The impact of mining activities in alteration of As levels in the surrounding ecosystems: An encompassing risk assessment and evaluation of remediation strategies

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ARTICLE INFO

ABSTRACT

A comprehensive field survey was conducted to explore the status of arsenic (As) contamination in soil and water systems surrounding numerous abandoned mine sites in Korea, which were previously applied with soil-topping (15 cm deep) and lime treatment for remediation purposes. This survey also aimed to assess the environmental stability of those reservoirs in relation to their established guidelines for As. To this end, a total of 5837 target soils (TS) were analyzed along with 305 control soils (CS) and 74 tailing (TA) samples. In addition, analyses were also extended to cover 1066 water and 329 sediment samples. Substantial evidence (e.g., differences in the mean As levels between TS ($12.7 \, mg \, kg^{-1}$) and CS ($0.69 \, mg \, kg^{-1}$) and the strong correlation between TS and TA) suggests a strong effect of previous mining activities. Soil-topping method was successful in confining As at the subsurface soil and restraining its dispersal. Although soil pH level also dropped with increasing As, it was restored to near neutrality by liming treatment. The mean values of As in water samples are comparable between dry (22.2) and wet seasons ($21.2 \, mg \, L^{-1}$), while its values frequently exceeded various guideline limits. The pollution status of the current land and water systems needs to be assessed properly along with a removal plan for mine wastes/tailings to limit the dispersion of As in the study area.

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1. Introduction

Mining activities, occurring in vast areas on the globe, have often been regarded as the major contamination sources of heavy metals and metalloids, including arsenic (As), in soil and aquatic systems [1]. As can be released into the environment through both natural (e.g., volcanism and rock weathering) and anthropogenic processes (e.g., mining and smelting) [2,3]. Being recognized as a prime carcinogen [4–8], As is considered as one of the most detrimental contaminants in soil/water systems [9–11]. Because As is present ubiquitously in the environment [12], its human intake may proceed through contaminated water, food, and soil [13].

Examinations of As contamination in the environment have often focused on water systems such as drinking water resources [6,14–16]. Similarly to excessive As in water bodies, contamination of soil systems with As has been viewed with great concern possibly due to its uptake by crops [17]. It is noteworthy that As-loaded water, if supplied to water crops in agricultural lands, may also act to propagate As in soils [13]. The environmental concerns on As contamination have thus been a phenomenal impetus towards boosting the demands for better knowledge with respect to As loads in waters and soils in and near mine sites [1,18].

In the case of Korea, vast land areas surrounding numerous abandoned mine sites are currently developed or used for various purposes (e.g., agriculture) without proper evaluation of land use suitability in relation to trace element loads and soil pH levels. Many of those mine sites had been surface layered (approximately 15 cm thick) with relatively uncontaminated soils. In addition, liming treatment was also applied to those areas to raise the soil pH level which is of primary concern for plant survival. Nonetheless, no attempts had been made to assess the status of As contamination in the surrounding water and sediment systems in which freshwater organisms thrive.

In order to assess the extent of As pollution from vast areas of abandoned mining sites across South Korea, a comprehensive field survey was undertaken by measuring its concentrations from soil samples along with water and sediment samples. The results of these analyses were examined in relation with previous mining activities for the assessment of their impacts on the surrounding ecosystem. The specific objectives of this study are (1) risk assessment of land areas near previous mining areas (within 4 km radius)

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on the basis of soil-As and pH levels, (2) quality assessment of water systems in terms of As load in relation to selected water parameters, (3) evaluation on the effectiveness of soil-topping method for the confinement of As contaminations to the sub-surface soil horizons or its reduction in the surface soil layer, and (4) ultimately drafting of rehabilitation plans tailored to the abandoned mine sites. A series of these efforts are expected to facilitate the amassing of a fundamental database for land use planning.

2. Materials and methods

According to a statistical survey conducted by the Korean Ministry of the Environment (KMOE) [19], there are a total of 936 abandoned metal mines in Korea. As part of preliminary reconnaissance survey, field sampling was conducted to select mining areas for intensive analysis by a number of criteria such as (1) agricultural soils exceeding the As warning level set by KMOE (6.0 mg kg^{-1}) [19], (2) areas potentially contaminated with heavy metals due to close proximity to mining sites, and (3) areas with mine waste and effluents from previous mining activities which are generating contaminated waters; once drained towards the surrounding environment, these waters can percolate into subsurface soils or infiltrate into surface and groundwater systems.

To comply with our experimental goals, a total of 100 abandoned metalliferous mines were selected as the target sites for the collection of soil and tailing samples in and around mine boundaries. Refer to both Fig. A1 and Table A1. Note that tailing samples were also taken, whenever available. Generally, the mines are located in the upland areas, and their immediate vicinity was covered with secondary forest growth. Lands at lower elevations surrounding the mines have been used for agricultural purposes after the mines were abandoned. The land use types of the study area can thus be categorized into: (a) paddy field (PF), (b) crop land (CL), (c) areas with fruit-bearing trees and secondary forest growth (SFL), and (d) household gardens/farms with multiple land use purpose (MLU). Consequently, soil samples collected from these agricultural areas were labeled by the four different categories above.

It is reasonable to assume that As and metals of geogenic origin can be found at deep layers of the soil profile (e.g., C horizon; >30 cm), while anthropogenic or mining-related As are confined to the upper soil layers (e.g., O, A, and B horizons; 0–30 cm). Hence, for the remediation purpose, soil-topping (approximately 15 cm thick) was applied to the neighboring areas of those abandoned mine sites. Moreover, liming (with calcium carbonate) was also treated to increase soil pH to near neutrality. However, agricultural activities (such as tillage) should have facilitated the mixing of this surface soil (0–15 cm) with the subsurface one (15–30 cm). Hence, in this study, we investigated both the surface and subsurface soil layers to quantify mining-related input of As that can be transferred to the surrounding crop plants. Approximately 50 surface soil samples were taken using a hand spade at specified intervals within 4 km downstream from each mine's working area and tailings storage site. This distance is generally recommended for the assessment of metal pollution by mining activities [19]. Subsurface soil samples were also taken concurrently using a hand auger (3.0 cm in diameter). Great care was taken to minimize the intermixing of soil materials.

Each target soil (TS) sample (with approximately 1 kg weight) was taken as a composite of five subsampling points. To learn more about the extent of As contamination, soil samples were also collected from reference points or control soils (CS). The collection of CS samples was also made from adjacent areas that were perceived to have experienced minimal disturbance, while being subject to similar natural pedological processes (e.g., climate, vegetation, water, relief, parent material, and biota) as the TS [20].

