Risk assessment of heavy metal contaminated soils with reference to aging effect

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Abstract
To estimate the effect of aging on the availability of heavy metals in soil, relationships between availability of metals in soil and period after contamination were investigated for a range of soils and metals. Five metals, Ni, Cu, Zn, Cd and Pb, were added as nitrate solution (2.5 mmol/kg: single or mixed, or 3 times of their background levels) to four soil samples with various chemical properties: dune soil, alluvial soil, red soil and volcanic soil. The soils were incubated at field capacity for 1day, 1 week, 2 weeks, 4 weeks or 6 months, and exchangeable and available fractions of the metals extracted with 1 *M* ammonium acetate and 0.005 *M* DPTA solution (pH 6), respectively, were determined by ICP-AES. The amounts of the metals in available fractions were generally in the order of Cu=Pb < Ni=Zn < Cd. Availability of the metals was in the order of volcanic soil < red soil < alluvial soil < dune soil. Temporal decrease of the metal availability, i.e. aging, was evident for all soils and metals, especially for red soil with high amount of oxides, and the changes became <3% / week after 4 weeks. These results enable us to understand natural attenuation of metal contamination and also to assess the risk of soil contamination by determining available fractions of metals in 4-week incubated soils after artificial contamination.

Key Words
Aging, availability, contamination, heavy metals, risk assessment, soil.

Introduction
Soil contamination with heavy metals has been a big issue worldwide (Alloway 1995; Nriagu 1996). It has been carried out intensively to investigate contaminated soils for evaluating the level of contamination in relation to human health and/or environmental conservation. It is also very important to investigate the process of soil contamination itself with special attention to available fractions because it directly relates to the management and prevention of soil contamination. It is generally known that availability of metals in soil decreases with time after contamination (Barrow 1998; Christensen 1984; Lock and Janssen 2003; Lu *et al.* 2005; Lim *et al.* 2002). This phenomenon known as "aging", however, has not been investigated comprehensively for a variety of soils with a range of metals. Based on this background, the objectives of this study were: 1) to investigate the aging effect of metals in soil with reference to the type of soils and metals, and 2) to propose a rational method to assess the risk of soil contamination by taking aging effect into account.

Methods
Soil samples
Four kinds of soil samples with variable physico-chemical properties were collected in Japan and used in this experiment: dune soil, alluvial soil, red soil and volcanic soil. According to Soil Taxonomy, they were classified as Psamments, Fluvaquents, Udults and Udands, respectively. Their general physico-chemical properties are listed in Table 1.

Contamination with metals
Five metals, nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb), were selected as heavy metals potentially toxic to the terrestrial ecosystems. They were added as nitrate solution to 4.0 g of soil sample in a 50mL plastic tube. Firstly, to investigate the effect of chemical characteristics of the metals on their availability, same level of metals were added to the soils; i.e. the level of 2.5 mmol/kg was arbitrarily selected, which was equivalent to 3 times of the background level of Ni (*c.* 150 mg/kg). Their nitrate solutions were added either individually or mixed together to the soils to compare mixed contamination with single one. Secondly, to investigate the aging effect on "realistic" level of contamination, the amounts of metals 3 times of their background levels (Bowen 1979) were added to the soils: 150 mg Ni/kg, 90 mg Cu/kg, 270 mg Zn/kg, 1.05 mg Cd/kg and 105 mg Pb/kg, respectively. In both cases, treatment without heavy metal addition was also prepared as a control. All the treatments were duplicated.

Table 1. General physico-chemical properties of the soil samples.

Soil	pH	EC mS/cm	TC %	TN %	C/N	Sand %	Silt %	Clay %	Texture
Dune soil (D)	5.6	0.06	0.76	0.06	11.8	98.5	0.8	0.7	S
Alluvial soil (A)	6.0	0.06	1.39	0.14	10.2	53.0	23.9	23.0	CL
Red soil (R)	5.5	0.19	0.15	0.04	3.8	35.7	8.0	56.3	HC
Volcanic soil (V)	5.6	0.20	7.10	0.48	14.9	41.5	34.3	24.2	CL

Soil	CEC	Exchangeable bases (cmolc/kg)				Total content（mg/kg)				
	cmolc/kg	Ca	Mg	K	Na	Ni	Cu	Zn	Cd	Pb
Dune soil (D)	3.2	1.9	0.48	0.19	0.01	0.6	14.0	43.7	0.0	6.3
Alluvial soil (A)	13.0	7.0	1.1	0.54	0.03	19.2	43.1	108	1.1	31.8
Red soil (R)	18.1	9.4	0.76	0.18	0.01	21.9	14.4	41.1	1.9	11.3
Volcanic soil (V)	37.1	13	3.5	1.4	0.09	16.4	45.1	75.9	3.8	17.0

Soil incubation, soil extraction and determination of metal concentrations

The soils were watered to reach at the field capacity and incubated for 1day, 1 week, 2 weeks, 4 weeks or 6 months at 25℃. Exchangeable and available fractions of the metals in soils were determined after incubation. Exchangeable fraction was extracted with 40mL of 1*M* ammonium nitrate solution (Symeonides and McRae, 1977), and available fraction was extracted with 20mL of 0.005*M* DPTA solution (pH 6) (Lindsay and Norvel, 1978). Concentrations of the metals in the extracts were determined by ICP-AES (Seiko Instruments Inc., SPS 1500VR).

