Research Article

Distinct Dispersion of As, Cd, Pb, and Zn in Farmland Soils near Abandoned Mine Tailings: Field Observation Results in South Korea

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We investigated the characteristics of metal(loid) transport and dispersion in agricultural soils near an abandoned metal mine. Topsoil samples were collected from 162 sampling sites in the study area, including 1 in the mine tailing dumps, to analyze the total concentrations of As, Pb, Cd, and Zn. Subsequently, the metal(loid) transport and dispersion characteristics were investigated using geographic information system (GIS) technology. The results of this study clearly demonstrated the variation in the dispersal of As, Cd, Pb, and Zn from the mine tailing dumps to nearby agricultural soils and the element-specific spatial variability in their respective transport and dispersion characteristics. These findings suggested that compared with the migration behavior of Cd, Pb, and Zn, that of As has a farther-reaching impact on agricultural soils owing to its geochemical cycling in the soil and groundwater environment. This impact differed significantly in magnitude from that of the other investigated metals. Therefore, special consideration must be given to the migration behavior of As.

1. Introduction

Globally, agricultural soil pollution caused by metal(loid)s from mining activities poses serious environmental concerns. Mine tailings, which are mine wastes derived from mining activities, contain several toxic metal(loid)s [1, 2]; thus, mine tailing dumps left untreated near abandoned metal mines are the primary sources of soil and water pollution in the surrounding areas [3–8]. Dispersal of metal(loid)s from mine tailing dumps into the ecosystems in the vicinity of such mining sites occurs primarily through two pathways: (1) dispersal of metal(loid)-bearing particles by the wind- and rainfall-driven erosion of mine tailings [2, 6, 9] and (2) infiltration of metal(loid)-bearing leachates into the soil below during rainfall–runoff processes

and subsequent migration into nearby soils and groundwater [6, 7, 9, 10].

Recent studies on the transport and dispersion of metal(loid)s in contaminated soils near mining areas have suggested that the spatial distribution of such metal(loid)s is determined primarily by the erosion of mine tailings, particularly by wind-driven erosion [1, 2, 6, 11, 12]. Moreover, the closer the location of the site to the mine tailing dumps, the higher the concentration of the contaminants, and vice versa [1, 2, 5, 11, 12]. Studies on the transport of metal(loid)s in soils by the leaching of metal(loid)s from mine tailing dumps have focused on the depth-dependent distribution of metal(loid)s within the soil profile, i.e., the vertical migration of metal(loid)s [9, 13–15].

On the contrary, in countries such as Korea that experience monsoon-driven rainfall and distinctly different dry and rainy seasons [16], the transport and dispersion of metal(loid)s migrating from mine tailing dumps to nearby soils may show different distribution patterns through complex pathways of erosion and leaching. Metal(loid)s infiltrating into the soil through leachates during rainfall-runoff processes tend to migrate to the groundwater via the soil pore water [17–19]. This suggests that soil metal(loid)s, driven by the hydraulic gradient, migrate not only vertically within the soil profile but also along the horizontal plane. Moreover, variations in groundwater cycling, irrigation, and level can release metal(loid)s back into the surface environment. Metal(loid)s can also undergo mobility changes in the soil and groundwater environment owing to various factors, such as pH, oxidation–reduction (redox) potential, organic matter content, and adsorption reactions between various minerals [4]. Therefore, the range of spatial dispersal of metal(loid)s from mine tailings into nearby soils can vary significantly depending on the extent of erosion as well as the different migration behaviors of individual soil metal(loid)s. Thus, a proper understanding of this complex phenomenon is imperative to adequately monitor soil metal(loid)s in areas affected by mining activities.

The objective of this case study is to elucidate the distinctive dispersion and distribution pathways of different metal(loid)s from mine tailing dumps to the surrounding agricultural soils. To this end, the following approaches were adopted. The total concentrations of metal(loid)s (As, Cd, Pb, and Zn) in the agricultural soils were surveyed extensively on-site. Then, we examined the spatial distribution of the metal(loid)s by identifying their horizontal variation according to distance from the mine tailing dumps and created a distribution map using a geographical information system (GIS). The results of this study provide important input for developing efficient monitoring schemes for metal(loid)s in agricultural soils and strategies for soil remediation in areas affected by mining activities.

