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THE DISTRIBUTION OF MANGANESE IN BRITISH COLUMBIA SOILS

By

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## ABSTRACT

A survey was undertaken to determine the manganese status of some of the more important soil associations of British Columbia. Three fractions of soil manganese, total, available and hydroquinone reducible were determined in the surface and parent materials of 45 uncultivated soil profiles.

The standard colorimetric procedure as described by Sandell was used for the determination of total manganese, with certain modifications introduced which made it especially suited for use with soil. Available manganese was estimated by replacement with ammonium acetate and the hydroquinone reducible fraction, using the same reagent with a 0.2% hydroquinone solution added.

The total manganese content of the samples was found to range from 0.007% to 0.494%. These values compared favorably with those reported for the soils of the United States, but proved to be somewhat higher than the values recorded for the soils of Australia. When the total manganese values obtained were compared by regions, the samples from the Lower Fraser Valley and Vancouver Island were generally highest and those from the Peace River Area lowest in manganese content. The samples from the Central Interior, Okanagan Valley, Rocky Mountain Trench and Kootenays were generally intermediate in total manganese content.

The available and hydroquinone reducible manganese content of the samples proved to be high also as compared to

ABSTRACT - Cont.

values reported from other countries.

The high values generally obtained for total, available and hydroquinone reducible manganese indicate that most soils in British Columbia are adequately supplied with this element. In fact, the indiscriminate use of manganese fertilizers might prove detrimental by increasing naturally high levels of available manganese to a point where it would prove harmful to plant growth.

Soils deficient in manganese for normal plant growth may occur in British Columbia. If such is the case, it is to be expected that the deficiency would be associated with such conditions as alkaline soil reaction, excessive use of lime, organic matter depletion and ion interference. Should manganese deficiency be suspected in a soil a very careful study of the condition should be made before manganese fertilization is recommended.

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## THE DISTRIBUTION OF MANGANESE IN BRITISH COLUMBIA SOILS

### INTRODUCTION

The occurrence and distribution in soils of such elements as copper, boron, cobalt, zinc and manganese is being given increasing attention. This maybe attributed to the growing recognition of the important roles played by these elements in plant and animal metabolism.

The investigation of manganese in soils and plants started with the work of Scheele (38) who in 1774 detected it in the ash residues of plants. It was not until nearly one hundred years later that Sachs (36) in 1864 undertook the first study of the role of manganese in plant growth. Although Sachs was apparently unable to satisfy himself as to the necessity of manganese to plant requirements, in all his later experiments manganese was added to ensure its presence in the culture medium. The later work of Bertrand (2) in 1897, Brenchley (3) in 1914, and McHargue (28) in 1922 demonstrated the essential role of manganese in plant growth.

The recognition of the important role played by manganese in plant growth prompted many studies of its occurrence and distribution in soils, and manganese defici-

encies have been reported from various parts of the world. From time to time suggestions have been made that some of the soils of British Columbia may be deficient in this element. Since no study of the manganese content of the soils of this province has been made, it was felt that an attempt should be made to investigate the manganese status of some of the soils of British Columbia. It was this fact that prompted the present study.

#### REVIEW OF LITERATURE

##### Properties of Manganese:

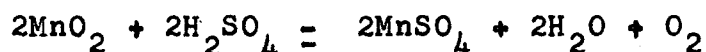
Manganese is a brittle non-magnetic metal which, like iron, can be hardened by alloying with carbon. It has a specific gravity of 8, melts at  $1225^{\circ}$  C. and boils at  $1900^{\circ}$  C. It is easily oxidised and decomposes water with the liberation of hydrogen gas at a temperature only slightly higher than room temperature. The metal is easily dissolved in dilute mineral acids and even in dilute acetic acid (25).

Manganese behaves much like most amphoteric elements; in many of its reactions it behaves as a base, while in others it acts as an acid. It forms many oxides of definite composition some of which are basic, e.g. manganoous oxide ( $\text{MnO}$ ), mangano-manganic oxide ( $\text{Mn}_3\text{O}_4$ ) (25).



The acidic oxides are: manganese trioxide ( $\text{MnO}_3$ ), manganese heptoxide ( $\text{MnO}_7$ ). The action of hydrochloric acid on manganese dioxide brings about the liberation of chlorine (25).

$$4\text{HCl} + \text{MnO}_2 = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$$
 sulfuric acid brings about the liberation of molecular oxygen.



The two reactions given above indicate the slight basic nature of manganese dioxide.

Manganese will combine to form double salts ( $\text{MnCl}_4$ ,  $2\text{KCl}$ ),<sup>and</sup> complex salts ( $\text{K}_2\text{MnCl}_6$ ). Manganic sulfate is formed by the action of concentrated sulfuric acid on manganese dioxide in the presence of heat (25) (42).

$$2\text{MnO}_2 + 6\text{H}_2\text{SO}_4 + \text{heat} = 2\text{Mn}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} + \text{O}_2$$
 Manganese dioxide when hydrolysed and treated with alkali solutions will form alums, e.g. ( $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ).

#### Manganese Minerals:

According to Treadwell-Hall (42) the most important manganese bearing minerals are pyrolusite ( $\text{MnO}_2$ ), polianite ( $\text{MnO}_2$ ), braunite ( $\text{Mn}_2\text{O}_3$ ), magnetite ( $\text{HMnO}_2$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), and rhodochrosite ( $\text{MnCO}_3$ ). This author states that pyrolusite is the richest source of manganese, the

purier samples being as much as 50% by weight manganese. He also makes mention of Wad, an impure mixture of oxides which is found in low-lying, damp areas.

In addition to the minerals mentioned above Dana (4) has recorded in some detail a list of the manganese containing ores and rocks.

Until recently very little attempt has been made to identify the actual nature of the manganese minerals occurring in soils. However, it seems likely that the more resistant of the minerals mentioned, together with various modified forms, persist.

In recent soil studies carried out in England Heintze and Mann (13) extracted soil free of their manganese using sodium hexametaphosphate. It was noted that most, if not all, of the manganese present was extracted using this reagent. Known amounts of manganese minerals - hausmannite ( $Mn_3O_4$ ), magnetite ( $HMnO_2$ ) and manganese oxide ( $Mn_2O_3 \cdot xH_2O$ ) were then added to the soils; these, too, were completely extracted by the phosphate solution. In the study of the phosphate extract Heintze and Mann (13) concluded that alkaline extracts contained divalent manganese<sup>and</sup>, that in neutral solution of the phosphate extract trivalent manganese could be formed by the interaction of divalent manganese and manganese dioxide ( $Mn^{++} = MnO_2$ ). It was suggested by these authors that the extracted manganese was

in the form of a mangani-pyrophosphate complex and occurred in soils as a hydrated manganic oxide ( $\text{Mn}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ).

Dion and Mann (5) extracted soils with pyrophosphate solution of varying molar concentrations. It was noted by these authors that the greater the phosphate concentration in the extractant, the greater the amount of manganese extracted. This fact, Dion and Mann suggest, was the result of interaction between phosphate ions and higher oxides of manganese which rendered them soluble. It was thought that the form which manganese combined with the pyrophosphate was in a manganipyrophosphoric acid complex ( $\text{HMnP}_2\text{O}_7$ ). Meyer and Merek (26) who carried on similar work suggested the formation of a manganidiorthophosphoric acid complex. However, more recently Kolthoff and Watters (21) have obtained a pyrophosphate manganate complex ( $\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3$ ).

Dion and Mann (5) proposed a method which they suggest could be used to determine the valency of manganese compounds in soils. They have postulated that manganese present in the soil might be in the form of manganic hydroxide ( $\text{Mn}(\text{OH})_3$ ) or as the hydrated manganic oxide ( $\text{Mn}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ ). This conclusion was made since manganic hydroxide added to the soil could be extracted with pyrophosphate solution similarly as the naturally occurring trivalent manganese compounds found in soils.

As yet absolute identification of <sup>the</sup> manganese compounds in soil has not been achieved. However, in recent years advances have been made toward this end, and undoubtedly methods will be devised which will aid greatly the problem of identification of manganese minerals which persist in soils

#### Occurrence of Manganese in Soils:

The manganese occurring in soils has been studied in three main fractions: total, available, and hydroquinone reducible (39) (13). The amount and proportion of soil manganese occurring in these various fractions has proved to vary from soil to soil, to change from one form to another and has been observed to be affected by many complex factors. Each of the various fractions will be considered in turn.

