3.12). For some of the samples, greater amounts of iron, aluminum and silicon were extracted. DisodiumEDTA dispersed the soil aggregates. Its chelating ability released some of the elements from the organic and inorganic complexes. The elements were thus more prone to attack by the subsequent reducing agent.

Hydroxylamine hydrochloride extraction after hydroxylamine hydrochloride and hydroquinone extractions

Very little manganese was extracted by hydroxylamine hydrochloride (Table 3.11). In samples already low in easily-reducible manganese, non-detectable amounts were extracted by hydroxylamine hydrochloride. More aluminum, iron and silicon were extracted by hydroxylamine hydrochloride following the two extractions. The milder effect of hydroquinone on the soil properties was shown by the concentration of manganese, iron, aluminum and silicon extracted by hydroxylamine hydrochloride (Tables 3.9, 3.10, 3.11, and 3.12). The reducing ability of hydroquinone is inferior to that of hydroxylamine hydrochloride, but the hydroquinone extractant was made in ammonium acetate solution and the ammonium ions have a strong displacing ability. This displacing ability may account for the extra iron, silicon and aluminum extracted by hydroxylamine hydrochloride.

CONCLUSION

L   Looking back at Bascomb's category of compounds:

	Inorganic		Organic	
Well-crystallized	Amorphous oxides "aged"	Amorphous oxides "gel"	Acid-soluble "Fulvate"	Acid-insoluble "Humate"

Both the lower and higher oxides of iron and manganese are present in the
these categories. The proportion of each oxidation state in each category is dependent on the redox potential of the system, relative aging and the stability constant of the oxides. The redox potential of a metal ion is modified once it is complexed. Generally, the higher oxides as well as the higher valenced elements have a higher stability constant than the lower valence form.

The extractant used in this study did not affect the well-crystallized forms of the oxides. Hydroxylamine hydrochloride extracted manganese and iron from the various portions by reducing and complexing. Since aluminummand silicon are not reducible it is safe to assume that they are complexed by hydroxylamine hydrochloride. Aluminum and silicon could have also been released as a consequence of manganese and iron reduction. The extent of reduction of these complexed elements by hydroxylaminehhydrochloride depends on the redox potential and the stability constant.

The strength, pH and other chemical properties of these reagents are important for their effects on the soil. Acid ammonium oxalate,

hydroxylamine hydrochloride, and sodium pyrophosphate have relatively more drastic effects than disodiumEDTA and hydroquinone. The concentration of elements extracted by hydroxylamine hydrochloride following the other extractants is dependent on the forms extracted. Complexing and chelating reagents often reduce the stability constant of organically-complexed elements and the higher oxides making them more susceptible to the following hydroxylamine hydrochloride reduction. Reducing agents are also known to reduce the stability constant of complexes.

Even though 100 mesh samples were used in this study, the extent of soil aggregation was still prominent enough to affect the results. Dispersion of these aggregates by the extractants often showed a significant increase in values. Therefore the concentration of elements extracted are dependent among other things on the extent of aggregation in the sample. This factor is particularly important in manganese, iron, aluminum and silicon analysis, since they are cementing agents in soils either in the form of sesquioxides or organic complexes.

It is a question of objectives that determine whether a researcher should carry out successive extraction analysis, or the arduous conventional procedure of using fresh samples for the different extractants. If the objective is to determine quantitatively the plant availability index, then successive extraction procedure is not recommended. Successive extraction procedures are warranted, however, for qualitative observations. This study indicated that the changes in the soil system affected by the preceding extractant did affect the results.

LITERATURE CITED

Bascomb, C. L. 1968. Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. J. Soil Sci. 19: 251-268.

Mortvedt, J. J., Giordano, P. M., and Lindsay, W. L. 1972. Micronutrients in agriculture. Soil Sci. Soc. Amer. Proc. Publishers.

Safo, E. Y. 1970. Manganese status of some Lower Fraser Valley soils developed from alluvial and marine deposits. M.Sc. (Agric.) thesis, Dept. of Soil Science, University of British Columbia.

Visentin, G. R. 1973. Aspects of inorganic amorphous system of humo-ferric podzols of the Lower Mainland of B.C. M.Sc. (Agric.) thesis, Dept. of Soil Science, University of British Columbia.

CHAPTER 4

THE EFFECT OF SOIL PRETREATMENTS ON THE EXTRACTION

OF MANGANESE, IRON, ALUMINUM, AND SILICON USING

HYDROXYLAMINE HYDROCHLORIDE AS THE EXTRACTANT

INTRODUCTION

Soil samples from the field are often treated and stored prior

to extraction. The treatment and storage duration and condition affect

extractability of the elements. Fujimoto and Sherman (1945) working

with Hawaiian soils, found that exchangeable manganese increased upon

air-drying. Oven-drying and steam-sterilization lead to an increase

from a few parts per million to approximately three thousand parts per

million. The release was found to be proportional to the duration and

temperature of incubation. Subsequent moistening of the soil to the

field capacity decreased the exchangeable manganese. They postulated

that dehydration of the hydrated manganese complex $[(MnO)_x(MnO_2)_y(H_2O)_z]$

causes the instability of the structure leading to the release of the

manganese oxide for the exchange sites. Later (1948) they also found

that steam sterilization increased the exchangeable and water-soluble

manganese but decreases the easily-reducible form. Christenson and

Toth (1950) suggested that products of organic matter decomposition

which increase with moisture content, form a strong complex with manganese.

95

Heintze and Mann (1947) showed that polycarboxylic and hydroxycarboxylic acids are responsible for complexing manganous and manganic ions.

An increase of up to six hundred percent was observed when air-dried samples were analyzed after being stored for one year (Boken, 1958). The increase was inversely proportional to the organic matter content. Hammes and Berger (1960) contradicted previous findings by showing that oxidation of organic matter upon air-drying released the organically-complexed manganese. It seems that there are two stages involved in the effect of organic matter on the extractability of manganese. At the early stage, products of decomposition of organic matter complexed with manganese. Further exposure will destroy these organic acids releasing the complexed manganese.

Nishita and Haug (1971) examined the changes in physical and chemical properties of the soil as a result of heating at different temperatures. They found that increased aggregation, due to calcination by iron oxides and aluminosilicates, takes place above 300°C. No changes were observed below this temperature. The cation exchange capacity was found to decrease after heating above 100°C. This reduction coincides with increased aggregation, dehydration and breakdown of the mineral crystal lattice. The pH of the soil decreased to a minimum as the temperature is increased to 200°C, and increased again with a further rise in temperature. The initial reduction in pH was due to oxidation of certain elements, dehydration of colloids and a relative increase of organic compounds. The ensuing increase in pH was due to the formation of oxides of many compounds. Nishita and Haug also investigated the

water and ammonium acetate extractable forms of manganese, iron, cobalt, chromium and copper as a result of incubation at temperatures of 100°C, 200°C, 300°C, 400°C, 500°C, 800°C, and 1,000°C. Incubating at 200°C lead to an increase in both extractable forms of most elements. At this temperature ashing of the soil samples and dehydration of the hydrated complexes may have taken place. Release from these complexes could therefore account for the marked increase at this temperature. The authors also realized the heterogeneity of the soil, because no definite conclusion could be derived from the study.

Manganese and iron are highly affected by the redox potential of the soil. Microbial activity, organic matter and moisture content are some of the factors that affect the redox potential. Meek et al. (1968) indicated that the combination of flooding, organic matter and high temperature increased the level of solubilized iron and manganese. Patrick and Turner (1968) found that conversion of easily-reducible manganese into exchangeable and water soluble forms is intense below 400 mV. Residual manganese (highly-crystallized) is not affected by redox potential. These findings stressed further the importance of easily-reducible forms, also known as the amorphous oxides.

The effect of soil treatments on aluminum and silicon was not mentioned in these studies, despite the occurrence of all four elements simultaneously. Little work has been done on the easily-reducible forms of manganese with different treatments. These forms are more reactive and should be more sensitive to changes.

The objective of this study was to investigate the extractability of manganese, iron, aluminum and silicon by hydroxylamine hydrochloride

with special emphasis on manganese. The different treatments were designed to evaluate the differences between in-situ extraction and the conventional air-drying procedures. An attempt was also made to see the effect of air-drying at two durations, one week and four months. Oven-drying at 50°C and 100°C were carried out to see the effect of enhanced drying of moist samples. The freezing treatment was carried out to show the effect of getting samples from the field in the winter and cold seasons. It is also hoped that freezing treatments together with the air-drying treatments will give some indication of the seasonal fluctuations on the extractability of manganese, iron, aluminum and silicon.

The experiments were designed to observe quantitatively the effect of different treatments on samples prior to extraction. The changes in physical and chemical properties of the soil brought about by the different treatments are realized. No attempt was made to determine what specific changes in physical and chemical properties lead to the quantitative observations. Hopefully this study will lay the basic ground work for future studies, and will also caution soil researchers about the variation in results obtained when no uniform sampling procedures is carried out.

MATERIALS AND METHODS

Five soil series from the Lower Fraser Valley were used in this study. They were Tsawwassen, Grevell, Blundell, Cloverdale and Sunshine. The general properties of these soils are given in Chapter 1. For a more detailed description of these soils refer to Luttmerding and Sprout (1967).

The general procedure involved shaking the soil for one hour in 0.1 M hydroxylamine hydrochloride in 0.01 M nitric acid, centrifuging at 2,500 rpm and filtering the supernatant solution. Centrifugation was repeated until the supernatant solution remained clear. The extract was made up to a volume of 250 ml and an aliquot was analyzed by the Perkin Elmer 306 atomic absorption spectrophotometer for manganese, iron, aluminum and silicon. A soil:extractant ratio of 1:20 was maintained for each extraction. Results were recorded, based on oven-dried soil weights.

Treatment of the soil prior to the general procedure involved:

A. <u>In-situ</u> extraction

Tared 100 ml of 0.1 M hydroxylamine hydrochloride solution in 250 ml centrifuge bottles were taken to the field. Approximately 10 gm of soil was sampled from the site, with minimum exposure to the atmosphere. This was done using a soil corer. Five sets of sample were taken from each horizon. A duration of five hours was allowed before carrying out the general procedure, so that the <u>in-situ</u> extraction was uniform for all the sites. The exact weight of the soils used was calculated by difference.

B. <u>Oven-drying at 50°C for one week</u>

This treatment was carried out on glass plates. Samples taken for the general procedure were not in contact with the glass plate to avoid silicon contamination. To ensure uniform heating of the samples, a thin layer of soil was used. Large aggregates of soil were broken up with a wooden roller.

C. <u>Oven-drying at 100°C for one week</u>

Procedure B was used but at the higher temperature.

D. <u>Air-drying for one week</u>

Air-drying was done on brown paper. Large aggregates of soil were crushed with a wooden roller.

E. <u>Storing moist in plastic containers for three months</u>

Soils in the field moist condition were used for this purpose. The plastic bags were sealed to reduce aeration, and loss of moisture from the soil.

F. <u>Air-drying for four months</u>

Pretreatment D was carried out except for a longer duration.

G. <u>Frozen for one month</u>

Field moist samples were frozen in the freezer. The samples were thawed after one month and analyzed.

<u>Statistical analysis</u>

Significant test for the interaction between treatments and horizons were carried out using computer. The program used was BMDIOV-General Linear hypothesis (No. 2) developed at the Health Sciences

Computing Facility, University of California, Los Angeles (1973).

This program can be obtained from the University of British Columbia

Computing Centre's Library. FLSD values were then calculated for the

different elements. The FLSD procedure for detecting the significant

differences between means was recommended by Carmer, S. G. et al. (1971)

The means and FLSD value for each element were tabulated in the Appendix.

RESULTS AND DISCUSSION

Tsawwassen series

The manganese results for the different pretreatments varied much more in the Ah horizon than in the C horizon (Figure 4.1). For the Ah horizon sampless, air-dried for one week showed the lowest value and those stored moist in plastic containers gave the highest extractable manganese. Storing in plastic containers may have reduced the higher oxides of manganese and made them more easily-reducible by hydroxylamine hydrochloride. Samples frozen for one month and the in-situ extractions also gave relatively high values. This observation was consistent with the C horizon. The higher results for the in-situ extraction was due to a reduced possibility for the manganese compounds to undergo further oxidation upon air-drying. Freezing the soil may have helped to break the soil aggregates, causing greater exposure of the soil particles to reduction. The other treatments did not differ significantly in their results. Higher results for in-situ extractions than the air-drying sampling preparation should caution workers on the use of conventional sampling procedures for measuring the plant availability indices.

