Excess Toxicity of Minor Metal Elements to Mulberry Plant

By HIDEJIRO TAKAGISHI

Chemistry Division, Sericultural Experiment Station

The nutritional problem of minor metal elements on mulberry plant had shown scant interest except a few studies on the quality of mulberry leaves as the diet for silkworm.

But recently, attention has been paid increasingly on the minor metal elements from two points of view in the cultivation of mulberry, namely, the one, which is due to the change of location of mulberry field, is the appearance of the deficiency of boron and the excess toxicity of nickel owing to the development of reclaimed mulberry fields in the mountainous area, and the other is the pollution of mulberry fields as well as that of other agricultural fields caused by the heavy metal elements such as Cd, Zn and Cu.

Owing to such circumstances, the study on the excess toxicity of minor metal elements in mulberry field was needed urgently, and the author has also performed some experiments on this point of view.

The outline of a pot experiment as an example of the approach to the study will be described hereunder[1].

Experimental design

This experiment was carried out with the pot of 1/2000 a, and the alluvial soil with sandy loam texture of the mulberry field, where mulberry trees had cultivated for more than 50 years without fertilizer application and correction of acidity, was used, and soil pH was very acidic below about 5.0.

Manure was applied according to the ordinary fertilization for pot culture, and metal elements were supplied to the soil as are shown in Table 1. To investigate the varietal difference of the resistivity against excess toxicity, Kenmochi var., Kairyonezumigaeshi var. and Roso var. were used as the representatives of *Morus bombysic* Koidz, *Morus alba* Linn and *Morus latifolia* Pollet respectively.

Relation between the supplied amount of minor metal elements and leaf yield

As is shown in Fig. 1, it was proved in this experiment that the leaf yield decreased with the increase of each element and these elements of high concentration rendered toxicity on mulberry, but the application of a little amount of Cu sometimes made the leaf yield increase reversely.

Table 1. Supplied dose of metal elements

Elements (Form of salts)		Cu ($CuSO_4 \cdot 5aq$)	Zn ($ZnCl_2$)	Mn ($MnSO_4 \cdot 4aq$)	Co ($CoCl_2 \cdot 6aq$)	Ni ($NiSO_4 \cdot 7aq$)
Supplied dose per pot (ppm)	Small	0. 5	10	96. 5	2. 5	2. 5
	Medium	1. 0	30	193	5. 0	5. 0
	Large	1. 67	80	—	12. 5	8. 35

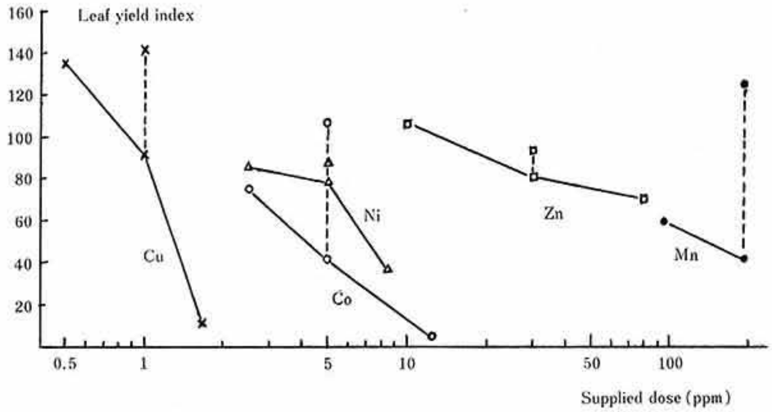

Fig. 1. Relation between metal element supply and leaf yield index in Kairyonezumigaeshi var.

As to the determination from the application of each element, the order of toxicity may be given as Cu>Co≒Ni≫Zn>Mn; the "half application amount" of each element, which reduces the leaf yield to a half by toxicity, was estimated to 1.3, 3.5, 7.0, 130 and 140 ppm respectively.

Though the excessive application of each element thus caused apparent decline of growth, no other specific visual symptom appeared.

The excessive absorption of a certain element cannot be only the effective factor to cause symptom, but the interaction with other coexisting elements is also important on the apperance of symptoms, and Iizuka[2] has examined this problem.

When the medium amount of each element was applied with dolomite powder to correct soil acidity, the restraining effect on the toxicity of each element was recognized remarkably as is shown with the dotted line in Fig. 1.

As for the varietal difference of the resistivity against toxicity, the resistance against the element of rather strong toxicity such as Cu or Ni is variable by varieties; that is, Kenmochi var. was the strongest and Kairyonezumigaeshi var. and Roso var. followed in succession, but any varietal difference against the element of comparatively mild toxicity was hardly recognized.