The samples were prepared and analyzed at the Soil Environment Laboratory at Sejong University, Seoul, Korea. Each soil sample was air-dried at room temperature for 7 days and crushed using a ceramic mortar and pestle. Ground soils were passed through a 2 mm (No. 10) mesh sieve, and some of them were subject to pH analysis in a soil to water mixture ratio of 1:5 (Orion 5 star pH meter, Thermo Co., USA). Approximately 100 g of < 2 mm sized soil samples were subsequently grounded to pass through a 0.15 mm (No. 100) mesh sieve. For the analysis of As in soil samples, the Korean Standard Method of Analysis (KSMA) was employed [19]. According to KSMA, 10 g of finely milled soil samples (< 0.15 mm) were initially decomposed in 50 mL of 1.0 M HCl solution. The mixture was then treated with 2 mL of 0.2% (w/v) potassium iodide and left to stand for 24 h. The concentrations of As were then measured by atomic absorption spectrophotometry (AAS: AA-240 model, Varian, Australia) with a hydride generation system [21]. In our preliminary study, a comparison was made by extracting As by both aqua regia and 1 M HCl. Results showed that their extraction ratios for low and high As-containing soils were found as 1.50:1 and 3.5:1, respectively. Hence, our As data should be significantly lower than those measured via aqua regia extraction. This should be taken into account, when comparing our As data with those of other studies.

The collection of water samples was made in the vicinity of the target areas (e.g., mine effluents, stream/river waters, and small reservoir/pools) in accordance with the standard water sampling procedure of KMOE [19]. Multiple stream points were selected for water sampling at 100–300 m distance intervals downstream (up to 4 km) of the mining sites. All clean plastic bottles (500 mL capacity) were rinsed with sample aliquots prior to actual sampling. Each bottle was inclined horizontally against the stream to collect samples without disturbing the stream bed. The collected samples were filtered with a hand-pump sampler using Whatman 0.45 μm membrane filter paper (47 mm diameter). These samples were then acidified with 1 to 2 drops of concentrated HCl to minimize the adsorption of As in the bottles. These acidified samples were stored in a cooling box (< 4 °C) for the continuing analysis. Quantitative analysis of As in each sample was carried out in the laboratory using AAS (AA-240 model; Varian, Australia) with a hydride generation system.

Important physico-chemical parameters in water systems (such as pH, redox potential (Eh), salinity, total dissolved solids (TDS), and electric conductivity (EC)) were measured on site using a portable water quality test kit (Orion 5 star model, Thermo Co., USA). To allow comparison of metal contents in waters between dry (end of spring: May and June) and wet seasons (end of summer: September and October), sampling between seasons was basically planned on a parallel basis. However, due to insufficiency of water during dry season, the data size between seasons differs inevitably. After each water sampling, sediment samples (each consisting of 10 subsamples with approximately 0.5 kg weight) were also collected whenever available using a stainless steel trowel. Stream sediment samples were air-dried, passed through a 100 mesh (<0.15 mm) sieve, and analyzed for As and pH in the same manner as the soil samples.

A rigorous quality control (QC) program was implemented such as reagent blanks, replicate samples, and in-house reference materials (soils from the Sangdong tungsten mine in Korea) with 1.5–1.9 mg As kg^{-1} soil. The minimum detection limit (MDL) of As in chemical analysis was 0.2 μg L^{-1} (or equivalent to 0.1 ng in absolute mass term). The accuracy of the analytical method, if assessed by the reference materials at 95% confidence interval, was within ±90%.

Table 1
Basic statistics of As concentrations ($mg\,kg^{-1}$) and pH levels in soil layers in relation to land use type and soil depth between the surface and subsurface layer.

Land use type[a]	Target soils (TS)						Control soils (CS)						z[c]	p-value[d]
	Mean	SD	Min.	Med.	Max.	N[b]	Mean	SD	Min.	Med.	Max.	N[b]		
(A) As in surface soil[e]														
CL	7.85	155	5.3E−03	0.58	5392	1326/1261	0.65	1.72	5.6E−03	0.28	13.0	73/63	1.6463	1.0E−01
PF	2.77	15.6	1.9E−03	0.80	392	1852/1741	0.69	0.81	5.0E−03	0.53	5.46	56/50	5.3267	1.0E−07
SFL	18.7	145	9.8E−04	0.79	4380	1218/1108	0.78	1.62	6.0E−03	0.30	10.5	53/45	4.1146	3.9E−05
MLU	10.4	64.9	9.3E−04	0.52	1222	590/508	1.28	3.44	2.1E−02	0.08	15.4	23/21	3.0674	2.2E−03
Mean[f]	8.83	110	9.3E−04	0.72	5392	4986/4618	0.77	1.80	5.0E−03	0.33	15.4	205/179	4.9433	7.7E−07
(B) As in subsurface soil[e]														
CL	30.0	379	6.7E−03	0.48	5597	232/218	0.35	0.39	2.0E−03	0.14	1.41	30/23	1.1559	2.5E−01
PF	3.32	19.8	8.3E−03	0.71	246	240/228	0.66	0.79	4.2E−02	0.57	4.36	35/31	2.0139	4.4E−02
SFL	69.3	636	1.0E−03	0.80	8118	295/274	0.50	0.59	1.1E−02	0.25	2.03	23/18	1.7918	7.3E−02
MLU	22.3	111	1.2E−02	0.71	897	84/69	0.50	0.59	2.3E−02	0.32	1.71	12/11	1.6336	1.0E−01
Mean[g]	35.3	426	1.0E−03	0.69	8118	851/789	0.52	0.63	2.0E−03	0.34	4.36	100/83	2.2918	2.2E−02
(C) All As data (surface and subsurface)	12.7	192	9.3E−04	0.72	8118	5837/5407	0.69	1.53	2.0E−03	0.34	15.4	305/262	2.0118	4.4E−02
(D) Tailings[h]	246	1028	6.0E−02	5.30	8417	74/71	–	–	–	–	–	–		
(A) Surface soil pH[e]														
CL	5.97	0.84	3.03	5.99	9.06	1326	5.99	0.87	3.90	5.95	8.38	73	−0.2436	0.8075
PF	5.83	0.70	3.85	5.78	9.50	1852	5.93	0.75	3.96	5.98	7.71	56	−0.9433	0.3455
SFL	5.89	1.00	2.42	5.82	9.88	1218	6.07	1.04	4.31	5.92	8.44	53	−1.1835	0.2366
MLU	6.45	0.89	3.02	6.42	8.76	590	6.57	0.95	5.20	6.53	8.19	23	−0.5732	0.5665
Mean[f]	5.96	0.86	2.42	5.90	9.88	4986	6.06	0.91	3.90	6.00	8.44	205	−1.5768	0.1148
(B) Subsurface soil pH[e]														
CL	6.01	0.90	3.03	5.96	8.91	232	6.03	0.84	4.33	6.14	7.86	30	−0.1274	0.8986
PF	5.83	0.68	4.23	5.78	7.99	240	5.89	0.59	3.99	5.87	7.09	35	−0.5572	0.5774
SFL	5.82	1.01	2.79	5.76	8.58	295	5.86	0.88	4.48	5.90	7.56	23	−0.2318	0.8167
MLU	6.34	0.98	4.32	6.43	8.86	84	6.38	1.25	4.74	6.05	8.43	12	−0.1069	0.9148
Mean[g]	5.93	0.91	2.79	5.88	8.91	851	5.99	0.84	3.99	5.98	8.43	100	−0.6675	0.5045
(C) All pH data (surface and subsurface)	5.95	0.87	2.42	5.90	9.88	5837	6.03	0.89	3.90	5.99	8.44	305	−1.5902	0.1118
(D) Tailings pH[h]	5.81	1.70	2.15	5.73	8.74	74	–	–	–	–	–	–		

