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Spatial distributions of metal(loid)s and their transport in agricultural soils around abandoned metal mine sites in South Korea

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Abstract

Purpose To develop efficient strategies and methods to remediate soils contaminated by metal(loid)s, it is vital to monitor the metal(loid)s in the soil by conducting field surveys and properly understanding their transport and spatial distribution characteristics. The present study aimed to elucidate the distinctive spatial distribution of anthropogenic arsenic (As) and metals from abandoned metal mine sites (AMMSs) to the surrounding agricultural soils.

Materials and methods In order to investigate transport and spatial distribution of the metal(loid)s from mine tailing dumps to the surrounding agricultural soils, extensive field surveys were conducted across agricultural fields located in the vicinity of five AMMSs, i.e., Gubong, Nakdong, Daema, Angang, and Sunyang mines. A total of 2371 soil samples were collected from the study sites during 2010–2014. The total concentration of metal(loid)s, i.e., As, lead (Pb), and zinc (Zn), in the soil samples was measured. Horizontal dispersion characteristics of As and metals transported from the AMMSs to the surrounding agricultural soils were analyzed using the spatial data and geoaccumulation index. Furthermore, the distribution of anthropogenic metal(loid)s was also mapped to analyze their distinct spatial distribution using a GIS tool.

Results and discussion Hot spots were formed within a 1-km radius of tailing dumps where anthropogenic As, Pb, and Zn in agricultural soils were highly concentrated. Among the anthropogenic metal(loid)s, As could be dispersed and distributed in a much wider region from the tailing dumps due to the high mobility of As through reductive processes in flooded paddy soils compared with other metals (Pb and Zn) whose transport and distribution are controlled primarily by the erosion process of mine tailing dumps (wind and water driven).

Conclusions The dispersion behavior of As has a relatively farther-reaching effect on agricultural soils due to its geochemical behavior in flooded paddy fields, which differs in magnitude from metals such as Pb and Zn. Therefore, the dispersion behavior of As should be focused on during the investigation, remediation, and management activities for agricultural soils contaminated by anthropogenic As and metals due to AMMSs.

Keywords Abandoned mine sites · Arsenic · Metals · Paddy soil · Spatial distribution

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1 Introduction

1.1 Objective

Agricultural soil contamination caused by metal(loid)s from mining activities has caused serious environmental concerns globally. To develop efficient strategies and methods to remedy soils contaminated by metal(loid)s, it is vital to monitor the metal(loid)s in the soil by conducting field surveys and properly understanding their transport and spatial distribution characteristics. The present study aims to elucidate the distinctive spatial distribution of anthropogenic arsenic (As) and metals from abandoned metals mine sites (AMMSs) to the surrounding agricultural soils. Total concentration of metal(loid)s, i.e., As, lead (Pb), and zinc (Zn), in all the agricultural soils located in the vicinity of five AMMSs, i.e., Gubong, Nakdong, Daema, Angang, and Sunyang mines, was measured. Then, the horizontal dispersion characteristics of As and metals were analyzed using the spatial data and geoaccumulation index (I_{geo}). Finally, the distribution of anthropogenic metal(loid)s in the agricultural soils was also mapped to analyze their distinct spatial distribution using a GIS tool.

1.2 Background and hypothesis establishment

Mine tailings are serious wastes derived from mining activities and contain several toxic metal(loid)s (Kim et al. 2014; Li et al. 2017); therefore, untreated mine tailing dumps left near AMMSs are the primary source of soil and water contamination in the surrounding areas (Jung 2001; Rodríguez et al. 2009; Rashed 2010; Mileusnić et al. 2014; Zhang et al. 2016; Gabarrón et al. 2018).

Releasing metal(loid)s into ecosystems primarily occurs through two pathways: (1) dispersal of metal (loid)-bearing particles by wind- and rainfall-driven erosion of mine tailings (Boussen et al. 2010; Mileusnić et al. 2014; Li et al. 2017) and (2) infiltration of metal(loid)-bearing leachates into the subsurface during rainfall–runoff processes and subsequent infiltration into subsurface and groundwater (Boussen et al. 2010; Mileusnić et al. 2014; Zhang et al. 2016; Ngole-Jeme and Fantke 2017). Recent studies based on the transport and dispersion of metal(loid)s in contaminated soils near mining areas have suggested that the spatial distribution of soil metal(loid)s near mine tailing dumps is primarily determined by the erosion of mine tailings, particularly wind- and water-driven erosion (Tembo et al. 2006; Meza-Figueroa et al. 2009; Kim et al. 2014; Mileusnić et al. 2014; Li et al. 2017). Moreover, the closer the location of the site to the mine tailing dumps, the higher the concentration of the contaminants and vice versa (Tembo et al. 2006; Meza-Figueroa et al. 2009; Kim et al. 2014; Mileusnić et al. 2014; Li et al. 2017).

In South Korea, agricultural lands [primarily paddy (flooding irrigation) and upland fields] are largely distributed around the AMMSs in forest areas, and therefore, such agricultural lands have a steep slope. Over 50% of agricultural lands comprise paddy fields in South Korea. To cultivate rice in such forest areas, paddies must be constructed to the type of terraced paddy fields.

Unlike upland fields (dry fields), paddy fields have a distinct cycle of flooded and non-flooded periods that lead to alternating reducing and oxidizing environments and accompanied by drastic redox potential changes (Takahashi et al. 2004; Yun and Yu 2015; Yun et al. 2017). Redox potential is considered as a key factor influencing the form and dispersion of arsenic (Pi et al. 2016). Flooding of soils, similar to that in paddy soil, leads to the mobilization of anthropogenic As adsorbed in iron oxyhydroxide phases, which is caused by both the reduction of As [As(V) to As (III)] and iron [Fe (III) to Fe (II)] under the reducing conditions (Meharg and Zhao 2012; Yun and Yu 2015; Chowdhury et al. 2017). During these reductive processes in flooded paddy soils, As can be continuously released into the soil pore water; arsenate is reduced to As (III), which has higher mobility