Accumulation of minor metal elements in leaves

Fig. 2 shows the relation between the

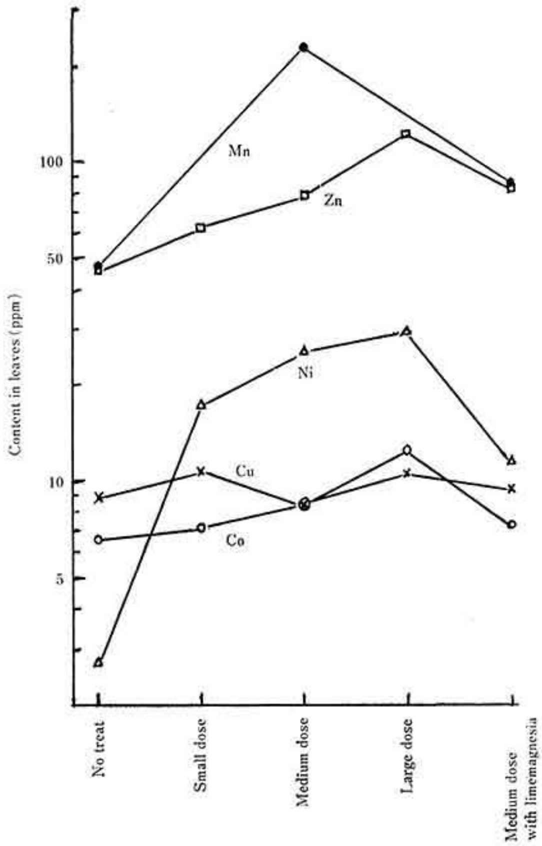

Fig. 2. Metal element contents in whole leaves of Kairyonezumigaeshi var.

applied amount of metal elements and the mean value of their contents in the leaf of Kairyo-nezumigaeshi var.. The mean values of contents were about 45 to 50 ppm for Mn and Zn, 6 to 9 ppm for Cu and Co, and 3 ppm for Ni when the mulberry was cultivated without metal element supply. When each element was applied to the original soil, the contents of Ni, Mn and Zn increased apparently according to the increase of applied amounts, and this trend was recognized more obviously with Ni.

On the contrary, the accumulated amount of Co was far less than that of Ni, neverthless it was applied as much as Ni.

As to Cu, its accumulated amount was scarcely changed in spite of the increase of application; it might be caused by the want of sufficient application.

Therefore it may be concluded that, though fairly much amounts of Cu and Co can be absorbed from ordinary soil, these elements cannot be absorbed and accumulated by mulberry to attain so high degree of concentration even if their contents in soil increased, and this trend is especially conspicuous with Cu.

On the other hand, the absorption of Ni by plant increased remarkably when its content in soil increased though its absorption from ordinary soil is rather little.

The increasing trend of the absorption of Mn and Zn accompanied with the increase of their contents in soil seems to be between those of Ni and Cu, Co, though the absorption of Mn and Zn from the ordinary soil is very much, compared with that of other elements described above.

If the "action coefficient" of Co, Zn and Ni in soil, which will be described later in detail are almost similar to each other, the difference of absorption and accumulation of these three elements seem to be related with the difference of the nutritio-physiological effects of the elements.

When the acidity of soil was corrected, the absorption of Mn and Ni was evidently restrained and that of Co was slightly restrained, while those of Cu and Zn were promoted a little. But the degree of this promotion is so little that it may be considered that almost no influence has been given.

On the difference of the contents of elements in leaves by the leaf order of Kairyo-nefiumigaeshi var., generally, the upper the position of leaf on shoot, the higher the contents of Cu, but the content gradient of other elements show reversal trend. The accumulation of each element in the upper order leaf increases according to the increase of absorption, but those in middle and lower order leaves increase more abundantly.

Therefore, the difference of element distribution between the upper and lower leaves is apt to be augmented. The maximum contents of each elements determined by this experiment were 15.5 ppm of Cu (in upper order leaves of abundant application plot), 204 ppm of Zn, 255 ppm of Mn, 15 ppm of Co and 33 ppm of Ni (these values are for the lower order leaves of abundant application plot).

Movement of minor metal elements in soil

The solubility of minor metal elements depends much upon the pH of solution. For example, the pH values when the elements begin to precipitate in the form of hydroxide in the solution of 0.01 M are reported[3] to be Mn^{2+} 8.5, Cd^{2+} 8.3, Co^{2+} 7.5, Ni^{2+} 7.2, Zn^{2+} 6.8 and Cu^{2+} 5.0, that is, Cu and Zn precipitate with acidic or weak acidic condition but other elements do with weak alkali or alkali condition.

Consequently, this problem was examined by means of the comparison of extraction rate of applied elements by ammonium acetate solution, since the availability of applied elements in soil may be variable according to the difference of acidity.

The element concerned and fertilizer were mixed with the air-dried soil of 50 g so as to make the same condition as that of pot culture test, and then the elements extracted wiht N-neutral ammonium acetate solution were determined after the incubation for two weeks under the water condition which corresponds to about 50 percent of field capacity.

As the result, the extracted amount of each element increased linearly according to the increase of application except that of Cu which was kept always nearly constant.

The regression coefficients between the applied and extracted amount of each element were Cu 0.17, Zn 0.22, Ni 0.29, Co 0.37 Cd 0.55 and Mn 0.70.

