Abstract

BACKGROUND: The concern over heavy metal(loid)s in arable land and agricultural products increases for public health in recent years. This study aims to identify transition characteristics of heavy metal(loid)s and to assess dietary risk in barley grown at the major producing districts in Korea.

METHODS AND RESULTS: The soil and barley samples were collected from 38 locations around the major producing districts at Jeollabuk-do in Korea for the purpose of examining the concentrations of heavy metal(loid)s. The 34 barley samples were separately purchased on the market for the same survey. The average concentration and range of arsenic (As), cadmium (Cd) and lead (Pb) in barley grown at the major producing districts in Korea were 0.037 (0.016-0.094), 0.028 (0.004-0.083) and 0.137 (0.107-0.212) mg kg\(^{-1}\), respectively. Currently, the maximum allowable level for barley Pb is set at 0.2 mg kg\(^{-1}\) in Korea, and the monitoring results suggested that some samples exceeded the maximum allowable level and required appropriate farming management. Bio-concentration factor values by heavy metal(loid)s in barley were high at Cd, copper (Cu) and zinc (Zn), similar to other crops, while As and Pb were low, indicating low transferability.

CONCLUSION: Human exposure to As, Cd and Pb through dietary intake of barley might not cause adverse health effects due to relatively low concentrations, although the Pb in some barley was detected higher than the maximum allowable level. Further study on uptake and accumulation mechanism of Pb by barley might be required to assess the human health risk associated with soil contamination.

Key words: Barley, Heavy Metal(loid)s, Lead, Monitoring, Risk Assessment

Introduction

As the quality of life improves, interest in agricultural product safety is also increasing. Continuously,
crop cultivation environment and criteria related to heavy metal(loid)s in agricultural products are expanded and supplemented. Therefore, a review of advanced data and scientific risk assessment is required. The Food and Agricultural Organization (FAO) and the World Health Organization (WHO) designated heavy metal(loid) in agricultural crops as monitoring pollutants as well as managed them safely. Among these heavy metal(loid)s in crops, there are remarkably damaging such as mercury (Hg), cadmium (Cd), lead (Pb) and arsenic (As) even in insignificant quantities.

Barley, one of the largest cereal grains around the world, is the second staple food in Korea and grown in winter used for food and forage purposes. Moreover, there are substantial economic benefits for healthy food and alcohol production using beta-glucan that could be found in whole grain [1]. In the re-evaluation report on the standard of heavy metal(loid)s in food in Korea in 2017, the concentrations of heavy metals in barley and brown rice were 0.0118 mg kg$^{-1}$, 0.0035 mg kg$^{-1}$ for Pb, and 0.021 mg kg$^{-1}$, 0.0124 mg kg$^{-1}$ for Cd, respectively, which showed highly those in barley than brown rice. However, the concentration of As in barley (0.011 mg kg$^{-1}$) was remarkably lower than that of As in brown rice (0.101 mg kg$^{-1}$). Nevertheless, the exposure of rice and barley to heavy metals is not high compared to other grains. In Korea, naturally, rice is cultivated from spring to fall, and barley is cultivated in the same paddy field from fall to the next spring. Although they are grown in the same soil, the reason that barley has a higher concentration of heavy metal(loid)s than rice may be differences in the absorption properties of crops. [2] showed that soil physicochemical factors (such as pH, cation exchange capacity, clay content) influence the accumulation of Pb in various parts of barley in contaminated soil by Pb from traffic pollution. Likely, [3] reported that the average lead concentration in barley (0.136 mg kg$^{-1}$) was higher than rice (0.099 mg kg$^{-1}$), some of which exceeded the maximum residual levels (MLs) of lead (0.2 mg kg$^{-1}$) established by the Codex, requiring continuous monitoring. In this study, in order to investigate the characteristics of transition from soil to barley, we evaluated human risks and suggested management for safe production of agricultural products through monitoring the heavy metal(loid)s of cultivated soil and barley in the major producing district in Korea.