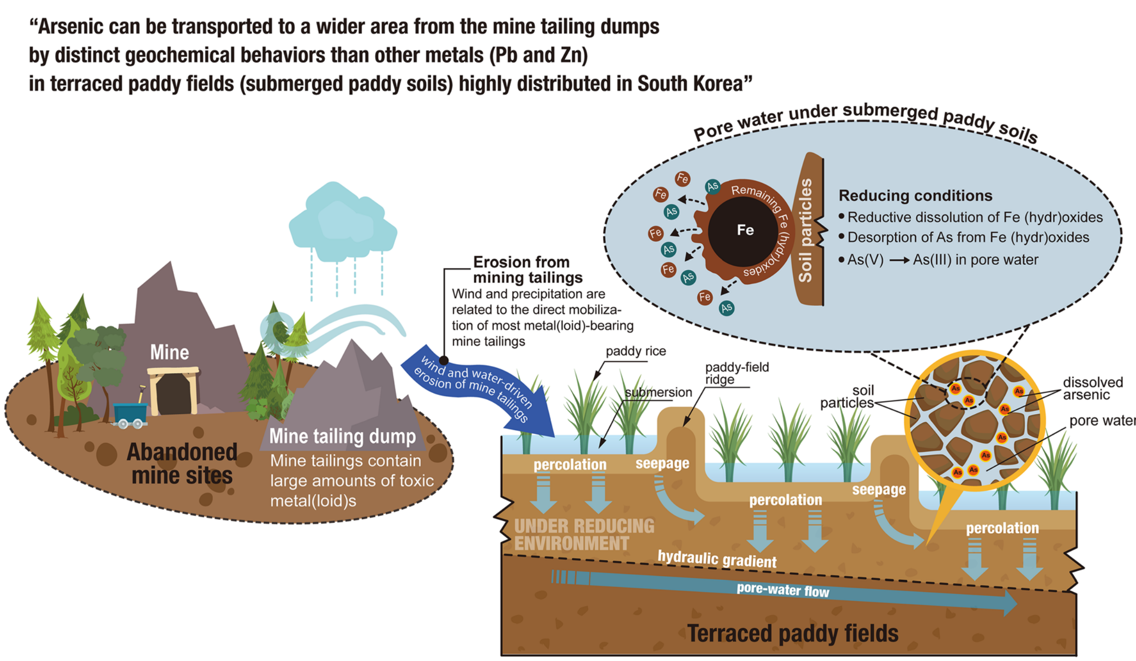


Fig. 1 Schematic of the transport processes of arsenic from the mine tailing dumps to the surrounding agricultural soils (terraced paddy soils)

and toxicity (Oremland and Stolz 2003; Moon et al. 2004; Vodyanitskii and Plekhanova 2014; Yang et al. 2015).

On the contrary, metals with constant valence under reducing conditions, i.e., flooded paddy soils, are likely to have lower mobility because they are immediately readsorbed by metallic oxides (e.g., aluminum (hydr)oxides and remaining Fe (hydr)oxides) and clay minerals (Takahashi et al. 2004). In addition, in the terraced paddy fields, water from a more elevated paddy will penetrate through a ridge and flow into a lower paddy; most of the water used to irrigate paddies will move in response to the hydraulic gradient beneath flooded paddy fields. Therefore, among metal(loid)s transported from mine tailing dumps to paddy fields, As can influence a larger geographical area than other metals because it has higher mobility in reducing conditions, as shown in Fig. 1.

Based on the above-mentioned content, the following hypothesis can be made regarding distribution characters of As

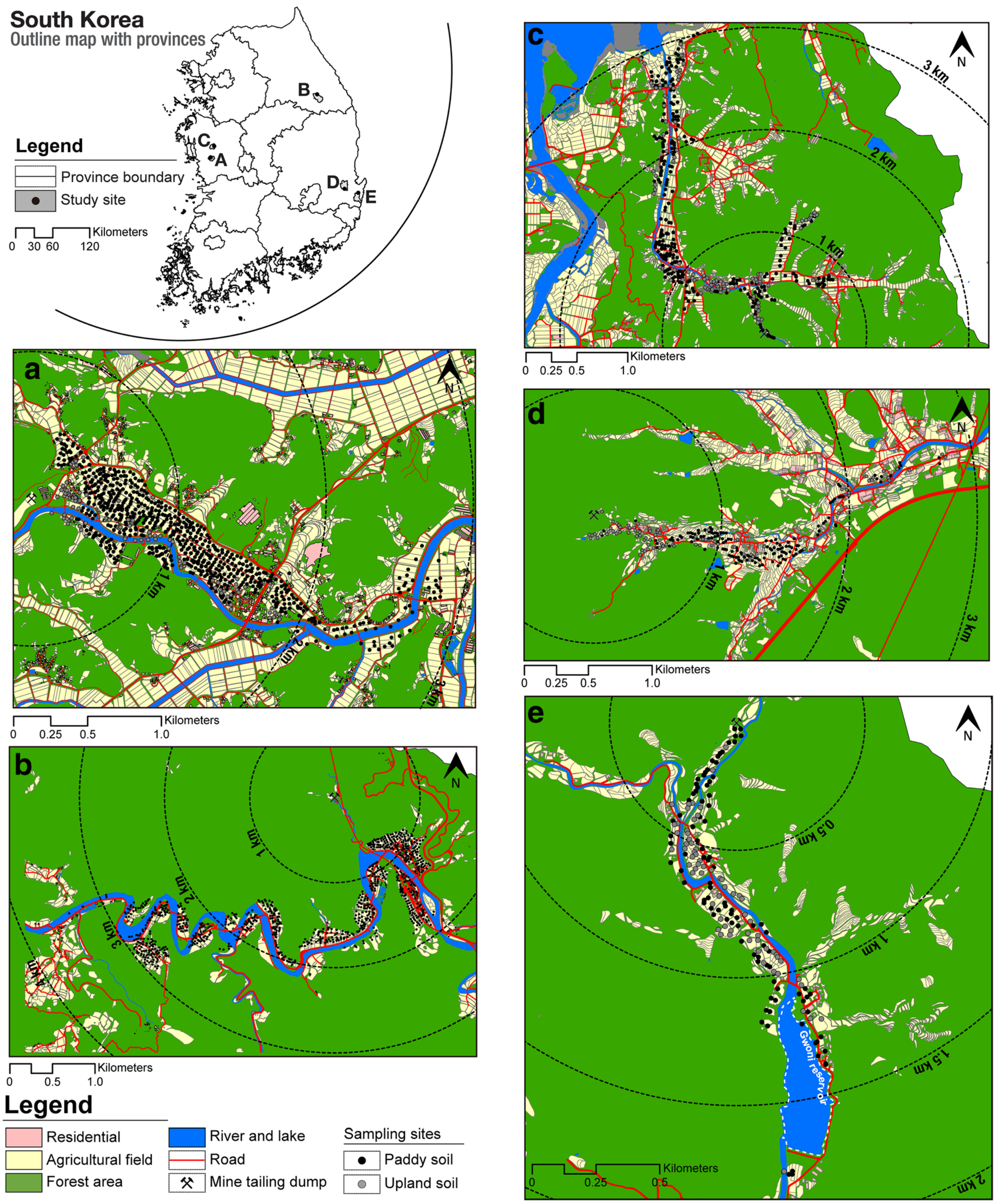


Fig. 2 Sampling points showing the distribution of land use types. **a** Gubong. **b** Nakdong. **c** Daema. **d** Angang. **e** Sunyang mines

and metals within agricultural lands around AMMSs in South Korea.

1. The agricultural soils located near the mine tailing dumps of the AMMSs must have been affected by tailing dump erosion (wind- and water-driven erosion), and the metal(loid)s must have directly moved to the surrounding agricultural soils through the erosion of tailing dumps.
2. Among the metal(loid)s, the As that moved to the agricultural soils through the erosion of tailing dumps would show a distinctive behavior in flooded paddy soils compared to other metals due to reductive processes (Fig. 1).
3. If the above hypothesis is correct, then the agricultural soils located near the tailing dumps must show a typical spatial distribution pattern of metal(loid)s based on the erosion process of tailing dumps.
4. As must have been moved and distributed across much wider areas from the tailing dumps in comparison to other metals with its high mobility due to reductive processes in flooded paddy soils; As and other metals would exhibit distinctive spatial distribution patterns.