Total Soil Manganese: This fraction embraces all the manganese present in soil and therefore includes the manganese present in the other two forms. Total soil manganese has usually been determined by acid extraction using sulfuric and hydrofluoric acids (37) although occasionally other extractants have been used (5) (13).

Leeper (22) working in Australia places the range of total manganese in soil from 0.1% maximum to a minimum of a few parts per million. In the case of the soils of the United States Robinson (34) (35) reports a range in total

manganese from 0.00% to 0.31% as manganese oxide. Soils up to 10.0% manganese oxide have been reported from Hawaii (1). Heintze and Mann (13) in England found mineral soils to be better supplied with respect to total than organic soils.

Climate has been found to have a pronounced effect upon the total manganese content of soil. Its effect is chiefly indirect through its influence on soil reaction (22) (7). In arid regions where precipitation is light basic ions accumulate which increase the soil alkalinity. In alkaline soils oxidation conditions are favored with the result that divalent manganese is oxidised quite readily and fixed as higher oxides of manganese. It is for this reason Sherman and Harmer (39) state divalent manganese is difficult to maintain in alkaline regions. However, under humid conditions sufficient precipitation falls to leach most of the soil bases from the soil which results in soil acidity. This increase in soil acidity brings about the solution of manganese compounds which are subsequently lost through leaching and runoff waters (27)(22). Considering climate only one would expect soils of arid regions to be supplied with greater quantities of manganese than soils of humid regions.

According to Leeper (22) eight factors influence the distribution of total manganese in the soil profile. These are:

1. Weathering of minerals and decay of organic matter.
2. Downward movement of manganese in drainage water.
3. Equilibrium between divalent manganese in solution and exchangeable cations on the surface of the soil colloidal complex.
4. Uptake of divalent manganese by roots and the subsequent deposition as litter on the surface.
5. Oxidation of divalent manganese to higher oxides of manganese by oxygen or bacteria.
6. Aging of manganic oxides from active to inert forms.
7. Reduction of manganic oxides by organic matter or bacterial action.
8. Direct absorption of manganic oxides by soil microorganisms and plants.

The first four factors, Leeper states, are common to most metals; while, the last four are specific for manganese.

As a result of these eight factors Leeper (22) suggests<sup>ed</sup> any one of the four types of manganese distribution through the profile:

1. A slight accumulation at the surface with a minimum in the subsurface, then a gradual increase with depths. Leached soils show this pattern. The concentration at the surface is attributed to plant action.
2. A steady decrease with depths found in certain leached soils, especially those with red tones.

3. A steady manganese value throughout the profile. This is characteristic of pedocols and unleached soils.
4. An accumulation in the subsoil just above the calcareous layer.

Available Manganese:

This fraction of the soil manganese is intended to include the manganese immediately available to the plant and is thought to comprise the manganese present in the soil solution together with that held in a replaceable form by the soil colloids. When estimating available manganese the usual practice is to leach the soil with neutral normal ammonium acetate (13) although some investigators have used calcium and magnesium nitrates,  $(\text{Ca}(\text{NO}_3)_2)(\text{Mg}(\text{NO}_3)_2)$  as extracting agents (12) (41). Ammonium acetate is usually preferred since it may be easily destroyed and the manganese in the residue determined colorimetrically using periodate (12) (13) (39).

Different extracting solutions have been found to remove different amounts of manganese and for this reason when reporting available manganese content of a soil the extracting reagent should be identified. This was well illustrated by Steenbjerg (41), working with heavily limed soils of Denmark, who found 0.5 molar magnesium nitrate  $(\text{Mg}(\text{NO}_3)_2)$  the most effective extractant in the determination of available manganese. He also found calcium

nitrate to be effective in the estimation of available manganese; while potassium, sodium and ammonium nitrate along with ammonium acetate to be ineffective. Heintze (12), on the other hand, states that on the alkaline soils of Romney Marsh, England, 0.5 m. calcium nitrate extracted four times as much soluble manganese as did magnesium nitrate of equal molar concentration.

From these results it is apparent that when considering the available manganese fraction the extracting solution should be clearly identified along with the nature of the soil and conditions of the test.

Active or Hydroquinone Reducible Manganese: This fraction of the soil manganese is intended to include the manganese present in oxidized forms which may be easily reduced to the manganous state (5) (39). The easily reducible manganese would therefore not be soluble and would not be available to plants. However, the fact that it may be easily reduced and so made soluble and available makes it an important potential source of manganese for plants. It is thought that if the conditions are favorable for its reduction during the growing season it may be an extremely important source of soluble manganese (22).

Various methods have been used to estimate the amount of easily reducible manganese present in soil and different methods have been found to give different results. There-



fore the complete definition of easily reducible manganese should include the method for its estimation but complete agreement has not been reached as to what method should be specified.

Heintze and Mann (13) suggested that the easily reducible fraction should be that removed by treating a soil with a 0.2% hydroquinone solution of neutral normal ammonium acetate for a period of 15 hours with intermittent shaking at the beginning and end of the experiment, or constant agitation for one hour. These investigators suggested that the more reactive portion of manganic oxides was extracted in this manner. For the 14 mineral soils they worked with they obtained an average recovery of 54% of the total manganese present, while an average of 15% recovery was obtained for the organic soils used. It was thought by the authors that the low figure for organic soils was due to the formation of a complex with organic matter thus fixing manganese in an insoluble state (13).

The definition given by Harmer and Sherman (39) for this fraction of the soil manganese was that portion of manganese dioxide which could be extracted in a period of six hours by a 0.2% hydroquinone solution of neutral normal ammonium acetate.

Leeper (22) at first suggested that a period of seven hours was required in order to leach a soil free of its

most active manganic oxides, using a 0.2% hydroquinone solution of ammonium acetate. He later suggested a half hour period was sufficient.

Gisiger (9), on the other hand, held the view that a three-minute period was sufficient time to remove the most active forms of manganic oxides from the soil. He suggested that a longer period of leaching with 0.2% hydroquinone in neutral ammonium acetate would remove the less reactive manganic oxides, thus obscuring the contrast between these and the most active forms. These less reactive forms of manganic oxides were extracted using neutral hyposulfite solution at pH 7 (22).

McCool (27) suggests another method of estimating this fraction of soil manganese which is adopted for use on highly acid soils. In his procedure the dry soil under study is stored for a period of a month at a temperature of 72° F. or higher and then extracted with water. This treatment was found particularly useful on highly acid soils which may accumulate toxic amounts of manganese by the interaction of organic matter and manganese oxides. He found that the method did not apply where microbial oxidation was appreciable or in moderately acid soils where water soluble manganese decreased with time of storage.

Two qualitative tests have been used to indicate the approximate amount of active or easily reducible manganese

in soils. One of the tests is colorimetric and uses benzidine salts. The manganic oxide has the ability to oxidise the benzidine salts in a neutral solution, resulting in the formation of a brilliant blue cation which is strongly absorbed and colors the soil blue (5). The other qualitative test is the catalytic destruction of hydrogen peroxide which can be studied either by the rise in temperature or by the rate of evolution of oxygen (34). These tests are not quantitative but are of value as indicators in the field.

On the basis of the investigations mentioned above, there can be no doubt as to the existence and importance of the active manganese fraction of soils. The exact nature of the fraction, however, is still in question as is the best method to utilize in its estimation. Of the methods that have been developed the most generally accepted involves the use of 0.2% hydroquinone as the reducing agent.

According to Leeper (22) the same pattern as was observed in the distribution of total manganese is noted in the case of <sup>the</sup> active fraction but with much stronger contrast between the horizons. Leeper reports that in leached soils there is a surface accumulation of active manganese while there is a marked decrease in the subsoil. Also, providing the subsoil is alkaline, there is a general increase in

the active manganese content with depth; otherwise it remains very low.