### Materials and Methods

#### Sampling Site and Preparation

Agricultural soil and barley samples were collected at Jeokkabuk-do province in Korea (e.g., Gunsan, Gimje, Jeongeup, Jeonju, etc.) from May to June 2019. Both plants and soil were sampled at the same point. All soil samples were air-dried, crumbled and passed through a 2 mm sieve. For the analysis of heavy metal(loid)s in soil, samples were ground to < 0.074 mm. Barley samples were dried at 60°C for a day. The air-dried barley was polished with rice barley using the experimental mill (SY21F, Sang Yong Inc, Korea), and then powdered homogenously for analysis. The thirty-four of the barley samples were collected at market for additional analysis.

#### Heavy Metal(loid)s Analysis in Soil and Barley

The analysis of heavy metals contents in soil were performed with the guideline of the Korean Ministry of the Environment (MOE) using an inductively coupled plasma-optical emission spectrophotometer (ICP-OES). Three grams of sieved soil was digested with aqua regia, 21 mL HCl + 7 mL HNO$_3$ (3:1) using Kjeldatherm (C. Gerhardt GmbH & Co., Northants, UK) at 30°C for 2 h, and then heated at 90°C for 2 h. After filtering, samples were adjusted to a final volume of 100 mL with 0.5M HNO$_3$.

The barley samples of about 0.25-0.5 g transferred into teflon vessel were digested with 8 mL 62% HNO$_3$, 1 mL H$_2$O$_2$ using microwave digestion system (ETHOS, Milestone, Italy) at 200°C for 20 minutes, continuously adjusted to a volume 20 mL with deionized water, and then filtered with 0.45 μm membrane filter. After that, the concentration of heavy metal(loid)s was analyzed by ICP-MS (Agilent Technologies, 7500a). The recovery test for elements were verified, obtaining recovery values between 81.4 and 100.3% for every heavy metal(loid)s analyzed.

#### Estimated BCF and Assessed Human Health Risk

The bio-concentration factor (BCF) was calculated using Eq. (1). It is the ratio of the concentration of heavy metal in plant compared to that in soil [3].

\[
\text{BCF} = \frac{\text{Heavy metal in barley (mg kg}^{-1} \text{ DW)}}{\text{Heavy metal in soil (mg kg}^{-1})} \quad (\text{Eq. 1})
\]

The CR (Cancer risk probability) and HQ values
(Hazard Quotient) were obtained from the average daily dose (ADD). ADD can be estimated from the heavy metal(loid)s concentration in barley to assess human health risk using the following Eq. (2) [4-6].

$$ADD = C \times IR \times ED \times EF \div (BW \times AT \times 365) \quad \text{(Eq. 2)}$$

- $C = \text{Conc. of As, Cd, Pb in barley (mg kg}^{-1} \text{DW})$
- $IR = \text{Intake rate of crop (0.00575 kg day}^{-1})$
- $ED = \text{Exposure duration (30 years)}$
- $EF = \text{Exposure frequency (365-day year}^{-1})$
- $BW = \text{Body weight (72.3 kg)}$
- $AT = \text{Averaging time (78 years)}$

$$CR = ADD \times SF \quad \text{(Eq. 3)}$$

- $SF = \text{Slope factor (1.5 mg kg}^{-1} \text{day}^{-1} \text{ for As)}$
- $HQ = ADD \div \text{RfD} \quad \text{(Eq. 4)}$

- $\text{RfD = Reference dose (0.0003 mg kg}^{-1} \text{day}^{-1} \text{ for As, 0.004 kg}^{-1} \text{day}^{-1} \text{ for Pb, 0.001 kg}^{-1} \text{day}^{-1} \text{ for Cd)}$

**Results and Discussion**

Total metal(loid) contents in 38 soils are given in Table 1. The average contents and ranges of As, Cd, Cu, Ni, Pb, and Zn in soils were from 9.59 (2.70-24.53), 0.28 (0.01-1.10), 22.4 (14.6-35.5), 28.2 (20.9-43.3), 57.9 (36.4-83.1) and 81.6 (58.6-132.4) mg kg$^{-1}$, respectively. The mean contents of heavy metal(loid)s were below the maximum allowable level of MOE, which was approximately 1/3~1/13 times lower. For the As content, it was slightly higher than the average As content of non-contaminated paddy soils (4.41 mg kg$^{-1}$) [7]. Other elements showed similar results or slightly higher tendency [7].

