Effects of organic matter application on the absorption and behavior of cadmium in a volcanic ash soil.

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To be presented in the IHSS 18 meeting in Kanazawa on September 13, 2016

Slide 1
Good morning, ladies and gentlemen. Dear my friends.
Welcome to Kanazawa.
I am very happy to have a chance of presenting my study in this occasion.
I was a member of the secretariat in the 5th IHSS meeting in 1990 held in Nagoya. I still remember the at home atmosphere during the meeting and the excursion.
I will retire from my university next March. I am very happy again to have this chance in time just before my retirement.

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Recently, as a method of remediating the soil polluted with a low concentration of heavy metals, much attention has been turned to phyto-extraction. The ability of the plant to absorb inherently toxic heavy metals may be related to the exudation of organic acids from the root, and to the synthesis of molecules contributing to the transportation or detoxification of the heavy metals. However, it is also important to establish the techniques for soil management which help the absorption of heavy metals.
Cadmium is an element which caused a serious disease called "Itai-Itai" disease in the lowland area of the neighboring Toyama prefecture, because the cadmium excreted from the zinc mine in the upper stream had contaminated the soils in the lower stream area. Cadmium is also used in various industrial products for

human life and is polluting the sewage drainage system and industrial wastes, and finally causing the pollution of soils.

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Among the soil borne factors, the effect of humic substance on the absorption of heavy metals have not been studied extensively.
Evangelou et. al. showed that adding 2000 ppm of humic acid in soil promoted the cadmium absorption by tobacco 30 – 40 %.
Halim et al also showed that 1 – 2 % of humic acid increased the plant available cadmium in soil.

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In this research, effects of humic and fulvic acids extracted from a volcanic ash soil in my university and that of peat humic acid from Sarobetsu mire in Hokkaido on the absorption of cadmium were examined.
For comparison, effects of EDTA and anaerobic digested cow slurry were also studied.

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The used plant was white mustard (Sinapis alba). The seed was bought from Takii company. This plant is a popular green manure plant and grow very fast and a large amount of biomass is produced. Brassica juncea, which belongs to the same group as Sinapis alba, has a high ability of absorbing cadmium.

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The used soil was collected from the experiment farm of our university. The soil layer is called Eniwa loam. It was a weathered sublayer soil, derived from a very old volcanic ash deposited around 17,000 years ago. The soil is a sandy loam, with neutral pH, very low in organic matter. The clay fraction is amorphous and rich in allophane.

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To the 300 g of soil in a 1 liter container, 500 ppm or 1000 ppm of humic acid, fulvic acid, or EDTA were added. Added rates of the anaerobic digested slurry were 2.5 % or 5 %. The added levels of cadmium were adjusted to 0, 10, and 50 ppm.

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This figure shows how plants were grown. In a plastic bottle of 1 liter, 100 mL of glass beads and 300g of test soil were placed. Necessary amount of fertilizers were also added and the moisture content of the soil was adjusted to 60% of maximum water holding capacity. After one week of stabilization, ten seeds of Sinapis alba were sown. Germinated seedlings were thinned to 5 after four days. Plants were grown for 30 days at 20 degree C in a green house.

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This figure shows the contents of carboxylic and phenolic hydroxyl groups in the used humic and fulvic acid samples.

Carboxyl group content was largest in the fulvic acid from andosol, and lowest in the humic acid from peat. Carboxyl group content in EDTA is calculated to be 10.8. Therefore, carboxylic group content in the fulvic acid was as large as that of EDTA.

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This figure shows the UV and visible absorption spectra of the used humic substances in a logarithmic scale.

Inclination of the humic acid from the andosol was very small, indicating the high degree of humification.

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This figure shows the FT-IR spectra of the used humic substances. Andosoil fulvic acid was charadterized by a very strong and sharp COOH peak. Andosol humic acid had also strong COOH peak, but

it accompanied the large peak of COO^-.
Peat humic acid showed very distinct aliphatic peaks.

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This figure shows the 13C-NMR spectra of used humic substances. Andosol HA had the strongest aromatic peak, Andosol FA had the strongest carboxylic peak, and peat HA had the strongest aliphatic peak.

Slide 13
Anaerobic digested slurry of cow manure was taken from the biogas plant of my university. Carbon content was 1.87 % and C/N was 5.36.

Slide 14
This photo shows the growth of Sinapis alba under different levels of cadmium. No organic matter was added to these pots. At 50 ppm of cadmium application, the leave color showed the symptom of chlorosis. Germination rate was almost 100 % in all plots.

Slide 15
When EDTA was added to soil, the growth of Sinapis alba was inhibited at all levels of cadmium application.

Slide 16
When the humic acid from andosol was added, Sinapis alba grew normally even at 10 ppm of cadmium. At 50 ppm of cadmium, the growth of Sinapis alba was inhibited and the symptom of chlorosis was shown.

Slide 17
By adding the anaerobic digested slurry, the growth of Sinapis alba was promoted even at 50 ppm of cadmium, though the color of the leaves became slightly yellow.

