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RAPID COMMUNICATION

Evaluation on bioaccessibility of arsenic in the arsenic-contaminated soil

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Abstract−Korea Ministry of Environment regulates the soil quality based on the pseudo-total content of metals extracted by *aqua-regia*, and the concentration of metals has been used in the risk assessment of the contaminated site. The pseudo-total content of metals can be accepted conservatively as a potentially risky concentration of metals in the soil. However, only some portion of metals in the soil are absorbed by plants, animals, and human beings, and the pseudo-total content used in the risk assessment tend to overestimate the risk of metal contamination. Therefore, the pseudo-total content does not reflect the real risk of the contamination. Bioavailability and bioaccessibility can be alternatives for the pseudo-total content to estimate the reasonable risk. Bioaccessible concentration can be analyzed as in-vitro by the amounts of metals extracted in the gastrointestinal situation, and the bioaccessible concentration is the maximum amount of metals to be absorbed. The bioaccessible concentration of As was evaluated, compared with the pseudo-total concentration of As, and the correlation between the concentration of As and physicochemical properties of soil was analyzed. The bioaccessible concentration can be estimated by the labile fractions of As, and Si, Al, and Mn content decrease the bioaccessible concentration of As.

Keywords: Bioaccessibility, Arsenic, Fractionation, Risk Assessment

INTRODUCTION

The management strategy for a metals-contaminated site can be classified into the pseudo-total content of metals and risk-based management [1]. In Korea, the Ministry of Environment sets the concerning and warning levels of contaminants in soil, and manages the soil quality based on the pseudo-total content of metals by the land use. By law, soil is considered as contaminated when the concentration of metals extracted by *aqua-regia* exceeds the concerning level in soil, which is the soil management based on content [2-4]. However, in risk-based management, the risk is used to determine if the soil is contaminated. The approach considers the soil as contaminated even though the soil contains a lower level of contaminats than the concerning (screening) level [5].

In Korea, we apply risk assessment to determine the remediation period, techniques, and target cleanup levels, and it is accepted that risk-based management is more reasonable than the management based on pseudo-total content [2]. However, on other points, the application of risk assessment to the site remediation is considered as the way to reduce total cost compared to the active remediation [6]. To date, we can apply risk assessment for the 14 contaminants, and the result can be used to manage the contaminated site. However, the law limits the application of risk assessment to only the site remediated by the government funding [7,8].

In Korea, the pseudo-total content of metals has been used in the human health risk assessment to estimate the risk of a contaminated site. "Content" means amounts of metals extracted by *aqua-regia* method, where the metals are extracted from the soil by strong acids and heat. However, the speciation and redox states are changed during the extraction, and it is unsuitable to estimate the real risk. Additionally, the metals uptaken through various exposure pathways are metabolized, absorbed, and distributed to the human body, and some portion of metals shows toxicity to human beings [9-11]. Therefore, the pseudo-total content is not suitable to be used in the risk assessment, but they can estimate a maximum risk in conservative point view [12]. However, the risk is overestimated because all metals in soil are not risky to humans, the remedial goal is too strict, finally, huge cost and long remediation time are required to meet the target cleanup level [13,14].

To date, reasonable exposure assessment considering the absorption has been studied to estimate realistic risk instead of the pseudo-total content of metals [15-18]. Bioavailability concept is one of the ways to achieve the goal because the concept means the potentially absorbable amounts of metals in the ingestion of metal-contaminated soil [14,18]. Bioavailability indicates the amounts of metals absorbed into the target organs among the amounts of metals ingested; an *in-vivo* assay using animals is required to be determined [19,20]. However, there are ethical problems during animal experiments and analytical limits for detection in the blood and organs, and the assay requires huge cost and time [20,21]. As an alternative to the bioavailability concept, the bioaccessibility concept was suggested, which means the amounts of metals to be absorbed into the human body through the human gastrointestinal tract. That is a maximum amount of bioavailable metals in the soil when the metal-contaminated soil is ingested [16]. Bioaccessibility is the extractable amount of metals by the artificial gastrointestinal through *in-vitro* experiments [22]. The amounts are bioaccessible metal, and bioaccessibility means the fraction of bioaccessible met-

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als with respect to the pseudo-total content of metal [16,23]. Some researches have reported the correlation between bioavailability and bioaccessibility, and suggested the estimation equation for bioavailability using the bioaccessibility of metals [11,21,24]. Furthermore, the US EPA proposed the estimation relationship of arsenic and lead using bioaccessibility [18]. Given the bioaccessibility of estimating the actual amount of heavy metal exposed to humans, it would be reasonably accepted rather than risk assessment based on total content.