2. Materials and Methods

2.1. Description of the Study Site. The surveyed site lies in the village of Gwoni in Gyeongju City, Gyeongbuk Province, Republic of Korea (Figure 1). The village of Gwoni is spread over an area of 7.97 km² and comprises forests (7.09 km²), paddy fields (0.48 km²), and dry fields (0.25 km²). According to the Korean Soil Information System [20], the soil types in the study site are classified as Inceptisols (7.56 km²), Ultisols (0.13 km²), Alfisols (0.10 km²), and Mollisols (0.01 km²), and the surface soil textures are loam (7.01 km²) and sandy loam (0.79 km²). The sandy loam occurs primarily in agricultural fields. The geology of the study site consists primarily of Cretaceous strata; Tertiary and Quaternary strata are unconformably distributed in the upper part (Figure 2) [21]. Hornblende-quartz-feldspar porphyry, hornblende-biotite granite, and granite, all belonging to the Bulguksa intrusive group of the Daedong supergroup, are distributed in the Cretaceous strata. In the upper part, andesite and tuff of the Tertiary Beomgockri group are unconformably distributed

and are not visible in the presented geological map; the strata are unconformably covered at the top by Quaternary alluvium. At the study site, farmland is mostly distributed in the Quaternary alluvium (Figure 2).

Gwoni Reservoir, which is a fill-type dam built in 1964, is downstream of the study area (Figure 1). However, this reservoir is used for irrigating agricultural fields in its vicinity, and the groundwater pumping wells have traditionally been used for irrigation of the agricultural fields in the study area, which was confirmed during the field survey (Figure S1).

The study area is affected by a typical temperate monsoon climate, with an annual mean temperature of 14.1°C and extreme maximum and minimum temperatures of 38.6°C and −12.7°C, respectively [22]. The annual mean precipitation is 842.9 mm, and its temporal distribution throughout the year is strongly heterogeneous. More than 54% of the total annual precipitation is recorded between July and October [22]. During the dry winter seasons, winds from the northwesterly quadrant are predominant, whereas hot and humid summers are dominated by southerly winds [23].

The Sunyang Mine (Figure 1), situated in the study region, was initially developed during the Japanese occupying period (1910–1945). Details of this abandoned Au mine are presented in Table 1. In the vicinity of the buried mine shaft, mine tailings of more than 2,500 m³, which is the main source of pollution, are piled together with waste rocks. The soil sampled near the mine tailing dumps, as indicated in Figure 1, has been reported to contain As, Cd, and Pb at concentrations far exceeding the prescribed thresholds [24]. During the field survey, we verified the presence of the mine tailing dumps and the collapsed stone wall piled up to contain the tailings (Figure S2).

2.2. Soil Sampling. An extensive investigation of the soil metal(loid) content was conducted in the study area in March 2014. Soil sampling was performed in the surrounding agricultural fields located downslope from the mine tailing dumps near the mine shaft of the Sunyang Mine to clearly determine the distribution patterns of metal(loid)s according to the distance from the mine tailing dumps (Figure 1). Soil samples were taken at depths of 0–30 cm from 162 agricultural fields, including 1 sample obtained from the mine tailing dumps (Figure 1). The sampling sites located in the forest areas shown in Figure 1 are currently used as agricultural fields, excluding the site located in the mine tailing dumps. Information about the locations of each sampling site is provided in Table S1. For each sample, five samples of surface soils were collected in a zig-zag pattern in each plot (<900 m²) of the agricultural fields and were mixed thoroughly to obtain a representative composite sample in accordance with the standard Korean method prescribed for collecting soil samples [28]. The soil samples were collected using a stainless steel hand auger and stored in prelabeled polyethylene zip bags. Appropriate care was taken at the sampling sites to avoid the collection of any obvious contaminants as well as plant leaves, gravel, and other debris.