The trend showed by Tsawwassen Ah and C horizons for iron was the same as manganese (Figure 4.2). Samples stored moist in plastic containers showed the highest results, followed by in-situ extraction and those frozen for one month. Air-drying for one week gave higher results than air-drying for four months, and oven-drying at 50°C. Air-drying for four months may have oxidized more iron into the "aged"
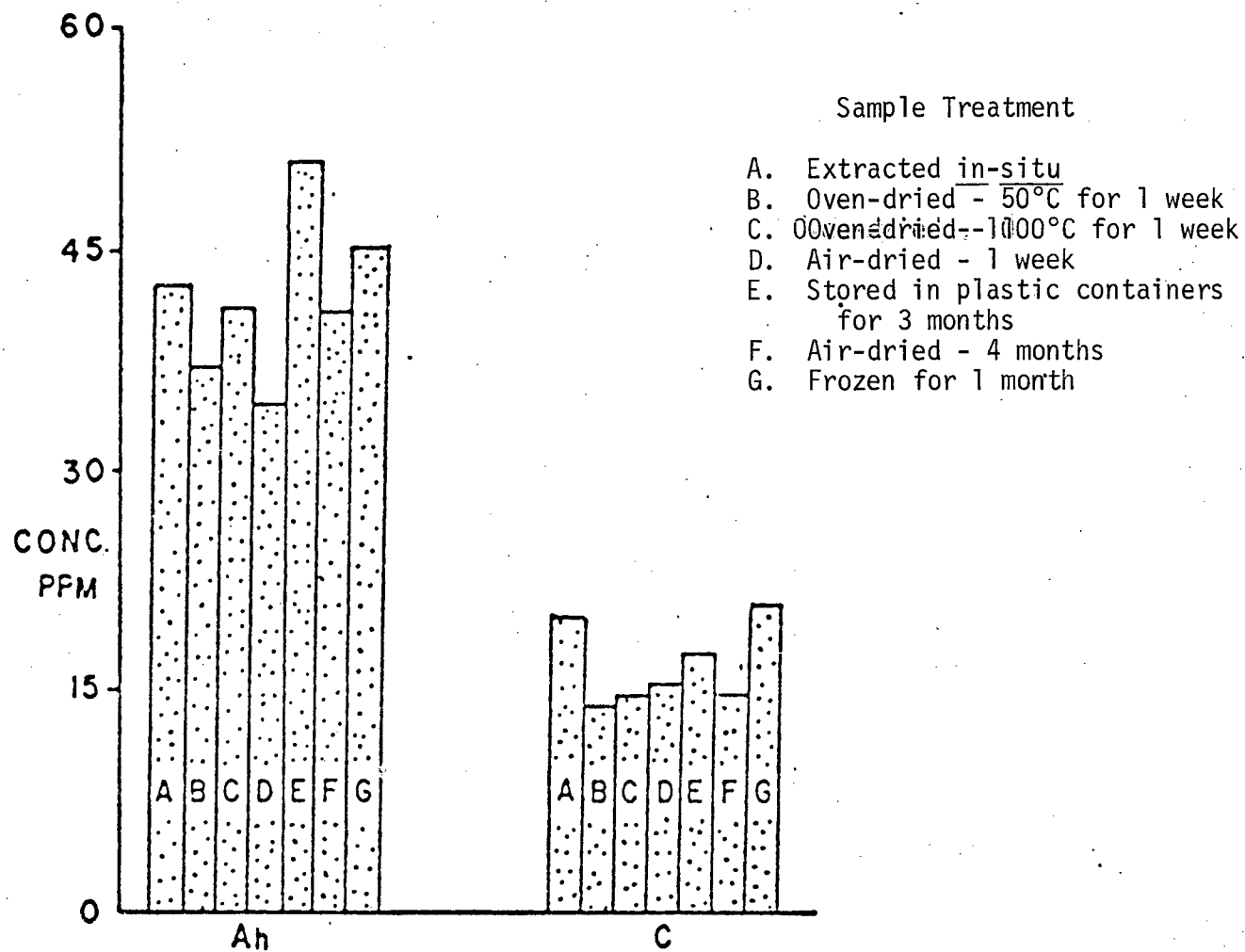
Figure 4.1. Tsawwassen - Concentration of hydroxylamine hydrochloride manganese extracted in relation to the different pretreatments.
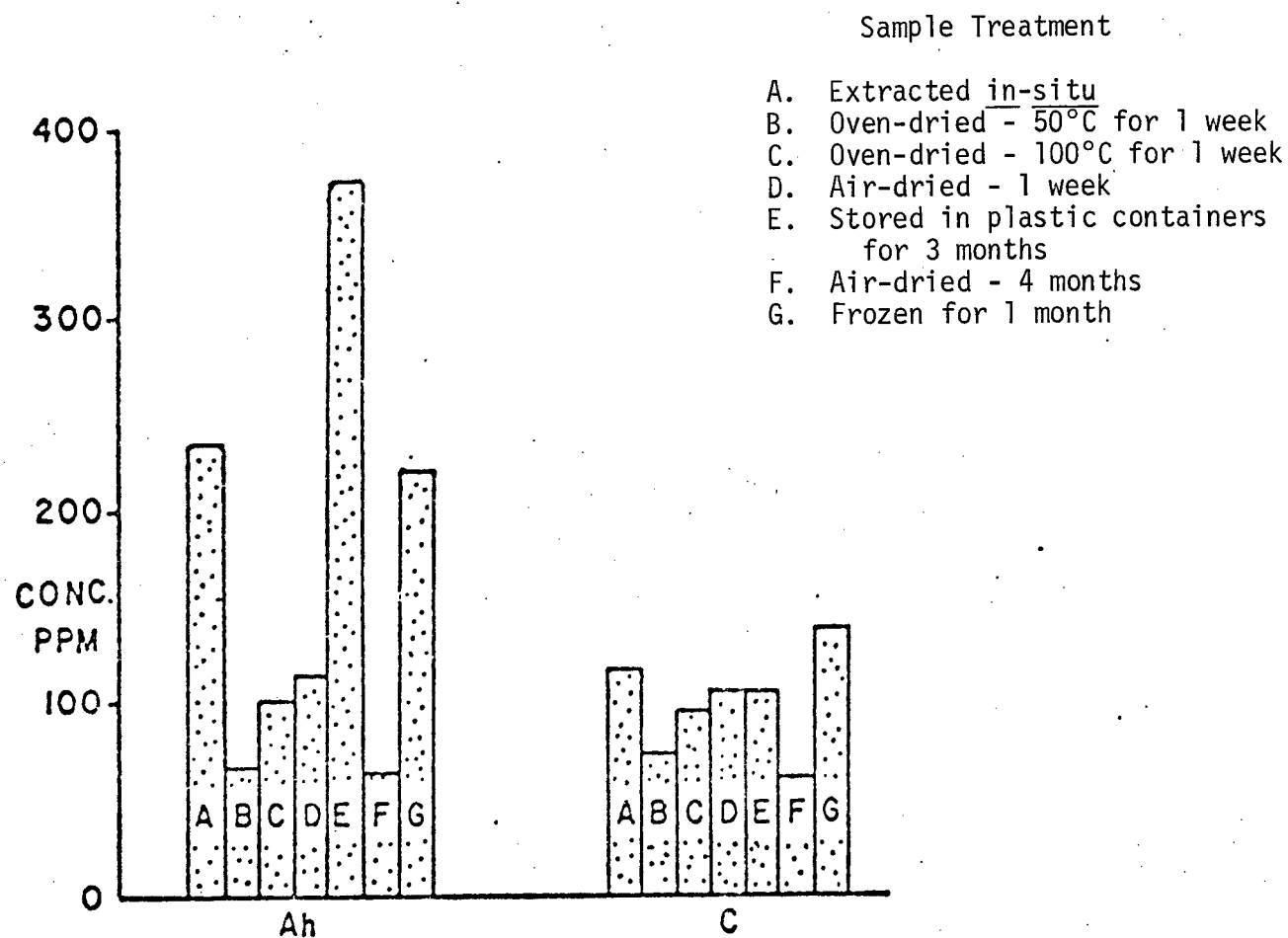
Figure 4.2. Tsawwassen - Concentration of hydroxylamine hydrochloride iron extracted in relation to the different pretreatments.

oxides. Oven-drying at 50°C may have dehydrated the soil aggregates,

making it more difficult for the dispersion by hydroxylamine hydro-

chloride. Oven-drying at 100°C may have decomposed some of the organic

portions and released more iron.

Storing samples moist in plastic containers did not give the

highest result for Tsawwassen aluminum values (Figure 4.3). Instead,

the highest values were given by oven-drying at 100°C for the Ah horizon

and frozen for one months for the C horizon. Oven-drying at 100°C

may have released more aluminum from the organic matter of the Ah horizon.

In the case oftthe C horizon, dispersion of the soil by freezing had a

greater impact on the aluminum complexed by hydroxylamine hydrochloride.

Both the Ah and C horizons showed the highest results for silicon

in samples stored moist in plastic containers (Figure 4.4). Air-drying

for one week was the next highest value for the Ah horizon. There was

no significant difference between the results of air-drying for four

months and in-situ extraction. Frozen samples showed non-detectable

amounts of silicon in the Ah horizon, but a relatively high concen-

tration in the C horizon.

The in-situ extraction procedure gave higher results than any

of the air-drying procedures for Tsawwassen iron and manganese (Figures

4.1 and 4.2). Air-drying values were close to that of in-situ extrac-

tion for all silicon results and Ah horizon aluminum. There was a

rowidexant difference between air-drying treatments and in-situ extrac-

tion for C horizon aluminum (Figure 4.3). Oven-drying at 100°C released

more manganese, iron, aluminum and silicon than oven-drying at 50°C

Sample Treatment

A. Extracted in-situ
B. Oven-dried - 50°C for 1 week
C. Oven-dried - 100°C for 1 week
D. Air-dried - 1 week
E. Stored in plastic containers for
   3 months
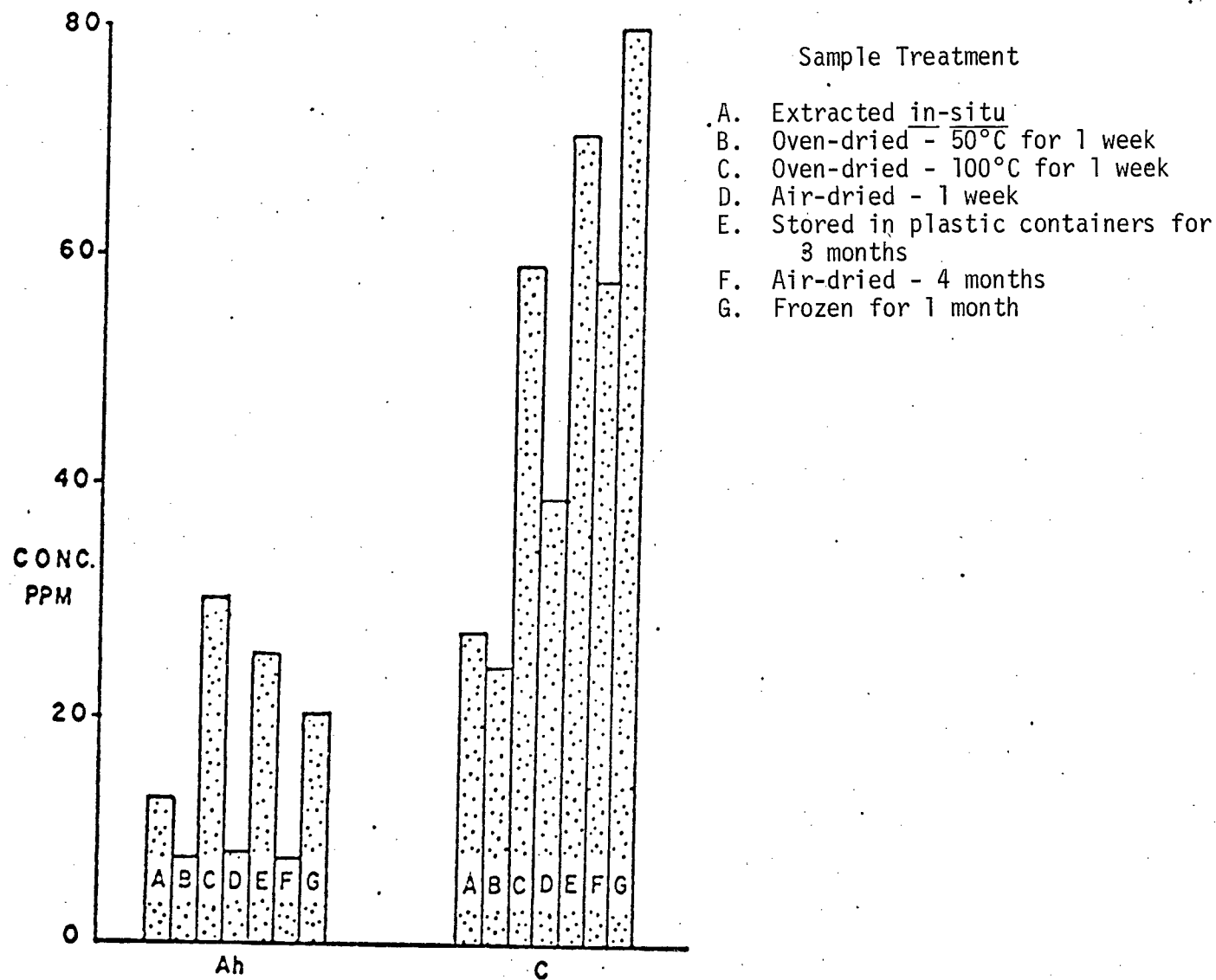F. Air-dried - 4 months
G. Frozen for 1 month

Figure 4.3. Tsawwassen - Concentration of hydroxylamine hydrochloride aluminum
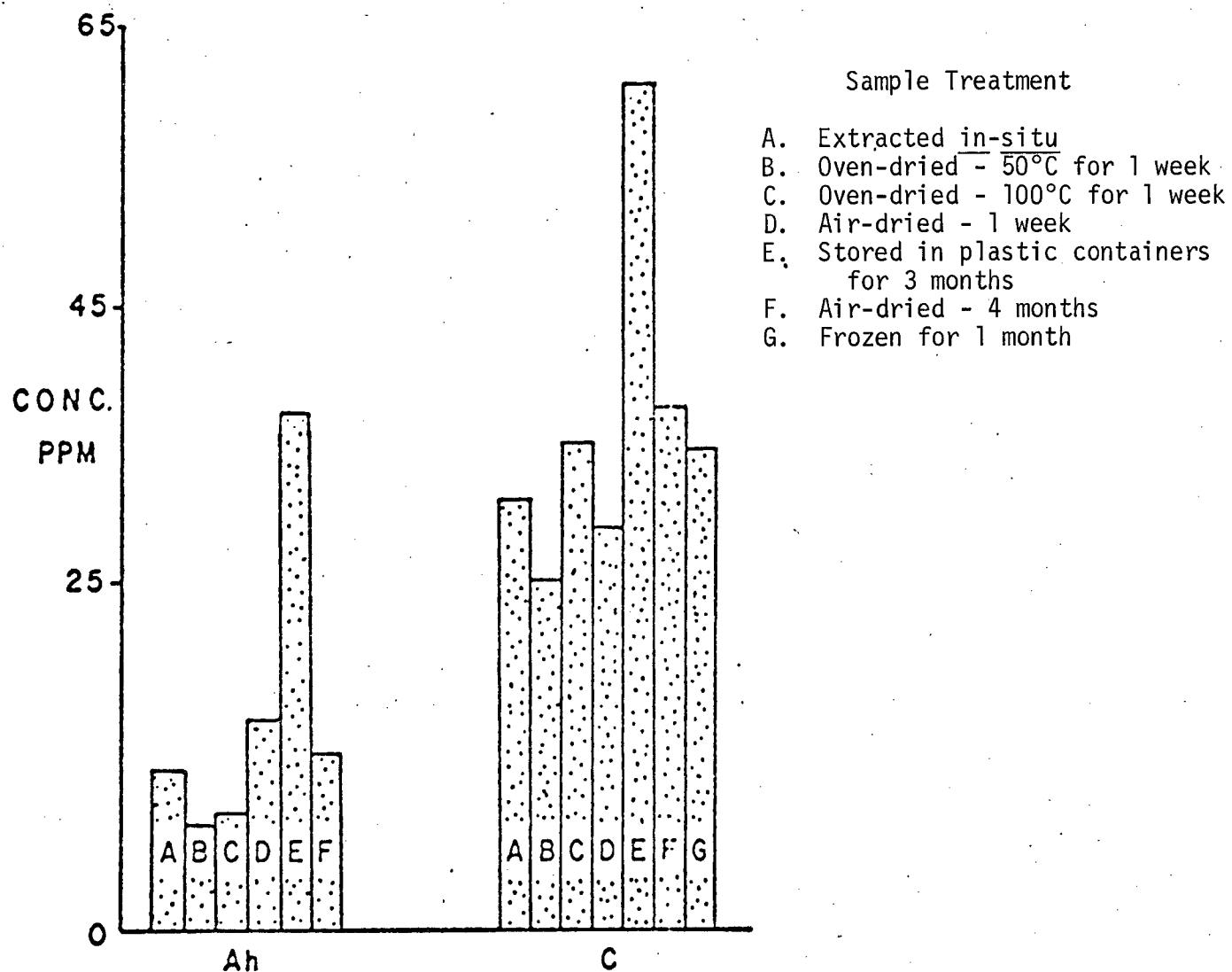extracted in relation to the different pretreatments.

Figure 4.4. Tsawwassen - Concentration of hydroxylamine hydrochloride silicon
extracted in relation to the different pretreatments.

(Figures 4.1, 4.2, 4.3, and 4.4). Freezing the sample gave higher
results than any of the air-drying procedures for manganese, aluminum
and iron (Figures 4.1, 4.2, and 4.3).

Grevell series

Oven-drying at higher temperatures did not lead to the extrac-
tion of a higher concentration of manganese (Figure 4.5). These results
contradict the observations for Tsawwassen and Sunshine samples (Figures
4.1 and 4.17). The texture of the soil could not be the reason for
these observations, since Tsawwassen has a similar texture as Grevell.
Probably the form of manganese present is different as Grevell is a
much more recent soil than Tsawwassen or Sunshine.

In-situ extraction results were lowest for the C horizon but
highest in IIC horizon (Figure 4.5). Samples stored moist in plastic
containers showed relatively high values for both C and IIC horizons,
but gave the lowest value for the Ah horizon. The moist steady con-
dition in the plastic containers was expected to create a reducing
condition and therefore the release of greater amounts of manganese,
but this was not found to be the case for the Ah horizon. The manganese
present in the Ah horizon may have been tied up with organic complexes,
while the manganese in the C and IIC horizons was in the form of higher
oxides.