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This figure shows the effect of organic matter application on the growth of Sinapis alba at different Cd levels.
When no organic matter was added, the growth of Sinapis alba was inhibited remarkably with the increasing level of cadmium.
By low application of Andosol humic acid, the growth of Sinapis alba was improved at 10 ppm of cadmium, however, the growth at 50 ppm of cadmium was not improved.
When high level of andosol humic acid was added, the growth of Sinapis alba was repressed slightly even when no cadmium was added. However, the growth at 10 ppm and 50 ppm of cadmium did not decrease compared with no cadmium plot. This means that the high level of humic acid decreased the toxicity of cadmium.
In the case of peat humic acid, the growth of Sinapis alba decreased with the concentration of cadmium.
Low level of fulvic acid protected the growth of Sinapis alba up to 10 ppm of cadmium, but the growth was inhibited at 50 ppm of cadmium.
Anaerobic digested slurry significantly improved the growth of Sinapis alba at 10 ppm and 50 ppm level of cadmium.
EDTA was not effective in protecting the growth of Sinapis alba at both low and high level of cadmium.

Slide 19
Short interim summary (skip)

Slide 20
This slide shows the scheme of cadmium in soil existing in different forms. We determined the cadmium in these five different forms in triplicate. Cadmium in the extracted solution was

determined by AAS after concentrated in MIBK solution.

Slide 21

This figure shows the proportion of different forms of cadmium in soils containing 10 ppm of cadmium and applied with different kinds of organic materials.

When EDTA was applied, water soluble cadmium increased and exchangeable cadmium decreased remarkably compared with the plot with no organic matter treatment.

Application of humic acids and fulvic acids did not influence the proportion of different forms of cadmium.

By applying anaerobic digested slurry, water soluble cadmium almost disappeared, exchangeable cadmium decreased, and inorganic bound cadmium increased.

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This figure shows the proportion of different forms of cadmium in soil containing 50 ppm of cadmium and applied with different kinds of organic materials.

The results were almost same as those from the soil containing 10 ppm of cadmium.

Proportions of exchangeable cadmium increased slightly in all treatments compared with the results from 10 ppm cadmium soils.

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Short interim summary (skip)

Slide 24

This figure shows the method of analyzing the leaves and shoots of Sinapis alba.

Dried plant sample was digested with nitric acid and sulfuric acid mixture and extracted with MIBK solution after transforming the cadmium to the tartrate chelate.

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This figure shows the cadmium concentration in the shoot of Sinapis alba grown at soil cadmium concentration of 10 ppm. Plants grown with humic substances application contained four times larger amount of cadmium. Cadmium concentration was also high in the plot applied with EDTA. Anaerobic digested slurry made the cadmium concentration in shoot lower than the control plot.

To the contrary, cadmium concentration in the shoot did not increase in the plots applied with humic substances and digested slurry. Probably the cadmium concentration attained to the maximum limit in these cases.

Cadmium concentration decreased in the plot applied with EDTA due to the growth inhibition. Peat humic acid which did not suppress the growth of Sinapis alba might have repressed the absorption of cadmium.

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This figure shows the total amount of cadmium absorbed to the shoot part of Sinapis alba.

In the plots of 10 ppm cadmium, total amount of absorbed cadmium increased remarkably in the plots applied with humic substances. EDTA was very slightly effective in cadmium absorption.

On the other hand, in the plots of 50 ppm cadmium, the anaerobic digested slurry was very effective in increasing the total amount of absorbed cadmium, while HA was slightly effective.

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This table summarizes the effects of organic material application on the cadmium absorption by Sinapis alba and those mechanisms were suggested.

When 10 ppm of cadmium was added to soil, all the humic substances promoted the absorption of cadmium by Sinapis alba.

The mechanisms are not limited to the chelate formation, but the hormone like activity of humic substances may also take part in.
Anaerobic digested slurry repressed the absorption of cadmium, by decreasing the water soluble and exchangeable cadmium in the soil.
Though EDTA increased the solubility of cadmium, but it also exerted the negative effects on the growth of Sinapis alba. As the combined effect, absorption of cadmium was promoted slightly.
In the soil with 50 ppm of cadmium, various humic substances showed different effects on the absorption of cadmium. Andosol humic acid promoted the absorption of cadmium. This may be due to the suppression of cadmium toxicity by changing the solubility of cadmium.
Anaerobic digested slurry promoted the absorption of cadmium at 50 ppm level. This may be due to the decrease in toxicity of cadmium and the promotion of the growth of Sinapis alba.
EDTA suppressed the absorption of cadmium at 50 ppm level. This may be due to increasing the toxicity of cadmium and suppression of the growth of Sinapis alba.

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Concluding summary.
Soil humic acid and fulvic acid, as well as EDTA, promoted the absorption of Cd at 10 ppm of pollution, while humic acids and fulvic acids were more effective than EDTA.
Anaerobic digested slurry was not so effective at 10 ppm Cd level, but promoted the Cd absorption remarkable at 50 ppm. This is because the digested slurry mitigated the toxicity of cadmium and promoted the growth of Sinapis alba even at a high cadmium level in the soil.

Slide 29. Scheme chart

Effects of organic materials in soil were not so simple.

A. Complex formation

1) Small molecule ---- EDTA, fulvic acid
   Accelerates the absorption
   Increase the toxicity of cadmium

2) Large molecule ---- Humic acids
   Retard the absorption
   Promote the slow absorption of Cd
   Decrease the toxicity of cadmium

B: Hormone like activity of humic substances and the nutritional effect of anaerobic digested slurry

Enhanced the growth of plants
Promoted the absorption of cadmium in total