FIGURE 1: Sampling points in the study area, showing the distribution of land use types.

The sampled soils were spread on steel pans in one layer with uniform thickness. The samples were then air-dried for one week to eliminate moisture. Then, the soils were crushed, passed through a 2 mm stainless steel sieve, and stored in airtight polyethylene containers.

2.3. Chemical Analysis for Total Metal(loid) Content. All soil samples were analyzed at a nationally accredited professional analysis institute in South Korea, National Environment Lab (NAPAI), which tests for pollution in soil samples. The NAPAI's official website can be accessed at <http://www.nelab.re.kr>. For the analysis of metal(loid)s, the dried soils were pulverized and sieved to pass a 100 mesh (<0.15 mm), and a 3 g sample of the sieved soil was digested with 28 ml of aqua regia (3:1, v/v, $\text{HCl} + \text{HNO}_3$) for 1 h at 70°C . The digested solution was filtrated through 5B filter paper, and the total concentrations of As, Cd, Pb, and Zn were then determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Optima 7300DV, Perkin Elmer, USA) [28]. A reference soil (Environmental Resource Associates, USA) was used to measure the recovery and relative standard deviation (RSD) of the elements studied. The recovery in the reference soil was between 70% and 130%, and the RSD was less than 30%.

2.4. Spatial and Statistical Analyses. Statistical analyses were conducted using SPSS 20.0 (IBM, USA). The data were

checked for normality via the Kolmogorov–Smirnov test with a confidence interval of 95% [29, 30]. A GIS tool (ArcGIS 10.2.2) was used to produce a land use map that indicates the soil sampling locations and distribution of the total concentrations of metal(loid)s in the agricultural fields in the study area. The GIS tool also enabled the analysis of the associated spatial data, such as the altitudes of the sampling locations and the distance from the mine. To investigate the transport and dispersion characteristics of the metal(loid)s released from the mine tailings, which is the primary anthropogenic pollution source in the study area, regression analyses were performed to determine the correlation between the spatial data and the total concentrations of the metal(loid)s. Graphs with curve fittings (regression models) were prepared using SigmaPlot 12.0 (Systat Software, Inc., USA).

3. Results

3.1. Total Concentrations of Metal(loid)s in Mine Tailings and Agricultural Soils. The total concentrations of the metal(loid)s in the sampled soil from the mine tailing dumps of the Sunyang Mine are presented in Table 2. The total concentrations of As, Cd, Pb, and Zn were measured to be 195, 11.9, 51,150, and 1,745 mg/kg, respectively, which significantly exceeded their respective upper national limits. In particular, the total concentration of Pb was found to be more than 250 times the national limit of 200 mg/kg.

FIGURE 2: Geological map of the study area.

TABLE 1: Description of the abandoned mine in the study area.

Operation period	Main geology	Type of mineralization	Ore minerals	Grade of ore body	Ore mineral associations	Pollution source	Reference
Japanese colonial period, 1961–1972	Biotite granite, felsophyre, granite porphyry	Au-bearing quartz vein	Au, Ag	Au: 0.0–2.4 g/ton, Ag: 281–1,467 g/ton	Pyrite, galena, sphalerite	Tailings (>2,000 m ³)	[24–27]

Table 3 presents descriptive statistics for the raw data of the metal(loid)s contained in the agricultural soils. The table also presents the background metal concentrations (BMCs) in unpolluted agricultural soils of South Korea [32] and soils worldwide (WSs) [33]. The total concentrations of the metal(loid)s at each site are presented in Table S1. The concentration ranges of As, Cd, Pb, and Zn were 0.78–25.0, 0.10–5.50, 8.78–567.9, and 37.7–646.8 mg/kg, respectively (Table 3). The As, Cd, Pb, and Zn concentrations exceeded the national limits at 1, 2, 9, and 11 locations, respectively. The mean concentrations of these elements were 5.99, 0.88, 76.20, and 128.93 mg/kg, respectively, which, except for As, exceeded the values of both BMCs and WSs. The coefficients of variation (CVs) for As (62.9%), Cd (98.5%), Pb (108%), and Zn (78%) indicated high variations.