Air-drying for four months gave lower results than air-drying
for one week for the C and IIC horizons (Figure 4.5). The reverse was
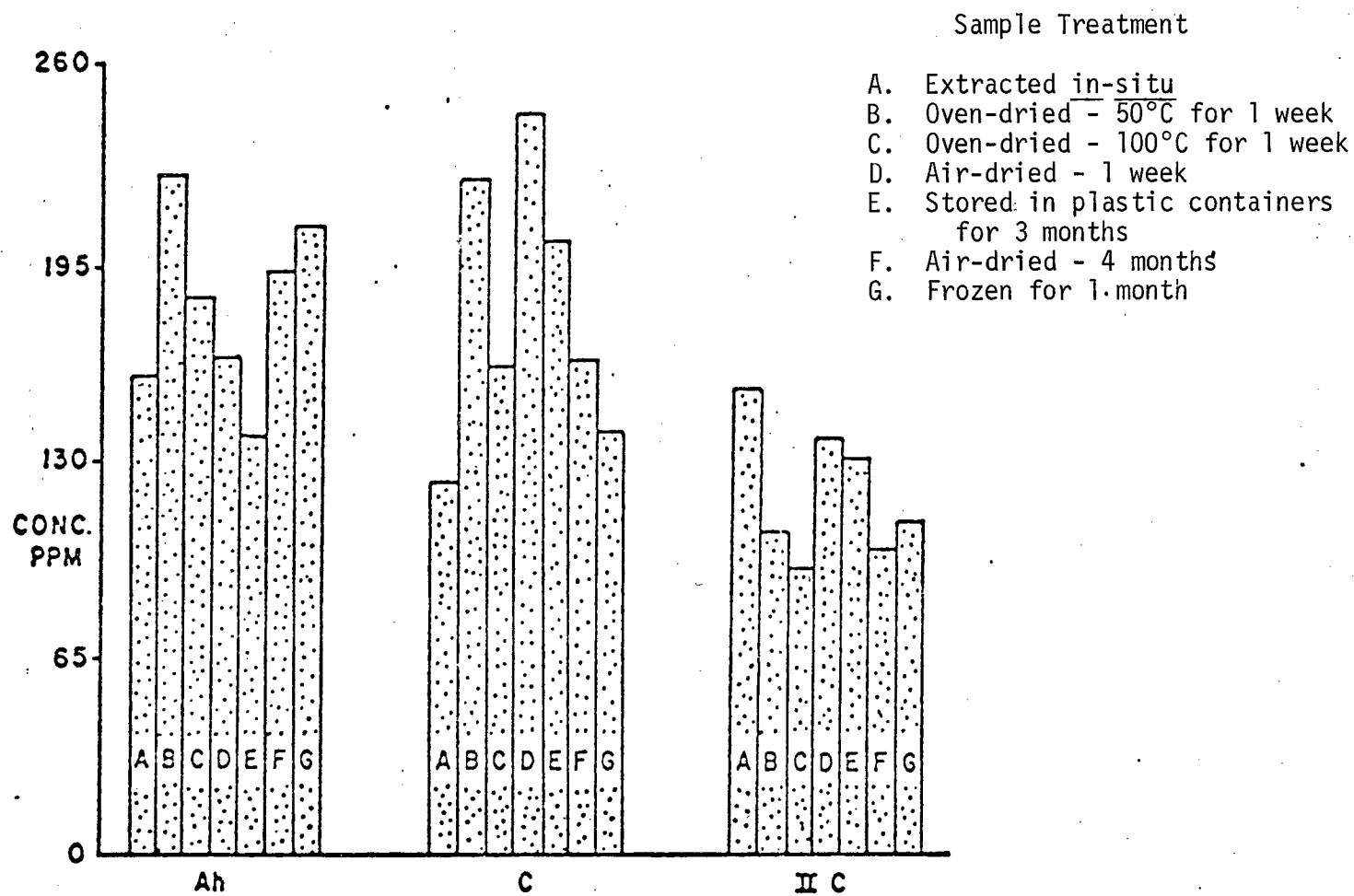true for Ah horizon. Decomposition of organic matter with time leads

Figure 4.5. Grevell concentration of hydroxylamine hydrochloride manganese extracted in relation to the different pretreatments.

to a greater release of manganese in the Ah horizon. In the lower horizons most of the manganese was in the form of oxides. A longer duration of air-drying would only lead to oxidation into the higher oxidation state.

The effect of freezing was not significant in the C and IIC horizons, but was so in the Ah horizon. This may have been due to the differences in texture. The Ah horizon was fine-textured and had micro-aggregates. Freezing may have broken these micro-aggregates. The C and IIC horizons were mainly sand-size particles.

Oven-drying at 50°C gave higher results than oven-drying at 100°C for iron in the Ah and C horizons (Figure 4.6). This trend was similar to manganese results. The IIC horizon showed otherwise. The longer the air-drying process, the lower the amount of iron extracted from all horizons. Freezing the soil did not affect the results significantly for Ah and C horizons but it did for the IIC horizon. However, the manganese result for the freezing treatment was among the highest in the Ah horizon. In-situ extraction gave the highest concentration for C horizon and relatively high values for Ah horizon, but was the lowest for IIC horizon. There did not seem to be any trend between treatments for the different horizons. The heterogeneity of the soil and the various forms of iron complexes responded differently to the different treatments. The results obtained are related to the concentration of the various forms in the soil.

Ah horizon had a very low amount of aluminum (Figure 4.7). No significant difference in results was observed for the different treatments. As in iron, in-situ extraction gave the highest value for the C
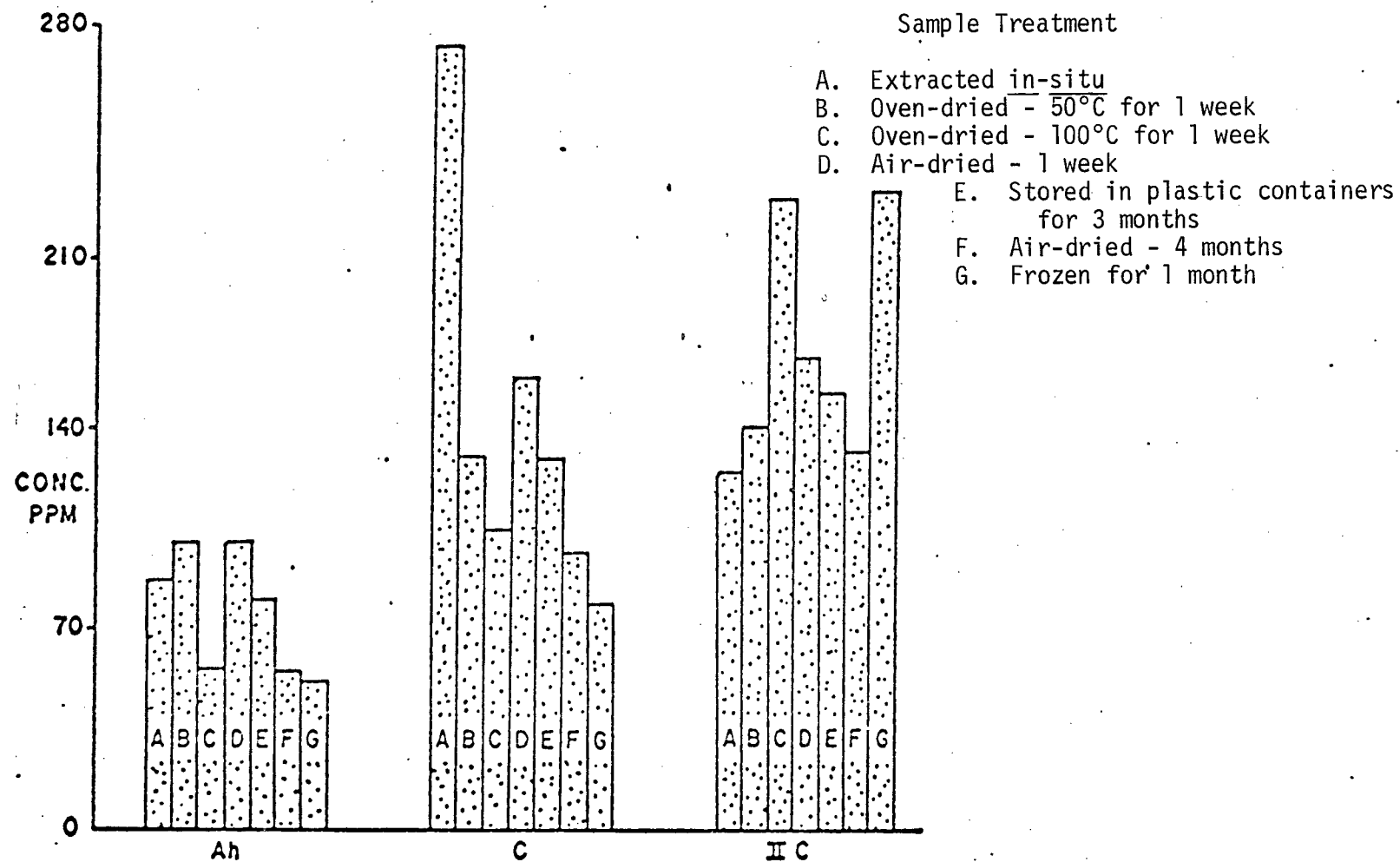
Figure 4.6. Grevell - Concentration of hydroxylamine hydrochloride iron
extracted in relation to the different pretreatments.

horizon. In-situ extraction results for IIC horizon were comparatively very low. Oven-drying at 100°C leads to a decrease in the amount of aluminum extracted compared to oven-drying at 50°C. The results obtained for manganese, iron and aluminum with regard to oven-drying at high temperatures were completely reversed from that shown by Tsawwassen samples. Greater length of air-drying also lead to the lower recovery of aluminum. The same trend was observed for iron. The aluminum may have combined with the higher oxides of iron, thus reducing its extractability. Storing samples moist in plastic containers gave relatively high extractable amounts of aluminum in the C and IIC horizons. This observation was the same as iron. Freezing the soil affects the IIC horizon positively in comparison with the in-situ extraction. However, in-situ extraction results were higher than the freezing treatment in the C horizon (Figure 4.7).

The in-situ extraction result for silicon was the lowest for Ah and IIC horizons but highest for the C horizon (Figure 4.8). Oven-drying at 100°C released greater amounts of silicon than oven-drying at 50°C. This result was contradictory to that observed for manganese and aluminum. One of the factors that could contribute to this is pH. Silicon is more soluble at alkaline pH. Aluminum and manganese are more easily extracted at low pH. The solubility of silica increases significantly above pH 7.0. Air-drying for a longer period again decreased the extractable amount of silicon. Freezing the soil increased the results significantly for the IIC horizon but not the Ah and C horizons. Storing in plastic containers did not give a high value for the Ah
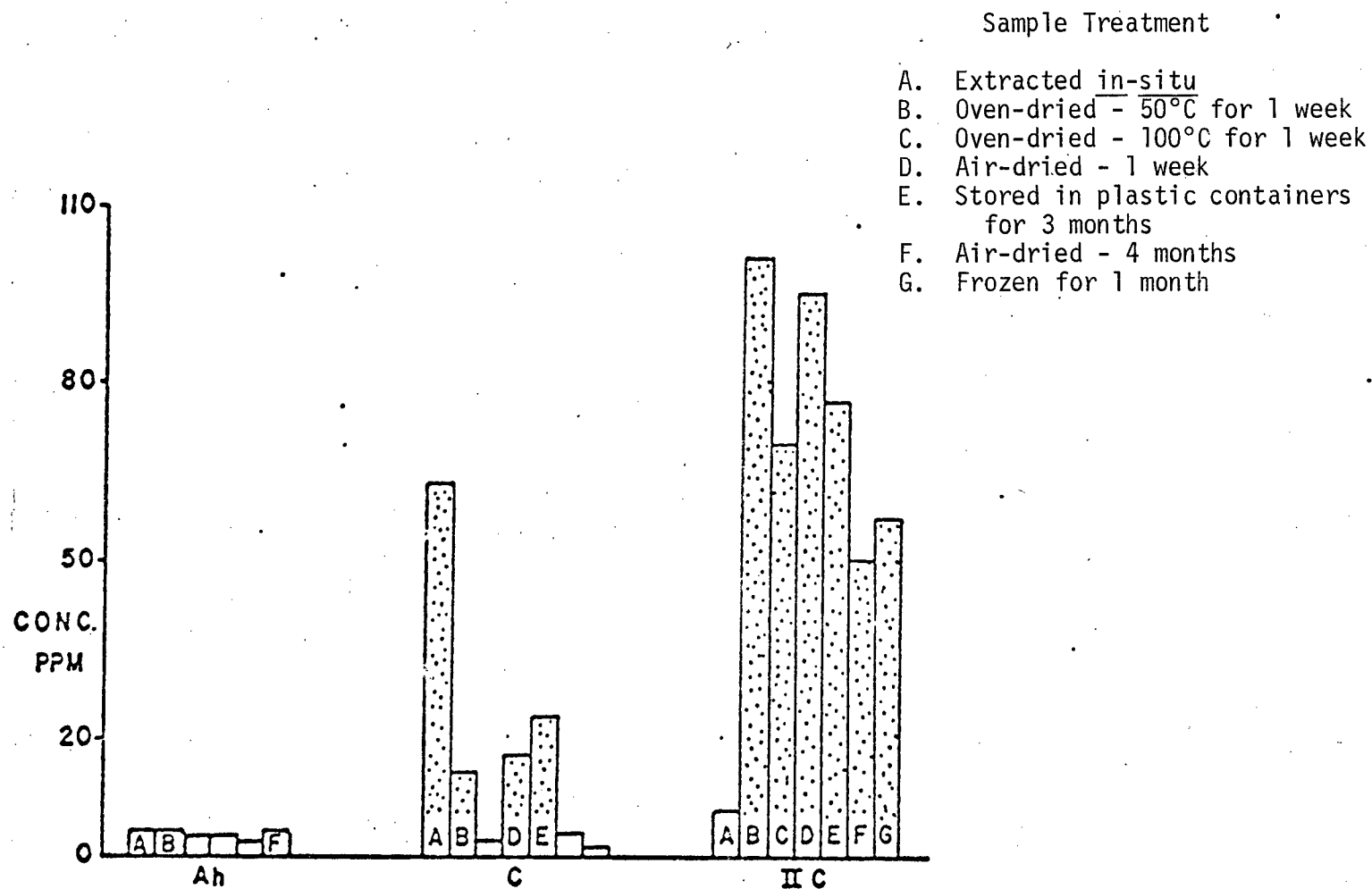
Sample Treatment

A. Extracted in-situ
B. Oven-dried - 50°C for 1 week
C. Oven-dried - 100°C for 1 week
D. Air-dried - 1 week
E. Stored in plastic containers
      for 3 months
F. Air-dried - 4 months
G. Frozen for 1 month