Alexander and Hendricks (14) have reviewed some interesting relationships in this regard. These authors point out that the same factors that favor the formation of kaolinite type clays in soil, i.e., acid conditions and strong leaching, also favor removal of active manganese. Similarly the conditions that favor the formation of montmorillonite type clays in soil, i.e., alkaline reactions and limited leaching, favor the accumulation of active manganese.

From the evidence available it appears that the distribution of active manganese in the soil is governed by the interaction of a number of factors that include reaction, extent of leaching, plants and the soil parent material.

#### Chemical Changes Affecting Soil Manganese

It was easily shown that the total manganese content of soil has little or no relationship to the amount of manganese that might be available in the soil for plant use (22) (39). This fact led to extensive study and discussion in regard to the chemistry and biology of soil manganese (22) (39). For some time it was generally considered that manganese present in soil was either in the available divalent form or in the tetravalent higher oxide state and unavailable to the

plant. Recently, however, Heintze and Mann (13), Quastel (33) and Dion and Mann (5) have given evidence of the existence of a third form, a trivalent compound of manganese. Dion and Mann (5) studied English soils which were known to be low in available manganese but well supplied with total concentrations of the element. Even after adding 1100 p.p.m. manganese as manganese sulfate to these soils they were able to extract only 10 p.p.m. available manganese. From this result Dion and Mann (5) suggested that the divalent manganese added to the soil was quickly oxidised either biologically or chemically to higher valent forms, perhaps trivalent and tetravalent.

Their reason for suggesting the presence of a trivalent form was based on an experiment in which benzidine salts were employed. This reagent is apparently specific for trivalent manganese since pyrolusite, a tetravalent form did not give the positive blue cation when tested. Benzidine, therefore, provides a specific test for trivalent oxidised manganese (14). Using a pyrophosphate extract from the same soils, these men carried out valency determinations, the results of which would indicate that a trivalent form of manganese was present in soils.

From their experiments Dion and Mann (5) postulate that:

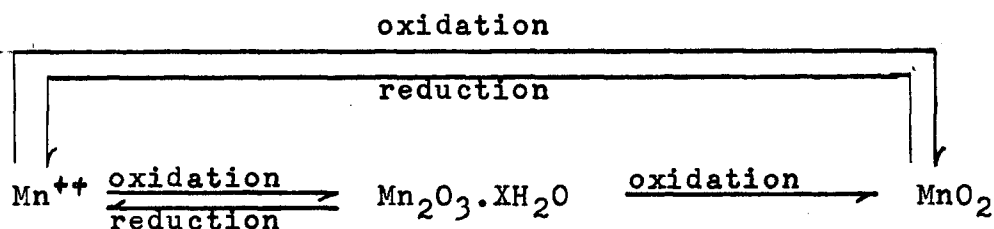
1. trivalent manganese is present in the soil at the expense of the divalent form.
2. trivalent manganese is the first product of oxidation.
3. trivalent manganese makes up about 23-24% of the total manganese concentration in soils.
4. trivalent manganese once formed can be either oxidised or reduced, depending upon soil conditions

Leeper (22) is of the opinion that the reactions outlined below take place in the soil:

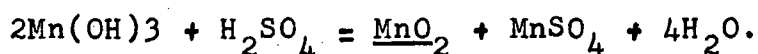


Leeper also states that oxidation to pyrolusite ( $\text{MnO}_2$ ) takes place quite rapidly in the presence of alkali and colloidal hydrated manganous oxide is oxidised to the inert oxide. This oxidation is accelerated in the presence of certain anions such as chlorides, etc. found in fertilizers (22) (39).

Although it is generally believed that oxidation of manganese in soils goes on at a much more rapid rate than reduction, it must not be assumed that reduction does not take place. In many acid organic soils reduction of higher oxides form the only source of divalent manganese (5) (33) (39). Both Quastel (33) and Dion and Mann (5) suggest the following manganese cycle in soils:



Quastel (33) maintains soil organisms participate actively in this cycle. According to Dion and Mann (5) trivalent manganese once formed in soils is subject to reduction particularly under acid conditions; at the same time, however, oxidation takes place. The probable reaction which takes place is:



Experiments were carried out by these investigators to determine the rate and proportion of the transformation of trivalent manganese in a range of pH values. When manganic hydroxide was used as a source of manganese the results obtained showed the rate of transformation varied directly with pH; 82% dismutation took place at pH 6.2 while only 10.7% was observed at pH 7.5. They conclude from this that manganic hydroxide is much more stable under alkaline than acid conditions and also the presence of divalent manganese is almost completely dependent upon the reduction of trivalent manganese. In acid soils trivalent manganese gives half its manganese to the divalent and half to the tetravalent forms.

It has been suggested that divalent manganese is oxidised to unavailable forms through the action of soil microorganisms (8) (23) (33). Leeper (23) has made the statement that organisms present in soils could oxidise divalent manganese to higher oxides at pH 5.5 and higher. He also reports that oxidation was accelerated when soils were well aerated. He arrived at this conclusion from results obtained in an experiment which involved applications of manganese sulfate to the soil in which the divalent manganese was slowly absorbed by the soil colloids and then oxidised by bacterial activity to higher oxides. The time required for the oxidation depended upon the temperature. Leeper concluded his study with the statement that non-biological oxidation of manganese is negligible below pH 8.

Gerretsen (8) confirmed Leeper's statements concerning the role played by organisms in the chemistry of soil manganese. He reported that deficiency symptoms in plants occurred in soils which were normally healthy after bacteria from a manganese-deficient soil had been incorporated. He then applied formalin to the deficient soil and found deficiency symptoms in the plants grown were less frequent. Hiltner (15) found the use of carbon dioxide reduced the occurrence of deficiency symptoms in plants. Presumably these substances inhibit bacterial oxidation of manganese.



Leeper's (23) conclusion that non-biological oxidation of manganese was negligible below pH 8 was refuted by Sherman et al (40) and Wain et al (45). These workers suggest that the oxidation of divalent manganese to higher oxides took place far too rapidly for biological activity. They have recorded an experiment in which the transformation took place in less than three hours.

Suggestions have been made that soil microorganisms can bring about the reduction of manganic oxides resulting in the liberation of divalent manganese. Quastel (33) and Leeper (23) have been the most vigorous supporters of this hypothesis. The fact that the organisms responsible have not been isolated as yet from the soil has not prevented Quastel from postulating their presence.

Fujimoto and Sherman (7), studying the soils in Hawaii noted that during the hot dry summer months the exchangeable manganese content of the soils increased markedly and resulted in a chlorotic condition in plants grown in these soils. This fact prompted further investigation as it suggested the possible reduction of higher oxides of manganese as a result of the action of heat.

In the process of their study Fujimoto and Sherman carried out experiments in which they tested the effect of air drying and heating on the level of exchangeable manganese in soils as shown in Figure I. It was noted that relatively high concentrations of available manganese were

liberated by oven drying and steam sterilisation processes. This phenomenon has been confirmed by several other investigators. Kelley and McGeorge (19) and McCool (27) have given evidence of a similar nature in which the exchangeable manganese was increased by heating a soil. The increase in the level of exchangeable manganese upon heating a soil was observed in all horizons; however, the greatest liberation was noted in the surface soil with a general decrease with depths (7). It was observed that the liberation of soluble manganese was very slow until about 70° C., when large quantities of manganese were liberated with an increase in temperature (7), (illustrated in Figures II and III). The resemblance of results obtained here with those obtained by oven drying suggest to these authors that the increase in divalent manganese may be the result of a physical rather than a chemical phenomenon. They postulate that the loss of water of hydration from the manganese complex tends to cause the compound to become unstable, resulting in the liberation of soluble manganese.

Another study was carried out by Fujimoto and Sherman to determine the effect of wetting and drying upon the valence state of manganese present in soils. It was found that soluble divalent manganese decreased with increased soil moisture content as shown in Figure IV. Fujimoto and Sherman (7) attribute this fact to either oxidation of

divalent manganese to insoluble forms, or it may be due to rehydration of the manganese complex. The second proposal seems the more logical to these men since the chlorotic condition of plants which were evident during the hot dry part of the growing season were observed to disappear during the months of lower temperatures.