The application of the Kolmogorov–Smirnov test ($p > 0.05$) confirmed that the raw datasets for metal(loid)s in the sampled soils were not distributed normally (Table 3). The distributions for As, Cd, Pb, and Zn were all strongly

positively skewed, with skewness values higher than 1.0, and their kurtoses were very sharp. Moreover, the distributions of these elements were still nonnormal after log- and square root-transformation.

3.2. Horizontal Variation of Metal(loid) Concentrations.

To determine the characteristics of metal(loid) transport and dispersion from the mine to the surrounding agricultural soils, the distance to the mine was used as an ancillary predictor. Figure 3 illustrates the concentrations of metal(loid)s in soil with increasing distance from the mine as predicted by the regression analysis with curve fitting (regression models).

The concentrations of Cd, Pb, and Zn in the agricultural fields were highest in the vicinity of the mine tailing dumps, at 80 m and 415 m for Pb and Cd-Zn, respectively. The levels rapidly decreased with increasing distance from the mine tailing dumps and reached relatively stable levels 600 m from

TABLE 2: Total concentrations of metal(loid)s in the mine tailing soil and the corresponding spatial data.

Metal(loid)s (mg/kg)				Spatial data	
				Transverse mercator (Tokyo datum)	Altitude (m)
As	Cd	Pb	Zn	X	Y
195.3	11.96	51,150	1,745	419,672	266,014
					203

Note. The national limits for As, Cd, Pb, and Zn are 25, 4, 200, and 300 mg/kg, respectively [31].

TABLE 3: Statistical summary of metal(loid) concentrations (mg/kg) in agricultural soils of the study area.

	Mean (N=162)	Median	Min	Max	SD	CV	Skew.	Kurto.	<i>p</i> (K-S test)	BMC	WS	NL	NL > BMC
As	5.99	5.14	0.78	25.00	3.77	62.9	2.871	10.194	0.00	6.24	6.00	25.00	1
Cd	0.88	0.66	0.10	5.50	0.87	98.5	2.627	8.946	0.00	0.14	0.35	4.00	2
Pb	76.20	49.44	8.78	567.95	82.85	108.7	3.678	15.405	0.00	20.07	35.00	200.00	9
Zn	128.93	93.73	37.67	646.78	100.60	78.0	2.593	8.083	0.00	71.07	90.00	300.00	11

SD: standard deviation; CV: coefficient of variation; Skew.: skewness; Kurto.: kurtosis; *p* (K-S test): *p* values of Kolmogorov–Smirnov test for normality of the raw data (for values higher than 0.05, the distribution is normal); BMC: background metal concentrations for unpolluted agricultural soils of South Korea [32]; WS: world soils unpolluted [33]; NL: national limits according to the soil quality standards of South Korea [31]; NL > BMC: number of samples with a concentration exceeding the national limit.

the mine (Figures 3(a)–3(c)). This spatial distribution pattern is in mathematical agreement with the exponential decay model ($y = y_0 + \alpha e^{-\beta x}$). In particular, the spatial distribution of Pb ($r = 0.626$) exhibited a relatively more pronounced exponential decay pattern as compared with Cd ($r = 0.367$) and Zn ($r = 0.362$). Zn and Cd showed similar distribution patterns in the agricultural soils (Figures 3(b) and 3(c), respectively), which were clearly distinguishable from that of Pb (Figure 3(a)).

The As content exhibited a distribution pattern (Figure 3(d)) that was distinct from those of Cd, Pb, and Zn. It showed the second-highest concentration, 24.78 mg/kg, at a point near the mine tailing dumps (46 m), which decreased until reaching a distance of 600 m from the mine. However, the As concentration began to increase continuously with an increase in the distance past that point. This behavior was in contrast to that of the other elements, which exhibited an exponential decay distribution and stabilized after 600 m onward. The highest As concentration, 25 mg/kg, appeared at the sampling site farthest from the mine, at 1,752 m. The distribution pattern of As showed the best fit with a quadratic model (convex down; $r = 0.724$), which suggests that the concentration of As in the study area decreased until reaching a specific distance from the mine and then increased steadily.

