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Soil Testing for Available Microelements in Japan

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Abstract

In the 1960s Japanese agriculture faced serious problems of soil pollution with As, Cd and other elements. Comprehensive investigations have been carried out on soil pollution and related subjects. The 1 M HCL/extraction method for diagnosing arsenic pollution in rice fields, the theoretical multi-step extraction method for zinc and other elements were developed during the period 1974-1983. The methods for evaluating soils with micronutrient deficiency were developed during the same period. This report reviews the development of applicable soil tests for such purposes in the last 20 years by Japanese soil scientists and explains why the content of extractable soil cadmium has not been adopted as a criterion of Cd toxicity in the pollution control law.

Discipline: Soils, fertilizers and plant nutrition
Additional key words: available soil cadmium, Chemical speciation, heavy metals, hydrochloric acid extraction, tannic acid extraction

Introduction

In Japan, for almost two decades from the 1970s onward, a large number of research reports on the influence of microelements upon crop production and human health were published. For studies on available microelements, the 1 M HCl/extraction method for As and the theoretical multi-step extraction method for zinc were developed.

For the soil microelement status, chemical speciation methods for As, Cr and I in soils, were developed along with extraction methods for available soil Mn/Co in deficient soils[10]. This short review describes the methods developed by Japanese researchers during the period 1974-1986 and the reason why the content of extractable soil cadmium has not been adopted as a criterion of Cd toxicity in the pollution control law.

Analysis of available soil microelements

1) Theoretical methods[11-13]

Although a single extraction is used for most routine soil testing purposes, the amount of nutrient extracted is affected by the solution : soil ratio. Watanabe[13] derived a formula for the solution : soil ratio and suggested the usefulness of the multi-extraction method expressed as follows:

$$1/S = K^n/St \cdot 1/V^n + 1/St$$

where S is the amount in μg of the extracted element in V ml of the solution used for extracting 1 g of sample soil, K and St are constants, and exponent n takes the value of 1/2 when cation salts used are monovalent, and 1 or 2 when they are divalent and trivalent. St is the theoretical amount of total extractable element when V approaches infinity. Since the St and K values change with ion strength and cation species, the St values do not represent the total amounts of element adsorbed on the soil particle surface but the total potential amounts that induce the equilibrium between solid and solution. The empirical equation may be considered to be another form of Henry's law.

The physiological significance of the solution : soil ratio and K values was demonstrated by experiments in which the availability of soil Zn for turnip plants

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(Zn intake) was compared with the amount of Zn extracted with divalent salt solutions at varying solution soil ratios. As the K value decreased, the proportion of plant Zn concentration (ppm) to St values (capacity), and also that to acid-extracted Zn, increased, i.e. the availability of soil Zn increased.

In conclusion, since the capacity and intensity factors are involved in the extraction method, the optimum solution : soil ratio is likely to depend upon the relative importance of the two factors.

2) 1 M HCl/extraction method for As pollution determination in paddy soil[6,7]

The phytotoxicity of As to rice plants which was investigated in relation to As forms bound to soil differed markedly from the forms in which As was added to the soils as follows: Na–, Ca–As were more toxic than Fe–, Al–As. Based on the calculation of the degree of toxicity in terms of GR50 (50% growth reduction in weight of old rice seedlings), and taking the toxicity level of Na–As as unity, Al–As was 1/4, and 1/2 while Fe–As was 1/6, and 10/1 as toxic as Na–As, respectively in kaolinitic and allophanic volcanic ash soils. The As forms in the contaminated soils were fractionated into Na–, Ca–, Al–, Fe–As. The content of each form of As averaged over the growing period was converted to the Na–As value of equivalent toxicity level. Significant relationships were detected among the reduction of grain yield, oxidation-reduction potentials in soils and the total equivalents of Na–As in soils.

For the determination of easily extractable As in soils 11 extractants were compared based on the relationship between the values obtained and the response of rice plants. One M HCl and 0.1 M HCl extractants were equally effective in predicting As phytotoxicity in the majority of the contaminated soils studied. However, the values obtained by 0.1 M HCl extraction did not show any correlation in volcanic ash soil. The best correlation for the response of rice plants obtained by the use of 1 M HCl extractant proposed by the authors was ascribed to the fact that the amount of arsenic extracted by 1 M HCl showed a significant correlation with the amount of Ca–, Al–, and Fe–As which were the main sources of available As in soils.

Several investigators have shown that the toxicity of As and heavy metals to crops varied markedly with the soil properties. In the case of volcanic ash soils, for example, the phytotoxicity was always lower than in the case of ordinary mineral soils.