Therefore, in this study, the bioaccessibility of As in the soil was investigated to evaluate the contamination of soil. The bioaccessibility was correlated with the pseudo-total concentration of As. In addition, the bioaccessible concentration of As was correlated with the fractionation analysis of As to propose the correlation between labile fractions of As and bioaccessible concentration of As.

MATERIALS AND METHODS

1. Materials

Total Ten soil samples (J) were taken from a site near a former refinery plant located in Janghang, Chungnam, Republic of Korea; another ten soil samples (D) were sampled from a site near a military site, Daejeon, Republic of Korea, and total 20 soil samples were used in this study. The soil was air-dried, sieved using a sieve with a 0.15 mm opening, and the soil samples with <0.15 mm were used for further analysis. The pseudo-total content of metals was analyzed by the Korean standard test method for soil [25]; organic matter (OM) was measured by mass loss after heating at 440 °C for 24 h (ASTM D2974-71, [26]). The fractionation of As was analyzed by the method suggested by Wenzel et al. [27]. The pH and electrical conductivity of soil were analyzed using a pH meter (pH-250L, Istek, Korea) and EC meter (EC-400L, Istek, Korea) according to the Korean standard test method for soil.

2. Bioaccessibility

The bioaccessible amounts of metal were measured using the method proposed by US EPA [18,28]. The extracting solution was a 0.4 M glycine buffer to simulate the gastric fluid. A mass of 0.3 g of soil and 30 ml of extracting solution was mixed at 37 °C for 1 h in an over-head shaker (FinePCR, Korea). The mixture was centrifuged at 8,000 rpm for 10 min; the supernatant was separated from the sample by filtration using a 5B filter, and the filtrate was used to analyze As concentration using ICP-OES (720-ES, Agilent Technologies, USA). Experiments were conducted in duplicate, and the average value was used.

The bioaccessible concentration of As was correlated with the fractionation analysis of As (labile fractions of As) and physicochemical properties of soil using IBM SPSS Statistics softwater (Version 21.0, USA).

RESULTS AND DISCUSSION

1. Physicochemical Properties of Soil Sample

The pH, EC, and OM of soil samples are summarized in Table 1. The pH range of soil was within the general pH value in Korea (5-7); however, a few samples (J7, J8, and J10) were slightly acidic. The average OM content of D and J soil was 6.7 and 4.6 wt%, respectively, which is slightly higher than the average OM in agricultural land, Korea. The EC values ranged 0.1-3.7 mS/cm. The oxide forms