To further elucidate the distinct distribution patterns of As, Cd, Pb, and Zn past the 600 m mark, linear regression analyses of the distribution patterns were performed for the section between 600 m and the sampling site farthest from the mine. The results are presented in Figure S3. In the post-600 m section, Cd, Pb, and Zn showed stable distributions with no significant variability as compared with the results of the pre-600 m section, with concentrations showing high variability depending on the distance (Figures S3a–S3c). Contrary to this trend, the As concentrations clearly tended to increase linearly with an increase in distance past the 600 m mark (Figure S3d).

3.3. Relationships between Metal(loid)s. Figure 4 shows the relationships between As, Cd, Pb, and Zn based on linear regression models. Such relationships can indicate transport pathways or mechanisms from the metal(loid) sources [34, 35]. Among the four elements investigated, Cd and Zn showed a high linear correlation ($r = 0.890$; Figure 4(e)), which supports the finding that Cd and Zn had similar distribution patterns in the agricultural fields located downstream of the mine tailing dumps (Figure 3). No statistically significant correlations were present among the other investigated metal(loid)s.

3.4. Spatial Distribution of Metal(loid)s in the Study Site. Figure 5 illustrates the spatial distribution of the total concentrations of As, Cd, Pb, and Zn in the soil samples collected from the study area. The sampling site and metal(loid) distribution maps given in the figure help to visualize the distance-dependent distribution patterns of the metal(loid)s shown in Figure 3. Pb occurs in hotspots characterized by high concentrations in a dense distribution at points that differ slightly from those of Cd and Zn, at about 80 m and 400 m distance, respectively. However, these three elements all occurred in hotspots at points located within 500 m from the mine tailing dumps, showing lower concentrations with increasing distance from the mine. On the contrary, higher As concentrations were observed at significantly farther points, past the 1,000 m mark from the mine tailing dumps, which occurred in hotspots at points farthest from the mine tailing dumps, past the 1,500 m mark. This distribution pattern differed distinctly from those of Cd, Pb, and Zn.

4. Discussion

The dispersion of metal-bearing mine tailings into nearby agricultural soils can be attributed to the elevated levels of

FIGURE 3: Scatter plots of metal(loid) concentrations in agricultural soils ($n = 162$) corresponding to an increasing distance from the mine tailing dumps for (a) Pb, (b) Zn, (c) Cd, and (d) As. The trend lines and 95% confidence (blue) and prediction (sky blue) bands are shown for the regressions. All p values (<0.0001) for the F -test in ANOVA were less than the specified significance level (0.005).

toxic metals observed in and around abandoned metalliferous mines [1, 2, 12, 36, 37]. Moreover, it should be noted that the primary ore body of the Sunyang Mine is a quartz vein containing Au and Ag that includes sulfide minerals, such as pyrite, galena, and sphalerite (Table 1). In addition, this quartz vein is commonly accompanied by arsenopyrite (FeAsS) [38–40], which is the most common As-bearing mineral [41, 42]. In general, the mine tailings generated by mining activities at Au or Ag mines in Korea contain high amounts of arsenopyrite [38]. Oxidation of the residual

sulfides releases Fe and other metal(loid)s from the mine tailings, such as Pb, Cd, and Zn [43, 44]. The wide variations of their concentrations in the agricultural soils of the study area can be attributed to the dispersion of the mine tailings (CVs in Table 3) because high CVs ($>50\%$) are often reliable indicators of anthropogenic activity [34, 35, 45–47]. Moreover, the hotspots of As, Cd, Pb, and Zn formed in the agricultural fields located downstream of the mine tailing dumps offer clear evidence for the dispersion of the mine tailings (Figure 5).

FIGURE 4: Relationships between (a) As and Cd, (b) As and Pb, (c) Cd and Pb, (d) As and Zn, (e) Cd and Zn, and (f) Pb and Zn concentrations in the agricultural soils ($n = 162$) of the study area.