[a] CL, crop land; MLU, multiple land use type; PF, Paddy field; and SFL, secondary forest land.
[b] N denotes the number of data; values on the left side of the slash denote the number of measurements, while the ones on the right side denote the number of measurements after excluding below detection limit (BDL) values.
[c] Results of the Z-statistic test to assess the statistical differences between two population means.
[d] Critical probability (or significance level).
[e] Surface and subsurface soil samples were taken at depths of 0–10 and 30–100 cm, respectively.
[f] Including all surface soil samples, regardless of land use type.
[g] Including all subsurface soil samples, regardless of land use type.
[h] Tailing data are treated separately from other soil data.

Table 2
Summary of mine sites with mean As concentrations (mg kg⁻¹) exceeding guidelines and regulations for soil As levels.

Criteria [a] (mg kg⁻¹)	Surface soils [b]								Subsurface soils [b]								Tailings	
	CL		PF		SFL		MLU		CL		PF		SFL		MLU			
	ID	As	ID	As	ID	As	ID	As	ID	As	ID	As	ID	As	ID	As	ID	As
(a) 15	12	361	19	34.3	78	201	14	140	12	1866	6	43.6	94	2736	14	144	11	8417
	78	55.7	26	32.9	12	103	21	30.8	21	130	18	34.9	78	1418	33	41.1	89	1495
	23	17.5	21	27.8	7	89.8	11	27.4	86	29.5	–	–	18	206	21	27.1	17	1163
	–	–	–	–	19	67.9	78	21.3	–	–	–	–	67	91.9	88	19.0	21	1032
	–	–	–	–	11	64.4	–	–	–	–	–	–	19	69.6	18	15.8	54	976
	–	–	–	–	34	62.6	–	–	–	–	–	–	64	63.9	–	–	50	801
	–	–	–	–	3	59.4	–	–	–	–	–	–	54	58.4	–	–	67	467
	–	–	–	–	79	50.9	–	–	–	–	–	–	79	58.2	–	–	3	462
	–	–	–	–	96	48.8	–	–	–	–	–	–	93	46.0	–	–	99	310
	–	–	–	–	64	45.0	–	–	–	–	–	–	87	40.0	–	–	64	204
	–	–	–	–	14	43.8	–	–	–	–	–	–	95	33.4	–	–	90	153
	–	–	–	–	17	43.7	–	–	–	–	–	–	50	30.6	–	–	2	140
	–	–	–	–	67	43.4	–	–	–	–	–	–	3	29.5	–	–	7	84.4
	–	–	–	–	18	39.6	–	–	–	–	–	–	82	29.5	–	–	86	33.8
	–	–	–	–	89	39.0	–	–	–	–	–	–	49	26.7	–	–	28	22.6
	–	–	–	–	94	28.6	–	–	–	–	–	–	17	20.9	–	–	19	19.5
	–	–	–	–	82	24.3	–	–	–	–	–	–	86	18.7	–	–	27	19.2
	–	–	–	–	95	23.9	–	–	–	–	–	–	–	–	–	–	39	17.5
	–	–	–	–	86	23.6	–	–	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	2	20.3	–	–	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	39	18.0	–	–	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	50	16.7	–	–	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	21	15.8	–	–	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	87	15.4	–	–	–	–	–	–	–	–	–	–	–	–
(b) 6	86	15.0	12	11.3	80	11.7	3	15.0	18	14.7	23	11.8	96	14.8	12	11.7	66	13.5
	26	13.6	86	11.0	54	11.5	40	12.2	53	12.7	–	–	40	11.7	34	12.6	55	8.59
	89	13.6	34	6.1	40	11.0	10	11.3	98	9.84	–	–	89	11.0	–	–	58	7.74
	79	12.8	33	6.1	30	7.3	88	10.9	17	7.72	–	–	98	10.7	–	–	53	6.30
	17	12.0	–	–	43	6.9	87	10.7	94	7.21	–	–	38	9.30	–	–	83	6.10
	50	11.7	–	–	38	6.0	34	8.74	23	6.81	–	–	2	7.28	–	–	59	6.03
	2	8.90	–	–	–	–	18	7.56	–	–	–	–	39	6.00	–	–	–	–
	21	7.00	–	–	–	–	7	7.44	–	–	–	–	–	–	–	–	–	–
	19	6.15	–	–	–	–	33	7.38	–	–	–	–	–	–	–	–	–	–
	98	6.05	–	–	–	–	31	6.78	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	–	–	80	6.34	–	–	–	–	–	–	–	–	–	–
	–	–	–	–	–	–	94	6.20	–	–	–	–	–	–	–	–	–	–

[a] Korean Ministry of the Environment (KMOE); (a) soil clean-up level (15 mg kg⁻¹) and (b) soil warning level (6 mg kg⁻¹) for agricultural soils, residential soils, parks and school grounds [19].

[b] Acronyms: ID, identification numbers; CL, crop land; PF, paddy field; SFL, secondary forest land; and MLU, multiple land use. Mean As values in higher categories also exceed the lower limits.

Table 3
Statistics of As concentration and the relevant parameters in water samples of four different water reservoir types (around 100 mining areas) between wet and dry seasons.