2 Materials and methods

2.1 Study sites

In total, five agricultural areas located in Gangwon, Chungnam, and Gyeongbuk provinces were considered; each of these areas has its own AMMSs (Gubong, Nakdong, Daema, Angang, and Sunyang), as shown in Fig. 2. Detailed information on the AMMSs is listed in Table 1. These AMMSs were locations where the surrounding agricultural soils have already been reported to be contaminated by metal(loid)s, particularly As, Pb, and Zn.

2.2 Soil sampling

Extensive investigations on soil metal(loid) contents were conducted during 2010–2014. Soil sampling was performed in the surrounding agricultural fields located downslope from the mine tailing dumps near the mine shaft (Fig. 2). The soil samples were taken at depths of 0–30 cm from agricultural fields, including one sample obtained from the mine tailing dumps (Fig. 2): Gubong (782 locations), Nakdong (823 locations), Daema (375 locations), Angang (233 locations), and Sunyang (163 locations). The location information for each site is provided in ESM 1 (Electronic Supplementary Material). From each sampling site, five samples of surface soils were collected in a zig-zag pattern and were mixed thoroughly to obtain a representative composite sample in accordance with the standard South Korean method prescribed for

Table 1 Description of the five abandoned mines in the study sites

Mine	Main geology	Type of mineralization	Target metal	Operation period	Grade of ore body	Ore mineral associations	Pollution source	Reference
Gubong	Biotite granite, granitic gneiss, lime-silicate	Au-bearing quartz vein	Au, Ag, Pb, Zn	1926–1977	Au: 6 ~ 8 g/ton, Ag: 5 ~ 6 g/ton	Arsenopyrite, pyrite, galena, sphalerite	Tailings (900,000 m^3)	Lee et al. 1997; Kim et al. 1999; Yi et al. 2003; KMoE 2005a
Nakdong	Granodiorite porphyry, quartz monzonite	Au-bearing quartz vein	Au, Ag, As, Bi	Japanese colonial, 1954–1959, 1968–1971	NA	Pyrite, arsenopyrite, galena, sphalerite	Tailings (29,837 m^3)	KORES 1974,
Daema	Granitic gneiss	Au-bearing quartz vein	Au, Ag	1934–1942, 1967–1989	NA	NA	Tailings (15,000 m^3)	KORES 1973, 1981; Kim et al. 2018
Angang	Quartz porphyry, shale	sulfide-bearing quartz vein	Zn	Japanese colonial, 1968–1970s	NA	Pyrite, sphalerite	Tailings (1400 m^3)	KORES 1975
Sunyang	Biotite granite, felsophyre, granite porphyry	Au-bearing quartz vein	Au, Ag, Zn	Japanese colonial, 1961–1972	Au: 0.0 ~ 2.4 g/ton, Ag: 281 ~ 1467 g/ton	Pyrite, galena, sphalerite	Tailings (8500 m^3)	KORES 1983, 1987; KMoE 2005b, 2008;

NA not available

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

Mine	Metal(loid)s (mg/kg)			Spatial data	
				Transverse Mercator (Tokyo Datum)	
	As	Pb	Zn	X	Y
Gubong	1320	1147	2754	178,130	322,974
Nakdong	582.2	10,956	3584	350,696	427,141
Daema	3803	1536	129.5	183,703	341,400
Angang	22.76	3501	2324	397,076	272,753
Sunyang	195.3	51,150	1745	419,672	266,014

The national limits for As, Pb, and Zn are 25, 200, and 300 mg/kg, respectively (KMoE, 2015)

collecting soil samples (KMoE 2013). The soil samples were collected using a stainless steel hand auger and were stored in pre-labeled polyethylene zip bags. Appropriate care was taken at the sampling sites to avoid collection of any obvious contaminants as well as plant leaves, gravel, and other debris. The sampled soils were spread on steel pans in one layer with uniform thickness. Then, the samples were air dried for 1 week to eliminate moisture. Then, the soils were crushed, passed through a 2-mm stainless steel sieve, and stored in airtight polyethylene containers.

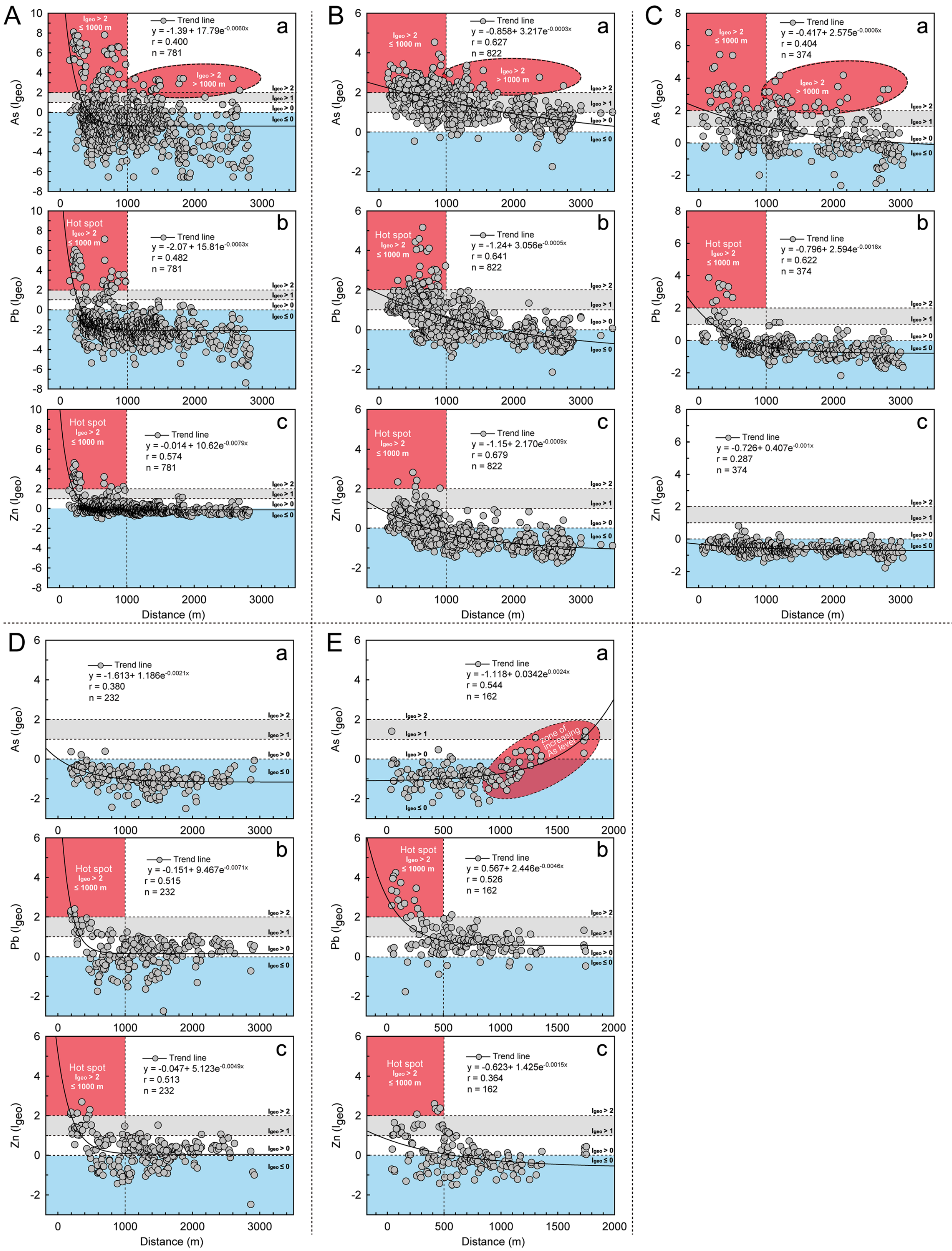
2.3 Chemical analysis for total metal(loid) contents