Results and discussion

Exchangeable and available fractions of the metals under single contamination

Rates of extraction of available fraction were higher than those of exchangeable fraction, as shown in Figure 1, reflecting the extractability of the solutions used. For both exchangeable and available fractions, rates of extraction were in the order of volcanic soil << red soil < alluvial soil < dune soil. This trend, especially clear for exchangeable fraction, would be due to highly reactive Al and Fe oxides in volcanic soil and red soil. Among metals, rates of extraction were in the order of Cu=Pb < Zn=Ni < Cd, reflecting their intrinsic chemical reactivity in soil. Temporal trend of the exchangeable and available fractions were also observed for all the five metals. In exchangeable fraction, there were sharp decline during the first 4 weeks of incubation and the decrease became rather slight after the period, even though the trend continued longer for Red soil. In available fraction, temporal decline of the rate of extraction continued slightly longer except for volcanic soil. It was concluded that decreasing trend of availability, i.e. aging, was clearly observed in both exchangeable and available fractions.

Exchangeable and available fractions of the metals under mixed contamination

In the case of mixed or multiple contaminations, similar patterns were observed as in the case of single contamination. General trend among metals and soils were quite similar but the rates of extraction of the mixed contamination were slightly higher than those of the single contamination. Figure 2 shows the relationship between the rates of extraction of the single and mixed contamination for the exchangeable and available fractions. It is clear that the rates of extraction of the mixed contamination were higher than those of the single contamination, especially for exchangeable fraction, in which the rates were relatively high for red soil and dune soil in terms of soil, and for Pb and Cu in terms of metals. In conclusion, mixed contamination enhanced the risk of soil contamination with metals compared with single contamination, especially for the exchangeable fraction.

Establishment of the risk assessment of heavy metal contaminated soils with reference to aging effect

Similar to the case of the same level of metal contamination, rates of extraction of the "realistic" soil contamination were in the order of volcanic soil, red soil < alluvial soil, dune soil (data not shown). Among metals, rates of extraction were in the order of Cu=Pb=Cd < Zn=Ni, reflecting relatively low concentration of Cd in soil. In this case, the period of time for the rate of aging (decrease of rate of extraction) to become < 3% / week was 4 weeks for any soil and for any metal. These results suggest that rate of extraction after artificial metal contamination can be assessed reasonably well after 4 week incubation, by taking aging effect into account. It was concluded, therefore, that risk assessment of soil contamination can be accomplished by the determination of exchangeable or available fraction of soil after 4 weeks incubation of soils artificially spiked with a metal equivalent to 3 times of the background level.