Water type	Dry season						Wet season						Z	p-value
	Mean	SD	Min	Med	Max	N[a]	Mean	SD	Min	Med	Max	N[a]		
(a) Mine waters (MW)														
As (μg L^{-1})	74.4	160	5.4E−04	24.2	853	46/30	47.2	65.6	1.8E+00	18.0	219	43/21	0.839	0.402
Temperature (°C)	18.9	3.37	1.2E+01	19.3	30.8	46	17.0	3.02	1.1E+01	16.4	24.2	43	2.825	0.005
pH	6.92	1.26	2.8E+00	7.25	8.37	46	6.83	1.24	2.5E+00	7.21	8.20	43	0.360	0.719
Eh (mV)	293	118	−1.3E+02	332	432	46	303	127	−1.1E+02	354	467	43	−0.375	0.708
Salinity (‰)	0.18	0.39	0.0E+00	0.10	2.70	46	0.17	0.24	0.0E+00	0.10	1.50	43	0.220	0.826
TDS (mg L^{-1})	189	386	2.6E+01	103	2650	46	147	215	3.0E+01	96.0	1430	43	0.636	0.525
EC (μS/cm)	348	667	5.5E+01	196	4550	46	272	399	5.7E+01	180	2660	43	0.665	0.506
(b) Groundwater (GW)														
As (μg L^{-1})	6.77	14.2	1.5E−01	2.16	88.0	175/85	10.6	18.1	5.1E−01	5.0	81.0	166/27	−0.996	0.319
Temperature (°C)	19.6	2.64	1.4E+00	19.7	27.2	175	18.2	2.62	1.2E+01	18.1	25.8	166	5.012	0.000
pH	6.98	0.71	4.5E+00	6.93	9.61	175	6.9	0.61	5.5E+00	7.00	8.40	166	0.574	0.566
Eh (mV)	241	142	−2.0E+02	314	427.8	175	238	153	−1.9E+02	305	431	166	0.236	0.813
Salinity (‰)	0.12	0.10	0.0E+00	0.10	1.00	175	0.11	0.09	0.0E+00	0.10	0.50	166	1.123	0.262
TDS (mg L^{-1})	114	85.5	1.5E+01	97.0	665	175	112	98.3	1.4E+01	89.5	735	166	0.256	0.798
EC (μS/cm)	213	149	3.2E+01	187	1040	175	210	174	2.8E+01	169	1087	166	0.218	0.828
(c) Small reservoir/pools (RP)														
As (μg L^{-1})	30.8	93.7	5.7E−01	1.97	327.7	13/12	14.5	24.3	1.9E+00	5.00	64.0	12/6	0.565	0.572
Temperature (°C)	24.8	5.02	1.6E+01	27.0	32.3	13	22.8	3.1	1.8E+01	24.2	28.1	12	1.206	0.228
pH	7.33	0.69	6.5E+00	7.30	8.9	13	7.02	0.60	6.4E+00	6.92	8.30	12	1.219	0.223
Eh (mV)	186	225	−2.4E+02	298	381.7	13	188	207	−1.9E+02	295	369	12	−0.020	0.984
Salinity (‰)	0.10	0.07	0.0E+00	0.10	0.3	13	0.03	0.03	1.2E−02	0.03	0.05	12	3.272	0.001
TDS (mg L^{-1})	68.1	45.5	2.2E+01	64.0	182	13	57.8	29.0	1.5E+01	56.5	125	12	0.677	0.499
EC (μS/cm)	133	86.5	4.6E+01	130	343	13	122	69.8	3.2E+01	107	263	12	0.330	0.742
(d) Stream water (SW)														
As (μg L^{-1})	19.9	45.1	5.0E−01	2.672	252	309/157	18.8	43.3	8.5E−01	6.00	353	302/92	0.186	0.852
Temperature (°C)	21.8	3.60	1.4E+01	21.8	33.3	309	18.4	3.4	1.1E+01	18.3	25.4	302	11.841	0.000
pH	7.28	0.64	3.9E+00	7.30	9.60	309	7.29	0.6	4.0E+00	7.30	9.20	302	−0.052	0.958
Eh (mV)	262	155	−2.5E+02	323	399	309	249	159	−1.9E+02	314	634	302	1.007	0.314
Salinity (‰)	0.10	0.22	0.0E+00	0.10	3.50	309	0.07	0.1	0.0E+00	0.10	0.40	302	2.025	0.043
TDS (mg L^{-1})	104	212	1.4E+01	76.0	3410	309	72.1	56.4	1.0E+01	56.0	383	302	2.574	0.010
EC (μS/cm)	199	417	1.9E+01	134	6660	309	133	105	1.5E+01	101	762	302	2.719	0.007
(e) All data[b]														
As (μg L^{-1})	22.2	67.1	1.5E−01	2.86	853	543/284	21.2	44.4	5.1E−01	6.00	353	523/146	0.182	0.856
Temperature (°C)	20.9	3.57	1.2E+01	20.8	33.3	543	18.3	3.21	1.1E+01	18.2	28.1	523	12.378	0.000
pH	7.16	0.75	2.8E+00	7.20	9.61	543	7.13	0.72	2.5E+00	7.20	9.20	523	0.506	0.613
Eh (mV)	256	151	−2.5E+02	320	432	543	248	157	−1.1E+02	315	634	523	0.812	0.417
Salinity (‰)	0.31	4.68	0.0E+00	0.10	109	543	0.09	0.103	0.0E+00	0.10	1.50	523	1.103	0.270
TDS (mg L^{-1})	114	202	1.4E+01	86.0	3410	543	90.6	96.1	1.0E+01	65.0	1430	523	2.413	0.016
EC (μS/cm)	215	381	1.9E+01	156	6660	543	168	176	1.5E+01	118	2660	523	2.581	0.010

[a] N denotes the number of data; values on the left side of the slash denote the number of measurements, while the ones on the right side denote the number of measurement data after excluding below detection limit (BDL) values.

[b] Including all samples, regardless of water type.

Table 4
Mines and water systems with strong acidity (pH $\leq$5) or excessive salts (salinity limits of 1000 mg L^{-1} TDS or 1500 µS cm^{-1} EC).