To explain the characteristics of transport and dispersion of As, Cd, Pb, and Zn in the investigated agricultural soils, the primary mechanisms by which the metal(loid) migrate from the mine tailing dumps were examined. The migration of metal(loid)s from mine tailing dumps to the surrounding soils largely occurs via two pathways. The first and direct migration pathway of metal(loid)-bearing particles is the erosion of the mine tailings. Improperly disposed mine tailings are exposed to two types of erosion: water erosion with transport during heavy rainfall events and wind erosion, which induces fine-particle dispersion [3, 6, 9, 12, 36]. Such erosion of mine tailings can be ascribed to natural factors, which significantly influence the spatial distribution of metal(loid)s in the surrounding regions [1, 2]. The second

migration pathway involves the infiltration of metal(loid)s dissolved in mine tailing leachates. The dissolved metal(loid)s infiltrate into the nearby soils with mine tailing leachates during rainfall-runoff processes and migrate with the soil pore water, thus, degrading the adjacent soil and groundwater environment [7, 10].

A common distribution pattern was observed for Cd, Pb, and Zn, which is characterized by an exponential decay in concentration with increasing distance from the mine tailing dumps (Figure 3). This spatial distribution is associated with the direct dispersion of metal(loid)s from anthropogenic sources. Typical examples of the exponential decay-type distribution pattern occur in areas near abandoned mines due to wind- and rainfall-driven erosion of mine tailings

FIGURE 5: Distribution maps of (a) Pb, (b) Zn, (c) Cd, and (d) As in the agricultural soils of the study area. The circle size indicates the relative degree of metal(loid) concentrations.

[35, 48, 49] and the anthropogenic metal(loid)s in the soils near industrial complexes or smelters/refineries by the deposition of airborne particles released from them [50–54]. Thus, the observed distribution pattern clearly indicates the presence of an anthropogenic contamination source. Similarly, the distribution patterns of Cd, Pb, and Zn in the soils of the agricultural fields suggest that they are closely associated with wind- and rainfall-driven erosion of the mine tailings. However, two slightly different tendencies were observed: Cd and Zn showed almost identical patterns that were distinguishable from that of Pb (Figure 3). Moreover, their hotspots were formed at sampling sites located farther from the mine tailing dumps than those of Pb, at 400 m versus 80 m, respectively (Figure 5). The high linear correlation between Cd and Zn, as illustrated in Figure 4, indicates that these elements have the same migration pathways. In nature, Cd occurs mainly in association with Zn ores, among which sphalerite (ZnS), the dominant mineral in the Sunyang Mine, is the primary geologic source of Zn and Cd (Table 1) [55]. Given that Cd, Pb, and Zn are anthropogenic inputs from the same contamination source (mine tailing dumps), the results shown in Figures 3–5 suggest that the migration mechanism of Cd and Zn is different from that of Pb and that As migration involves a mechanism different from those of Cd, Pb, and Zn.

In addition to the erosion of mine tailings, another pathway for metal(loid) dispersal from the mine tailings is through the migration of soil pore water by downward percolating rainwater and readjustment of the groundwater table. Metals may also move upwards to the topsoil through

evaporation and osmotic suction [56]. Given that soil metal(loid)s migrate only with the soil pore water, their mobility can be strongly influenced by the adsorption preferences between different types of soil minerals and the dissolved metal(loid)s [57–60]. In general, the adsorption preferences of soil minerals for metal(loid)s are known in the order of $\text{Cr} \geq \text{Pb} \geq \text{Cu} > \text{Co} > \text{Zn} > \text{Ni} \geq \text{Cd}$ [61]. Because mobility and adsorption preference are inversely related, Pb has a lower mobility than Zn and Cd, which explains why Pb hotspots occurred much closer to the mine than Zn and Cd hotspots. This finding is consistent with the results of column leaching tests performed in other studies, which suggest that the Pb concentration in leaching solutions is very low, even in mining-impacted soil containing high concentrations of Pb [62–64].