The 1 M/HCl extraction method for As determination was adopted as a criterion of As toxicity in the pollution control law for arable land.

3) Tannic acid extraction of Mn and Co[3-5]

To estimate the amounts of available Mn in volcanic ash soils in terms of the correlation between the contents of extracted Mn and Mn in orchardgrass, 4 extractants (neutral 1 M ammonium acetate [AmAct], 0.2% hydroquinone/neutral 1 M AmAct [hydroquinone method], DTPA (diethylene-triamine-pentaacetic acid), and 1 M dihydrogen ammonium phosphate were compared for their efficiency. Neutral 1 M AmAct gave a low correlation value $(r = 0.529)$ and negative values were obtained with the other three extractants.

In order to identify a more suitable extracting reagent of organic nature, water solutions were prepared respectively from five components which were systematically extracted from fresh orchardgrass, and, along with water as control, were tested on soil samples. The solution of ethanol extract showed the highest ability of extracting Mn from soil among the six. As the ethanol extract contained 1 to 3% of crude tannin, tannic acid was tested for extraction efficiency. Values of soil Mn obtained by the tannic acid method showed a good correlation with the Mn contents of orchardgrass, suggesting that it may be a suitable extracting reagent.

The solubility of Mn is influenced by the redox potential of soil, where a reduced condition enhances the solubility of manganese oxides. Hydroquinone also solubilizes manganese oxides under a reduced condition. However, hydroquinone extraction occurred at the neutral pH maintained by the acetate buffer. On the other hand, since the tannic acid method can be applied in aqueous solutions of different pH levels depending on the soil conditions, better extraction can be achieved.

Acetic acid extraction for estimating the content of soil Co has long been used in studies on Co nutrition of forage plants. However, tannic acid has been proposed as another extractant to obtain a better parameter for soil Co availability in situ, especially in the soils of volcanic ash origin.

The content of Co in orchardgrass was found to be positively correlated with the soil Mn content.

On the other hand, since the coexistence of Co and Mn in the nodules of Mn oxides in soils had been revealed, available Co in soils was considered to be contained in nodules of Mn oxides in soils. The positive correlation between the Co and Mn contents in orchardgrass may reflect the status of available Co and Mn in soils.

The Mn oxides in soils were dissolved in a 0.5% tannic acid solution. The amount of extracted soil Co by tannic acid gave a much higher correlation with the Co content in orchardgrass than that extracted by standard 2.5% acetic acid. The content of Co in orchardgrass, however, is also influenced by the soil pH and Eh and a higher Co content in the plant is observed under lower soil pH and Eh conditions. As tannic acid extraction of air-dried soil is not affected by these soil pH and Eh conditions, it only reveals the potential availability of soil Co.

Extraction with 4% tannic acid is recommended instead of 0.5%, because the former gives a higher rate of extraction of soil Co contained in Mn oxides.

Chemical speciation analysis

The chemical forms in soil have been determined by fractionation using several characteristic extractants, i.e. Na–, Ca–, Al–, organic-P/As. In the last two decades, chemical speciation techniques have been mainly developed in the field of oceanography. Chemical speciation methods which enable to determine the chemical species extracted from soil with an extractant without concomitant change of their status, separate each chemical species bound with an element of constant valency or some organic component. Chemical speciation methods have been reported for As, Cr and I in soil as follows:

1) Arsenic[8]

To determine the amounts of As compounds, such as arsenate, arsenite, monomethylarsonate (MMA), and dimethylarsinate (DMA) in soils, Takamatsu et al.[8] developed an analytical method that included solvent extraction, anion exchange chromatography, and final determination of As by flameless atomic absorption spectrometry. This method was successfully applied to typical As-polluted soils in Japan. As a result, arsenate was found to be the major component, and lower levels of DMA and MMA were also detected in most of the samples. The pH and the amounts of arsenite and DMA increased with the reduction of soil under flooded conditions, whereas the pH decreased and the amounts of arsenate and MMA increased under upland conditions.

2) Chromium[9]

Chromium which is used in industrial processes is also an essential nutrient in its trivalent oxidation state. However, chromate and dichromate are toxic and their levels must be monitored. Parts per billion amounts of Cr (III) and Cr (VI) in soils are determined by graphite furnace atomic absorption spectrometry after pretreatments, as follows. Sample solution is prepared by 0.1 M Na_2HPO_4/extraction. Cr (III) can be recovered by the ferric hydroxide coprecipitation method, unlike Cr (VI). On the basis of the results, an analytical method for the determination of Cr (III) and Cr (VI) in soils was developed.

