Fundamental Studies on the Biogeochemical Prospecting for Manganese

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Most of the manganese ores of economic importance in Japan form very small ore bodies near the surface, and the mining industries are generally of very small scale. Systematic prospecting has not yet been performed but only groping has been carried on. Geochemical prospecting for manganese ore by the analyses of soil and surface water has been studied by M. Shima[1] in this country and he suggested such possibilities in several mines. Surface water is not always available; when a representative soil sample is required, the sampling method may become rather complicated. These considerations led the authors to make an attempt of a geochemical prospecting for manganese by use of plant leaves as an aid.

Principle

Several problems are underlying in the application of plant material in practice as an indicator for manganese level in soil. Those problems could be briefly described as follows:

(1) Correlation of manganese level between soil and plants.

Numerous investigators performed experiments on some culture plants by use of water and sand culture method and positive correlation of manganese level between the medium and the plant has been confirmed. This relationship is likely to be applied to natural plants, herbs and trees, although the direct evidence has not been submitted.

Above mentioned correlation is only appropriate for manganese in solution. In our case, the matter in question is the correlation between mineral content of manganese in soil and manganese level in plants. Fortunately, several problems on the soil manganese conditions were solved by G. D. Sherman and P. M. Harmer in 1942[2], and we can use their results as the basis for further research.

(2) In practice, to obtain the plant samples which are as representative as possible, a tree is preferred to small herbaceous plants, because the latter are sensitive to small local variations in soil. Only two grams or less in dry weight is required for the analysis of manganese in plant leaves; two problems arise about the sampling method to avoid variations.

1) M. Shima, "Geochemical Prospecting" (in Japanese) Maruzen Co., Ltd., Tokyo (1955) p. 180.

2) G. D. Sherman and P. M. Harmer, *Soil Sci. Soc. Amer. Proc.*, **7**, 398 (1942).

One of the variations of manganese content is due to the difference in age and position of leaves of a tree, and the other is due to the age of the tree. The dimensions of those variations must be confirmed at the beginning of the experiment.

Experimental

In the chemical analysis of manganese and iron in plant leaves, the air-dried (100°C for 6 hours) samples were first ashed in a porcelain dish over an open flame. The ash was moistened with water, decomposed with 5 ml. of nitric acid (1 : 1) and 2 ml. of sulfuric acid, evaporated to dryness, and then heated to fumes. When the resultant liquid was dark colored, one ml. of hydrogen peroxide solution and 2 ml. of concentrated nitric acid were added and again heated to fumes. To the colorless or pale-yellow liquid was added hot water and insoluble matter was filtered. The filtrate was made up to 50 ml., and a 40 ml. aliquot was used for colorimetric determination of manganese as described in A. O. A. C. official methods of analysis[3], and 10 ml. aliquot for iron determination by use of thiocyanate colorimetric method as usual[4].

Soil extractions were made on freshly taken soil samples, and a separate portion was taken for moisture determination. Further procedure was the same as that of Sherman and Harmer[5].

The manganese mineral content in soil was determined as follows. One to ten grams of soil sample was taken in a beaker and 5 to 30 ml. of concentrated sulfuric acid and 20 to 100 ml. of concentrated nitric acid were added. This was heated gently until brown fumes diminished, and boiled until white fumes appeared. Phosphoric acid was added, boiled for a few minutes and after cooling made to 100 ml. or one litre. A suitable quantity of the clear supernatant solution was taken and the manganese determined as described before. The manganese extraction methods for the various states in soil are schematically shown in Fig. 1.

	State of Mn in soil	Extractant
Active-Mn	Water-soluble	H_2O
Active-Mn	Exchangeable	1 N-NH_4-acetate
Active-Mn	Easily-reducible	1 N-NH_4-acetate and hydroquinone
	Acid-soluble	$HNO_3+H_2SO_4$

Fig. 1. State of manganese in soil and extractants.

3) "Official Methods of Analysis of the A. O. A. C." 7th ed. Association of Official Agricultural Chemists, Washington (1950).

4) E. B. Sandell, "Colorimetric Determination of Traces of Metals" 2nd Ed., Interscience Publ., Inc., New York (1950).

5) Care must be taken for hydroquinone in use, because commercial hydroquinone frequently contains a considerable amount of manganese.

Errors in the colorimetric analyses of manganese and iron were calculated from the quadruplicate determinations on a powdered and well-mixed plant sample (*Chamaecyparis obtusa* Endlicher, "Hinoki"). The results are shown in Table I. The relative error was 0.4% for manganese and 1.3% for iron.

TABLE I
ERRORS IN THE COLORIMETRIC ANALYSES OF MANGANESE AND IRON IN PLANT MATTER
(On fresh basis)

Chamaecyparis	Mn (p.p.m.)	Fe (p.p.m.)	Mn/Fe
obtusa	78.9	222	0.355
	77.3	216	0.358
	76.9	209	0.368
	77.4	225	0.344
Mean	77.6	218	0.356
Average deviation	0.31	2.8	0.0034

Results and Discussion

Culture Experiments.—At first, a water-culture experiment was carried out with about thirty-days seedlings of tomato plants. The plants had been cultured for two weeks in glazed clay pots with a perfect universal culture solution[6] when the solution was replaced by those of six levels of manganese concentrations. After twenty days culturing with occasional renewal of the solution, the plants were harvested and the leaves were analyzed for manganese.