Aqua regia digestion was conducted to determine the total contents of As, Pb, and Zn in sampled soils. The dried soils were pulverized and sieved to 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, $HCl + HNO_3$) for 1 h at 70 °C. The digested solution was filtrated through 5B filter paper; then, the total concentrations of the metal(loid)s were determined using an inductively coupled plasma optical emission spectrometer (ICP–OES; Optima 5300DV, Perkin Elmer, USA) in accordance with the standard South Korean method (KMoE 2013). All soil samples were analyzed in duplicate, and their mean values were used for statistical and geostatistical analysis. A reference soil (Environmental Resource Associates, USA) was used to measure the recovery and relative standard deviation (RSD) of the elements investigated. Recovery in the reference soil

Table 3 Statistical summary of metal concentrations (mg/kg) in agricultural soils of the study sites and some soil properties

Mine		Mean	Median	Min	Max	SD	CV	Skew.	Kurto.	p (K-S test)	BMC	WS	NL	NL > BMC
Gubong (*N* = 781)	As	54.3	4.59	0.10	2554	231	425	6.58	49.3	0.00	6.24	6.00	25.0	105
	Pb	45.0	8.42	0.18	4242	223	495	11.5	179	0.00	20.07	35.0	200	29
	Zn	133	98.9	52.0	2613	185	139	8.02	79.4	0.00	71.07	90.0	300	27
Nakdong (*N* = 822)	As	28.2	22.8	2.8	217	18.1	64.0	2.78	17.6	0.00	6.24	6.00	25.0	370
	Pb	53.7	37.4	6.77	1076	67.2	125	8.08	92.8	0.00	20.07	35.0	200	14
	Zn	97.2	77.2	31.4	755	62.3	64.1	3.62	24.4	0.00	71.07	90.0	300	8
Daema (*N* = 374)	As	29.2	15.4	1.5	1047	66.0	226	11.1	158	0.00	6.24	6.00	25.0	110
	Pb	31.0	22.8	6.67	439	41.6	134	6.43	47.3	0.00	20.07	35.0	200	6
	Zn	72.6	70.4	31.1	187	16.9	23.2	1.72	7.34	0.00	71.07	90.0	300	0
Angang (*N* = 232)	As	4.96	4.83	0.99	12.3	1.60	32.2	0.90	3.52	0.00	6.24	6.00	25.0	0
	Pb	43.0	39.0	4.47	160	25.6	59.4	1.91	4.95	0.00	20.07	35.0	200	0
	Zn	144	130	19.1	691	89.4	62.0	2.432	8.85	0.00	71.07	90.0	300	12
Sunyang (*N* = 162)	As	5.99	5.14	0.78	25.0	3.77	62.9	2.87	10.2	0.00	6.24	6.00	25.0	0
	Pb	73.6	49.4	8.78	568	81.8	111	3.68	15.4	0.00	20.07	35.0	200	9
	Zn	129	93.7	37.7	647	101	78.0	2.59	8.08	0.00	71.07	90.0	300	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 (KMoE 2014), *WS* world soils unpolluted (Adriano 2001), *NL* national limits, the soil quality standards of South Korea (KMoE, 2015), *NL > BMC* number of samples with a concentration that exceeded the national limit


A
As (Igeo)
Trend line
y = -1.39 + 17.79e-0.0060x
r = 0.400
n = 781
Igeo > 2 ≤ 1000 m
Igeo > 2 > 1000 m
Pb (Igeo)
Hot spot Igeo > 2 ≤ 1000 m
y = -2.07 + 15.81e-0.0063x
r = 0.482
n = 781
Zn (Igeo)
y = -0.014 + 10.62e-0.0079x
r = 0.574
n = 781
B
y = -0.858+ 3.217e-0.0003x
r = 0.627
n = 822
y = -1.24+ 3.056e-0.0005x
r = 0.641
n = 822
y = -1.15+ 2.170e-0.0009x
r = 0.679
n = 822
C
y = -0.417+ 2.575e-0.0006x
r = 0.404
n = 374
y = -0.796+ 2.594e-0.0018x
r = 0.622
n = 374
y = -0.726+ 0.407e-0.001x
r = 0.287
n = 374
D
y = -1.613+ 1.186e-0.0021x
r = 0.380
n = 232
y = -0.151+ 9.467e-0.0071x
r = 0.515
n = 232
y = -0.047+ 5.123e-0.0049x
r = 0.513
n = 232
E
y = -1.118+ 0.0342e0.0024x
r = 0.544
n = 162
zone of increasing As level
y = 0.567+ 2.446e-0.0046x
r = 0.526
n = 162
y = -0.623+ 1.425e-0.0015x
r = 0.364
n = 162
Distance (m)

◀ **Fig. 3** Scatter plots of geoaccumulation index (I_{geo}) values for metal(loid)s in agricultural soils corresponding to increasing distance from the mine tailing dumps located in the study sites. **a** Gubong (n = 781). **b** Nakdong (n = 822). **c** Daema (n = 374). **d** Angang (n = 232). **e** Sunyang mines (n = 162). a As, b Pb, and c Zn. The trend lines are shown on regressions that correlate with the significance. The hot spot (red) area indicates that I_{geo} values are above 2.0 within 1 km of the mine tailing dump. $I_{geo} < 0$: practically uncontaminated, $0 < I_{geo} < 1$: uncontaminated to moderately contaminated, $1 < I_{geo} < 2$: moderately contaminated, and $2 < I_{geo} < 3$: moderately to heavily contaminated

was between 70 and 130% and RSD was less than 30%.

2.4 Assessment of metal(loid) pollution

The geoaccumulation index (I_{geo}) was used to evaluate the degree of metal(loid) pollution in the soil samples obtained from the study sites, which can be calculated using the following equation (Muller 1969):

$$I_{geo} = \log_2\left({}^{C_m}/_{1.5C_b}\right),$$

where C_m is the concentration of element m measured in the soil obtained from the study area, C_b is the geochemical background value (denoted as background metal concentrations (BMC) in Table 2) for element m, and 1.5 is the background matrix correction factor due to the lithogenic effect. The I_{geo} comprises seven grades or classes: Class 0 (practically uncontaminated): $I_{geo} < 0$; Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated): $1 < I_{geo} < 2$; Class 3 (moderately to heavily contaminated): $2 < I_{geo} < 3$; Class 4 (heavily contaminated): $3 < I_{geo} < 4$; Class 5 (heavily to extremely contaminated): $4 < I_{geo} < 5$; and Class 6 (extremely contaminated): $5 < I_{geo}$.