Fujimoto and Sherman concluded their study with the statement that the increased concentration of divalent manganese as a result of these several physical treatments was due predominantly to the processes of hydration and dehydration, although oxidation-reduction processes were still considered active in determining the valency of manganese in soils.

The varying moisture content has been shown to have a marked influence of the divalent manganese concentration in most soils. In water saturated soils reducing conditions are favored, thus Piper (31) and Leeper (22) both working with Australian soils were able to detect appreciable increase in the water soluble manganese when the soils were saturated. These findings are in accord with those given by McCool (27) and Fujimoto and Sherman (7).

One of the main factors affecting the valency of manganese in the soil is its reaction. It plays a prominent role in determining the valence state displayed by soil manganese (33) (39). In very acid soils the formation of di-valent manganese is enhanced since oxidation by bacterial

or chemical means is practically nil; while reduction is at a maximum (22). On the other hand, neutral or alkaline conditions divalent manganese is almost completely oxidised to trivalent and tetravalent forms (5) (22) (33) (39) (40)(45). Leeper (22) suggests that reduction is negligible above pH5.5.

On the basis of presently available information, it appears that at least three valence forms of manganese may occur in most soils and that any one or a combination of all may be present. However, those factors which exert the greatest influence in any particular soil will govern the form taken by the manganese present.

FIGURE I

The effect of air drying upon the liberation of exchangeable manganese.\*

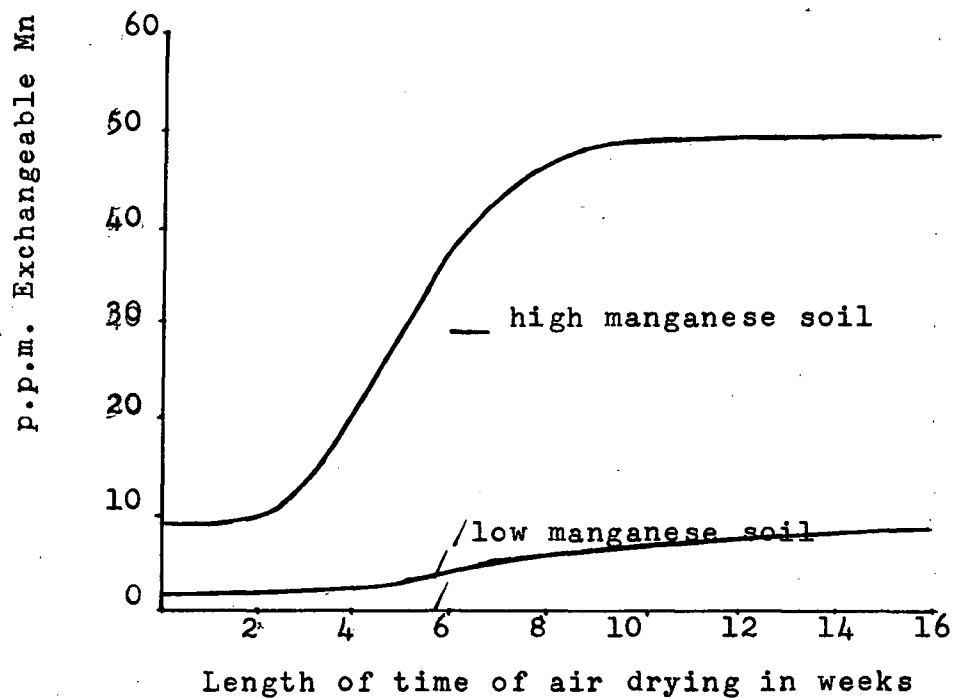
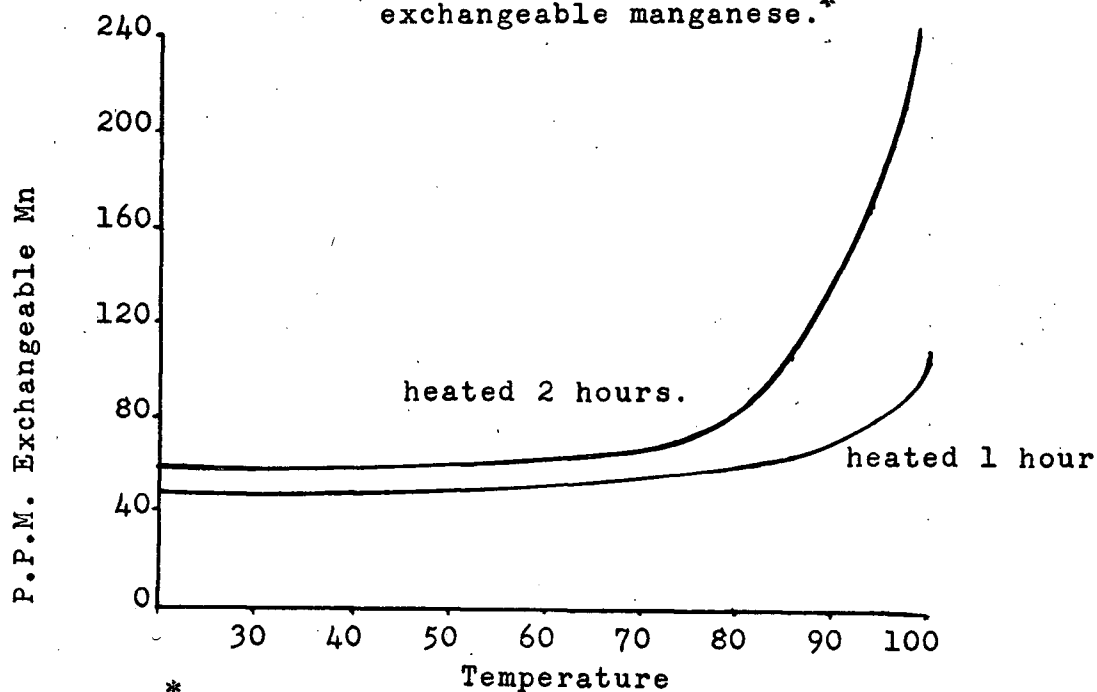


FIGURE II

The effect of temperature upon the liberation of exchangeable manganese.\*



\* Fujimoto and Sherman.

FIGURE III

The effect of the incubation temperature upon the liberation of exchangeable manganese.\*