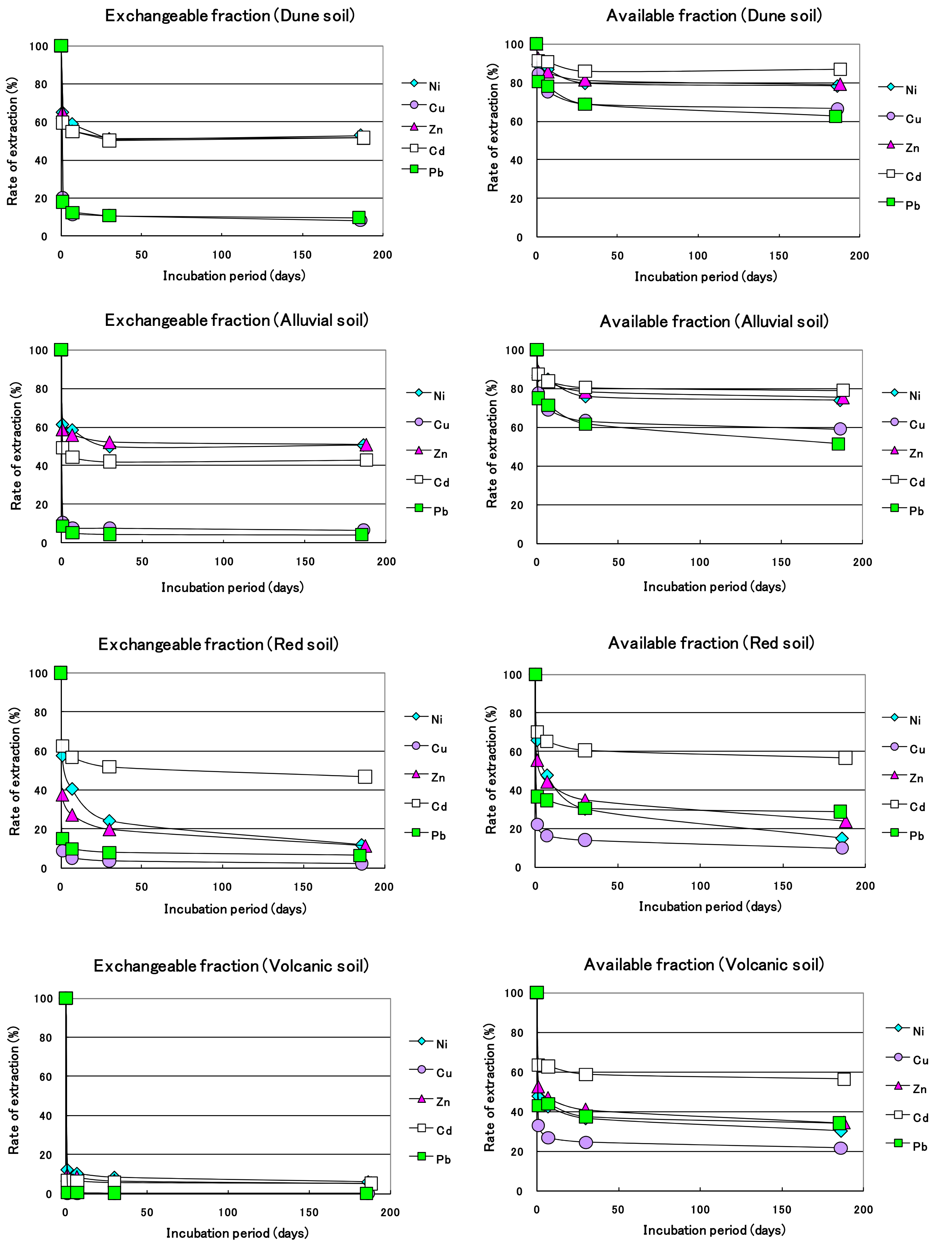

Figure 1. Temporal change of exchangeable and available fractions of the five metals in four soil samples investigated (single contamination).

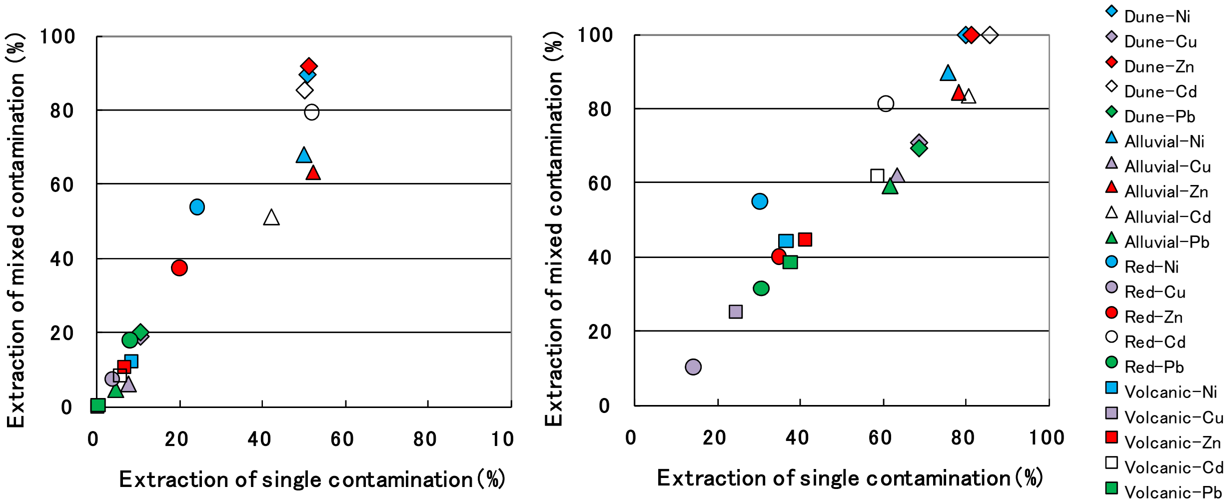

Figure 2. Relationship between the rates of extraction of the metals of the single and mixed contamination for the exchangeable (left) and available (right) fractions.

Conclusion

Effect of type of metals and soils on the metal availability in soil was clearly observed: Cu=Pb < Ni=Zn < Cd for metals and volcanic soil < red soil < alluvial soil < dune soil for soils. Mixed contamination considerably increased metals in exchangeable fraction, especially Pb and Cu, compared with single contamination. Natural attenuation of the metal availability, i.e. aging, was also evident for all soils and the changes generally became <3% / week after 4 weeks. These results enable us to assess contamination risk of soil contamination *prior to* contamination by assessing available fractions of metals in 4-week incubated soils after artificial contamination.

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