Mine ID	Water type[a]	pH ($\leq$5)	TDS (ppm)	EC (µS/cm)	Salinity (‰)
(A) Dry season					
29	SW	–	1220	2450	1.2
32	MW	2.8	2650	4550	2.7
43	SW	–	3410	6660	3.5
45	MW	3.6	–	–	–
61	MW	4.2	–	–	–
68	MW	4.4	–	–	–
68	SW	4.0	–	–	–
68	SW	3.9	–	–	–
69	GW	4.5	–	–	–
69	SW	4.9	–	–	–
88	MW	3.9	–	–	–
88	SW	5.0	–	–	–
(B) Wet season		–	–	–	
32	MW	2.5	1430	2660	1.5
45	MW	3.0	–	–	–
61	MW	5.0	–	–	–
68	SW	4.0	–	–	–
68	SW	4.2	–	–	–
88	MW	3.8	–	–	–
99	SW	5.0	–	–	–

[a] MW, mine water; GW, groundwater; and SW, stream water.

3. Results and discussion

3.1. The basic features of soil As distribution and comparison with guidelines

A statistical summary of As and pH data collected from both TS and CS is presented in Table 1. To evaluate the general trend of As distribution in the study area, all the TA samples with strong eccentricity were treated separately (as a distinct group). TA-based mean As concentration was measured as 246 mg kg^{-1} with a pH value of 5.81. The mean for TS-based As concentrations (12.7 mg kg^{-1}) from all areas in and nearby mine sites showed an 18-fold enhancement relative to its CS counterpart (0.69 mg kg^{-1}). The findings of enhanced As levels in TS samples of both surface (8.83) and subsurface (35.3 mg kg^{-1}) soil layer relative to their respective CS counterpart (mean of 0.77 and 0.52 mg kg^{-1}) were seen consistently in each land use type (Table 1). Hence, one may speculate that As levels in these soils were raised considerably due to previous mining activities. As levels in all of our CS samples (mean = 0.69 mg kg^{-1}) are much lower than those reported in uncontaminated soils worldwide, which fell between 6 mg kg^{-1} [22] and 7.4 mg kg^{-1} [23]. As already discussed in the method section, notably low As levels in our study relative to others should be accounted for by the less strong extraction treatment for our samples. As such, our data are not directly comparable to those treated in a different way.

Evaluation of the soil profile indicates notably higher As levels in subsurface (35.3 mg kg^{-1}) than in surface soil layers (8.83 mg kg^{-1}) (Table 1). This observation is also manifested in all land use types (e.g., CL, PF, SFL, and MLU) (Table 1). Although the vertical profile of As was distinguished to a certain extent, their differences were in most cases not statistically significant in four land use categories as defined above. As the PF soils are plowed periodically, such activities might have contributed to the fairly homogeneous distribution of As in its surface (2.77) and subsurface (3.32 mg kg^{-1}) soil horizons. This observation of relatively enhanced As in subsurface layer coincides with the fact that most mining sites in the study area were covered previously with relatively clean soils (15 cm thick) to suppress its vertical and horizontal migration (i.e., soil-topping). It thus confirms that such treatment has been successful in lowering the surface As concentration to a degree. This type of treatment is important, as As can be transported to other ecosystems by water, wind, animal carriages, and human activities and thereby hamper various components of those ecosystems. An evaluation of the soil pH data however indicated that under no circumstances did pH display any significant difference in all possible assemblages (between CS (6.03) and TS (5.95) or between surface and subsurface soils of various land use types). This indicates that the effort to raise soil pH should have been successful on areas affected by mining activities.

In a number of countries, standards or guidelines have been established to remediate or to regulate As levels in soil. These reference values are generally categorized by the land use types (e.g., industrial, residential, or agricultural) because of the differences in land utilization patterns and the associated impacts. As a simple means to assess the effect of such variables, our As data exceeding such guidelines were sorted out and arranged in the order of their magnitude (Table 2). In the case of common soils (e.g., agricultural, residential, parks, and schools), the Korean Ministry of the Environment (KMOE) has established an As 'warning level' and an 'action (or clean-up) level' at 6 and 15 mg kg^{-1}, respectively [19]. There were 54 soil samples from 36 mines that were above the former but below the latter criteria. If this comparison is extended to cover the KMOE soil action/clean-up level for agricultural soils (15 mg kg^{-1}), nine samples (i.e., 1 CL, 5 SFL, and 3 TA) from three mines exceeded such criterion.

3.2. As in water systems and the relevant physico-chemical parameters

As a companion study of our comprehensive monitoring for As in the soil system and the associated assessment task, our investigation was extended further to measure its contamination in the nearby water systems between dry (winter) and wet (summer) seasons (Table 3). The seasonal mean values of As in those waters were fairly comparable between dry (22.2 ± 67.1) and wet season (21.2 ± 44.4 mg L^{-1}), although dry season values were slightly enhanced relative to wet season (except groundwater) without statistical significance. The pattern observed in surface water, however, contrasts sharply with that of the groundwater, as the mean for wet season (10.6 mg L^{-1}) is much larger than its

Table 5
List of water systems with As levels ($\mu g\,L^{-1}$) exceeding specified guideline limits.