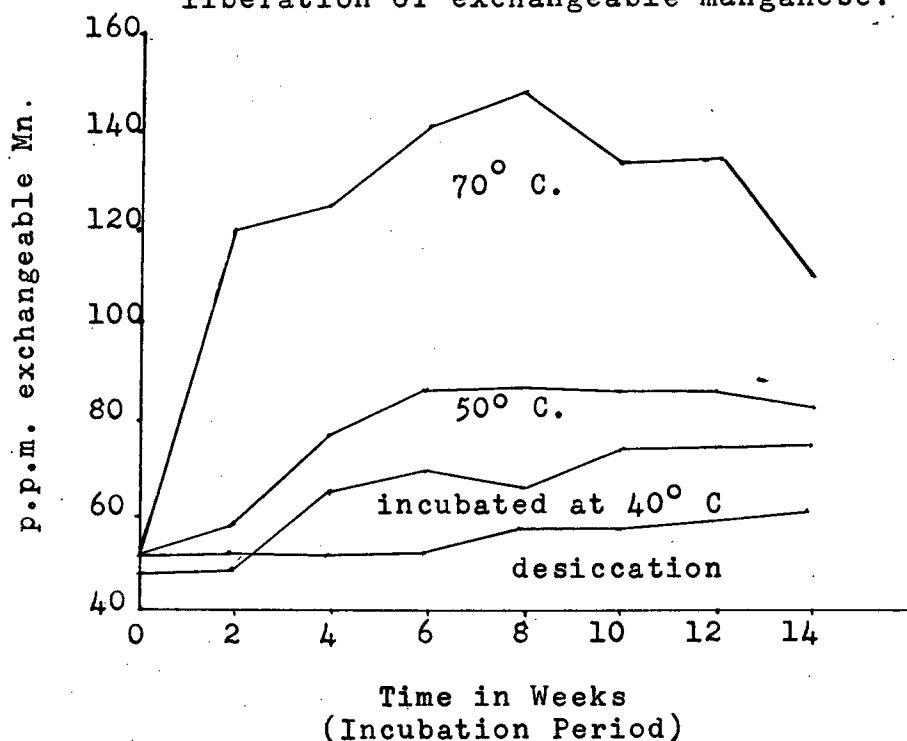
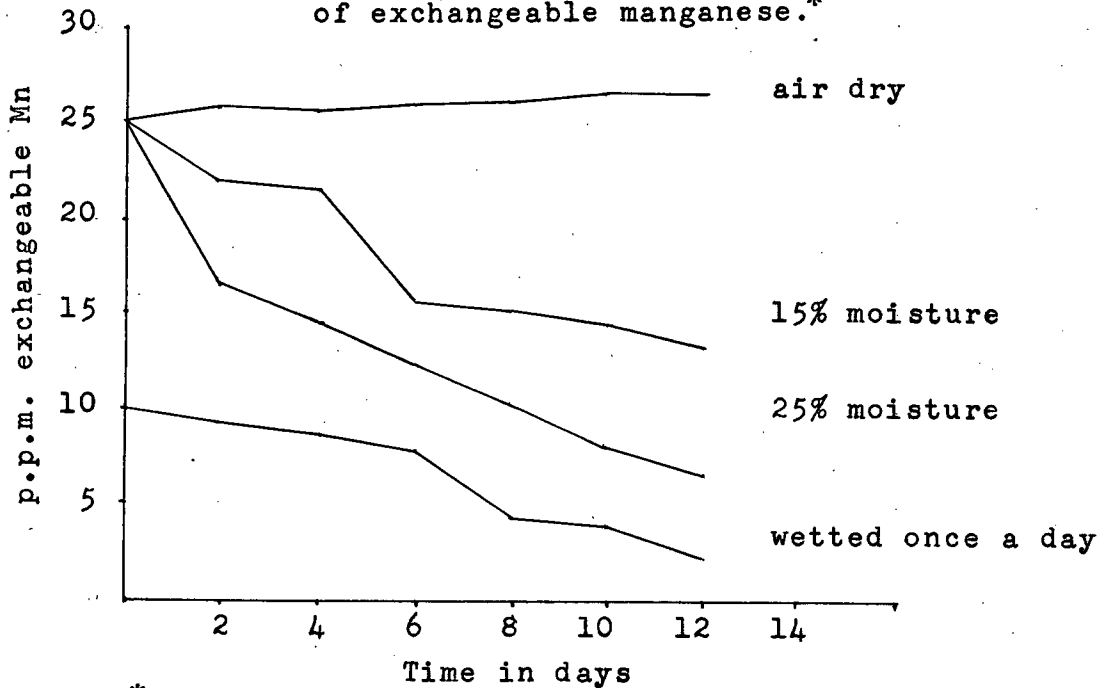


FIGURE IV

The effect of moisture content upon the liberation of exchangeable manganese.\*



\* Fujimoto and Sherman.

Soil Manganese-Plant Relationships:

Manganese deficiency has been observed to occur in many plant species with different visual symptoms for different species (20). For example, conditions known as gray speck of oats and marsh spot of peas are attributed to manganese deficiency (32) (12). This apparent deficiency of the element in the soil in reality may not be an actual lack but may be due to certain factors which render the manganese present in soils unavailable for plant growth. The amount of manganese present in the soil for plant requirements depends largely upon the soil reaction (13) (33) (39).

The valence state of manganese used by the plant is invariably in the reduced form which is available from the soil and the soil colloids (7) (12) (31). Plants showing deficiencies are generally associated with neutral or alkaline soils (5) (13) (33). Thus Leeper reports that most soils which show a manganese deficiency have a pH of 6.5 or over, usually over pH 7. Total manganese is of no significance so far as availability to plants is concerned (22) (33) (39). Excess use of lime has been observed to produce manganese deficiency symptoms in plants (33) (39) (40).

Only rarely have deficiency symptoms been noted on acid soils and from this it has been concluded that acid soils are well supplied with manganese available to plants (31) (32) (39). However, some acid soils have been

reported to contain insufficient available manganese as a result of excessive leaching in areas of high rainfall (22) (39).

It has been found difficult to establish the amount of available manganese necessary in the soil to prevent the occurrence of deficiency symptoms in plants. For example, Steenbjerg (41), working on the soils of Denmark, set the limit between healthy and sick soils with respect to available manganese at 2 to 3 p.p.m. Steenbjerg found this limit quite satisfactory but others have reported sick soils containing more than this minimum and healthy soils with less than 1 p.p.m. (11) (40).

Various explanations may be offered for such discrepancies and one of the most important factors undoubtedly has to do with the active or hydroquinone reducible manganese fraction and its relation to available manganese. Leeper (22) suggested this fraction of manganese to be the most active portion of manganic oxides which is more or less taken into solution during the growing season through the reducing action of plant roots. He stated that an alkaline soil which normally contained 100 p.p.m. of this hydroquinone reducible manganese would produce plants free of deficiency symptoms. However, if these soils contain less than 15 p.p.m. of such manganese, abnormalities might and most likely would occur. Further (22) (39) if oxidative



conditions were prolonged this active manganic oxide would be made inert and thus would no longer form a supplement to the available manganese. These observations of Leeper and Harmer and Sherman were, for the most part, corroborated by Twyman (43) and Sherman et al (40). Therefore it seems almost certain that the active manganese fraction of soil manganese governs to a considerable degree whether or not a soil would be deficient when available manganese is marginal.

Sherman (38a), studying the soils of Hawaii concluded that manganese deficiencies in plants was not necessarily related to the level of manganese in the soil, or the level of manganese uptake by the plant; it was the ratio of iron to manganese. Plants may be chlorotic with 500 p.p.m. manganese, due to an upset in the iron-to-manganese ratio. In general, if this ratio is about 2 to 1, plants will be normal.

Various chemicals such as sulfur, quinone, glucose, thiols, calcium and magnesium thiosulfates, and copper sulfate have been added to soils to study their effects on manganese availability (5) (13) (22) (33) (39). These materials were observed to increase the amount of soluble manganese. In the case of sulfur, quinone, glucose, and thiols the increase in available manganese was attributed to the effect of increased soil acidity (33). The thio-sulfates of calcium and magnesium also increased the soil

acidity, but demonstrated the additional effect of reduction of higher manganic oxides. The effect of copper compounds as yet has not definitely been determined. Leeper (22) suggested that it did not affect oxidation of manganese compounds, while Sherman et al (40) showed it retarded oxidation through its antagonistic effect upon the manganese ion.

Methods of applying manganese compounds have also received considerable study. Leeper (22) suggested that spraying manganese or injecting it into the plants showing deficiencies gave better results than applying it to the soil. This has been confirmed by McLachlan (29) working with the alkaline soils in Ontario. McLachlan found no benefit from the broadcast of manganese to the soil but was able to cure deficiency symptoms through spray applications directly to the plant. Similar results have been reported by Quastel (33).

Although the absolute status of soil manganese has yet to be achieved, advances toward this end have been made. The years of study that soil scientists and plant nutritionists have given this element have led to the recognition of its essential and indispensable role in plant metabolism.

## EXPERIMENTAL

Since the purpose of the study was to examine some of the soils of British Columbia with respect to their content of total, available and active manganese, the first step was to obtain adequate and representative soil samples. The samples used were selected with the aid of soil survey maps and reports (16) (17) (18) (47) (48) (49). Reference was also made to the study by Fennell of the boron distribution in British Columbia soils (6). The sampling sites were selected to represent as well as possible in a general way the more important agricultural soil areas of the province.

The actual sampling was done on the basis of the soil profile and samples were taken from each horizon. However, manganese determinations were made using only the A and C horizons. In the case of the A horizons the A<sub>1</sub> and A<sub>2</sub> horizons from each profile were composited with a view to obtaining a sample which would represent the soil to approximately plow depth. The C horizon in each case represented the parent material from which the soil was derived. All samples with the exception of two were from sites that had not been cultivated.

Preparation of Soil Samples:

All soil samples which were used in the total manganese determinations were air dried and ground to a fine powder to pass through a 100-mesh bolting cloth sieve. The samples used in the available and hydroquinone reducible manganese determinations were ground to pass through a  $\frac{1}{2}$  mm. sieve. All the samples were used in the air dry state and the calculations were based upon this weight of soil.