Figure 4.7.   Grevell - Concentration of hydroxylamine hydrochloride aluminum
extracted in relation to the different pretreatments.
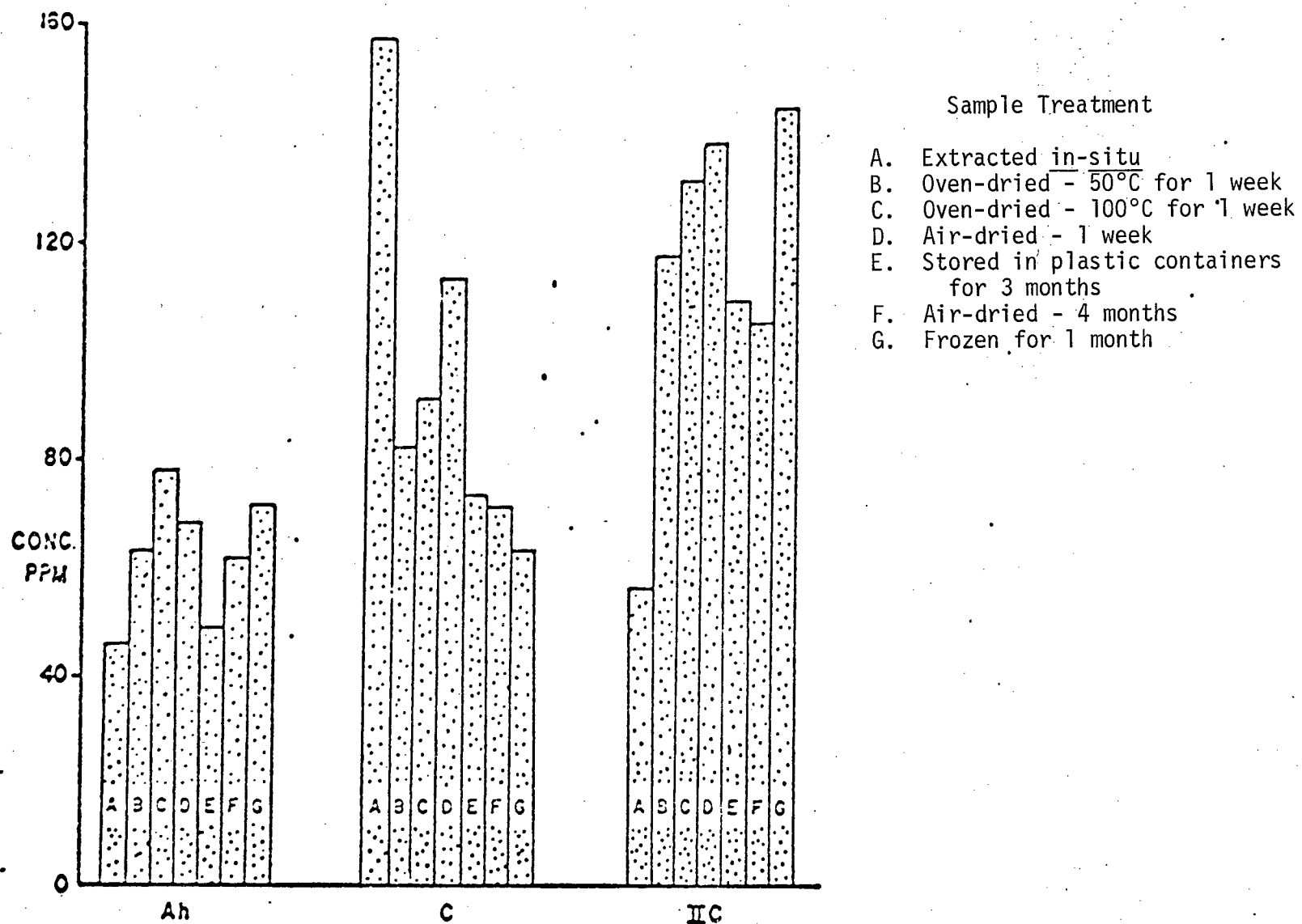
Figure 4.8. Grevell - Concentration of hydroxylamine hydrochloride silicon
in relation to the different pretreatments.

Sample Treatment

A. Extracted in-situ
B. Oven-dried - 50°C for 1 week
C. Oven-dried - 100°C for 1 week
D. Air-dried - 1 week
E. Stored in plastic containers
    for 3 months
F. Air-dried - 4 months
G. Frozen for 1 month

horizon but the result was close to that of air-drying for four months in the C and IIC horizons (Figure 4.8).

Blundell series

A greater amount of manganese was extracted when the samples were oven-dried at 100°C compared to at 50°C (Figure 4.9). The Blundell soil is fine-textured, having a relatively high organic matter content. Heating at high temperature may have released more manganese from the organic matter. Dehydration of the samples would also have destabilized the hydrated manganese $[(MnO)_x(MnO_2)_y(H_2O)_z]$ releasing MnO_2 and MnO.

Freezing the sample gave the highest results for the Ap and Cg horizons (Figure 4.9). There was no significant difference between treatments for the Bg horizon. In-situ extraction results were higher than the air-drying procedure. When the samples were extracted in-situ, it was still moist and easily dispersed by the extractant. Drying the soil increased the cohesion between soil particles. Storing the samples moist in plastic containers released greater amounts of manganese. The reducing environment may have released more easily-reducible manganese from the nodules which are prominent in these samples.

Freezing and storing moist in plastic containers lead to greater release of iron in all horizons (Figure 4.10). This trend was similar to that shown by manganese and iron in Tsawwassen samples. Drying the soil at two different temperatures did not show significant changes. Manganese, on the other hand, showed an increase when heated to 100°C.

A. Extracted in-situ
B. Oven-dried - 50°C for 1 week
C. Oven-dried - 100°C for 1 week
D. Air-dried - 1 week
E. Stored in plastic containers
       for 3 months
F. Air-dried - 4 months
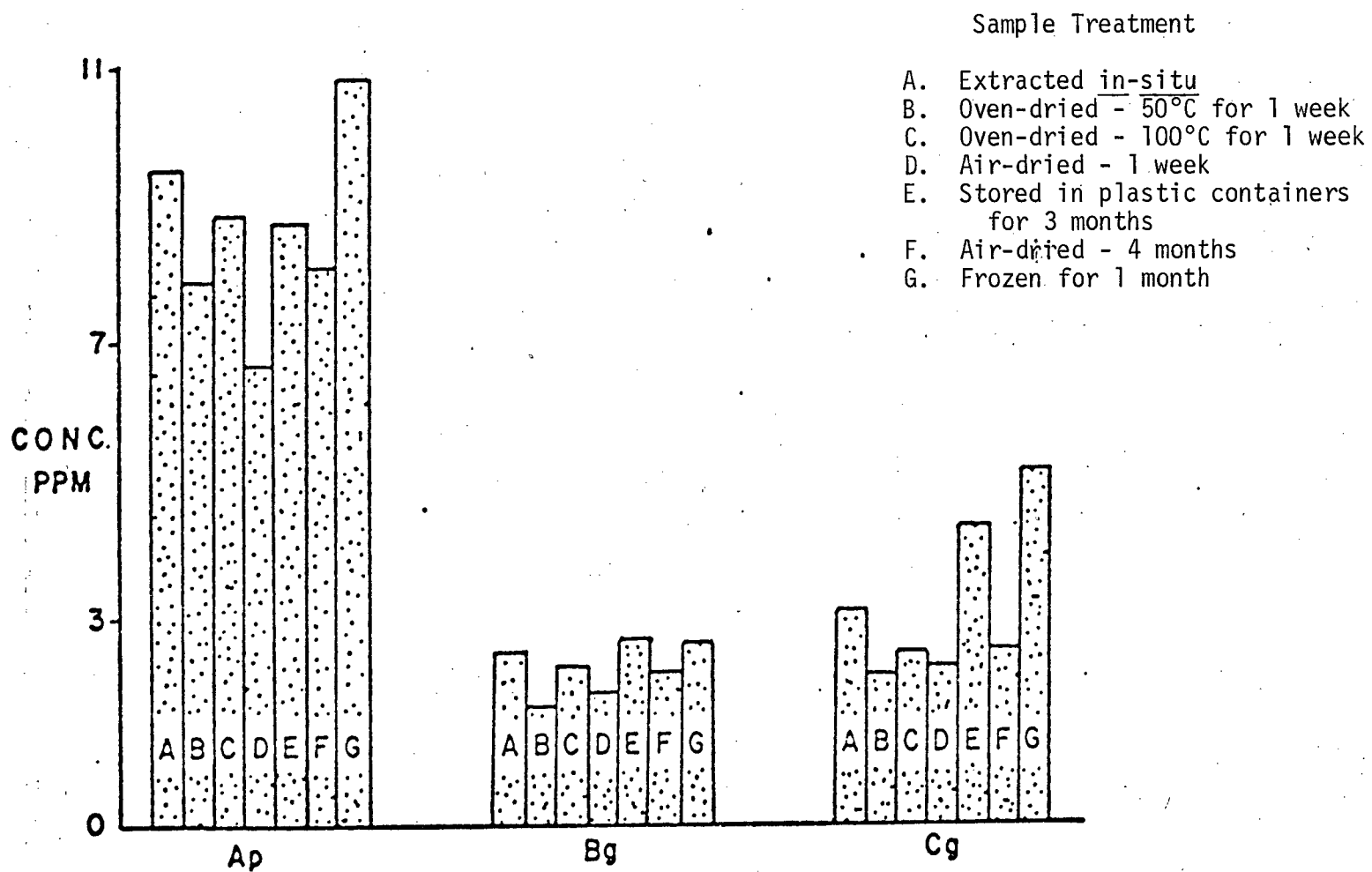G. Frozen for 1 month

Figure 4.9.   Blundell - Concentration of hydroxylamine hydrochloride manganese
              extracted in relation to the different pretreatments.
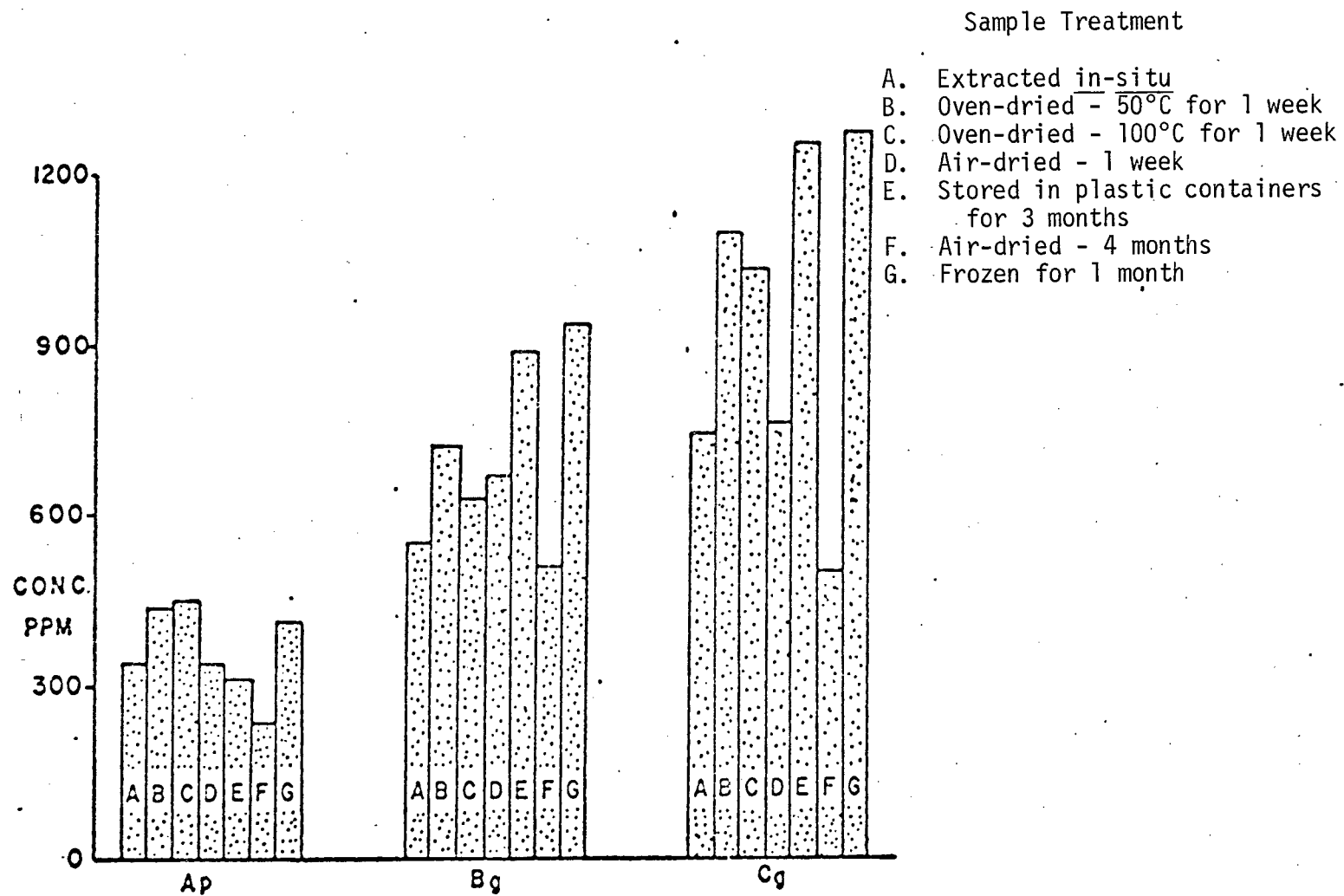
Figure 4.10. Blundell - Concentration of hydroxylamine hydrochloride iron extracted in relation to the different pretreatments.

Prolonged air-drying again decreased the iron extracted (Figure 4.10) and this is indicated by the low results in relation to in-situ extraction results. Increase in pH and oxidation to higher oxides may account for this observation.

Storing moist in plastic containers again gave significantly higher results than most of the other treatments for aluminum (Figure 4.11). Reduction of manganese and iron may also lead to release of aluminum from the complex. Increased duration of air-drying showed a greater release of aluminum. This result was similar to manganese (Figure 4.9) but opposite to that of iron (Figure 4.10). One possible effect of air-drying may have been the decomposition of organic matter and the subsequent release of aluminum and manganese. Iron is much more strongly coordinated with organic compounds than either manganese or aluminum.

Drying at a higher temperature also released greater amounts of aluminum. In-situ extractions gave higher results than any of the air-drying procedures for the Ap horizon and also higher results than air-drying for one week, for Bg and Cg horizons.

The highest amount of silicon was extracted when the samples were stored moist in plastic containers (Figure 4.12). This was followed by the freezing treatment. There was no significant difference between the air-drying treatments for Ap and Bg horizons, however, longer duration of air-drying reduced the amount extracted for Cg horizon. This observation coincided with that of iron. The formation of ferro-silicate compounds upon prolonged air-drying could be a possibility. No changes