2.5 Statistical analyses and GIS mapping technique

Statistical analyses were conducted using SPSS 20.0 (IBM, USA). The mean, range, standard deviation, and coefficient of variation (CV) of the elements were calculated to obtain the trend and pattern of variation among the different sampling points. The statistical distribution of the data was checked via the Kolmogorov–Smirnov test for normality with a confidence interval of mean 95%. To determine the influence of metal mine sites on the metal(loid) distribution in soil, the distance to the metal mine was used as an ancillary predictor and linear regression was performed on data obtained from the sampling points using SigmaPlot 12.0 (Systat Software, Inc., USA). A GIS tool (ArcGIS 10.2.2) was used to produce spatial distribution maps for metal(loid)s in the study sites and analyze the associated spatial data, i.e., distance from the mine and land use.

3 Results and discussion

3.1 Total metal(loid) concentrations in mine tailings and agricultural soils

The total concentration of metal(loid)s in the sampled soils from the mine tailing dumps of the AMMSs is presented in Table 2. The total concentration of As, Pb, and Zn was 1320, 1147, and 2754 mg/kg, respectively, for Gubong; 582, 10,956, and 3584 mg/kg, respectively, for Nakdong; 3803, 1536, and 129.5 mg/kg, respectively, for Daema; 22.76, 3501, and 2324 mg/kg, respectively, for Angang; and 195.3, 51,150, and 1745 mg/kg, respectively, for Sunyang mine, which significantly exceed their respective national limits except for As in the Angang mine.

Table 3 lists the descriptive statistics for the raw data of metal(loid)s in the agricultural soils considered. Additionally, the BMCs in unpolluted agricultural soils of South Korea (KMoE 2014) and world soils (WSs) (Adriano 2001) are listed. The total concentration of the metal(loid)s at each site is presented in ESM 1 (Electronic Supplementary Material). The mean concentration of As, Pb, and Zn was 54.3, 45.0, and 133 mg/kg for, respectively, Gubong; 28.2, 53.7, and 97.2 mg/kg, respectively, for Nakdong; 29.2, 31.0, and 72.6 mg/kg, respectively, for Daema; 4.96, 43.0, and 144 mg/kg, respectively, for Angang; and 5.99, 73.6, and 129 mg/kg, respectively, for Sunyang mine as listed in Table 3. The mean concentration of As, Pb, and Zn in the sampled soils of the study sites was higher than that of the BMC or WS, except for As in the Angang and Sunyang mine and Zn in the Daema Mine, as listed in Table 3.

Table 4 Coefficients of exponential equations for As, Pb, and Zn (I_{geo} value)

Mine	Element	y_0	α	β	r
Gubong (N = 781)	As	− 1.39	17.8	− 0.0060	0.400
	Pb	− 2.07	15.8	− 0.0063	0.482
	Zn	− 0.014	10.6	− 0.0079	0.574
Nakdong (N = 822)	As	− 0.858	3.22	− 0.0003	0.627
	Pb	− 1.24	3.06	− 0.0005	0.641
	Zn	− 1.15	2.17	− 0.0009	0.679
Daema (N = 374)	As	− 0.417	2.58	− 0.0006	0.404
	Pb	− 0.796	2.59	− 0.0018	0.622
	Zn	− 0.726	0.407	− 0.0010	0.287
Angang (N = 232)	As	− 1.61	1.19	− 0.0021	0.380
	Pb	− 0.151	9.47	− 0.0071	0.515
	Zn	− 0.047	5.12	− 0.0049	0.513
Sunyang (N = 162)	As	− 1.12	0.034	0.0024	0.544
	Pb	0.567	2.45	− 0.0046	0.526
	Zn	− 0.623	1.43	− 0.0015	0.364

The CVs of As, Pb, and Zn were 425%, 495%, and 139%, respectively, for Gubong; 64.0%, 125%, and 64.1%, respectively, for Nakdong; 226%, 134%, and 23.2%, respectively, for Daema; 32.2%, 59.4%, and 62.0%, respectively, for Angang; and 62.9%, 111%, and 78.0%, respectively, for Sunyang mine, as listed in Table 3. Most of the CVs for As, Pb, and Zn showed significantly high variations, with all values above 50%, except for Zn and As in the Daema and Angang mines, respectively. The wide variation in their concentrations in agricultural soils could be attributed to dispersion of the mine tailing dumps because high CVs (> 50%) are often reliable indicators of anthropogenic activity (Chen et al. 2008; Guo et al. 2012; Mihailović et al. 2015). Sulfide minerals, such as arsenopyrite (FeAsS), pyrite (FeS_2), galena (PbS), and sphalerite (ZnS), which are associated minerals of the AMMSs in the study sites, are the primary geologic source of As, Pb, and Zn (Table 1). Oxidation of the residual sulfides releases Fe and other metal(loid)s from mine tailings, such as As, Pb, and Zn (Talavera-Mendoza et al. 2007; Dótor-Almazán et al. 2017).

The application of the Kolmogorov–Smirnov test ($p > 0.05$) confirmed that the raw datasets for metal(loid)s in sampled soils were not distributed normally (Table 2). The distributions for As, Pb, and Zn were all strongly positively skewed, with skewness values higher than 1.0 and their kurtoses were also very sharp.

3.2 Horizontal distribution and transport of metal(loid)s in agricultural soils

To determine the influence of wind- and water-driven erosion resulting from the mine tailing dumps on the metal(loid) distribution in soil, the distance to the mine tailing dump was used as an ancillary predictor. Since the changes in the