Method of Analysis:

The method first used to detect the presence of manganese was that described by Sandell (37). In this procedure 0.5 grams of finely divided sample were transferred to a platinum crucible together with 5 millilitres of 1:1 sulfuric acid and 3-4 mls. of hydrofluoric acid. The contents were mixed and heated carefully first on a hotplate, then more strongly until fumes of sulfuric acid were given off. The solution was allowed to cool and the sides of the vessel were washed down with water and 2-3 mls. of dilute sulfuric acid and a few drops of nitric acid.

The mixture was evaporated again to white fumes of sulfuric acid, allowed to cool and water added to dissolve the soluble salts. Filtration was carried out through a small

filter paper and the residue washed with hot water, but the total volume of washings was not allowed to go beyond 50 mls. To the filtrate 3 mls. of concentrated sulfuric acid, 2 mls. 85% phosphoric acid and 0.3 grams potassium periodate were added. The solution was then heated to boiling and allowed to digest for 5 minutes at 100° C. It was then cooled, diluted to a volume of 100 mls. After the solution was thoroughly mixed and the full permanganate color was allowed to develop the transmittancy of the solution was compared against a standard manganese solution.

The standard manganese solution was prepared using potassium permanganate according to the method proposed by Sandell (37). The potassium permanganate was standardised according to the procedure given by Vogel<sup>"</sup> (44). A standard curve was plotted using solutions containing different concentrations of manganese. Using this standard curve the manganese content of the soil was determined by comparison.

#### Determination of the Different Fractions of Manganese:

Total manganese determinations were made using a procedure more or less similar to that used by Sandell (37) but with certain modifications. The procedure as originally suggested by Sandell had several objects when it was used to determine the total manganese content of soils. These limitations included:

1. The loss of material through spattering when strongly heated as suggested in the method.
2. The failure of sulfuric-nitric acid mixture to completely remove organic matter.
3. The soils high in calcium salts caused large precipitates to form in the presence of sulfuric acid.
4. The procedure as suggested was very time-consuming.
5. The loss of manganese through adsorption brought about by the use of the filter paper, occlusion and post precipitation (30).
6. The lack of agreement between duplicate determinations.

To overcome these objections, modifications to Sandell's procedure were introduced and the total manganese determinations made using the following revised method. One half gram of oven dried soil was placed in a crucible, transferred to a muffle furnace and ignited at  $600^{\circ}$  C. for two hours. This method of removal of the organic matter eliminated the use of the sulfuric acid-nitric acid mixture which was the cause of considerable loss of material through spattering. One ml. of perchloric acid was used along with 10 mls. of hydrofluoric acid and the mixture was gently digested to dryness on a steam bath. The change to perchloric acid reduced the time required for analysis. Water was then added to the dried residue along with 3 mls. of sulfuric acid and 2 mls. of phosphoric acid; the whole

solution was then heated gently to bring all soluble materials into solution. The contents of the crucible were then transferred to a beaker without filtering and a little water and 0.3 grams of potassium periodate was added. The solution was boiled, digested for 5 minutes at 100° C., cooled, made to volume of 100 mls., and the transmittancy of this solution was compared with a similar standard solution.

This modified Sandell method worked well and was considerably less time consuming. It gave results that were comparable to those obtained with the standard procedure and it was found that better agreement between duplicate tests could be obtained with it than with the original procedure. A comparison of results obtained on four soil samples by the two methods is given in Table A.

TABLE A

A comparison of the results obtained using Sandell's method and the revised method used in this study.

Soil Association	Percent Transmittancy Sandell's Method			Percent Transmittancy Revised Method		
	Sample	Sample	Average	Sample	Sample	Average
	1	2		1	2	
Custer Loam	84.20	85.00	84.60	84.80	85.20	85.00
Lynden Silt Loam	58.00	59.20	58.60	58.80	58.80	58.80
Alderwood Sandy Loam	56.00	55.30	55.70	55.30	55.30	55.30
Langley Clay Loam	45.1	44.90	45.00	44.40	44.80	44.60

Note: Figures shown are for the A horizon of some of the Fraser Valley soils.

Available Manganese:

Determinations for this fraction of manganese were carried out using the ammonium acetate replacement procedure (5) (13) (37). This procedure involved leaching of a soil with neutral normal ammonium acetate for a period of 12 hours. An aliquot of the leachate was removed and evaporated to dryness on a steam bath. The organic matter was destroyed by hydrogen peroxide (6%) in acid solution. The residue was then taken up in a little water, 3 mls. concentrated sulfuric acid,



2 mls. of 85% phosphoric and 0.3 grams of potassium periodate. The solution was then brought to the boil, digested at that temperature (100° C.) for five minutes, cooled to allow the permanganate color to develop fully, and compared for transmittancy with a standard prepared in a similar manner.

Active or Hydroquinone Reducible Manganese:

Soil manganese included in this category was determined by leaching a soil with a 0.2% solution of hydroquinone in neutral normal ammonium acetate for a period of 12 hours. An aliquot was removed from the leachate, was evaporated to dryness, organic matter destroyed with 6% hydrogen peroxide in acid solution. The residue was taken into solution with a little water, 3 mls. sulfuric acid, 2 mls. 85% phosphoric acid and 0.3 grams of potassium periodate. The solution was then brought to the boil, digested at that temperature for 5 minutes, cooled, made to volume, shaken to allow full permanganate color to develop and then compared to the standard manganese solution.

Distribution of Manganese in British Columbia Soils:

Soil samples were taken from several naturally occurring regions of British Columbia for comparison.

Peace River Block:

The total, available and hydroquinone reducible manganese found in the soil samples selected from the Peace River are given in Table I.

It will be noted from this table that a wide range in total manganese exists, the range being from 74 to 1250 p.p.m. in the A horizon and from 66 to 1150 p.p.m. in the C horizon. No consistent trends in total manganese may be observed in the data. However, it will be noted that both the A and C horizons do compare favorably with the figure given by Leeper (22). It will also be noted that the content in the C horizons or parent materials tends to be greater than that of the surface or A horizons. This, too, is in accordance with the work of others, since the soils are all slightly acid and leached in the surface horizons and alkaline in the subsurface.

The sample representing the Alcan association is lowest in total manganese in both surface and subsoil. This is of particular interest for several reasons for, besides being the lowest in total manganese, it is the most acid; in particular it is very acid in the C horizon. It is also of interest to note that it represents the only soil thought to be developed chiefly from parent material brought from the West, that is the Rocky Mountain area. All other soil parent materials were more influenced by materials from the East.

Although all the soils represented in table I are well supplied with all fractions of manganese, it is quite apparent that the degraded black soils are more adequately supplied than the gray wooded or slough podsoles. This is particularly noticeable in the strongly degraded black soils.

Upon examination of the figures given in Table I for available and hydroquinone reducible manganese one is led to conclude that sufficient manganese is present in the soils of the Peace River area to prevent the development of manganese deficiencies under normal conditions. This last statement is supported by the fact that leguminous plants which are ordinarily sensitive to manganese deficiency grow very well in the Peace River area.

Okanagan Valley Area:

The data given in Table II indicate that the samples representing this area are well supplied with total, available and hydroquinone reducible manganese.

It will be noted here; however, that the total manganese content of the A horizons is higher than that of the C horizons. This could be expected since both surface and subsoil are alkaline. Thus manganese present in the surface horizon would be, for most part, in the oxidised state which is not leached since it is insoluble in water.

It is of interest to note the very high content of available and hydroquinone reducible manganese in these soils, particularly in the A horizon, especially in view of the fact that these soils are quite alkaline. Apparently these soils are well supplied with a very reactive oxide form of manganese.

The deep black soil from Armstrong is supplied with greater total manganese content than any of the other soils; however, all soils in Table II are high in total concentration of manganese. The shallow black soil from Kamloops was used for comparative purposes only, and as expected it falls between the deep black and dark brown soils.

It is interesting to note that the manganese content of the three glacial till soils is higher than the alluvial soil. This might be due to the fact that some of the manganese content of the alluvial soil was washed out as it was deposited in running water. This is true for the other two fractions of soil manganese as well.