Considering these behaviors, the dispersal of metal(loid)s from mine tailings to nearby agricultural soils can be attributed to two mechanisms with some varying details. The primary pathway of Pb, Cd, and Zn migration is the direct dispersion of metal(loid)-bearing particles through erosion of the mine tailings. Moreover, given its extremely low mobility in soil, Pb mainly migrates via erosion, which is in good agreement with the Pb distribution pattern observed in this study, which also showed the best fit with the exponential decay model. In contrast, Cd and Zn have higher mobility in soil, which may explain their farther migration as compared to Pb, along with the leachates of mine tailings and the soil pore water in which they are dissolved. Therefore, the dispersal mechanisms for Cd and Zn are much more complex than a simple erosion-induced dispersion. A similar

distribution pattern between Cd and Zn suggests that the soil in the study site was clearly affected by tailing dumps (Figures 3–5). The similarity in the distribution patterns of Cd and Zn in the soil during the metal(loid) dispersal processes also validates the distribution patterns of Pb and As observed in this study (Figure 3).

On the contrary, the spatial distribution of the As concentration cannot be explained by the erosion of mine tailings alone. As previously mentioned, another metal(loid) migration pathway involves the infiltration of metal(loid)s dissolved in the mine tailing leachates into the soil during rainfall-runoff processes and migration to the surrounding soils with the soil pore water. To examine the As transport and dispersion characteristics, we investigated the geochemical behaviors of As in the soil and groundwater environment.

The geochemical behavior of As differs completely from that of other metal(loid)s because it undergoes various geochemical processes, such as adsorption/desorption, precipitation or coprecipitation, and oxidation/reduction [65–68]. These processes change the forms of As, which further changes its behavior in the environment and affects its fixation or migration [68, 69]. In nature, As exists mainly in the forms of arsenate [As(V)] and arsenite [As(III)]. Although the major factors responsible for its states have not been clearly identified [68] thus far, the redox potential is considered to be a key factor influencing the form and migration of As [70]. Under oxidizing conditions, As exists predominantly as As(V); however, under reducing conditions with a low redox potential, arsenate is reduced to As(III), which has higher toxicity and mobility [70–72].

Moreover, the mobility of As is enhanced by the reductive dissolution of Fe/Mn (hydr)oxides under reducing conditions [73, 74]. This phenomenon can be attributed to the fact that Fe/Mn (hydr)oxides in soil, which are present in aerobic environments, absorb various trace elements containing metal(loid)s in high concentrations [75, 76]. This is corroborated by the fact that the ore body of the abandoned mine in the study area is a quartz vein containing Au and Ag, including the sulfide mineral pyrite (Table 1); the mine tailing dumps near the mine can be closely associated with this sulfide mineral. Its main components are Fe and S, which are regarded as the primary sink for As [77–79].

Metals with a constant valence under reducing conditions, such as Cd, Pb, and Zn, are likely to have lower mobility because they are immediately readsorbed by soil oxides (e.g., aluminum (hydr)oxides and remaining Fe (hydr)oxides), even under the reductive dissolution of Fe/Mn (hydr)oxides [80]. Pinto et al. [81] reported that under oxidizing conditions, Cd, Pb, and Zn in mine tailing soils have much higher mobility as compared with reducing conditions. In contrast, the valence of As is dependent on the redox potential; therefore, it can be continuously released into the soil pore water through reduction from As(V) to As(III) and reductive dissolution of Fe/Mn (hydr)oxides.

Moreover, several studies have reported that the primary As migration mechanism in soil and groundwater is associated with the reductive dissolution of Fe(III) (hydr)oxides and a consequent release of adsorbed and coprecipitated As [82–87].