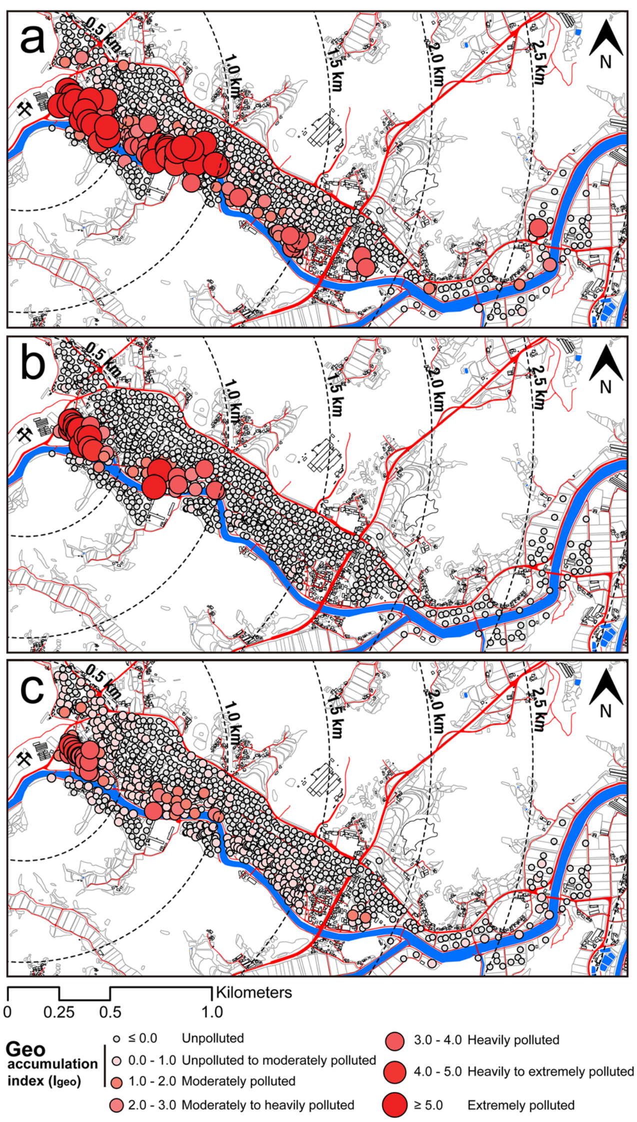


Fig. 4 I_{geo} value distributions of the metal(loid)s in agricultural soils near the Gubong mine. **a** As, **b** Pb, and **c** Zn. The size of the circles shows the relative degree of metal(loid) pollution

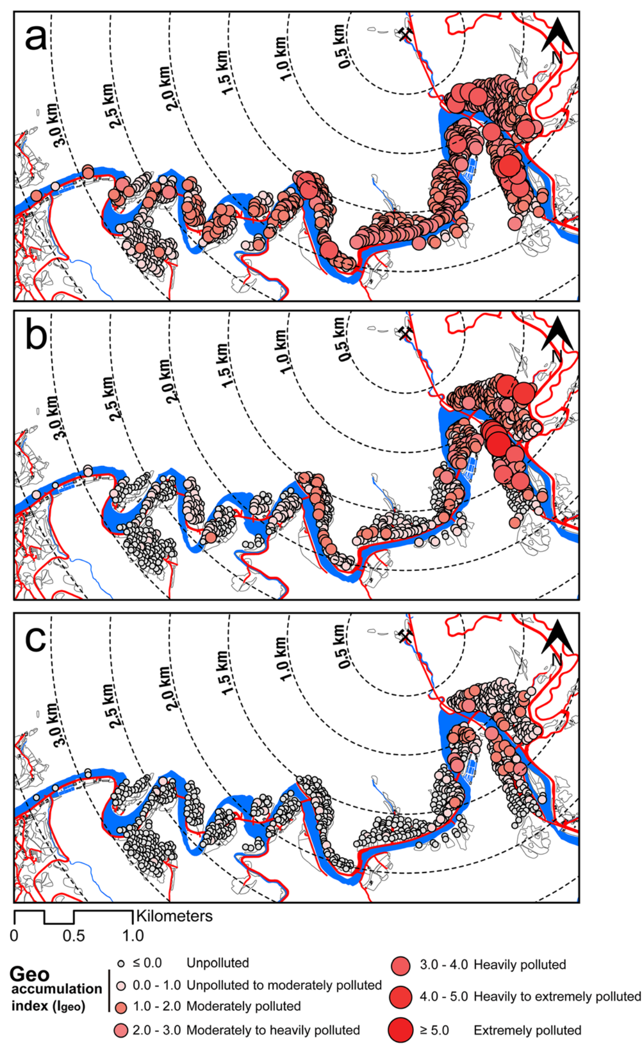


Fig. 5 I_{geo} value distributions of the metal(loid)s in agricultural soils near the Nakdong mine. **a** As, **b** Pb, and **c** Zn. The size of the circles shows the relative degree of metal(loid) pollution

concentration of metal(loid)s in agricultural soils around AMMSs are extremely high, I_{geo} value has been used as a proxy variable to indicate the degree of accumulation of metal(loid)s within the soil, instead of using the concentration of metal(loid)s in this research.

Figure 3 illustrates the I_{geo} values of metal(loid)s in soil with increasing distance from the mine tailing dumps derived using the exponential decay model. The I_{geo} values of As, Pb, and Zn decrease with the distance from the mine tailing dumps (Fig. 3). Mathematically, the distribution patterns for As, Pb, and Zn were relatively well fitted with the exponential decay model, as shown by the following equation:

$$y = y_0 + \alpha e^{-\beta x} \text{ (general form)}$$

where α and β are the coefficients and x is the distance from the mine tailing dump. The coefficients of exponential equations for As, Pb, and Zn by the study sites are listed in Table 4. The α represents the theoretical maximum value (I_{geo} value) of the metal (loid)s. The β indicates the rate of decrease in the I_{geo} values. The I_{geo} value of an element with a relatively higher β value decreases more rapidly with distance than that with a lower β value.

These distribution patterns (exponential decay) of metal(loid)s are 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 water-driven erosion of mine tailing dumps (Roberts and Johnson 1978; Jung and Thornton 1996; Yun et al. 2017) and anthropogenic metal(loid)s in the soils near industrial complexes or smelters/refineries due to the deposition of airborne particles released from them (Bi et al. 2006; Wu et al. 2011; Li et al. 2015; Yun et al. 2018). Therefore, the distribution patterns of As, Pb, and Zn in the soil suggest that they are closely associated with wind- and water-driven erosion of the mine tailing dumps (Fig. 3). However, the distribution of I_{geo} values for Zn and As in the Daema and Angang mines, respectively, were $I_{geo} \leq 0$ (practically uncontaminated), in most of the areas, and they had a low suitability with the exponential decay model (Fig. 3 c(c) and d(a)). These elements within each corresponding research area had an average concentration lower than that of BMC or WS. In addition, CV was also low at under 35% (Table 3), indicating that the elements were not anthropogenic elements from mine tailing dumps but were related to natural sources such as soil parent materials.

The I_{geo} value distribution regarding anthropogenic As, Pb, and Zn in soils commonly showed the formation of hot spots ($I_{geo} > 2$) in a 1-km radius of the tailing dumps and showed a considerable decreasing tendency after 1 km (Fig. 3). However, As, among the anthropogenic components, showed a distinctive distribution character. In Fig. 3a–c, Pb and Zn