Mine ID	As	Water type[b]	Mine ID	As	Water type[b]	Mine ID	As	Water type[b]	Mine ID	As	Water type[b]
(a) >500 ppb[a]			99	73.9	MW-WS	50	28.0	SW-WS	79	16.1	SW-DS
	853	MW-DS	100	73.1	GW-DS	51	28.0	GW-DS	12	16.1	SW-WS
(b) >100 ppb[a]			18	69.8	SW-WS	79	27.6	MW-DS	75	16.0	SW-DS
19	353	SW-WS	18	64.0	RP-WS	50	27.0	SW-WS	30	15.8	MW-DS
18	328	RP-DS	12	61.4	SW-WS	26	25.6	SW-DS	40	15.7	GW-WS
54	252	SW-DS	23	61.0	MW-DS	21	25.1	SW-DS	80	15.0	SW-DS
50	248	SW-DS	55	60.0	SW-DS	68	25.0	MW-DS	89	15.0	SW-WS
50	235	SW-DS	62	60.0	SW-DS	25	24.3	MW-DS	23	14.6	SW-DS
94	230	MW-DS	55	56.0	GW-WS	54	24.0	SW-WS	80	14.5	SW-DS
19	219	MW-WS	63	55.0	SW-DS	54	24.0	SW-WS	12	14.2	SW-DS
78	217	MW-WS	54	54.0	SW-DS	92	24.0	MW-DS	98	14.2	SW-WS
19	193	SW-WS	(d) >10 ppb[a]			92	24.0	GW-DS	67	14.0	SW-WS
	190	SW-DS	40	49.6	SW-DS	3	23.2	SW-DS	80	14.0	SW-DS
54	190	MW-DS	27	48.0	SW-WS	40	22.7	SW-WS	19	13.6	SW-WS
55	180	MW-DS	62	48.0	GW-DS	54	22.0	SW-WS	30	13.3	GW-DS
55	162	SW-DS	22	47.8	GW-DS	18	21.8	MW-WS	60	13.0	SW-WS
18	156	SW-DS	67	47.0	SW-WS	78	21.4	SW-WS	94	12.1	GW-DS
90	141	MW-DS	40	46.5	SW-DS	21	21.1	RP-DS	42	12.0	MW-DS
50	135	SW-DS	6	44.6	MW-DS	17	21.0	SW-DS	75	12.0	SW-DS
54	133	SW-DS	61	42.0	MW-DS	40	20.6	SW-WS	54	12.0	SW-WS
94	121	MW-WS	68	42.0	MW-WS	21	20.5	SW-DS	60	12.0	MW-WS
27	116	SW-DS	50	40.0	SW-WS	54	20.0	SW-WS	57	12.0	MW-WS
90	105	MW-WS	54	39.0	SW-DS	6	19.2	MW-WS	94	11.8	SW-DS
(c) >50 ppb[a]			96	39.0	MW-WS	79	19.2	SW-DS	23	11.8	GW-DS
18	94.7	SW-DS	96	37.0	SW-WS	17	18.9	SW-DS	34	11.6	SW-DS
55	94.0	SW-DS	50	36.0	SW-WS	41	18.9	MW-DS	23	11.6	GW-DS
62	94.0	MW-DS	1	35.8	MW-DS	79	18.4	SW-DS	17	11.0	SW-DS
55	88.0	GW-DS	25	35.1	MW-WS	96	18.0	SW-WS	22	11.0	GW-WS
32	87.7	MW-DS	78	34.3	SW-WS	54	18.0	MW-WS	17	11.0	SW-DS
96	86.7	MW-DS	54	32.0	SW-DS	79	17.3	GW-DS	12	10.8	SW-DS
96	86.3	SW-DS	12	31.1	GW-WS	60	17.0	SW-WS	80	10.5	SW-DS
55	84.0	SW-DS	78	30.5	SW-WS	88	17.0	MW-WS	42	10.4	SW-DS
50	81.0	SW-WS	23	29.6	SW-DS	55	17.0	MW-WS	14	10.3	SW-DS
57	81.0	SW-WS	96	28.5	SW-DS	88	17.0	MW-DS			
67	81.0	GW-WS	56	28.0	SW-DS	18	16.3	SW-WS			

[a] Regulation guideline code for As ($\mu g\,L^{-1}$) in water: (a) 500 for wastewater [19]; (b) 100 for industrial use [19] or As threshold level for crop production [30]; (c) 50 for drinking water, household use and agricultural use [19] or rice production [30]; and (d) 10 for drinking water [28].

[b] Acronyms: GW, groundwater; MW, mine water; RP, small reservoir and pools; and SW, stream water. Mean As values of the upper categories also exceed the lower counterparts.

dry counterpart ($6.77\,mg\,kg^{-1}$). It is reasonable to expect that most surface waters (e.g., mine waters (MW), small reservoir and pools (RP), and stream waters (SW)) tend to maintain higher As contents during the dry season with the strong evaporation and low dilution effect (reduced water supply) [10]. Meanwhile, As levels in groundwater declined with the insufficient water supply (loaded with As) to percolate down the soil profile during the dry season. This vertical profile of As during the dry season tended to be reversed, as more precipitation occurred. Hence, in this research, the level of As pollution in groundwater systems appears to be supported by the combination of seasonal factors and the related water supply conditions.

If the mean pH levels in water systems are compared between seasons, there were no significant differences between dry (7.16) and wet (7.13) seasons (Table 3). Moderately acidic conditions were prevalent in MW (pH range of 2.5–8.37). In contrast, more basic conditions were seen from those of GW (4.5–9.61), RP (6.4–8.9), and SW (3.9–9.60) in both dry and wet seasons. It is important to note that surface water chemistry (e.g., pH) can be altered greatly by the type and composition of soil, rock, and sediment materials through which water flows [27]. In addition, both materials leached from the land and various detritus in water can affect the pH levels throughout the seasons. In 1982, Jones reported that a drop of pH to 5 (or lower) would cause damage to aquatic ecosystems ([24] and references therein). In this study, 17 out of 1066 water samples (during both seasons) maintained water pH at or below 5 (Table 4). In case of the dry season, 10 out of 543 samples showed pH below

5.0 which consisted of 5 samples (0.9%) from MW (pH 2.8–4.4), 4 (0.74%) from SW (ranging from 3.9 to 5.0), and 1 (0.18%) from GW (4.5). In contrast, during the wet season, 7 out of 523 cases fell into such category with 4 (0.76%) from MW (pH 2.5–5.0) and 3 (0.57%) from SW (pH 4.0–4.96). Hence, acidification of water systems should have proceeded in at least some of the studied mine sites.

The amount of total dissolved solids (TDS) in the water is often used to estimate salinity. The relationship between TDS and electric conductivity (EC), although not constant in all situations, is known to exhibit a strong correspondence with each other, e.g., $TDS = 0.64 \times EC$ [25]. As changes in the salt content (or their relative proportions) can alter such relationships, so can changes in geographical factors [25]. In this study, the mean values of salinity, TDS, and EC were generally high during the dry season (0.31‰, $114\,mg\,L^{-1}$, and $215\,\mu S/cm$, respectively) relative to the wet season (0.09‰, $90.6\,mg\,L^{-1}$, and $168\,\mu S/cm$, respectively) (Table 3). Because of a linear relationship between the two parameters (i.e., TDS ($mg\,L^{-1}$) $= 0.53 \times EC$ ($\mu S/cm$) with $R = 0.99$) in this study, it is reasonable to infer that the studied water bodies should have maintained enhanced salinity relative to common waters. As salt can suppress plant growth considerably, it can exert lethal effects above certain levels [26]. Consequently, if salinity increases in freshwater environments, most of its biota cannot survive. Usually such a crisis can be induced at TDS level above $1000\,mg\,L^{-1}$ (or 1500 EC) [27]. In our study, 3 sites (mine ID: 29, 32, and 43) had such large TDS values in their systems (Table 4), while two of them may be

Table 6
Mean As levels in sediments and the associated pH data collected from three types of aquatic environments in the vicinity of target mining areas.