3) Iodine[14]

Four kinds of I forms, i.e. I^-, I_2, IO^{3-} and CH_3I exist in nature. Four I forms in the soil solution were separated by toluene/aqueous solution-extraction based on the redox reaction. After separation, iodine was determined by neutron activation analysis. Dominant forms were I^- in paddy, and IO^{3-} in upland soils.

Why the method of extractable Cd in soils has not been adopted in the pollution control law?

The soil pollution control law for arable land was enacted in 1970, and Cd, Cu, As, and their compounds were designated as harmful elements. For identifying polluted areas, the threshold concentrations defined by the law are as follows: Cd, 1 mg/kg in brown rice taken from rice plants in the field, Cu, 125 mg/kg in paddy soil and As, 15 (10–20) mg/kg in paddy soil.

The authorized extraction methods consist of 0.1 M and 1 M hydrochloric acid for Cu and As, respectively. On the other hand, for the determination of Cd, the Cd content in brown rice has been adopted, though the 0.1 M HCl/extraction method was used for assessing Cd-polluted soil based on a ministerial bylaw enacted in 1971. Why was the plant test selected as the method for assessing Cd pollution in soil instead of the soil test? The author proposed an

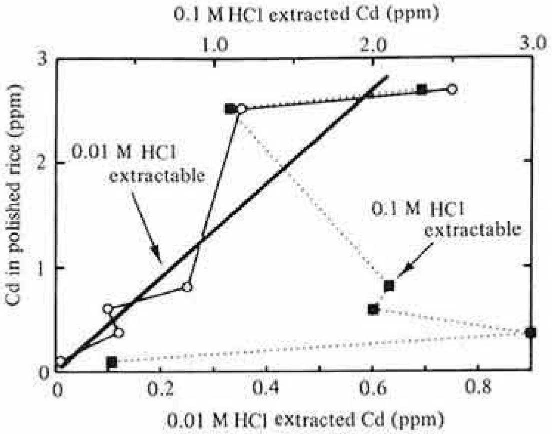

Fig. 1. Relationship between the amount of soil cadmium extracted by diluted hydrochloric acid and its concentration in polished rice

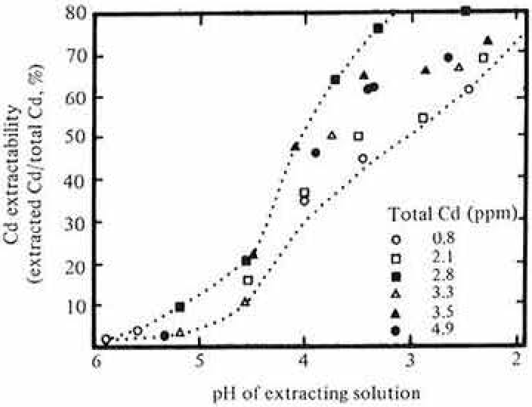

Fig. 2. Effect of pH on extractability of cadmium in soil

explanation to justify this decision as follows:

Before the ministerial regulation was issued, the researchers of the National Institute of Agricultural Sciences (National Institute of Agro-Environmental Sciences at present) had already observed that there was no significant correlation between the Cd content in soils determined by the 0.1 M HCl/extraction method and that in brown rice. They proposed the use of the 0.01 M HCl[2] or 0.1 M pH 4.5 AmAct/extraction method[1] instead of the 0.1 M HCl/extraction method. Earlier studies revealed that there was a significant correlation between the Cd contents in soil determined by the 0.01 M HCl/ extraction method and those in polished rice, but none between the Cd values in soil determined by 0.4–0.02 M HCl extractants and the latter. Fig. 1 shows the relationship between the Cd concentrations in soil obtained by 0.01 M and 0.1 M HCl extractants and those in polished rice.

Why does the diluted HCl extract better reflect the available Cd form in soils? Fig. 2 shows the presence of a close relation between Cd extractability (extracted Cd/total-Cd, %) and the pH of the extracting solution, but no correlation between the total Cd concentrations and the latter. The extractants below pH 4 can extract more than 30% of total-Cd, namely, solutions with an HCl concentration higher than 0.05 M extract the values related to total-Cd. These facts suggest that, to estimate the amount of available Cd, the extractant solution should reflect the soil pH with a low buffer action. However, the method by 0.01 M HCl extractant was not adopted by the law due to its low precision and reproducibility based on the fact that a low buffer extractant can extract only a trace of the element present in soil.

In addition another reason may be related to the methodology. While at current levels the pollution by As and Cu influences only crop growth, that by Cd affects human health. In this regard, the effect of cadmium toxicity to human is more related to the content of the element in foodstuffs than in soil.

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