Sample Treatment

A. Extracted in-situ
B. Oven-dried - 50°C for 1 week
C. Oven-dried - 100°C for 1 week
D. Air-dried - 1 week
E. Stored in plastic containers
      for 3 months
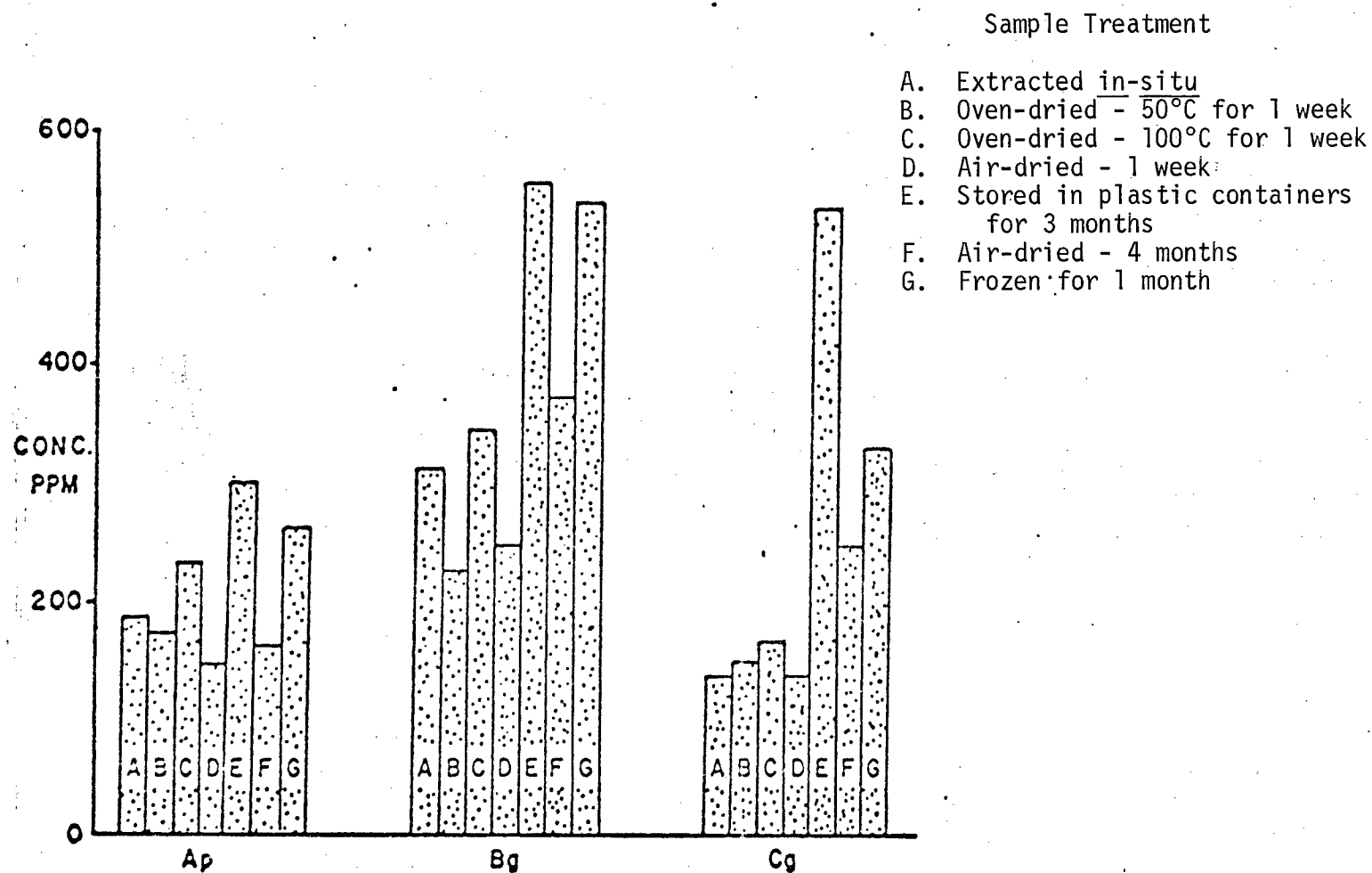F. Air-dried - 4 months
G. Frozen for 1 month

Figure 4.11.   Blundell - Concentration of hydroxylamine hydrochloride aluminum
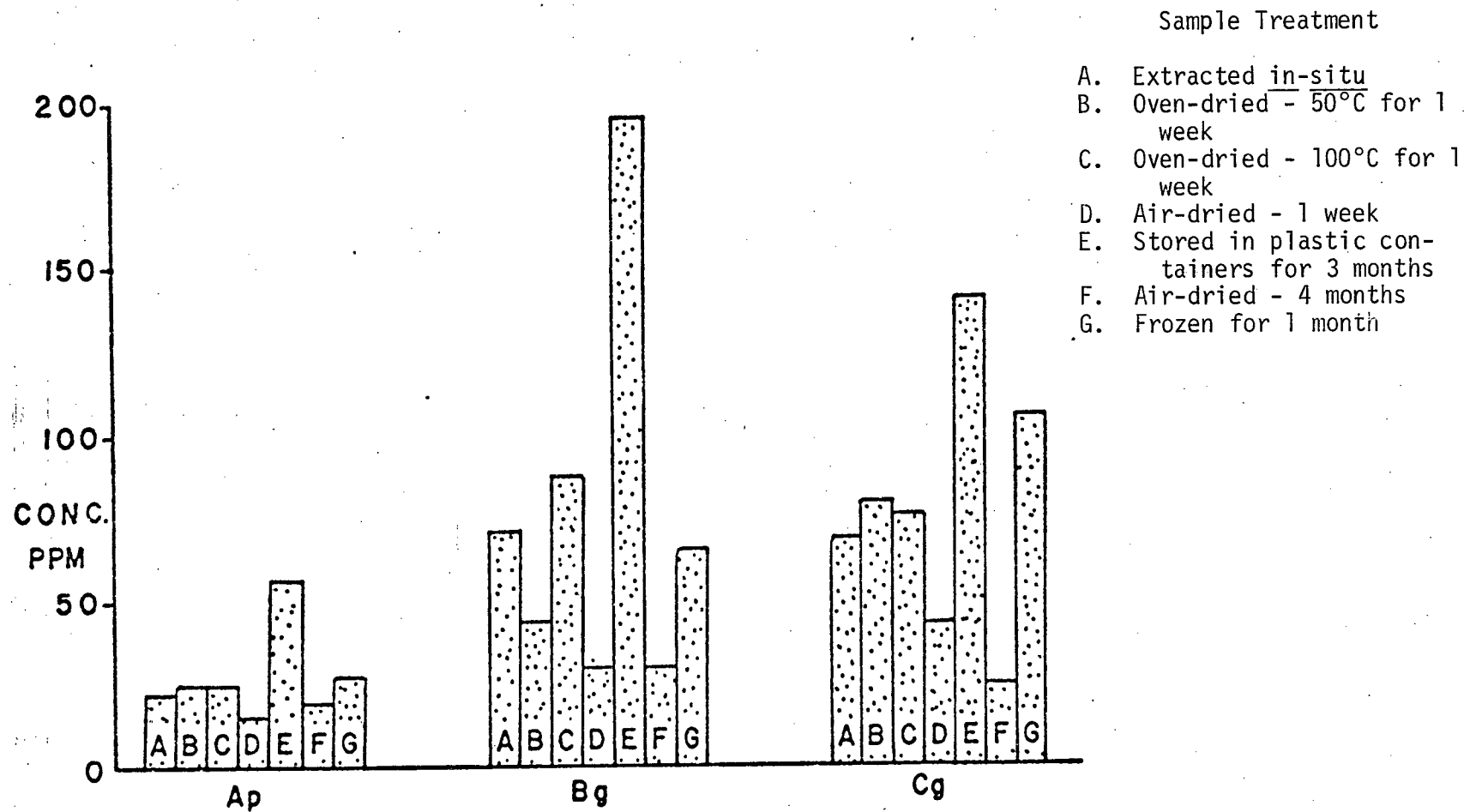extracted in relation to the different pretreatments.

Figure 4.12. Blundell - Concentration of hydroxylamine hydrochloride silicon extracted in relation to the different pretreatments.

were observed between the two oven-drying treatments for Ap and Cg horizons (Figure 4.12). Heating at higher temperature released greater amounts of silicon in the Bg horizon only. In-situ extraction gave higher results than any of the air drying treatments.

Cloverdale series

Oven-drying at 100°C compared to oven-drying at 50°C released greater amounts of manganese in the Ah1 and Ah2 horizons and lower amounts of manganese in the mineral horizons (Figure 4.13). The high temperature may have decomposed the organic matter, resulting in greater extractable manganese in the Ah horizon. A longer duration of air-drying released greater amounts of manganese in the Ah1 and Ah2 horizons. The reverse was true for Bf, Cg1, and Cg2 horizons. The effect of freezing the soil on extractable manganese values decreased with depth. Storing moist in plastic containers gave relatively high results for the subsurface horizons. No definite trend was observed between in-situ extraction and any of the air-drying treatments. In some cases in-situ extraction results were lower than air-drying results, in others it was higher. The results obtained for the various treatments showed a difference in effects on the different forms of manganese present in the soil. Two distinct forms of manganese can be seen from this obser-vation, the organically-complexed form and the oxides form.

The effect of oven-drying at 100°C for iron was more prominent than any of the other treatments in Ah1, Ah2, Cg1 and Cg2 horizons. (Figure 4.14). No significant difference was observed between these
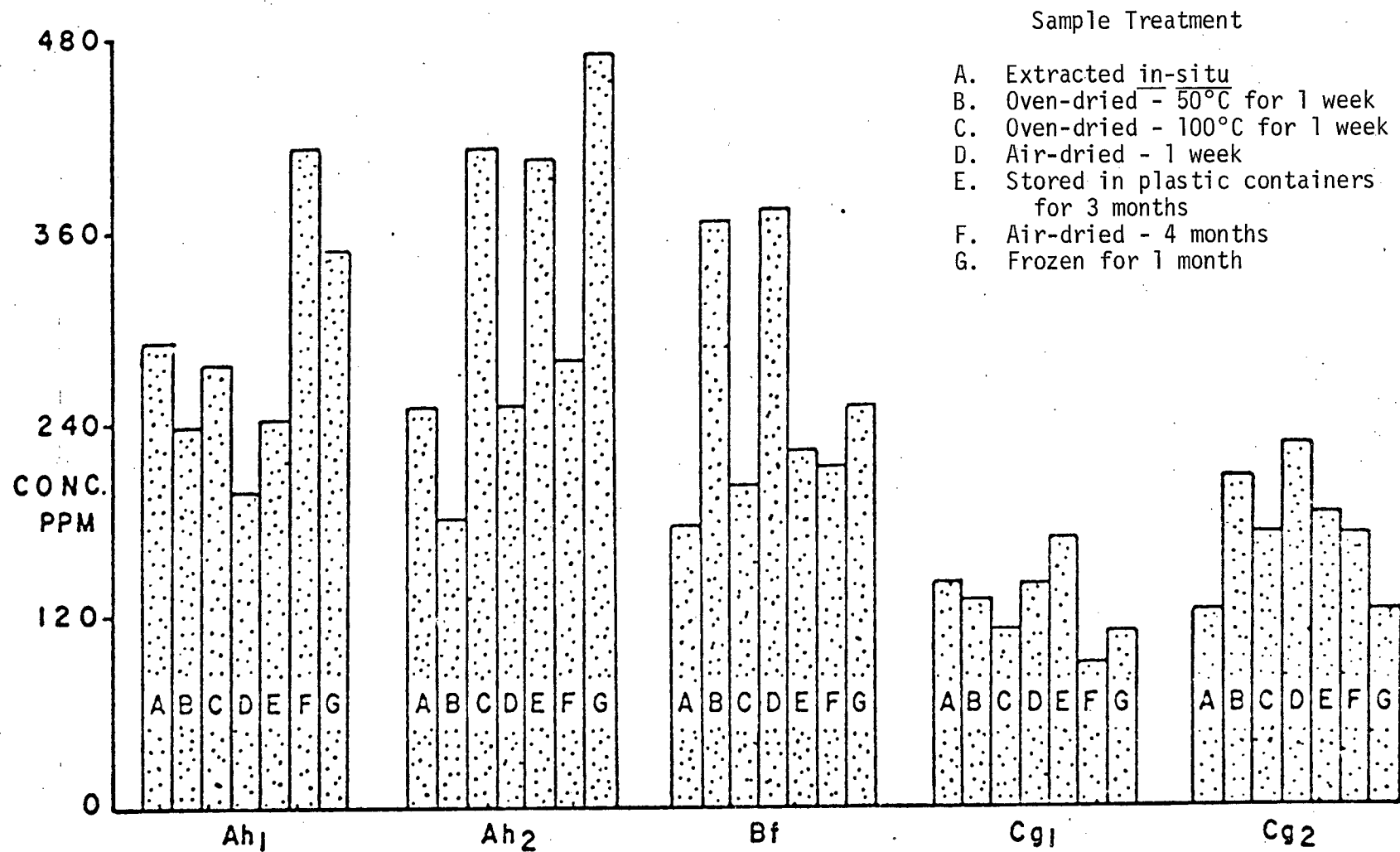
Figure 4.13. Cloverdale - Concentration of hydroxylamine hydrochloride manganese
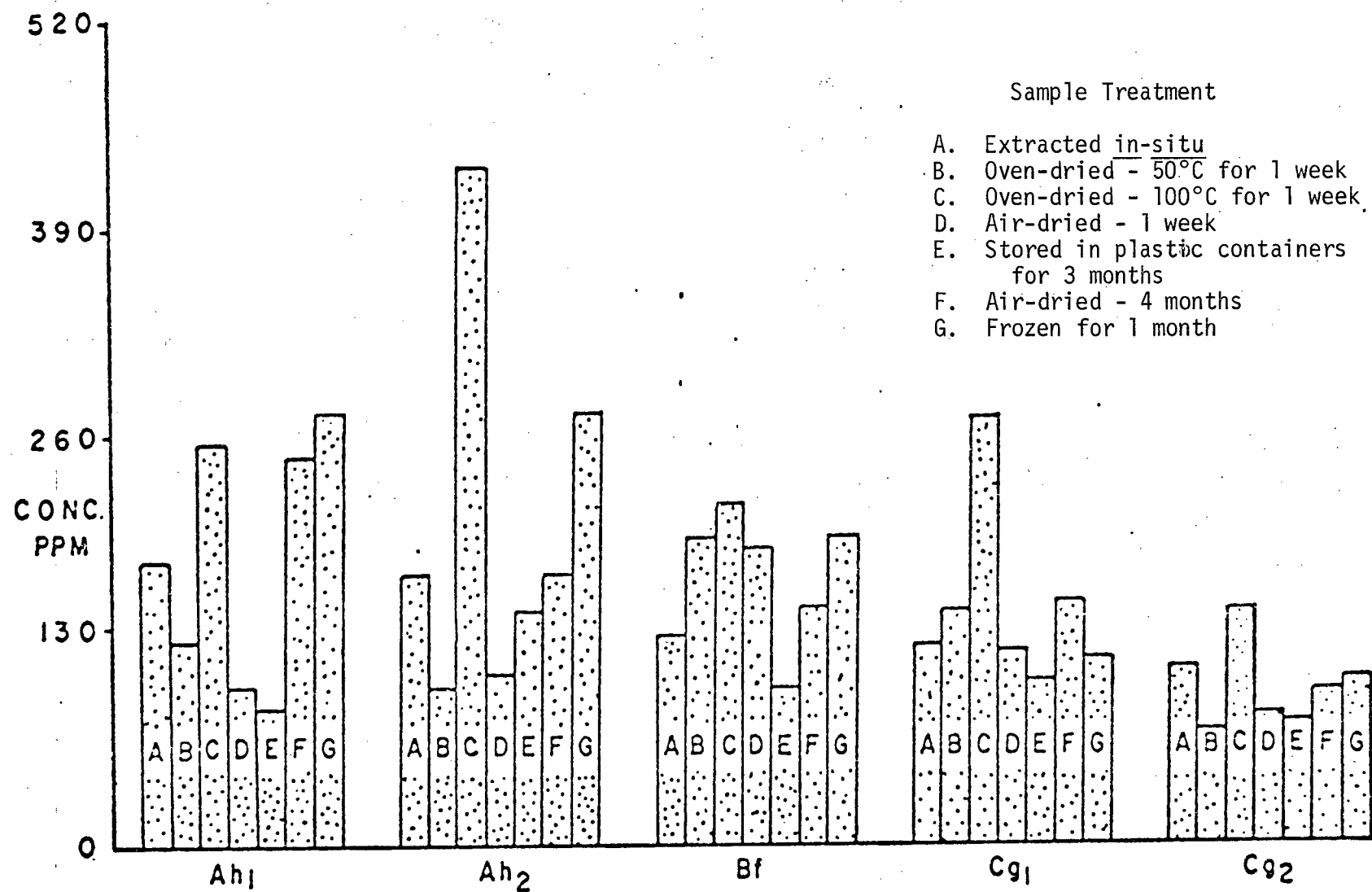extracted in relation to the different pretreatments.

Figure 4.14.   Cloverdale - Concentration of hydroxylamine hydrochloride iron extracted in relation to the different pretreatments.

treatments for Blundell's iron. The Cloverdale samples had many root remnants and tubular nodules. The extra manganese released upon heating at higher temperature may have been derived from this form. Again longer duration of air-drying released greater concentrations or iron in Ah1, Ah2, Cg1, and Cg2 horizons but not in the Bf horizon. The effect of freezing the soil was more significant in the upper horizons. In-situ extraction results were relatively higher than air-dried for one week treatment for Ah1, Ah2 and Cg2 horizons, but not sorin Bf and Cg1 horizons. This observation indicates some common properties of iron in the surface horizons and the parent material. Iron in the middle of the soil profile reacts differently to the different treatments. It is in more of a transition state in this horizon.