Water type	Mean	SD	Min	Med	Max	N[a]
(a) Stream water						
As (mg kg^{-1})	6.73	23.9	0.01	0.66	332	318/311
pH	6.73	0.71	3.25	6.72	8.62	318
(b) Reservoir/pools						
As (mg kg^{-1})	1.30	2.54	0.05	0.09	7.89	9
pH	6.45	0.42	5.80	6.50	7.05	9
(c) Mine waters						
As (mg kg^{-1})	253	340	12.2	253	493	2
pH	5.75	0.55	5.36	5.75	6.14	2
(d) All data						
As (mg kg^{-1})	8.11	35.9	0.01	0.67	493	329/322
pH	6.72	0.70	3.25	6.70	8.62	329

[a] N denotes the number of data; values on the left side of the slash denotes the number of measurements, while the ones on the right side denote ones after excluding below detection limit (BDL) values.

considered brackish (salinity range of 0.5–30‰: mine IDs 29 and 43). These water systems are inappropriate for irrigation (or agricultural) purposes, as there is a large potential to hamper plant populations. Hence, clearing (or removal) of their salt sources is desirable to restrict their migration into nearby soil–water systems.

3.3. Concentration of As in water systems and its environmental implications

For comparative purposes, the mine sites with excessively high water As levels were sorted out for evaluation against various guideline limits set for aqueous As levels (Table 5). In light of the fact that As can cause cancer and/or other harms to humans, the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) lowered its permissible level in drinking water to 10 μg L^{-1} ([28] and references therein). Likewise, in Korea, a guideline for both drinking water and household use is set at 50 μg L^{-1}. If the guideline of WHO and USEPA is concerned, 134 samples (12.6%) from various water systems (a total of 45 mines) exceeded this limit.

The supply of water systems with high As load can cause degradation of crop quality due to excessive As levels [29]. The As threshold level in agricultural water is set by WHO at 100 μg L^{-1} (except for rice production set at 50 μg L^{-1}) [30]. This contrasts with the guideline of KMOE for agricultural waters (50 μg L^{-1}) [19]. If one takes into consideration of the guidelines for rice production recommended by both WHO and KMOE (50 μg L^{-1}), 43 water samples (23 SW, 14 MW, 4 GW, and 2 RP) taken from 19 mines were above such criterion. Moreover, 21 water samples (11 SW, 9 MW, and 1 RP) from 9 mines exceeded WHO's limit for agricultural soils (100 mg L^{-1}). Note that this guideline is identical to those set for industrial waters in Korea. Hence, these waters are unsuitable for both agricultural and industrial purposes. Because small reservoirs are utilized for the irrigation of agricultural fields, RP in mine site 18 is unlikely to be suitable for agricultural purposes. If our As water data are compared with less rigid guideline of KMOE for wastewater (500 μg L^{-1}), there remains a single site (mine ID 18) that exceeds such criterion. Consequently, policy makers and land use planners should consider the significance of As contamination in these mine sites to

Table 7
Results of the Pearson correlation (ρ) analysis: comparison of significantly correlated cases.

Matching pairs	ρ	p-value	n
(A) Soil parameters			
(1) All soil data			
Soil As vs. distance	−0.0343	1.2E−02	5407
Soil As vs. soil pH	−0.0575	2.3E−05	5407
Distance vs. soil pH	0.1281	3.2E−21	5407
(2) Soil data grouped according to depth: surface and subsurface			
Surface soil As vs. distance	−0.0365	1.3E−02	4617
Surface soil pH vs. distance	0.1370	8.7E−21	4617
Surface soil As vs. subsurface soil As	0.1426	5.8E−05	789
Surface soil As vs. surface soil pH	−0.0707	1.5E−06	4617
(3) Tailing samples			
Soil As vs. soil pH	−0.3187	5.6E−03	74
(4) Mean data from control soils (CS) and target soils (TS) for each mine site			
pH CS vs. pH TS	0.4105	2.2E−05	100
(B) Water parameters (no significant correlation between water As and water parameters)			
(C) As in soil, tailings, water, and sediment for each mine site			
As in tailing vs. As in TS	0.8998	3.5E−18	48
As in TS vs. As in sediments	0.3694	2.0E−04	97

Table A1
Basic information of the 100 selected abandoned mining areas in this research.