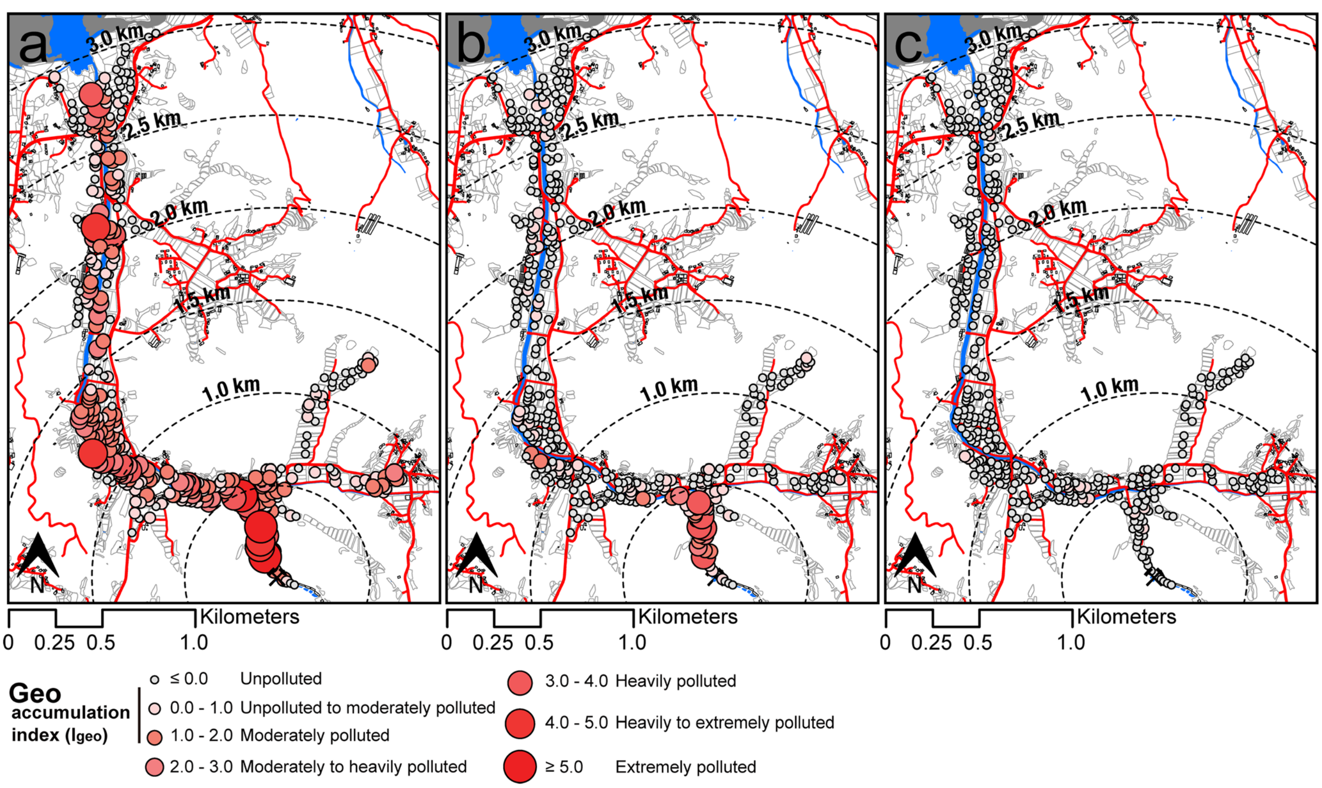


Fig. 6 I_{geo} value distributions of the metal(loid)s in agricultural soils near the Daema mine. **a** As, **b** Pb, and **c** Zn. The size of the circles shows the relative degree of metal(loid) pollution

commonly showed points where $I_{geo} > 2$ is concentrated within the 1-km radius from the tailing dumps. However, As shows points where $I_{geo} > 2$ are relatively distributed in wider areas across the entire research areas even over 1 km. In addition, although the range of I_{geo} value was widened to $I_{geo} > 1$, the distribution characters of As, Pb, and Zn could be equally described with that of $I_{geo} > 2$. Such a distribution pattern indicates that As has a higher mobility than Pb and Zn. In addition, in the exponential decay equations proposed in Table 4, if β are compared, then As has a relatively lower β value than Pb and Zn in anthropogenic metal(loid)s for each research area. This indicates that Pb and Zn would have I_{geo} values more rapidly reduced than As because they dispersed farther away from the tailing dumps.

In the study areas, all the anthropogenic metal(loid)s in the agricultural soils around the tailing dumps showed a typical distribution pattern based on the erosion process of tailing dumps. Furthermore, among the anthropogenic metal(loid)s, high concentrations of As were more highly distributed to farther distances than Pb and Zn over the whole research area. Such a result is consistent with the hypothesis outlined in Sect. 1.2. The anthropogenic metal(loid)s disperse from the tailing dumps to the surrounding agricultural soils mainly as particulate matter due to wind- and water-driven erosion. In addition, among the anthropogenic metal(loid)s, As could be dispersed and distributed in a much wider region than other metals such as Pb and Zn from the tailing dumps because of its high mobility based on reductive processes in flooded paddy soils, as shown in Fig. 1. The distribution pattern of metal(loid)s in the agricultural soils in the study areas indicated such characteristics.

The distribution pattern of metal(loid)s in agricultural soils nearby the Sunyang mine, as shown in Fig. 3e, indicated a clear distinction between As and other metals. Similar to other study areas, Pb and Zn had hot spot formation within the 1-km radius of the tailing dumps and showed a tendency toward having the degree of accumulation reduction in the form of exponential decay as they dispersed farther away from the tailing dumps (Fig. 3 e(b) and (c)). It was indicated that As was mostly accumulated at a point relatively closer to the

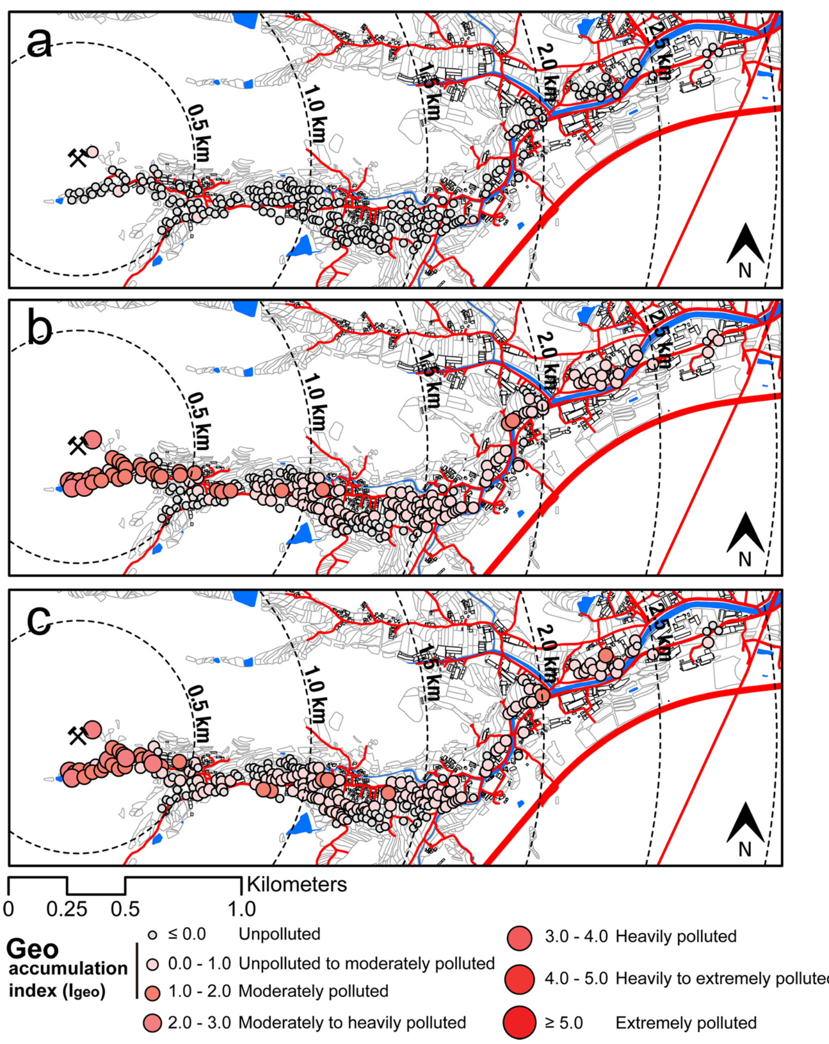


Fig. 7 I_{geo} value distributions of the metal(loid)s in agricultural soils near the Angang mine. **a** As, **b** Pb, and **c** Zn. The size of the circles shows the relative degree of metal(loid) pollution

tailing dumps (approximately 50 m) (Fig. 3 e(a)). However, it showed a distribution pattern of exponential growth in which the degree of its accumulation increased rapidly after approximately 900 m away from the tailing dumps (Fig. 3 e(a)). It is difficult to accurately explain the cause for the distribution characteristic for As as shown in Fig. 3 e(a) in the range of this research. However, this distribution characteristic was also expected to be related to the geochemical behavior of As, which is distinct from that of other metals in flooded paddy soils, as described in Sect. 1.2. The causes for this expectation are as follows.