Table 1. Physicochemical properties of soil samples

Soil sample No.	pH	EC (mS/cm)	OM (%)	Aqua-regia extractable concentration (mg/kg)			
				Fe	Al	Mn	As
D1	6.66±0.05	0.70±0.01	6.2	38037.4±395.4	23967.9±91.6	817.6±3.4	10.7±0.3
D2	6.20±0.04	0.46	8.3	39522.9±137.5	26904.5±130.6	746.5±4.0	13.9±1.0
D3	5.46±0.05	0.12	3.9	44835.0±381.2	28182.5±12.0	509.5±2.4	17.2±0.5
D4	5.33±0.04	0.19	4.3	51867.3±1414.8	33198.8±309.5	610.9±1.4	19.3±1.8
D5	5.98±0.05	0.16	3.7	48629.0±230.6	15560.7±99.4	1176.0±2.1	21.6±4.3
D6	5.59±0.05	0.36	8.0	80881.4±1874.6	31849.5±766.6	629.6±3.0	30.3±7.3
D7	6.46±0.01	1.32	14.5	71531.0±972.2	23906.4±57.1	649.7±12.4	30.5±4.5
D8	5.30±0.01	0.24	3.2	51247.9±1179.6	16214.2±126.8	717.9±5.8	44.8±0.9
D9	5.85±0.03	0.66	6.9	45584.3±466.7	23149.2±286.7	488.9±0.1	46.7±1.7
D10	5.49±0.01	0.49	8.2	52272.3±7.5	30914.9±19.6	820.2±8.6	52.9±1.9
J1	6.18±0.01	2.95±0.05	1.3	25986.6±33.3	13190.3±158.9	667.2±0.7	26.8±0.4
J2	5.49±0.01	0.24	5.2	39545.0±194.6	24763.5±107	493.7±0.7	29.2±3.1
J3	6.13±0.03	1.58±0.01	1.2	27102.7±143.3	13561.2±22.8	569.7±4.5	29.9±0.7
J4	7.14±0.02	0.29	4.0	33314.5±299.9	21620.6±28.6	694.8±0.3	35.2±1.2
J5	5.36	1.59	3.5	33132.7±49.9	19570.0±20.7	527.7±1.8	61.5±0.5
J6	5.89±0.01	3.67±0.07	1.9	23380.3±193.6	15105.3±16.5	374.3±0.6	70.5±4.4
J7	4.87±0.01	1.09	8.8	42117.6±723.9	21492.0±354.6	305.3±4.5	74.6±0.9
J8	4.60	0.99	8.6	43768.7±177.5	20493.6±108.2	334.5	75.5±3.2
J9	5.53±0.05	0.22	4.3	26872.4±3.4	7256.9±126.5	152.3±0.7	116.6±8.3
J10	4.49±0.01	0.57	7.6	31596.6±124.6	14504.5±9.7	293.5±1.7	119.7±0.3

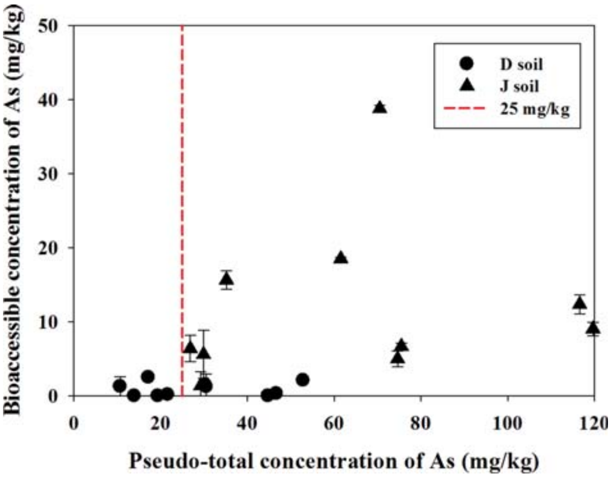

Fig. 1. The scatter plot of bioaccessible concentration by the total concentration of soil samples.

of Fe, Al, and Mn affect the fate and transport of As in soil due to the great affinity of the metal oxides with respect to As [29-31]. The amounts of Fe, Al, and Mn extracted by *aqua-regia* solution were 23,380.3-80,881.4, 7,256.9-33,198.8, and 152.3-1,176.0 mg/kg, respectively. There was no significant difference between the two sites.

Arsenic concentration in D site was lower than that in the J site; all samples in the J site exceeded the concerning level of As for residential and agricultural land use. In the D site, some sample was contaminated by As (D6-D10), and others were not contaminated, by law.

2. Evaluation of As Contamination Using Bioaccessibility

The bioaccessible concentration of As in the simulated human gastrointestinal tract was analyzed (Fig. 1). The As content and bioaccessible concentration of As in the soil un-contaminated, by law (that is, the As content is lower than 25 mg/kg) were 16.5±4.4 and 0.8±1.1 mg/kg, respectively, and the contaminated soil (>25 mg/kg of As) showed 56.3±29.6 mg/kg of As content and 8.3±9.9 mg/kg of bioaccessible As. The result indicates that the bioaccessible concentration of As is proportional to the As content (pseudo-total concentration). However, the bioaccessible concentration of As is relatively high in some un-contaminated soil (that is, the soil with <25 mg/kg of As). The observation indicates there are other factors to be considered in the assessment of the bioaccessible concentration of As.