Oven-drying at 100°C released lower amounts of aluminum than oven-drying at 50°C for most horizons (Figure 4.15), however, the effect was insignificant for Cg1 and Cg2 horizons. The same trend was observed for Grevell samples. Freezing gave a more favorable effect for aluminum in the surface horizon. Prolonged air-drying released lower amounts of aluminum. Storing in plastic containers did give high values for the subsurface horizons, but not foraAh1ehorizon. In-situ extraction was lowest for Bf and Cg1 horizon but was relatively high for the other horizons.

Greater amounts of silicon were extracted when the samples were oven-dried at 100°C compared to 50°C for all Cloverdaleahorizons. horizons (Figure 4.16). This result is contradictory to that observed for aluminum, as shown in Figures 4.15. Fig. In-situ extraction.

520 —

390 —

260 —

CONC.
PPM

120 —

0

Ah₁ Ah₂ Bf Cg₁ Cg₂

A B C D E F G H

FigureSample Treatment

A.   Extracted in-situ
B.   Oven-dried - 50°C for 1 week
C.   Oven-dried - 100°C for 1 week
D.   Air-dried - 1 week
E.   Stored in plastic containers
        for 3 months
F.   Air-dried - 4 months
G.   Frozen for 1 month

Figure 4.15.   Cloverdale - Concentration of hydroxylamine hydrochloride aluminum
extracted in relation to the different pretreatments.

Sample Treatment

A. Extracted in-situ
B. Oven-dried - 50°C for 1 week
C. Oven-dried - 100°C for 1 week
D. Air-dried - 1 week
E. Stored in plastic containers
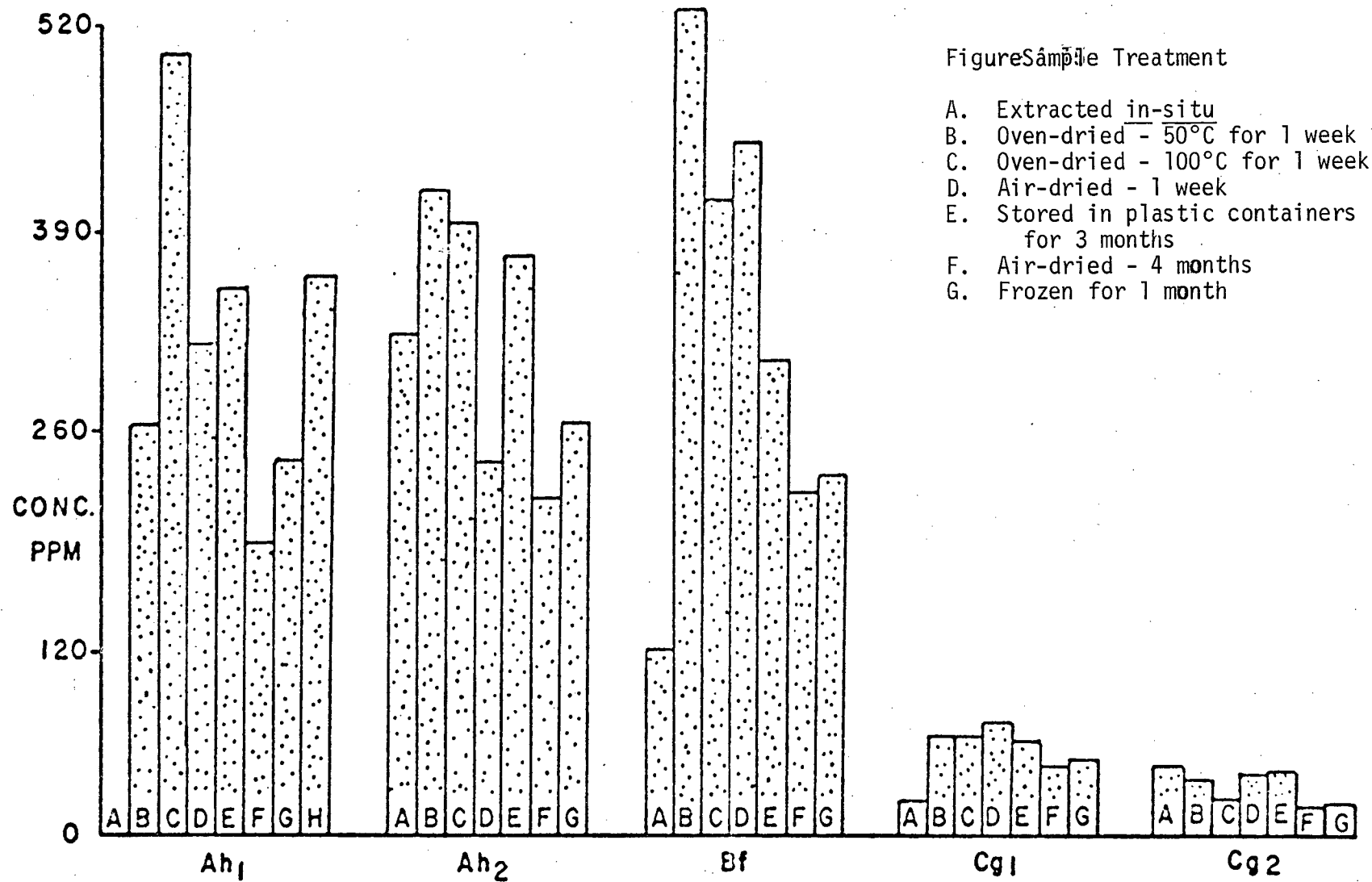   for 3 months
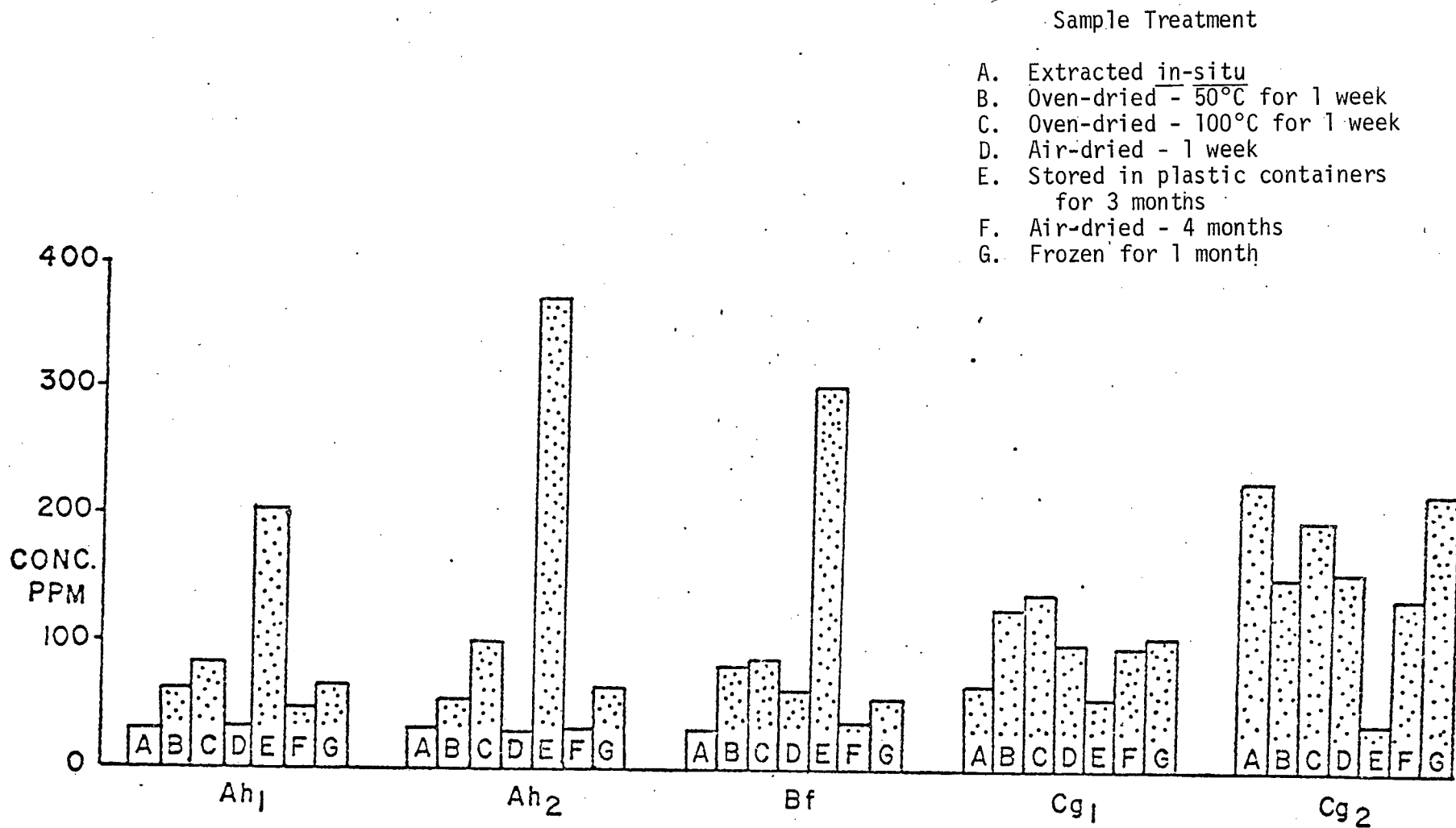F. Air-dried - 4 months
G. Frozen for 1 month

Figure 4.16.   Cloverdale - Concentration of hydroxylamine hydrochloride silicon
extracted in relation to the different pretreatments.

results were relatively low for Ah1 and Ah2 horizons (Figure 4.16).
The effect of storing in plastic containers was more significant in
the upper horizons. Longer air-drying released a lower concentration
of silicon in Bf1, Cg1, and Cg2 horizons, but higher amounts in Ah1
and Ah2 horizons. The effect of freezing the soil was even greater
in the lower horizons, however, this does not coincide with the results
of aluminum (Figure 4.15).

Sunshine series

The differences in results due to the different treatments were
more significant for the surface horizons (Figure 4.17). This coin-
cided with the higher organic matter content, and the relatively recent
and unstable nature of the various compounds in the upper horizon.
Freezing samples for one month gave the highest manganese results for
the Ah and Bf horizons. Air-drying for four months showed the lowest
results for these horizons. In-situ extraction was relatively high
for the Ah horizon, but was close to the results of the other treatments
for Bf1, Bf2 and BC horizons. Oven-drying at 100°C released greater
concentration of manganese than oven-drying at 50°C. Similar obser-
vations were obtained in the Tsawwassen series. The higher temperature
not only released nutrients tied up in the organic matter, but also
weakened the soil aggregates. The difference in results for the two
treatments was often greater for the Ah horizon. This indirectly re-
flects the greater effect of temperature on the extractability of nut-
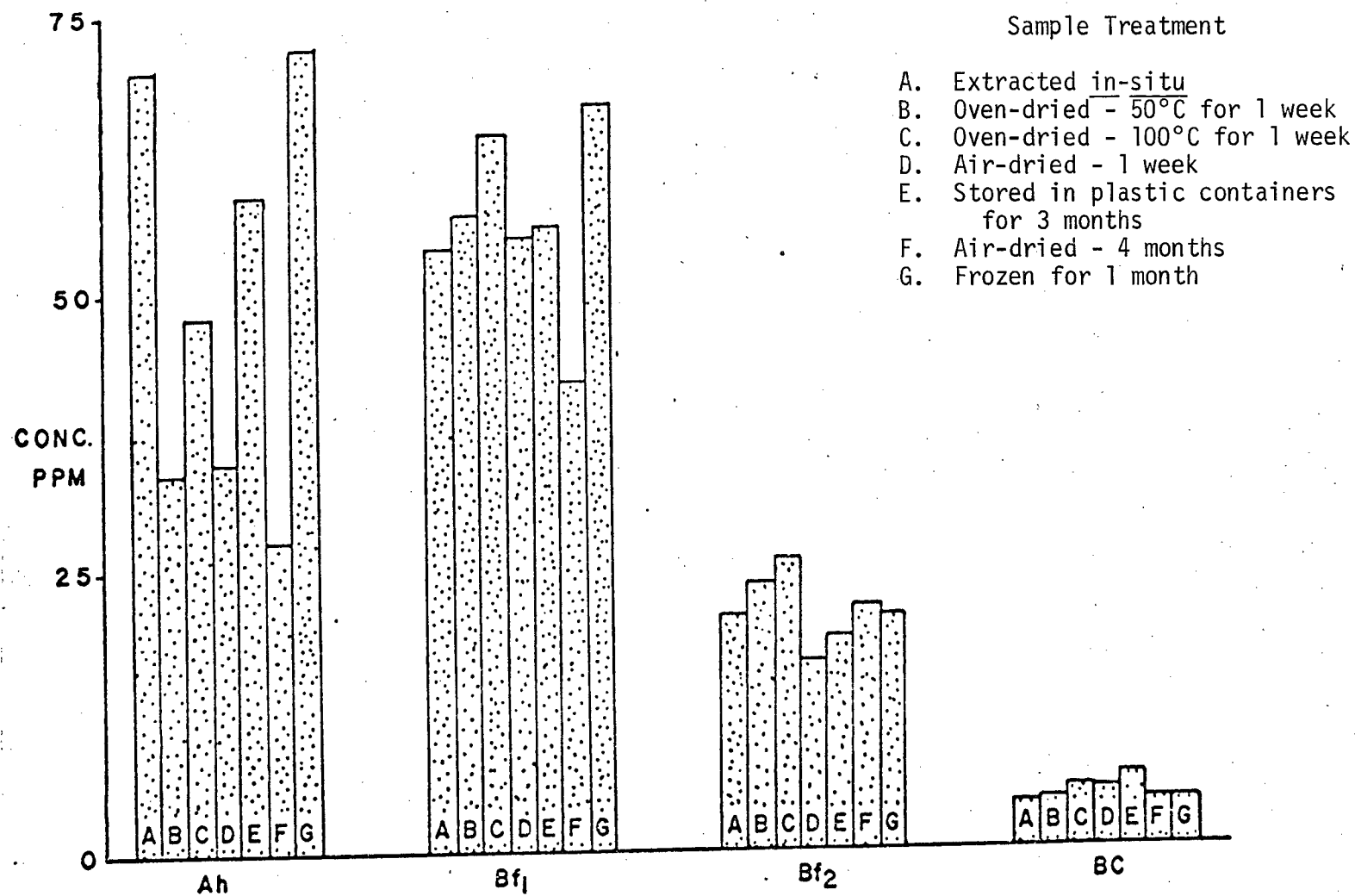rients for soils high in organic matter content.

Figure 4.17. Sunshine - Concentration of hydroxylamine hydrochloride manganese
extracted in relation to the different pretreatments.

Air-drying for one week was among the lowest results for all horizons. It was quite close to the results for oven-drying at 50°C in Ah and Bf horizons. The effect of both treatments might be the same for both horizons. There was no significant difference in results for the different treatments in the BC horizon.

Oven-drying at 100°C gave the highest result for iron in the Ah horizon (Figure 4.18). This was followed by air-drying for one week and oven-drying at 50°C. There was no significant difference in results between the in-situ extraction and the other treatments. Oven-drying at 100°C again gave the highest results for the Bf1, Bf2 and C horizon. Considering the lower amount of organic matter in these horizons, the higher value could be due to increased dispersion of the soil aggregates or increased rate of weathering of the soil at high temperatures. In-situ extraction results were quite similar to the results of air-drying for four months, but lower than air-drying for one week.