Table 2 shows heavy metal(loid)s in 38 barley collected at the major producing districts in Korea. The Cd concentrations of barley were in the range of 0.004-0.083 mg kg$^{-1}$, those were not exceeded the maximum...
allowable level of Cd (0.1 mg kg\(^{-1}\)). On the contrary, the maximum Pb concentration of 0.212 mg kg\(^{-1}\) was observed in barley, which exceeds the maximum allowable level in barley. Besides, those values were similar to the previous study in that the Pb contents in barley range of 0.034-0.041 mg kg\(^{-1}\) [3]. The As concentrations varied from 0.016 mg kg\(^{-1}\) to 0.094 mg kg\(^{-1}\) among these plants, which was similar to the previous study in the As concentration in barley range from 0.004 mg kg\(^{-1}\) to 0.050 mg kg\(^{-1}\). Even though rice and barley plants are grown in similar cultivation fields, the As level was higher in rice and the Cd and Pb levels were higher in barley [3]. This may result in the difference between the absorption characteristic of barley and rice plant and water management practices, for example, rice cultivated in irrigated water and barley cultivated in non-irrigated water. The alternate wetting drying (AWD) and row treatment reduced the As level in brown rice by 32-60% but increased the Cd level [8]. This result shows that heavy metal(loid)s can be reduced through water management during the harvest season. In addition, crops grown under the same soil conditions may have different levels of accumulation due to their different resistance and affinity to each heavy metal [9,10]. [11] also reported that the difference in the level of heavy metal absorption of wheat and barley growing under the same conditions was due to the surrounding environment of the crop, competition and concentration between heavy metals, and the affinity for heavy metal ions of the crop.

The heavy metal(loid) concentrations of barley collected at the market were presented in Table 3. The average concentration and range of As, Cd, and Pb in barley were found to be 0.036 (0.004-0.183), 0.017 (0.010-0.026), and 0.057 (0.025-0.136) mg kg\(^{-1}\), showing the maximum allowable level below the Food Sanitation Law in Korea. It was confirmed that the average and range of As, Cd and Pb concentration in barley, which were investigated by the Ministry of Food and Drug Safety, differs from 0.011 (nd-0.1014), 0.0209 (0.0091-0.0603) and 0.0118 (nd-0.082) mg kg\(^{-1}\), respectively, but had a similar concentration range. In addition, the fact that the heavy metal content of the market barley was lower than that of the major producing district could be estimated as the dilution of the heavy metal concentration of the market barley, which was mostly distributed at low concentration and diluted as well.

The concentrations of Cd and Pb in barley collected by distance from the highway passing through the major producing district in Korea were shown in Fig. 1. According to a survey of highway separation distances of up to 300 meters or more, Cd and Pb concentration in barley were believed to be rarely affected by highways. In general, as the distance from the highway increases, the content of Cd and Pb in the soil decreases estimating to be the effect of the highway. However, there is no significant difference between two variables (Fig. 2). In addition, higher contents of Cd and Pb in soil tend to increase the Cd and Pb concentration in barley, but significant differences between two variables are also not. The Pb concentration of some samples of barley earlier exceeds the standard and is expected to flow pollutants from the road as another factor. [12, 13] reported that the concentration of heavy metals in the soil collected within 5 m of the

<table>
<thead>
<tr>
<th>Items</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.036</td>
<td>0.017</td>
<td>2.968</td>
<td>1.268</td>
<td>0.057</td>
<td>15.369</td>
</tr>
<tr>
<td>SD</td>
<td>0.041</td>
<td>0.004</td>
<td>0.582</td>
<td>0.568</td>
<td>0.022</td>
<td>5.038</td>
</tr>
<tr>
<td>Min</td>
<td>0.004</td>
<td>0.010</td>
<td>2.029</td>
<td>0.487</td>
<td>0.025</td>
<td>10.401</td>
</tr>
<tr>
<td>Max</td>
<td>0.183</td>
<td>0.026</td>
<td>4.772</td>
<td>2.373</td>
<td>0.136</td>
<td>33.773</td>
</tr>
<tr>
<td>Median</td>
<td>0.020</td>
<td>0.016</td>
<td>3.011</td>
<td>0.998</td>
<td>0.055</td>
<td>13.862</td>
</tr>
<tr>
<td>95P</td>
<td>0.135</td>
<td>0.022</td>
<td>3.929</td>
<td>2.199</td>
<td>0.094</td>
<td>23.177</td>
</tr>
</tbody>
</table>