In the soil environment, the reduced state is developed in a saturated soil layer beneath the groundwater table [70]. The As concentration in groundwater may vary depending on the depth of the groundwater table and alterations to the flooding cycle [87]. More specifically, the groundwater level rises closer to the surface through the rise of the groundwater table, thereby facilitating the contact of groundwater with the mine tailing dumps. If the groundwater table rises up to the topsoil, the soil environment alters to a reduced state, making it easier for As to be released into the pore water through the processes of reduction from As(V) to As(III) and reductive dissolution of Fe(III) (hydr)oxides. Given that Korea experiences concentrated rainfall during a specific period, the groundwater table may rise up to the surface. In addition, most of the agricultural fields in the study area are paddy fields (Figure 1), which are periodically flooded and drained during the rice-growing season. Yun et al. [34, 35] noted that As transported to paddy soil can affect a wider area owing to the reducing conditions of the paddy soil and the hydraulic characteristics. Moreover, in this area, the traditional irrigation method is groundwater pumping, which has been maintained even after the construction of the reservoir in 1964 (Figure S1). The As released from the mine tailing dumps to the soil and groundwater environment migrates vertically and horizontally by vertical and horizontal hydraulic gradients. Its concentration is likely to increase in groundwater that flows longer and to a wider area under reducing conditions, in which the As mobility increases. Polizzotto et al. [88] reported that the concentrations of As released from near-surface wetland sediments to the groundwater tended to increase in proportion to the period of time and distance traveled by the groundwater. The As input into agricultural fields through groundwater pumping tends to remain in the topsoil due to oxidation, adsorption, and coprecipitation under oxidizing conditions in the topsoil layer [89].

Considering the geochemical behaviors of soil As and the role of soil as the major sink for released metal(loid)s, the groundwater circulation in the study area provides clues for the observed characteristics in the As distribution.

As indicated in Figure 6, As, Cd, Pb, and Zn released to the soil environment by processes other than the dispersion pathways common to all metal(loid)s, i.e., by the wind- and rainfall-driven erosion of mine tailings, are likely to have different mobilities depending on the redox state. However, As, driven by a substantially increased mobility owing to reduction from As(V) to As(III) and reductive dissolution of Fe(III) (hydr)oxides, can migrate to a wider area and, thus, has a stronger impact on agricultural soils than Cd, Pb, and Zn through groundwater cycling.

FIGURE 6: Conceptual diagram illustrating the transport processes of metal(loid)s from the mine tailing dumps to the surrounding agricultural soils in the study area.

5. Conclusions

In this study, we used field surveys and GIS mapping to identify the distinct transport and dispersion characteristics of different metal(loid)s by tracing the migration pathways of As, Cd, Pb, and Zn from the mine tailing dumps of an abandoned mine to nearby agricultural fields. The results of this study show a common migration pathway for As, Cd, Pb, and Zn: direct dispersion of metal(loid)-bearing particles in the tailings through the wind- and rainfall-driven erosion. In addition, As, Cd, Pb, and Zn released to the soil environment from the mine tailing dumps during rainfall-runoff processes adopt different migration patterns. The dispersion and spatial distribution characteristics of these patterns are dependent on the soil and groundwater environment as well as the adsorption preferences of various soil minerals for individual metal(loid)s. In particular, As can influence a larger geographical area than do other metals owing to its distinct geochemical behavior.

To efficiently manage and remediate the surrounding agricultural fields that have been polluted by anthropogenic sources, such as abandoned metal mines, the area of influence must first be accurately set for the environment surrounding the anthropogenic source. However, in Korea, pollution management and remediation activities are generally only conducted in agricultural fields that are within a 1-2 km radius of an abandoned mine. The results of this research clearly show that the existing distance, especially for

the area of influence of As, may be underestimated. Therefore, special consideration should be given to the migration behavior of As during the development of appropriate soil remediation activities, such as soil management, for agricultural soils contaminated by anthropogenic metal(loid)s as a result of mining activities.

Data Availability

The data used to support the findings of this study are included within the paper and Supplementary Materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Figure S1: overview of the pumping well for irrigation in the study area. Figure S2: overview of the mine tailing dumps

located in the study area. Figure S3: scatter diagrams of metal(loid) concentrations in the agricultural soils ($n = 162$) and increasing distance from the mine tailing dumps. Table S1: total concentrations of metal(loid)s in the studied samples of agricultural soils and their corresponding spatial data. (*Supplementary Materials*)

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