The aluminum results for different treatments varied throughout the horizons (Figure 4.19). Again, drying at 100°C gave higher values than oven-drying at 50°C for all horizons. In-situ extraction results were lower than any of the air-drying results for Ah horizon. This trend was the same as for iron (Figure 4.18). Air-drying for four months released greater amounts of aluminum than air-drying for one week in the Bf1, Bf2 and BC horizons. Conversely, the effect was the opposite in the Ah horizon.

Storing moist in plastic containers and freezing the soil gave the highest values for the Bf1, Bf2 and BC horizons. This observation

Figure 4.18. Sunshine - Concentration of hydroxylamine hydrochloride iron extracted in relation to the different pretreatments.

Figure 4.19. Sunshine - Concentration of hydroxylamine hydrochloride aluminum extracted in relation to the different pretreatments.

was similar to that of Tsawwassen aluminum. There was no significant
difference between the other treatments for the BC horizon.

Oven-drying at 100°C contributed the highest result for silicon
in the Ah horizon (Figure 4.20). This was followed by storing moist
in plastic containers. In-situ and air-drying for four months showed
the lowest values. There was no significant difference between the
other three treatments. In-situ extractions values were significantly
lower than the other pretreatment values in Bf1 and BC horizons. On
the other hand, air-dried for one week results were significantly dif-
ferent from the other pretreatments in Bf2 horizon. Further study is
necessary before a more definite conclusion can be attached to these
observations
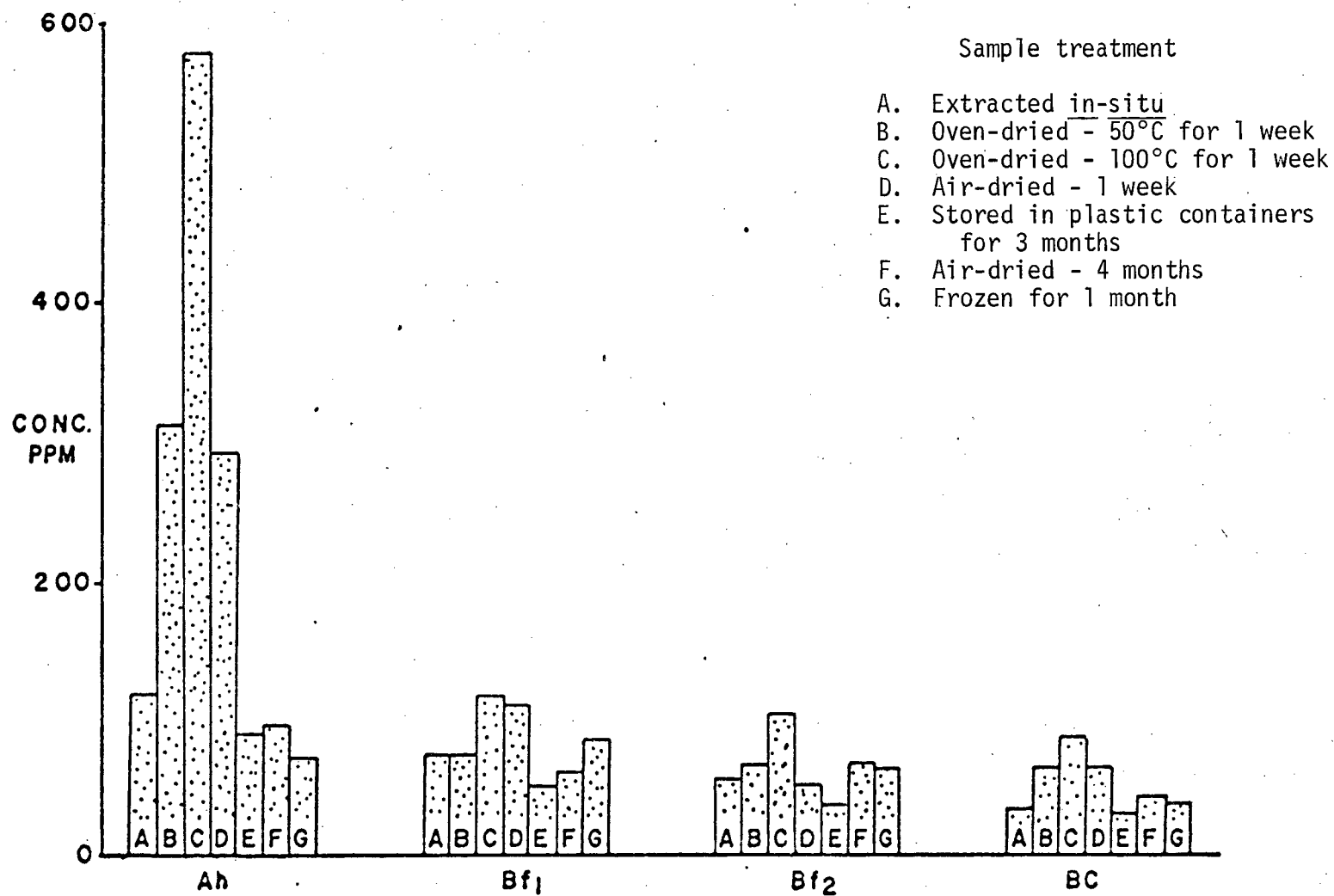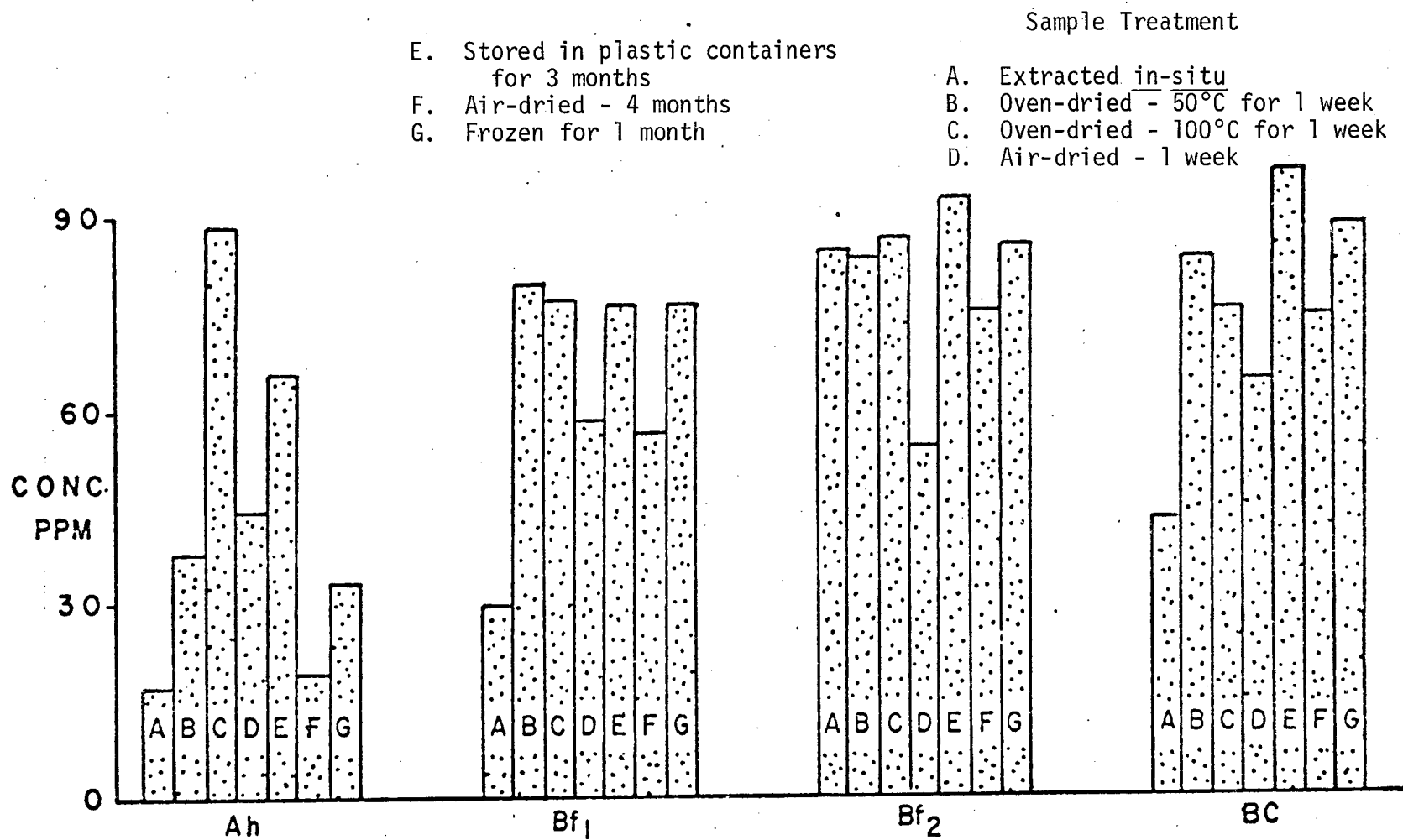
Figure 4.20.   Sunshine - Concentration of hydroxylamine hydrochloride silicon
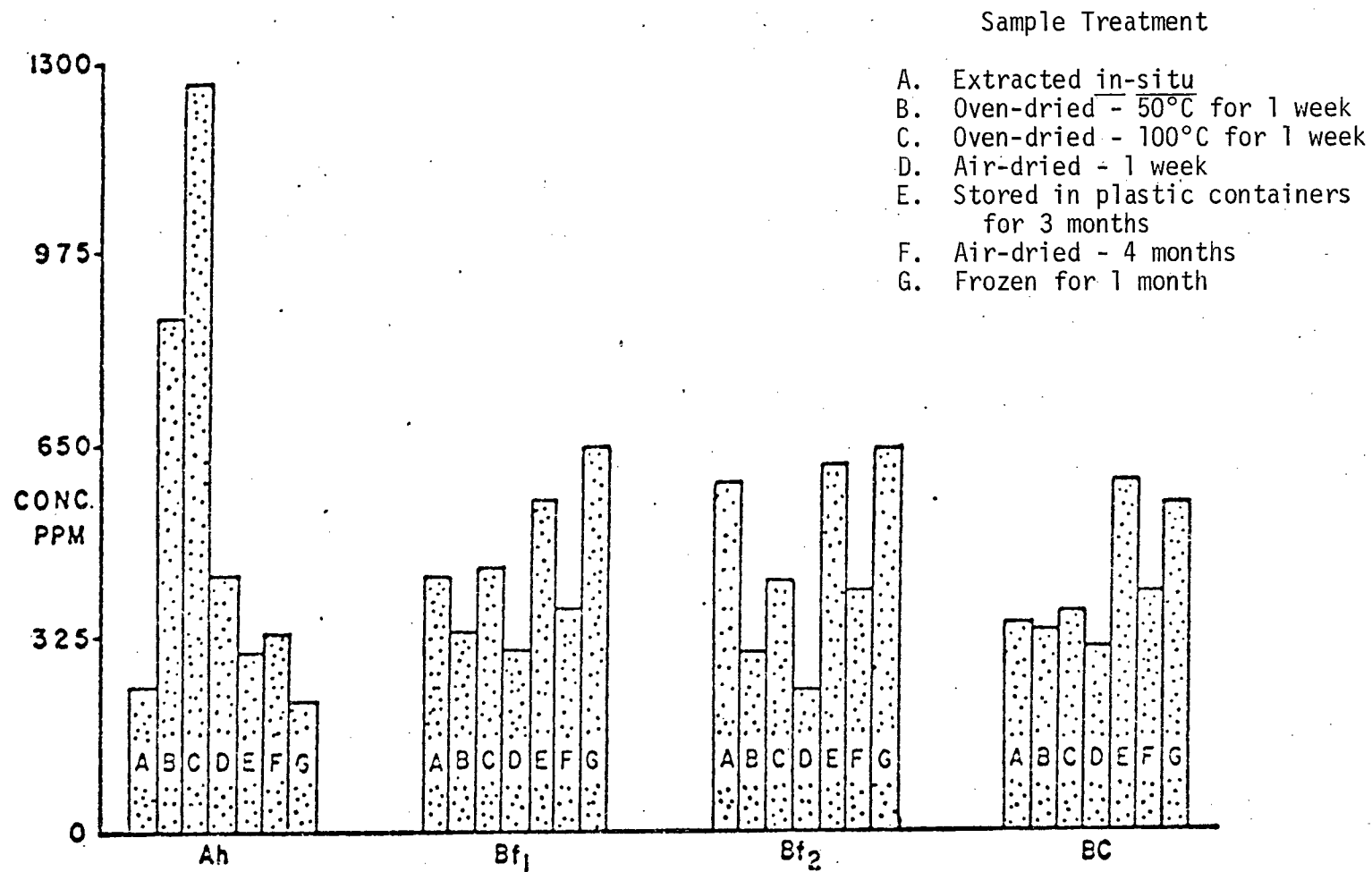extracted in relation to the different pretreatments.

CONCLUSION

No definite trend could be observed with the effect of the

various treatments on the extractability of manganese from the soils.

In general, increasing the oven temperature from 50°C to 100°C often

lead to greater release of manganese. This effect was shown more sig-

nificantly in the surface horizons, where the organic matter content

was high. However, in Grevell series and certain subsurface horizons,

the reverse trend was observed. Further studies are necessary to

explain these observations. Freezing the samples produced higher re-

sults than any of the air-drying procedures in most surface horizons.

The concentration extracted from samples which were frozen was also

higher than oven-drying treatments except for Grevell-Ah horizon.

The trend showed by in-situ extraction results vary in different soil

series and different horizons. Ittdid not coincide with any of the

air drying procedures. Storing the samples moist in plastic containers

generally brought out relatively high concentrations of manganese.

Iron results indicated that in-situ extractions showed higher

values than air-drying - 4 month values for Blundell, Tsawwassen

and Grevell samples and no observable difference in Sunshine and Clover-

dale samples. Longer air-drying duration decreased the amount of iron

extracted in Blundell, Grevell, Sunshine and Tsawwassen series; however,

there was an increase in concentration with time for Cloverdale samples

except for the Bf horizon. These results are contrary to that observed

for aluminum and silicon. Oven-drying at 100°C released more iron

than oven-drying at 50°C for Sunshine, Cloverdale, Tsawwassen samples and for Grevell IIC horizon. However, Grevell Ah and C horizons showed a decrease in extractable iron with higher temperature drying. Blundell samples did not show any distinct differences for the two oven-drying treatments.

Storing moist in plastic containers lead to release of greater amounts of iron in Blundell Bg and Cg, and Tsawwassen-Ahₐwₐₐₛₛₑ⁻ ⁻⁻ horizons. Only slight differences were observed between storing moist in plastic container results and air-drying results for Sunshine and Cloverdale samples. Freezing was found to affect the soil samples significantly except for Sunshine series.

The response of aluminum and silicon to the different pretreatments was very similar. Generally freezing and storing moist in plastic containers contributed very high results. Oven-drying at 100°C released more aluminum and silicon than oven-drying at 50°C. This was more prominently observed in certain horizons. Again, in-situ extraction results did not coincide with any of the air-drying values. ⁻⁻⁻ For Sunshine Tseries, significant differences between the seeₑₑ ᵤₕₐₛ ᵤₕₐₛ treatments were observed in the Ah horizon.

The portion of these elements extracted by hydroxylamine hydrochloride ais derived from both the amorphous organic and inorganic complexes. These forms are very sensitive to temperature, oxidation-reduction potentials, moisture regime, and length of time exposed to the treatment. Temperature would affect the microbiological activity. Microorganisms are responsible for decomposing organic matter, oxidizing

and reducing of oxides and the weathering of minerals and rocks in
the soil. Temperature also affects the rate of reactions in the soil.
Extremely high temperatures decompose the organic matter releasing
nutrient elements. Oxidation-reduction potentials are affected by
the moisture regime of the soil, aeration, length of time exposed to
the different treatments and the microbiological activity. It can
be seen that these factors are interacting with each other dynamically.
The quantitative results that we observed are the penultimate results
of these interactions. The interactions vary with different types
of soil and for different horizons since proportions of the substances
making up a soil vary.