Available and hydroquinone reducible manganese as reported is very high also. With such concentrations of available and reducible manganese there is little possibility of a deficiency of the element in these soils. Since the annual precipitation in this region is low, less than 20 inches, loss of available manganese through leaching is negligible.

TABLE I

MANGANESE CONTENT AND RELATED DATA PERTAINING TO VIRGIN  
SOILS OF THE PEACE RIVER AREA OF BRITISH COLUMBIA

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Slightly Degraded Black	Lacustrine	Rolla	A	654.0	5.6	296.0	--
			B(ca)	427.0	9.8	158.6	--
Degraded Black	Alluvial	Fort St. John	A	1150.0	7.2	8.2	6.7
			C	720.0	5.6	8.2	7.4
Degraded Black	Till(Modified)	Montney	A	464.0	6.6	8.6	6.8
			C	1250.0	6.0	106.0	7.2
Degraded Black	Lacustrine	Arras(1)	A	154.0	20.8	101.0	--
			C	468.0	7.4	18.0	--
Degraded Black	Lacustrine	Arras(2)	A	210.0	10.0	80.0	--
			C	420.0	6.7	100.0	--
Strongly Degraded Black	Till	Mytron Solodic member	A	96.0	8.2	17.4	6.6
			B(SO <sub>4</sub> )	406.0	8.2	109.2	7.6
Strongly Degraded Black	Rocky Mt. & Keewatin Till	Mytron Solonetzic member	A	116.0	33.6	66.0	6.5
			C	692.0	7.2	172.6	8.0
Strongly Degraded Black	Till(Modified)	Farmington	A	890.0	8.8	155.2	5.6
			C	596.0	8.0	12.2	6.2
Grey Wooded	Alluvial	Judah	A	72.0	18.6	6.6	6.5
			C	350.0	10.2	83.4	8.0

TABLE I - Cont.

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Grey Wooded	Till	Singer	A	544.0	10.0	26.6	6.2
			C	262.0	8.2	148.2	7.8
Grey Wooded	Rocky Mountain Till acid	Alcan	A	66.0	10.2	6.8	4.9
			C	74.0	33.0	27.0	4.4
Grey Wooded	Till(Modified)	Bessborough	A	690.0	35.6	75.6	6.8
			C	890.0	12.4	128.2	7.6
Podsol(Slough)	Till (Poorly drained)	Cuthbert	A	190.0	7.8	20.4	5.4
			C	250.0	10.4	12.4	6.0

N.B. -- Figures for Manganese analysis in all Tables is an average for Duplicate Determinations.

TABLE II

MANGANESE CONTENT AND RELATED DATA PERTAINING TO VIRGIN SOILS OF THE OKANAGAN VALLEY  
OF BRITISH COLUMBIA

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Brown	Alluvial	Penticton	A	1216.0	22.0	148.0	7.6
		Silt Loam	C	1140.0	13.0	102.0	8.6
Dark Brown	Glacial Till	Kelowna	A	1588.0	82.0	363.0	7.5
		Gravelly sandy loam	C	1550.0	40.0	158.0	8.9
Shallow Black	Glacial Till	Kamloops	A	1800.0	90.0	258.0	7.3
			C	1760.0	22.0	160.0	8.6
Deep Black	Glacial Till	Armstrong	A	2200.0	54.0	346.0	7.3
		Gravelly sandy loam	C	2030.0	14.0	136.0	8.6

Vancouver Island Area:

The total, available and hydroquinone reducible manganese determinations for the soils representing this region are recorded in Table III.

An examination of the figures given in Table III reveals more or less the same general pattern of distribution as observed in the Peace River Block, with the principal exception that the figures exhibited here are much higher for total manganese content. Although, once again, no consistent trends are observed it will be noted that both the A and C horizons are well supplied with total manganese. The figures given here are very high when compared with those given by Leeper (22); however, they compare favorably with the determinations of the soils of the United States made by Robinson (35) who reported a range of 0.00 to 0.32% in the manganese content of some American soils. Here again the C horizon or parent material is supplied with a greater manganese content than the A horizon. The surface soil is more acid than the subsurface soils, thus a portion of the soluble manganese in the surface is carried into the subsoil in drainage waters.

The figure given for the Cedar association is very high in both surface and subsoil samples. This might be due to the fact that the parent material is a residual shale. This parent material is a sedimentary rock and is thought to



have been deposited during the upper Cretaceous which was the last period in the Mesozoic era. It is also of interest to note that this rock is the only residual parent material known in our Pacific Coast soils. The parent materials for the other soil samples have all been transported.

It was noted that the lacustrine soil, Cowichan clay loam, had present a layer of black material coating some of the soil aggregates in the C. horizon. It was thought it might be the impure mixture of manganic oxides known as "Wad" (25) (42). When analysed it was found to be approximately 0.2% manganese.

The content of available manganese in the A and C horizons of the Cowichan Soil Association were very nearly the same in both A and C horizons.

The hydroquinone reducible manganese is in high concentrations particularly in the C horizons. It is of interest to note that wherever the total manganese content of a horizon was high, the hydroquinone reducible manganese was high also.

As with the other regions so far studied, it is thought that the soils contain sufficient available manganese to meet plant requirements.

TABLE III

MANGANESE CONTENT AND RELATED DATA PERTAINING TO VIRGIN SOILS OF THE SOUTH EASTERN  
PORTION OF VANCOUVER ISLAND OF BRITISH COLUMBIA

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Brown Podsolie	Alluvial	Qualicum Loamy Sand	A	534.0	10.6	83.4	4.9
			C	360.0	12.0	26.6	5.5
Brown Podsolie	Residual shale	Cedar	A	2366.0	45.0	820.0	5.0
			C	4020.0	47.0	1040.0	5.2
Brown Podsolie	Glacial Till	Bainbridge Loam	A	140.0	8.4	12.5	4.7
			C	800.0	6.0	223.4	5.3
Brown Podsolie	Glacial Till	Keating Sandy Loam	A	1510.0	22.4	161.0	6.2
			C	--	--	--	--
Alluvial	Alluvial	Chemainus Loamy sand	A	1620.0	26.8	178.0	5.8
			C	2256.0	25.6	170.0	6.0
Brown Podsolie	Lacustrine	Cowichan Clay Loam	A	1180.0	65.0	160.0	5.2
			C	1856.0	66.0	288.0	6.2
Brown Podsolie	Lacustrine	Black Stained Cowichan C.L.	C	1864.0	--	--	6.2

Nechako Plateau - Central Interior

This area represents the north central portion of the Nechako Plateau which extends from the American border well into the northern regions of the province (6).

A study of the data given in Table IV reveals the distribution of manganese in the soils selected from this region of the province. It will be noted that a wide range in total manganese exists in both A and C horizons. No consistent trends with regard to total manganese are evident. There appears to be no relationship between total content and pH as was evidenced in the soils of the Peace River area. For example, the Vanderhoof association shows a higher total manganese content in the A horizon than in the C horizon, although the A horizon is more acid than the C horizon. However, in the case of the sample from the Pineview association, one sees that the more acid A horizon is considerably lower in total manganese than the alkaline C horizon. This, of course, is expected and is in accordance with the observations of other investigators (22) (39).

The degraded black soils of this region are generally a little higher in all fractions of manganese than are the grey wooded soils. Total concentrations of manganese given in Table IV more closely approximate Robinson's results (34) for some American soils than they do for the Australian soils studied by Leeper (22).

That which has been said for total manganese more or less holds for the other two fractions of manganese. It appears from the samples tested that the soils of the Nechako Plateau should, under normal conditions, contain sufficient available manganese for plant growth.

South Eastern Portion of British Columbia

Only three samples were analysed from this large section of the province, one from Big Bend, one from Columbia Lake and one from Creston. The results are included in Table V. It will be noted from Table V that the total manganese contents do not differ particularly from those reported for other areas of the province.

The Creston area is of considerable interest from the standpoint of soil manganese since reports have been made from time to time of benefits obtained from the use of manganese fertilizers in that area. However, no conclusive evidence of manganese deficiency appears to have been obtained. When the manganese status of the Creston soil samples is considered in respect to this situation one would conclude that only under particular circumstances would manganese deficiency likely occur. This might be the case because the total manganese content of the samples appears satisfactory but the soil is alkaline and thus under strong oxidising conditions might lead to low manganese availability.