The soil was classified into un-contaminated and contaminated

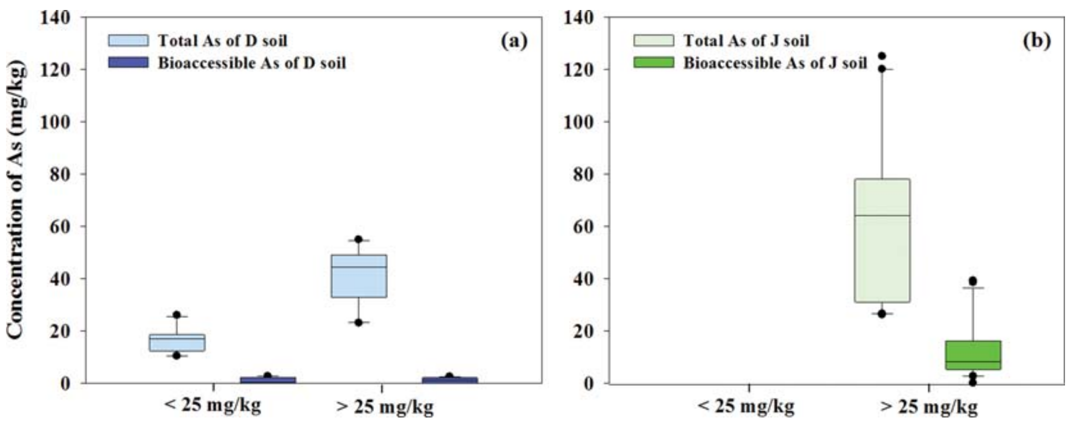

Fig. 2. Distribution of bioaccessible concentration. Bioaccessible value of soil samples was classified according to As-reference value (25 mg/kg); (a) D soil (b) J soil.

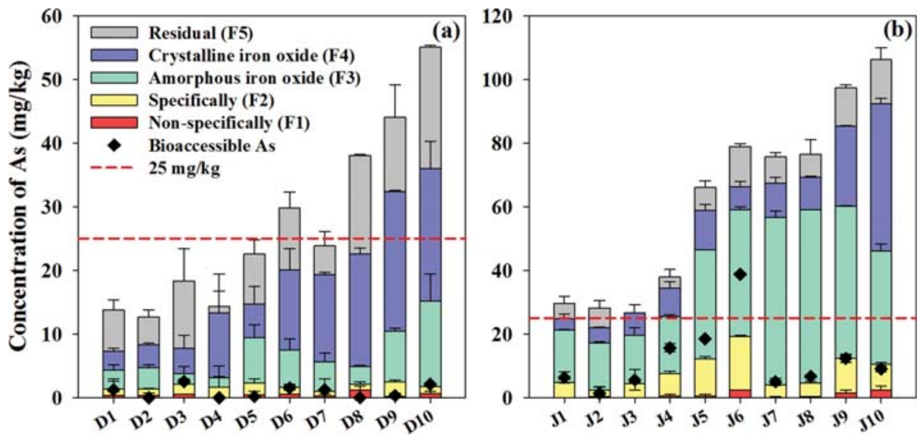

Fig. 3. Bioaccessible As and fractionation of As by sequential extraction procedure; (a) D soil, (b) J soil.

Table 2. Correlation between bioaccessible concentration and fractionation of As

Correlation coefficient	Compare with Bioaccessible concentration of As		
	F1	F1+F2	F1+F2+F3
Pearson**	0.523*	0.933*	0.680*
R^2***	0.273	0.871	0.463

*The correlation coefficient is significant at the 0.01 level

**Indicates the linear correlation of bioaccessible As and labile fractionation of As

***Indicates the coefficient of determination

based on the concerning level, that is, 25 mg/kg, and the average and range of pseudo-total concentration and bioaccessible concentration is plotted in Fig. 2. There is no difference in the bioaccessible concentration of As even though the average pseudo-total content of As was three-times higher in the contaminated soil than that in un-contaminated soil for D site. In the case of J soil, the average concentration of As in the contaminated soil was slightly higher than that in D soil; however, the bioaccessible concentration was much higher than the value in D soil.