Results obtained from this study signify the importance of
uniform sample treatments prior to soil analysis. The extractable con-
centration of the different elements also varies with seasons. This
is shown by differences between the freezing results and the air-drying
and in-situ results. The most appropriate procedure for extracting
soil should be the in-situ extraction. This procedure reduces the
alterations that could take place with the samples. However, in-situ
extraction has several limitations too. It is time consuming, and
many sets of samples are required to ensure correct sampling. Particle-
size distribution is also important in determining the reliability of
in-situ extraction. Fine-textured soils containing an uneven distri-
bution of coarse particles would lower the precision of the analysis.

LITERATURE CITED

Baker, J. 1950. Distribution of manganese in British Columbia soils.
   M.Sc. (Agric.) thesis, Dept. of Agronomy (Soils),University of
   British Columbia.

Boken, E. 1958. Investigations on the determination of the available
   manganese content of soils. Plant and Soil 9: 269-283.

Carmer, S. G. and Swanson, M. R. 1971. Detection of differences be-
   tween means: A Monte Carlo study of five pairwise multiple com-
   parison procedures. Agron. J. 63: 940-945.

Childs, F. D.,and Jencks, E. M. 1967. Effect of time and depth of
   sampling upon soil test results. Agr. Journal 59: 537-540.

Christensen, P. D., Toth, S. J. and Bear, F. E. 1950. The status of
   soil manganese as influenced by moisture, organic matter and pH.
   Soil Sci. Amer. Proc. 15: 279-282.

Cline, M. G. 1944. Principles of soil sampling. Soil Sci. 58: 275-
   288.

Fujimoto, C. K. and Sherman, G. D. 1945. The effect of drying, heating
   and wetting on the level of exchangeable manganese in Hawaiian
   soils. Soil Sci. Soc. Amer. Proc. 10: 107-112.

Hammes, J. K. and Berger, K. C. 1960. Chemical extraction and crop
   removal of manganese from air-dried and moist soils. Soil Sci.
   Soc. Amer. Proc. 25: 361-364.

Heintze, S. G. and Mann, P.J.G. 1947. Soluble complexes of manganic
   manganese. J. Agr. Sci. 37: 23-26.

Luttmerding, H. R. and Sprout, P. N. 1967. Preliminary report of
   the Lower Fraser Valley Soil Survey. British Columbia Dept. of
   Agric., Kelowna, B.C.

Meek, B. D., Mackenzie, A. J. and Grass, L. B. 1968. Effect of organic
   matter, flooding time, and temperature on dissolution of iron
   and manganese from soil in situ. Soil Sci. Soc. Amer. Proc. 32:
   634-638.

Nishita, H. and Haug, R. M. 1971. Some physical and chemical charac-
   teristics of heated soils. Soil Sci. 113: 422-430.

Nishita, H. and Haug, R. M. 1973. Water and ammonium acetate-extractable zinc, manganese, copper, chromium, cobalt and iron in heated soils. Soil Sci. 118: 421-424.

Patrick, W. H. and Turner, F. T. 1968. Effect of redox potential on manganese transformation in waterlogged soil. Nature 220: 476-478.

Safo, E. Y. 1970. Manganese status of some Lower Fraser Valley soils developed from alluvial and marine deposits. M.Sc. (Agric.) thesis, Dept. of Soil Science, University of British Columbia.

SUMMARY

The total manganese content of the Lower Fraser Valley soils has previously been investigated. The results obtained differed significantly. In this study, the perchloric-hydrofluoric acid mixture digestion procedure was carried out to measure the total manganese, aluminum and iron in the soils studied. Total manganese concentration was found to be higher than those reported by Safo (1970), even though the soil samples were derived from the same area. Total manganese ranged from 1,365 ppm in the Cloverdale-Ah horizon to 297 ppm in the Blundell-Ap horizon, and the total iron content was found to range from 2.6 percent in the Grevell-C horizon to 6.2 percent in the Cloverdale-Bg horizon. The total aluminum concentration was highest at 8.2 percent in the Cloverdale-Cg horizon and lowest at 4.5 percent in the Monroe-Btj horizon. No definite trend was observed between the results obtained and the parent material of the soil. The distribution of iron and manganese in the soil pedon was, however, closely related. Other selected chemical properties of the soil were also determined to characterize the soils for the subsequent studies.

Soil manganese was extracted according to its oxidation states and its reducibility from the higher oxidation state. This was felt rather unnatural since manganese in the soil is mostly present as mineral crystals or as amorphous organic and inorganic complexes,

139

frequently in combination with iron, aluminum and silicon. An evaluation was therefore felt to be necessary for the extraction of manganese with:

1. Acid ammonium oxalate,

2. Sodium pyrophosphate,

3. DisodiumEDTA,

4. Hydroxylamine hydrochloride, and

5. Hydroquinone.

The trends showed by hydroxylamine hydrochloride, acid ammonium oxalate, disodiumEDTA and hydroquinone were generally the same in the soil pedons studied. Only the relative concentrations were different. Hydroquinone was only effective for extracting manganese, while disodiumEDTA, acid ammonium oxalate, sodium pyrophosphate and hydroxylamine hydrochloride extracted detectable amounts of iron and aluminum also. Only acid ammonium oxalate and hydroxylamine hydrochloride were found to extract silicon. The former extracting a higher concentration than the latter. Sodium pyrophosphate results were not consistent with the other extractants. Further studies are necessary to explain this phenomena. No relationship was observed between sodium pyrophosphate and disodiumEDTA extractions, even though both have chelating properties. The difference in pH, i.e. disodiumEDTA being 4.5 and sodium pyrophosphate 10.0, may account for this observation.

DisodiumEDTA and hydroxylamine hydrochloride results were very similar in most cases. There is a possibility that the form of manganese, iron and aluminum extracted by both reagents is the same.

Hydroxylamine hydrochloride extracted higher amounts of manganese than hydroquinone. This is the result of the fact that the former has stronger reducing capability.

Successive extraction analysis using hydroxylamine hydrochloride followed by one of the other extractants, then hydroxylamine hydrochloride again, was undertaken to investigate the origin of reducible forms of manganese and the other elements extracted by hydroxylamine hydrochloride. This study also investigated the reliability of successive extraction procedures. Results indicated that the easily-reducible portion of manganese and iron are derived from the organically and inorganically complexed forms. Since the oxidation reduction potentials of these complexed metal ions are altered as a result of the complexation, the extent of reduction by hydroxylamine hydrochloride varies with the type of compounds in the soil.

The properties of the preceding extractants are important in affecting the concentration of manganese, iron, aluminum and silicon extracted by hydroxylamine hydrochloride in the successive extraction studies. Only very small amounts of manganese were extracted by hydroxyl-amine hydrochloride after the samples had been extracted by hydroxyl-amine hydrochloride and any of the other extractants successively. Generally, more iron, aluminum and silicon were extracted by hydroxyl-amine hydrochloride after either acid ammonium oxalate or disodiumEDTA extractions than hydroxylamine hydrochloride prior to these extractants. The differences were more significant in fine-textured soils. More aluminum and silicon were also extracted by hydroxylamine hydrochloride

after sodium pyrophosphate and hydroxylamine hydrochloride extractions. These results indicate the changes in the soil system initiated by the preceding extractant. The reliability of successive extraction procedures for quantitative analysis is therefore questioned.

The effects of sample pretreatments on the extractability of manganese, iron, aluminum and silicon by hydroxylamine hydrochloride were also studied. The pretreatments were:

A. In-situ extraction,

B. Oven-drying at 50°C for one week,

C. Oven-drying at 100°C for one week,

D. Air-drying for one week,

E. Storing moist in plastic containers for three months,

F. Air-drying for four months, and

G. Freezing the soil for one month.

Significant differences in results were observed between in-situ extractions and the air-drying procedures for some horizons. Oven-drying at 100°C compared to oven-drying at 50°C often lead to greater extractability of these elements in most horizons. Generally a longer duration of air-drying resulted in a smaller concentration of extractable elements. Freezing and storing moist in plastic containers gave distinctly higher values for most samples. Hydroxylamine hydrochloride extracts the easily-reducible portion of manganese, iron and the associated aluminum and silicon. The complex chemistry of these elements, and the greater reactivity of this portion of manganese, iron, aluminum and silicon, made it impossible to show a definite trend on the effects of the different pretreatments on the soils studied. The results did, however, lay the basic ground work for further studies.

APPENDIX 1

Concentration of Manganese by Pretreatments
for Significant Test Using FLSD
FLSD = 20.7
(0.05)

Soil	A*	B*	C*	D*	E*	F*	G*
Blundell							
Ap	9.5	7.9	8.8	6.7	8.8	8.0	10.8
Bg	2.5	1.7	2.3	1.9	2.7	2.2	2.6
Cg	3.1	2.2	2.5	2.3	4.3	2.5	5.1
Tsawwassen							
Ah	42.7	37.1	41.2	34.5	51.2	40.7	44.9
C	19.9	14.2	14.5	15.4	17.3	14.4	20.9
Grevell							
Ah	157.0	224.3	182.5	162.7	143.0	191.5	206.0
C	121.1	220.7	160.0	241.9	202.4	162.6	137.9
IIC	153.8	116.6	92.6	137.4	129.9	100.0	108.9
Cloverdale							
Ah1	291.9	235.7	245.1	195.8	242.4	408.8	349.7
Ah2	249.5	179.2	412.3	250.0	403.3	276.2	471.1
Bf	174.9	366.7	196.7	372.3	220.9	212.2	248.5
Cg1	138.1	129.2	108.6	137.5	168.0	88.5	108.9
Cg2	122.4	204.2	168.4	225.3	182.7	168.2	121.3
Sunshine							
Ah	69.8	33.9	48.1	34.8	59.2	28.0	71.9
Bf1	53.5	56.6	64.3	54.5	56.2	42.3	66.9
Bf2	20.9	23.8	25.9	17.1	19.4	22.3	20.8
BC	4.0	4.5	5.8	5.4	6.8	4.7	4.8

A - In-situ extraction
B - Oven-dried at 50°C for one week
C - Oven-dried at 100°C for one week.
D - Air-dried for one week.
E - Stored moist in plastic containers for three months
F - Air-dried for four months
G - Frozen for one month

Concentration of Iron by Pretreatments
for Significant Test Using FLSD
FLSD = 51.0
(0.05)

Soil	A*	B*	C*	D*	E*	F*	G*
Blundell							
Ap	340.1	446.0	454.2	343.7	309.1	231.7	406.5
Bg	547.9	718.0	630.7	675.9	884.8	561.5	903.3
Cg	738.1	1,088.4	1,028.2	752.5	1,480.1	503.0	1,257.4
Tsawwassen							
Ah	234.5	69.4	98.3	113.6	369.5	62.3	219.1
C	114.9	73.3	94.5	103.0	105.4	61.3	136.4
Grevell							
Ah	86.0	101.6	55.2	100.5	80.4	54.4	52.3
C	272.6	130.8	105.2	157.9	129.6	98.1	79.0
IIC	125.2	142.8	199.4	105.7	151.6	131.7	221.5
Cloverdale							
Ah1	180.6	129.9	254.0	96.7	88.1	244.0	274.4
Ah2	170.5	100.9	428.1	109.2	148.5	171.1	270.8
Bf	132.7	192.9	279.1	186.1	97.6	146.5	192.6
Cg1	125.1	148.3	265.4	120.8	102.9	154.3	117.2
Cg2	110.3	72.5	145.3	79.7	77.5	96.3	103.6
Sunshine							
Ah	115.2	311.1	574.0	288.8	88.1	93.4	70.1
Bf1	70.8	72.0	113.3	108.7	50.3	57.1	80.9
Bf2	54.4	62.1	102.2	47.5	35.9	63.5	59.4
BC	31.9	59.1	80.5	58.5	26.9	39.6	35.9

A - In-situ extraction
B - Oven-dried at 50°C for one week
C - Oven-dried at 100°C for one week
D - Air-dried for one week
E - Stored moist in plastic containers for three months
F - Air-dried for four months
G - Frozen for one month

Appendix 3

Concentration of Aluminum by Pretreatments
for Significant Test Using FLSD
FLSD = 68.0
(0.05)

Soil	A*	B*	C*	D*	E*	F*	G*
Blundell							
Ap	185.3	170.0	237.3	145.0	299.7	161.4	260.7
Bg	309.6	223.5	344.4	245.4	551.5	370.4	532.3
Cg	132.9	143.3	157.8	139.1	528.8	245.8	324.9
Tsawwassen							
Ah	12.3	7.5	29.6	7.9	25.0	7.5	20.0
C	227.4	24.4	59.0	39.2	71.0	58.2	80.1
Grevell							
Ah	3.7	3.7	3.7	4.2	2.4	3.7	-
C	66.2	14.2	3.0	16.7	24.0	3.5	2.0
IIC	7.2	102.9	68.0	95.3	76.6	50.1	56.5
Cloverdale							
Ah1	264.0	500.7	316.4	347.5	188.7	239.8	357.7
Ah2	319.7	412.8	396.8	241.3	373.1	218.4	265.0
Bf1	119.8	528.8	406.9	442.6	304.3	218.9	233.2
Cg1	24.0	64.0	65.8	73.3	61.2	45.0	48.0
Cg2	42.6	37.1	22.9	39.2	40.9	18.3	20.7
Sunshine							
Ah	245.8	864.3	1,260.1	430.3	300.1	328.1	219.9
Bf1	427.5	336.1	446.5	302.1	559.6	374.5	638.9
Bf2	595.7	303.7	422.8	236.2	617.1	407.2	648.7
BC	354.0	338.2	367.3	304.3	590.1	404.7	546.1

A - In-situ extraction
B - Oven-dried at 50°C for one week
C - Oven-dried at 100°C for one week
D - Air-dried for one week
E = Stored moist in plastic containers for three months
F - Air-dried for four months
G - Frozen for one month

Appendix 4

Concentration of Silicon by Pretreatments
for Significant Test Using FLSD
FLSD = 17.0
(0.05)

Soil	A*	B*	C*	D*	E*	F*	G*
Blundell							
AP	22.2	25.0	25.7	15.0	56.5	19.0	27.2
Bg	70.6	42.8	86.7	28.6	194.4	30.4	64.1
Cg	67.5	79.1	75.0	41.8	139.5	22.8	104.8
Tsawwassen							
Ah	11.1	7.5	8.3	15.0	37.0	12.5	-
C	30.8	24.9	35.0	29.1	61.0	37.5	34.8
Grevell							
Ah	45.3	62.3	77.2	66.7	47.6	60.8	69.8
C	156.6	81.3	89.6	112.4	72.0	70.1	62.3
IIC	54.8	116.6	128.5	137.4	108.1	104.5	142.6
Cloverdale							
Ah1	229.4	262.3	84.3	37.6	203.2	48.1	64.4
Ah2	330.7	154.8	100.1	29.2	373.1	32.9	64.5
Bf	130.5	81.2	86.6	62.7	304.3	37.8	56.3
Cg1	68.7	129.1	141.4	104.2	61.1	101.7	108.9
Cg2	231.3	156.5	203.4	162.7	40.9	142.9	220.1
Sunshine							
Ah	17.0	36.8	88.3	44.1	65.2	18.7	33.2
Bf1	29.4	79.1	77.7	58.3	76.0	55.8	76.1
Bf2	84.2	83.3	86.0	54.1	92.3	74.7	84.6
BC	43.6	83.3	75.0	63.9	96.1	74.3	87.9

A - In-situ extraction
B - Oven-dried at 50°C for one week
C - Oven-dried at 100°C for one week
D - Air-dried for one week
E - Stored moist in plastic containers for three months
F - Air-dried for four months
G - Frozen for one month