If agricultural soil is flooded, the water table rises to the ground surface, and a reducing environment is formed in subsurface. As shown in Fig. 1, the As that was dispersed from the tailing dumps to the agricultural soil could be released to groundwater, and its concentration could be increased in groundwater, which flowed for a relatively longer time in the reducing environment. The result of Polizzotto et al. (2008) showed that As, which was released from near-surface wetland sediments to groundwater, had a high concentration in groundwater. Furthermore, the As that flowed into agricultural lands with irrigated water through agricultural wells was able to mostly accumulate on the topsoil, and this was due to the oxidation, absorption, and coprecipitation of As in the oxidizing environment of the topsoil (Kumarathilaka et al. 2018). Unusually, although the present study area (Sunyang mine) has a reservoir that was constructed in 1964, as can be seen in Fig. 2e, an agricultural well was used long before it was utilized for agricultural activities.

3.3 Spatial distribution of metal(loid)s in the study sites

Figures 4, 5, 6, 7, and 8 show the spatial distributions of the I_{geo} values of As, Pb, and Zn in the soil samples collected from the study areas. The sampling location and metal(loid) distribution maps in Fig. 3 help to understand the distance-dependent distribution patterns. The anthropogenic metal(-loid)s in agricultural soils in the research areas commonly showed the formation of hot spots within the 1-km radius of the tailing dumps, and distribution pattern of reducing I_{geo} values after that point (Figs. 4, 5, 6, 7, and 8). As showed clearly a distinctive distribution pattern from Pb and Zn in which its I_{geo} values were distributed in the wider region at a

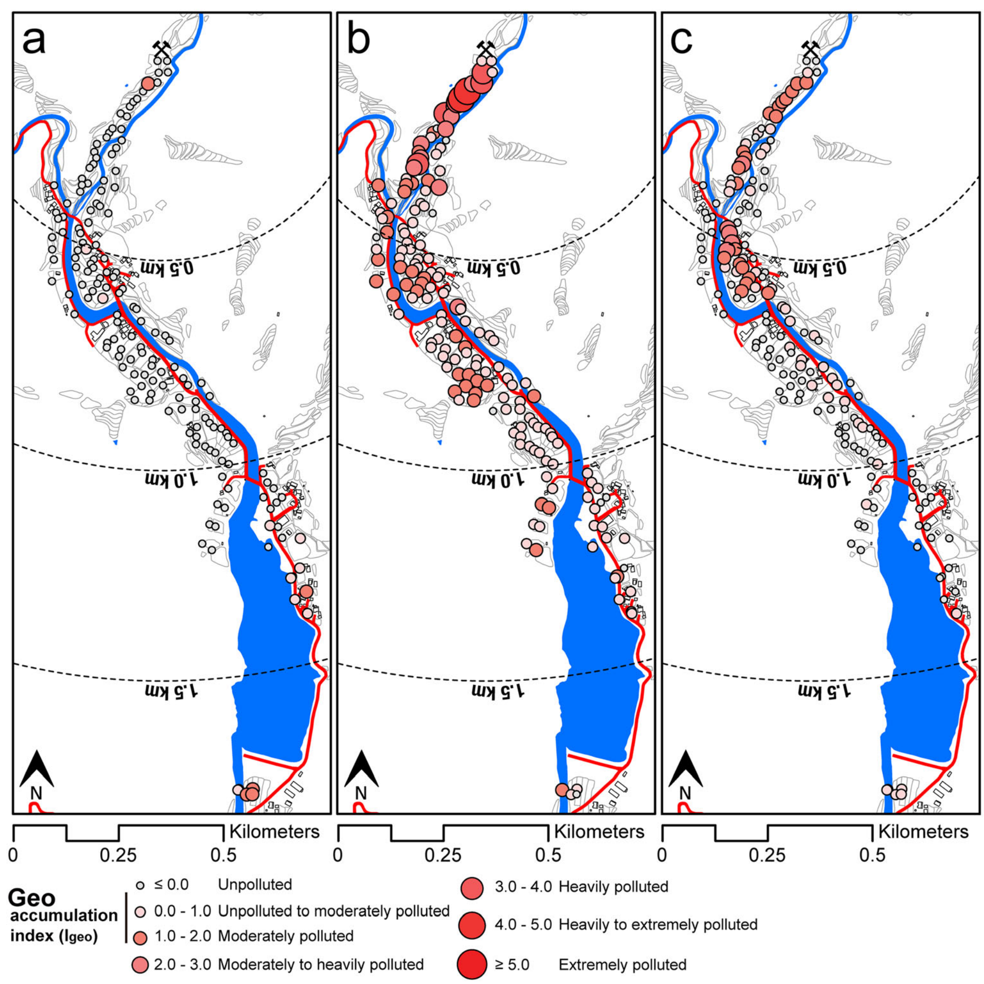


Fig. 8 I_{geo} value distributions of the metal(loid)s in agricultural soils near the Sunyang mine. **a** As, **b** Pb, and **c** Zn. The size of the circles shows the relative degree of metal(loid) pollution

higher level than Pb and Zn. Especially, the As in the agricultural soils near the Sunyang mine showed a tendency for I_{geo} values increasing from 900 m away from the tailing dumps and such a distribution pattern of As is very distinctive from that of other metals. The spatial distribution patterns of As, Pb, and Zn in the Sunyang mine were shown more clearly in the distribution maps of metal(loid) concentrations, which were provided in ESM 2 (Electronic Supplementary Material), than those of the I_{geo} values of the other sites.

4 Conclusions

The present study investigated the transport and distribution characteristics of anthropogenic metal(loid)s from the tailing dumps to agricultural soils in the vicinity of five AMMSs. It was shown that the metal(loid)s derived from the tailing dumps commonly dispersed to surrounding agricultural soils, which could be attributed from the erosion process of tailing dumps. It was also shown that As distributed to a much wider spatial range than Pb and Zn due to its distinct geochemical behavior in flooded paddy soil. As the results, special attention should be paid to the distribution behavior of As during the investigation, remediation, and management activities for agricultural soils contaminated by anthropogenic metal(loid)s as a result of AMMSs.

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