The result shown in Table II indicates a fair correlation between the manganese content in plants and the manganese level

TABLE II
WATER CULTURE EXPERIMENT WITH
Solanum Lycopersicum L

Pot No.	Mn level in culture sol. p.p.m.	Mn content in cultured plant p.p.m. (dry basis)	Conc. ratio
1	0.03	74.5	2500
2	0.1	126	1260
3	0.3	196	650
4	1	302	300
5	3	323	100
6	10	1029	100

in culture solution which ranged from 0.03 to 10 p. p. m. But, the concentration ratio of manganese by a plant grows small when the manganese level in solution is raised. In other words, the magnitude of

6) Devised by the authors grounded on the distribution of chemical elements in natural plants; *Japan Analyst*, **6**, 75 (1957).

TABLE III

CULTURE EXPERIMENT ON THE SOIL MIXED WITH RHODONITE

(p. p. m. on dry basis)

Pot No.	pH of soil	Acid soluble Mn	Active Mn			Plants Mn	
			Water soluble Mn	Exchange-able Mn	Easily reducible Mn	Aster sp.	Carex sp.
Contrast	7.1	700	0	7.1	92	95	6.2
1	7.1	710	0	2.4	138	109	13
2	7.0	1400	1.0	11	163	118	17
3	7.0	2350	3.2	23	504	168	33
4	7.0	5440	9.3	52	958	379	71
5	7.0	7000	10	116	1940	622	113
6	7.0	18500	—	—	—	—	3090*

* died in two weeks

TABLE IV

CULTURE EXPERIMENT ON THE SOIL MIXED WITH HAUSMANNITE

(p. p. m. on dry basis)

Pot No.	pH of soil	Acid soluble Mn	Active Mn			Tomato plant	
			Water soluble Mn	Exchange-able Mn	Easily reducible Mn	Mn	Mn/Fe
Contrast	7.2	700	0	7.1	92	174	1.58
1	7.0	1480	2.9	0	239	219	0.90
2	7.2	2130	2.0	1.0	495	203	2.42
3	7.3	4810	3.7	2.1	1700	256	4.57
4	7.3	12900	23	6.5	4520	419	5.66
5	7.3	22800	34	11.5	5740	393	9.82

fluctuations in the manganese content of a plant is smaller than that of manganese in the medium. The former is only 1/24 of the latter in this experiment, and the relationship is also valid in the soil experiments as described later.

Soil culture experiments were carried out with two kinds of manganese mineral mixed with a normal soil. The soil was mixed with various quantities of rhodonite[7] and hausmannite[8] minerals separately and plants were cultured on them for about one month in pots. At the same time when the cultured plants were harvested, fresh soil samples were collected from the pots and extraction of manganese in various states was performed, and then a separate portion of the sample was used for soil reaction test with 100 ml. distilled water by use of glass electrode pH meter. The results are shown in Tables III and IV.

Addition of rhodonite to the soil slightly increased acidity of the soil and vice versa in the case of hausmannite, but the extent of increase or decrease was not remarkable.

When the two soils mixed with almost the same quantity (in acid soluble-manganese) of rhodonite and hausmannite, were compared with respect to their manganese status, the levels of water-soluble and the easily reducible manganese are of comparable order in both soils, but the level of exchangeable manganese in the soil mixed with rhodonite (Table III) is much higher, about twenty times or more, than that in the other soil.

In accordance with the variation of acid-soluble manganese in soil, the manganese content of *Aster* sp. and *Carex* sp. varied from 95 to 622 p. p. m. and from 6.2 to 113 p. p. m. respectively. The magnitude of fluctuation is about 6.5 in the former, and 18 in the latter; in this sense, *Carex* sp. can more sensitively indicate the manganese level in soil than *Aster* sp. but its response for manganese is lower.

In the case of the culture experiment with hausmannite, a tomato plant was used and the magnitude of fluctuation was only about 2 when acid soluble manganese varied from 700 to 22800 p. p. m. In this case iron content of the plant was also determined and Mn/Fe ratio calculated. As shown in Table IV, the fluctuation of Mn/Fe is much greater than that of

7) Contained a small amount of hausmannite and braunite.
8) Contained a small amount of braunite.

manganese content itself. Thus, under certain circumstances, we can employ the ratio of manganese to iron in a plant as the more sensitive indicator for the manganese level in soil.

Variation of Manganese and Iron Content due to the Sampling Position of a Tree.—A "Hinoki" tree (*Chamaecyparis obtusa* ENDLICHER), about thirty years of age, was chosen in the campus of our college. Four samples of leaves, about 200 grams each were pulled off from the south, the east, the north and the west side of the tree, and young leaves were collected from the top of the tree. Those samples were separately analyzed in the same way as described before. The result shown in Table V indicates that the variation due to the sampling position of a tree is great enough to be beyond the errors in determination. Thus, it can be concluded that to obtain leaves which are as representative as possible, a composite sample must be taken from around the tree.