TABLE IV

MANGANESE CONTENT AND RELATED DATA PERTAINING TO VIRGIN SOILS NECHAKO PLATEAU  
(CENTRAL INTERIOR) OF BRITISH COLUMBIA

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Grey Wooded	Lacustrine	Vanderhoof Clay	A	1584.0	26.6	156.6	6.7
			C	1380.0	21.6	128.0	7.6
Grey Wooded	Lacustrine	Pineview Clay (1)	A	--	--	--	--
			C	1830.0	17.6	526.0	7.1
Grey Wooded	Lacustrine	Pineview Clay (2) Prince George	A	186.0	21.6	72.0	4.7
			C	2368.0	39.2	277.0	7.5
Grey Wooded	Glacial lacustrine	Bednesti Silt loam	A	--	--	--	--
			C	1940.0	31.2	386.0	6.8
Degraded Black	Lacustrine	Fort St. James Clay	A	4936.0	324.0	876.0	--
			C	1856.0	162.0	864.0	--
Degraded Black	Lacustrine	Nulki Clay	A	700.0	44.0	212.0	--
			C	1260.0	12.6	516.0	--
Degraded Black	Glacial Till	Driftwood Loam	A	--	--	--	--
			C	1100.0	88.0	458.0	7.2
Degraded Black	Glacial Till	Mapes Loamy Sand	A	2334.0	236.6	788.6	5.2
			C	1550.0	55.2	357.2	6.5

TABLE V

MANGANESE CONTENT AND RELATED DATA PERTAINING TO VIRGIN SOILS OF THE SOUTHEASTERN  
PORTION OF BRITISH COLUMBIA

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Brown Podsollic	Glacial Till	Big Bend	A	144.0	--	--	4.4
			B <sub>2</sub>	1990.0	--	--	5.9
			C	3080.0	--	--	7.8
Rendzina	Limestone	Columbia Lake	A	1090.0	--	--	7.5
			B <sub>2</sub>	786.0	--	--	7.8
			C <sup>2</sup>	1158.0	--	--	8.3
Alluvial	Alluvial	Creston	A	600.0	54.0	110.0	7.55
			C	760.0	14.0	80.0	7.80

Lower Fraser Valley Area:

This area involves some 350,000 acres of arable lands, alluvial and glacial soils extending inland from the mouth of the Fraser River for some 80 miles. The soils naturally divide themselves into groups: ground water soils, recent alluvial, and raised delta (5).

An examination of Table VI reveals that the soils of the Fraser Valley are extremely high in total manganese as compared to the average for soils elsewhere. Of particular interest, also, is the fact that the surface samples are as high or higher in total manganese than the parent material samples. This is rather surprising since the surface soils are more acid than the subsoils and therefore in an area of high precipitation and leaching such as the Fraser Valley one would expect considerable downward movement of manganese (22) (39).

No consistent relationship may be observed in the figures for total manganese and the mode of deposition of the parent materials.

The results given in Table VI also show the virgin soils of the Fraser Valley to be high in available manganese. The figures given for available manganese in each sample are much higher in the A horizon than in the C horizon. This fact can be explained on the basis of pH. In the A horizons the acid condition present favors reduction and with the very high total content of manganese

reported for these horizons one could reasonably expect to find higher quantities of divalent manganese. It would seem from an analysis of the data given in Table VI a more consistent relationship exists between available manganese and pH than between total manganese and pH.

There is apparently no consistent trends illustrated between available manganese and parent material, some of the more lighter textured soils being better supplied with available manganese than some of the heavier textures ones.

The remarks made with respect to available manganese can be applied to hydroquinone reducible manganese. Soil acidity or pH influences this fraction of soil manganese much the same as it does the available manganese.

Upon a review of the data given in Table VI it is quite evident that, when compared to other British Columbia soils, the soils from this region are very well supplied with all fractions of soil manganese. In view of this fact it would seem very unlikely that a deficiency of this element would be experienced. Harris (10) noted that the applications of manganese fertilizers to these soils had little, if any, effect on the yield of carrots and turnips. However, it should be noted here that manganese applications increased the keeping quality of carrots and turnips. Harris concluded his work by suggesting that no visible evidence of a micro-element deficiency was apparent.



TABLE VI

MANGANESE CONTENT AND RELATED DATA PERTAINING TO VIRGIN SOILS OF THE LOWER FRASER VALLEY OF BRITISH COLUMBIA

Great Soil Group	Parent Material	Soil Association	Horizon	P.P.M. Manganese			pH
				Total	Available	Reducible	
Brown Podsollic	Coarse Alluvial	Everett Loamy sand	A	2460.0	238.0	740.0	5.9
			C	1830.0	17.6	52.0	5.6
Brown Podsollic	Fine Alluvial	Lynden Silt loam	A	2520.0	78.0	530.0	5.8
			C	1700.0	17.6	280.0	5.7
Brown Podsollic	Glacial Till	Alderwood Sandy loam	A	2400.0	103.0	514.0	5.6
			C	1520.0	9.0	52.0	6.0
Brown Podsollic	Glacial Till(old)	Whatcom Silt	A	3460.0	86.0	832.0	5.4
			C	1880.0	8.0	28.0	6.8
Brown Podsollic	Glacial Till (old)	Whatcom Silt Loam	A	1060.0	30.0	18.0	5.4
			C	1360.0	14.0	32.0	6.8
Brown Podsollic	Lacustrine	Haney clay	A	1830.0	100.0	306.0	5.3
			C	1560.0	11.0	30.0	5.2
Groundwater Podsol	Alluvial	Custer Loam	A	800.0	18.0	46.0	5.0
			C	1030.0	10.0	32.0	7.1
Gleizolic	Lacustrine	Langley clay loam	A	4000.0	188.0	503.0	5.3
			C	1430.0	12.0	24.0	7.3
Gleizolic	Lacustrine	Milner clay loam	A	830.0	38.0	80.0	5.0
			C	1340.0	9.0	20.0	5.6
Alluvial	Alluvial	Monroe Clay loam	A	2060.0	174.0	416.0	5.6
			C	2080.0	35.0	192.0	5.9

SUMMARY:

1. A survey was made of the status of manganese in some of the more important soil associations of British Columbia. Three fractions of manganese, total, available and hydroquinone reducible were determined in surface and parent materials of 45 uncultivated soil profiles.
2. Total manganese content of the samples was found to range from 0.007% to 0.494%. The values compared favourably with those reported for the soils of the United States and were generally higher than those reported from soils in Australia.
3. When the total manganese values obtained were compared by regions the samples from the Lower Fraser Valley and Vancouver Island were generally highest and those from the Peace River lowest in total manganese content. The samples from the Central Interior, Okanagan, Rocky Mountain Trench and Kootenays were generally intermediate in content of total manganese.
4. Downward movement of manganese in the soil profiles was most frequently indicated by the samples from the Peace River area. The Okanagan samples indicated no downward movement of manganese. In the soil samples of the Lower Fraser Valley the surface samples were frequently higher in total manganese than the corresponding parent

material samples indicating some upward movement of manganese.

5. Available manganese content of the samples was found to range from 5.6 to 324 p.p.m. The values were generally high when compared to values reported elsewhere. Availability of manganese was related more to soil reaction than to total manganese.

6. The range in hydroquinone reducible manganese found in the soil samples was from 8.2 to 1040.0 p.p.m. The results were generally high compared to values reported for soils elsewhere.

7. The high values generally obtained for total, available and hydroquinone reducible manganese indicate that most soils in British Columbia are adequately supplied with this element. In fact the indiscriminate use of manganese fertilizers might prove detrimental by increasing naturally high levels of available manganese to a point where it would be harmful to plant growth.

8. Soils deficient in manganese for plant growth may occur in British Columbia. If deficiency symptoms do occur they are to be expected as a result of such conditions as alkaline soil reaction, overliming practices, excessive destruction of soil organic matter and ion interference.

If a soil manganese deficiency is suspected a careful appraisal of each individual situation should be made before manganese fertilizer applications are recommended.

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