The rate of extraction against application amount is very much different by the elements. The extracted rate of Cu and Zn decreased according to the increase of application, but those of other elements increased slightly or showed no great change.

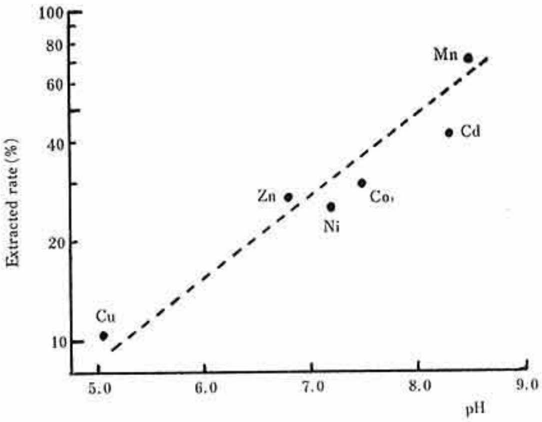

Fig. 3. Relation between pH at which metal elements would be expected to precipitate as hydroxide and extracted rates by neutral amm. acetate solution

Fig. 3 shows the relation between the logarithm of the mean values of extracted rates and the pH values[3] at which metal elements would be expected to precipitate as hydroxide. That is, apparent correlation exists between them, and the extracted rate of Cu, which precipitate at rather low value of pH, was very low, about 10 percent, and that of Mn, which would be expected to precipitate at the alkali side of pH 8.5, attained to 70 percent.

Discussion on concentration of toxicity of minor metal elements

The movement of each elements in the soil is closely related to the soil acidity and the proper chemical characters of each element. Therefore, a certain action coefficient must be considered in the examination of the concentration of toxicity, as the toxicity of elements is not always directly related to the applied amount.

For example, since the order in largeness of the regression coeffcient between the applied amount of each element and the amount extracted with N-neutral ammonium acetate solution perfectly coincides with the order in highness of pH which makes each element precipitate as described above, this regression coefficient may be regarded as a kind of action coefficient in the comparison of the movement of each element under a certain condition. For example, the coefficient of Zn is small because it precipitates at the pH of low value next to Cu, while that of Mn is large because it precipitates at alkali side.

If the value obtained from the multiplication of the "half application amount" by this "action coefficient" is designated as "half acting concentration", the "half acting concentration" of Zn goes down far below that of Mn in spite of their nearly same "half application amount".

The action coefficient proposed in this case must be, naturally, variable according to the kind of soil, chemical character and the extraction condition of elements.

In the examination of the toxicity of elements with reference to the "half acting concentration", the order of toxicity corresponds very well with the order of Pauling's electronegativity[4] as is shown in Table 2. This relation may be also applicable to bacteria and other crops, though some irregularities are found in the order.

If such a relation can be recognized as a general rule, the unknown toxicity of elements may be presumable to a certain extent. For

Table 2. Toxic concentration of minor metal elements to mulberry growth

	Cu	Co	Ni	Ce	Zn	Mn
A. Supplied dose making leaf yield to reduce to half (ppm)	1. 3	3. 5	7. 0	(4–70)	130	140
B. Active concentration making leaf yield to reduce to half (ppm)	0. 22	1. 3	2. 0	(2–30)	29	98
C. Mean content in leaf corresponded to A (ppm)	10	7–8	25–30	—	160–170	200<

( ) Estimated value. Refer to the text

example, the toxicity of Cd, which is an element of Zn group like other elements studied in this experiment, is presumed to be weaker than that of Ni and stronger than that of Zn (from the order of electronegativity), consequently its "half acting concentration" may be estimated to be between 2 and 30 ppm.

But Cd possesses higher basicity than Ni or Zn, and its "action coefficient" may be estimated to be 0.55 from the experimental results described above; therefore, its "half application amount" seems to come into the range of 4 to 70 ppm.

This problem was also examined in other pot experiment using acidic soil, where its "half application amount" ranged from 15 ppm to 30 ppm, and the "half acting concentration" was calculated to be about 8 ppm to 16 ppm; consequently, the toxicity of Cd seemed to be rather similar to that of Ni[5].

Table 2 shows also the mean content of the elements contained in the leaves of mulberry tree which suffered from the toxicity and therefore gave a half yield level.

References

1) Takagishi, H., Goto, A. & Sato, T.: Injury concentration of minor metal elements to mulberry growth. (1970). [In Japanese, summary of oral presentation]
2) Iizuka, T.: Interaction among nickel, iron and zinc in mulberry tree grown on serpentine soil. *Soil Sci. Plant Nutr.* [In press]
3) Charlot, G.: L'analyse qualitative et les réaction en solution. [translated into Japanese by K. Sone and M. Tanaka (1964): Teisei Bunseki Kagaku, 279, Kyoritsu Shuppan KK, Tokyo] (1957).
4) Japan Chemical Society: Kagaku Binran (Handbook of Chemistry, Fundamental Volume), 1133, Maruzen, Tokyo (1966).
5) Takagishi, H. & Sato, T.: Unpublished data.