TABLE V

VARIATION DUE TO THE SAMPLING POSITION OF A TREE

(*Chamaecyparis obtusa* leaves, on fresh basis)

Sampling position	Mn p.p.m.	Fe p.p.m.	Mn/Fe
East side leaves	25.1	125	0.201
West side leaves	23.2	131	0.177
South side leaves	20.0	121	0.165
North side leaves	29.8	130	0.229
Top young leaves	23.4	82.4	0.284

Variation due to the Age of the Tree.—Five "Hinoki" trees of different ages were chosen in the campus and composite samples were taken for analyses. The result shown in Table VI indicates the increasing manganese content and Mn/Fe ratio of plant in consequence of the growing age. So, it can be concluded that to guess manganese levels in soil we must take foliar samples from the trees of an age as similar as possible, e.g. from twenty to thirty years.

TABLE VI

VARIATION DUE TO THE AGE OF A TREE

(*Chamaecyparis obtusa* leaves, on fresh basis)

Proximate age Years	Mn p.p.m.	Fe p.p.m.	Mn/Fe
3	25.6	265	0.097
10	20.8	155	0.13
20	49.8	169	0.29
30	34.8	133	0.26
40	77.1	212	0.36

Possibility of the Practical Application.—In order to find out whether this method of manganese analysis was applicable to the practical soil investigation and the prospecting of ores and to examine how much the manganese content of a plant varied with circumstances, the authors collected, in September 1956, a number of samples in the mine district near the river Kiriu, about four kilometers from the city of Kiriu.

The bed rock consists of paleozoic chert and slate, and the principal manganese ore consists of rhodochrosite, rhodonite, tephroite, penwithite and various oxide minerals.

Five samples of "Hinoki" (20—30 years) leaves were collected in a non-mineralized district near the river Kiriu about one kilometer away from the mineralized district where eight samples were collected. As shown in Table VII, even in the non-mineralized district, the trees contained much larger quantities, about three times

TABLE VII

VARIATION OF MANGANESE CONTENT OF "HINOKI" IN MINERALIZED AND NON-MINERALIZED DISTRICTS

In mineralized district			In non-mineralized district		
Location No.	Mn p. p. m. dry basis	Mn/Fe	Location No.	Mn p. p. m. dry basis	Mn/Fe
6	569	19.4	1	246	4.6
7	629	13.4	2	169	2.6
8	1228	26.8	3	109	2.1
9	832	29.1	4	196	3.6
10	505	10.1	5	215	4.6
11	817	21.7	Av.	187	3.5
12	485	9.1			
13	656	17.8			
Av.	715	18.4			

TABLE VIII

CORRELATION OF MANGANESE LEVELS BETWEEN SOIL AND PLANT IN THE MINERALIZED DISTRICT

Location No.	pH of soil	Acid soluble Mn p.p.m.	Active Mn: Water soluble Mn p.p.m.	Active Mn: Exchangeable Mn p.p.m.	Active Mn: Easily red.-Mn p.p.m.	*Quercus acutissima* Mn p.p.m.	*Quercus acutissima* Mn/Fe	*Chamaecyparis obtusa* Mn p.p.m.	*Chamaecyparis obtusa* Mn/Fe
1	7.3	350	0	1.2	16.8	265	4.2	337	5.7
2	7.4	300	0	0.2	19.7	244	3.4	414	9.6
3	7.0	425	0	1.8	71.1	1020	16.4	924	16.4
4*	7.0	1737	0	1.2	424	875	11.6	917	16.8
5*	7.1	5565	0	0.9	720	1050	21.3	671	12.5

* near the deposits.

as much manganese and less iron than those trees in the campus (Table VI).

The Mn/Fe ratio indicates more sensitively those relationships: the ratio in the non-mineralized district is 3.5 on average and this value is more than ten times as great as those in the campus. The ratio grows as big as 29.1 in the mineralized district. The antagonistic behavior of manganese and iron in relation to plant uptake is a very interesting object of physiological research, although it is beyond the scope of this article.

Each of five samples of "Hinoki" and also *Quercus acutissima*, a latifoliate tree which showed as vast distribution as "Hinoki" was collected at five locations in the mineralized district. Soil samples were also taken at those locations and analyzed. The results are shown in Table VIII. Acid-soluble and easily reducible manganese contents in the soils at the locations No. 4 and 5 which stand on or near the deposits are considerably high and the foliar analyses also seem to indicate the deposits. Both *Quercus* and "Hinoki" are applicable to the prospecting but the latter is better, because its leaves are available all the year round.

Summary

The possibility of practical application of foliar analyses for geochemical prospecting for manganese were examined. A positive correlation of manganese level between soil and plants was revealed by the experiments using water and soil culture.

For the practical application, a tree, *Chamaecyparis obtusa* was chosen to avoid small local variations, and the sampling variations due to age and position were determined.

The Mn/Fe ratio was found to be a more sensitive indicator than the manganese content itself and its average value in the mineralized district was 18.4; on the other hand, it was only 3.5 in non-mineralized district.

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