**Table 3. Total concentrations of heavy metal(loid)s in barley commercially purchased at the market in Korea**

† Average content of heavy metal(loid)s in barley collected at the markets in Korea
†† Maximum allowable level (DW basis) of heavy metal(loid)s in barley enforced by Food Sanitation Act
road was higher than that of soil collected in the distance. In addition, similar results were found in plants collected from the same site, which were estimated to be accumulated due to lower soil acidity and increased plant-based efficacy of heavy metals in agricultural areas near roads. [14] reported that the concentration of Pb in the soil more than 80 m from the road was not affected by the road, and the concentration of Pb in barley was not affected by the road.

Bio-concentration factors (BCF) of heavy metal(loid)s in barley grown at the major producing districts in Korea were given in Table 4. The mean and range of the BCF of As was 0.006 (0.002-0.025). In comparison with other crops, the BCF of As in barley was relatively low compared to 0.101 for rice, which is high [3]. This is consistent with the relative inhibition of uptake compared to the state of reduction due to flooding condition. The mean and range of the BCF of Cd was 0.165 and 0.005-0.507, respectively. The level was higher than the BCF of the brown rice, 0.121, which was esti-
mated that dry soil condition promoted the absorption of Cd [8]. The mean and range of the BCF of Pb were 0.002 and 0.001-0.00, respectively, similar to those of brown rice. The BCF for each element of barley was high in copper (Cu), zinc (Zn), and Cd, and low in As and Pb. This was similar to the previous results of reporting the BCF of leafy vegetables and medicinal crops in order of Cd>Zn>Cu>Pb>As> chromium (Cr) [15,16].

Table 5 shows the hazard quotients (HQ) and cancer risks (CR) for the monitored results of As, Cd and Pb in barley were determined in this survey. The calculation result of non-carcinogenic hazard for each component was below 1, which was very unlikely to cause cancer through barley. In addition, the combined results of As, Cd and Pb were 6.76 × 10⁻², CR risks averaged 2.06 × 10⁻⁶, and a maximum value of 9.50 × 10⁻⁶, below the acceptable level of 10⁻⁴. The level of non-carcinogenic and carcinogenic hazards of market barley was also lower than that of the barley samples collected in the major producing districts.

Therefore, the agricultural safety management in barley must be considered to have been carried out from the production stage. Furthermore, it is assumed that Pb from other factors than soil may have been introduced among barley, and it is assumed that studies related to the physiological characteristics of agricultural materials and crops that affect the absorption of Pb crops should be carried out.

### Note

The authors declare no conflict of interest

### Acknowledgement

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### References


### Table 5. Mean and maximum value of HQ and CR for As, Cd and Pb concentrations in barley cultivated at the major producing districts and purchased on the market in Korea

<table>
<thead>
<tr>
<th></th>
<th>Hazard quotients (HQ)</th>
<th>Cancer risk (CR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Cd</td>
</tr>
<tr>
<td>Cultivated barley</td>
<td>4.57 × 10⁻³</td>
<td>9.85 × 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>(2.11 × 10⁻³)</td>
<td>(2.92 × 10⁻³)</td>
</tr>
<tr>
<td>Commercial barley</td>
<td>4.22 × 10⁻³</td>
<td>5.98 × 10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>(2.15 × 10⁻³)</td>
<td>(9.15 × 10⁻⁴)</td>
</tr>
</tbody>
</table>

§ Maximum value of HQ and CR

### Conclusion

This study was carried out to understand the characteristics of the transition of heavy metal(loid)s into soil-plant and to derive appropriate management practices for production of safe agricultural products. The soil and barley samples were collected from 38 locations around the major producing districts at Jeollabuk in Korea to examine the concentrations of heavy metal(loid)s. Separately, 34 barley samples were purchased on the market for the same survey. The Pb concentration of barley purchased at the market did not exceed the maximum allowable level of 0.2 mg/kg designated by the Food Sanitation Act. However, the Pb level exceeded the acceptable level at some sample of barley produced in the major producing districts.
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