3. Fractionation of As and Bioaccessible Concentration of As

Fractionation analysis was used to determine the labile portion of As in soil, and the amount of As was accepted as the leachable concentration of As [27,32]. The fractionation of As, pseudo-total content of As, and the bioaccessible concentration of As are summarized in Fig. 3. The bioaccessible concentration of As was 12% of the pseudo-total content of As, and the contamination by law does not make a significant difference in the bioaccessible concentration of As. The result implies that the pseudo-total content of As in the risk assessment will overestimate the risk of the contaminated site.

The bioaccessible concentration of As was correlated to the summation of each fractionation of As (Table 2). The analysis shows that the amounts of bioaccessible As were similar to those of F1(non-specifically adsorbed)+F2(specifically adsorbed). The labile fraction of As is bioaccessible fractionation in both soils. The other fractions of As are bound to the soil strongly, which means that it is hardly desorbed or dissolved in the digestion fluid. Thus, the fractionation analysis can be used to determine the bioaccessible concentration of As instead of the independent *in vitro* analysis. The fractionation analysis has been widely used to estimate the mobility and leaching potential [33,34], and the first two fractions can be considered as bioaccessible amounts of As. In the site characterization stage, the fractionation analysis or bioaccessibility can be carried out. However, this result indicates that the fractionation analysis can be used to determine the bioaccessible concentration of As. In other words, the pseudo-total content in the risk assessment considers the stable or non-labile fractions of As as potentially harmful amounts of As, which may overestimate the risk of As-contaminated sites.

4. Physicochemical Properties of Soil and Bioaccessibility

Chemical properties of soil affect the bioaccessibility of As greatly, and the properties shown in Table 1 were correlated with the bioaccessibility of As (Table 3). The EC shows a relatively strong positive correlation with bioaccessibility. However, the amounts of Fe, Al, and Mn show a negative correlation because the oxide forms of Fe, Al, and Mn are sinks for As in the soil [35]. The more Fe, Al, and Mn means that the soil can immobilize the As in the soil, which decreases the bioaccessibility of As. Thus, the bioaccessible As in the soil can be stabilized and immobilized by the addition of Fe, Al, and Mn. The addition has been proved as a remediation technique to reduce the mobility of As and to increase the stability of As in soil [36]. The method is effective to lower the bioaccessible concentration.

Generally, the soil pH shows some relationship because a higher pH of soil changes the surface charge to negative, which increases the mobility of As or desorption of As from the soil [37]. However, in this study, there was no relationship between pH and bioaccessible As.

CONCLUSIONS

Bioaccessibility can assess the contamination of As in soil instead of pseudo-total content of As. The bioaccessible concentration of As is proportional to the pseudo-total content of As by aqua-regia in the contaminated soil, that is, the soil with >25 mg As/kg. However, in the non-contaminated soil, there was no distinct relationship between the content and bioaccessible concentration. Slightly higher bioaccessible As was observed even in the soil with lower content of As. Therefore, the use of pseudo-total content in the risk assessment can overestimate the real risk of the As-contaminated soil. In addition, the bioaccessible concentration shows a strong correlation with the labile fractions of As in the fractionation analysis. The bioaccessible concentration decreased with the increase in the content of Fe, Al, and Mn in soil because the metals can stabilize As by forming complexes, which indicates that the bioaccessible As can be controlled by stabilization technique using Fe, Al and Mn oxides. This study suggests that bioaccessible concentration of As is more suitable than the total content to estimate the real risk of As-contaminated site.

Table 3. Correlation between bioaccessible concentration and physicochemical properities

Correlation coefficient	Compare with Bioaccessible concentration of As					
	Ph	EC	OC	Fe	Al	Mn
Pearson	0.045	0.670**	−0.374*	−0.548**	−0.429**	−0.405**
R^2	0.002	0.449	0.140	0.300	0.184	0.164

*The correlation coefficient is significant at the 0.05 level

**The correlation coefficient is significant at the 0.01 level

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