Mine ID	Province[a]	City	Mine's name	Mineral(s) mined	Longitude	Latitude
1	GG	Gapyeong-gun	Myeongbo (Buyeong)	Au	127:23:11	37:43:34
2	GG	Gapyeong-gun	Jeil (Yongseok-jeil)	Au	127:24:19	37:45:35
3	GG	Yangpyeong-si	Geumgye	Au, Ag, Cu, Pb, Zn	127:46:02	37:27:52
4	GG	Yangpyeong-si	Geumdong	Au, Ag, Cu, Pb, Zn	127:40:42	37:24:55
5	GG	Yangpyeong-si	Yangdong	Au	127:44:49	37:28:58
6	GG	Yangpyeong-si	Hwanggeo	Au	127:43:38	37:28:12
7	GG	Yeoju-gun	Yeosu, Samjeong, Palbo	Au, Ag	127:29:15	37:24:55
8	GG	Yongin-si	Dokseong	Au	127:18:07	37:10:05
9	GG	Pocheon-si	Geumdong, Chilsung	Au	127:08:29	37:55:44
10	GG	Incheon-si	Dong	Au, Ag, Cu, Pb, Zn	126:21:53	37:31:57
11	GW	Wonju-si	Sinrim, Seokgwang	Ag	128:05:36	37:14:40
12	GW	Hongcheon-gun	Seokdam	Au, Ag, Cu, Pb	127:34:10	37:41:13
13	GW	Hongcheon-gun	Jinheung-heungcheon	Au	128:00:47	37:52:08
14	GW	Hongcheon-gun	Hwajeon-daemyeong	Au, Ag	127:44:00	37:36:45
15	GW	Jeongsun-gun	Deokil, Dongbok (Cheonpo)	Au, Ag	128:47:46	37:20:45
16	CN	Boryeong-si	Pyeongchon	Alluvial gold	126:34:18	36:27:37
17	CN	Cheonan-si	Sijang, Daejang	Au, Ag	127:14:12	36:53:19
18	CN	Cheonan-si	Daeheung	Au, Ag	127:13:19	36:52:41
19	CN	Cheonan-si	Daeheung1	Au, Ag	127:13:43	36:51:43
20	CN	Cheonan-si	Mangwang	Au, Ag	127:14:56	36:51:20
21	CN	Cheonan-si	Ilbo	Au, Ag	127:15:35	36:54:07
22	CN	Yesan-gun	Daeduk	Au	126:52:42	36:35:16
23	CN	Cheongyang-gun	Gubong (Geumbong, Sayang)	Au, Ag, Cu, Pb, Zn	126:45:39	36:24:17
24	CN	Cheongyang-gun	Mangwolsan, Cheongyang	Au, Ag	126:51:46	36:20:21
25	CN	Cheongyang-gun	Samchang	Au, Ag	126:54:39	36:22:59
26	CN	Hongseong-gun	Gyeolseong	Au, Ag	126:30:43	36:32:22
27	CN	Hongseong-gun	Sindong	Au	126:44:05	36:30:29
28	CN	Hongseong-gun	Wolrim	Au	126:39:49	36:31:50
29	CN	Hongseong-gun	Hongseong-geumsan	Au	126:42:09	36:31:28
30	CB	Jecheon-si	Wolak (Jangpung, Manjang)	Au, Ag, Pb, Zn	128:08:57	36:52:46
31	CB	Jecheon-si	Seogok, Daeyang (Yeongseong)	W	128:10:46	36:58:26
32	CB	Jecheon-si	Gukchang	Au, Cu, Zn	128:10:40	36:59:48
33	CB	Jecheon-si	Danjemori	Mo	128:13:21	36:58:09
34	CB	Jecheon-si	Boksu	Au, Ag, Cu, Pb, Zn	128:12:05	36:57:09
35	CB	Jecheon-si	Jeokduk	Fe	128:09:19	37:03:31
36	CB	Jecheon-si	Hwangseok	Fe	128:08:21	37:02:19
37	CB	Cheongju-si	Cheongju	Au, Ag	127:31:43	36:38:28
38	CB	Danyang-gun	Danyangcheol	Fe	128:15:58	36:58:03
39	CB	Danyang-gun	Yujin	Au	127:14:04	37:01:48
40	CB	Goesan-gun	Manjang	Cu	127:58:57	36:48:03
41	CB	Jincheon-gun	Geumam	Au, Ag	127:22:45	36:49:07
42	GN	Geochang-gun	Ssangbong	Au, Ag	127:51:27	35:52:13
43	GN	Gosung-gun	Daeduk	Pb, Cu	128:16:48	34:54:46
44	GN	Gimhae-si	Gimhae (Samdeok)	Fe	128:56:38.0	35:15:26.0
45	GN	Gimhae-si	Geumrim	Au, Ag, bronze, Zn	128:50:03.7	35:20:36.8
46	GN	Namhae-gun	Changsun (Nogu, Namheung)	Cu, Pb, Zn	127:59:36	34:50:14
47	GN	Milyang-gun	Jeonggak	Bronze, Bi	128:54:32.7	35:32:47.2
48	GN	Yangsan-si	Eungok (Ingok)	Ag, bronze, Pb, Zn	128:57:47.3	35:22:10.9
49	GN	Sacheon-si	Waryong	Amethyst (SiO$_2$)	128:06:10	34:58:59
50	GN	Uiryeong-gun	Garye	Au, Ag	128:13:46.5	35:23:49.1
51	GN	Changnyeong-gun	Yongran (Taeho)	Au, Ag, bronze, Zn	128:33:54.5	35:32:58.7
52	GN	Changwon-si	Daewon	Au, Ag, bronze	128:35:24.3	35:19:20.0
53	GN	Masan-si	Yongjang	Au, Ag, bronze, Pb	128:30:04.6	35:15:41.3
54	GN	Haman-gun	Namseon	Au, Ag, bronze, Zn	128:17:56.0	35:14:20.3
55	GN	Haman-gun	Yeohang	Au, Ag, bronze, Zn	128:25:07.9	35:12:39.2
56	GN	Hapcheon-gun	Jangbang	Au	128:09:25.5	35:45:10.1
57	GN	Hapcheon-gun	Gahoe	Au, Ag, bronze, Zn	128:03:28.4	35:28:47.5
58	GN	Hapcheon-gun	Dukchon (1)	Au, Ag	128:01:34.0	35:26:09.1
59	GN	Hapcheon-gun	Dukchon (2)	Au, Ag, bronze, Pb	128:01:07.0	35:26:18.0
60	GN	Hapcheon-gun	Bong (Bongsan)	Au, Ag, bronze, Zn	127:59:44.8	35:33:54.2
61	GN	Hapcheon-gun	Yaro	Au, Ag, Pb, Zn	128:12:24.3	35:42:46.7
62	GN	Hapcheon-gun	Yongju (Gaho)	Au, Ag, bronze, Pb	128:04:25.7	35:32:51.2
63	GN	Hapcheon-gun	Yongbong	Au, Ag, bronze, Pb	128:06:45.0	35:34:35.0
64	GN	Busan-si	Busan	Fe	129:00:11.3	35:06:34.9
65	GN	Busan-si	Dongbo (Gyeongchang)	Au, Ag, bronze, Zn, W, Mo	129:00:35.0	35:10:54.9
66	GB	Ulju-gun, Ulsan-si	Ulju	Au, Ag, bronze, Zn, Fe	129:09:21.0	35:42:26.1
67	GB	Gyungju-si	Manguembong	Au, Ag, bronze	129:01:13.6	35:49:15.0
68	GB	Gyungju-si	Namgyeongsang	Bronze, iron sulfide (FeS), Au, Ag, Pb	129:03:26.4	35:43:51.9
69	GB	Gyungju-si	Seonyang	Au, Ag	129.26.4.0	35.51.55.5
70	GB	Gyungju-si	Gyeongju (Seobu, Dong)	Fe, Mn	129.26.04.8	35.51.56.5
71	GB	Mungyung-si	Mungyeong	Fe, Mn	128:08:37	36:49:44
72	GB	Mungyung-si	Daemi Mori	Fe	128:19:27	36:47:31
73	GB	Bonghwa-gun	Samyong	Au	128:55:03.2	36:52:19.5
74	GB	Bonghwa-gun	Sampung (Samdong)	Au, Ag	128:55:41.3	36:51:44.7

Table A1 (*Continued*)

Mine ID	Province[a]	City	Mine's name	Mineral(s) mined	Longitude	Latitude
75	GB	Bonghwa-gun	Dadeok3	Au	128:50:26	36:53:49
76	GB	Bonghwa-gun	Nakguk	Au	128:53:40	36:53:18
77	GB	Bonghwa-gun	Geumdangyeon	Au, Ag, Pb, Zn	128:49:40	37:02:30
78	GB	Bonghwa-gun	Gakhui (Geumjeong1)	Au, Ag, Pb	128:49:23	37:04:11
79	GB	Bonghwa-gun	Gakhui (Geumjeong2)	Au, Ag, Pb	128:47:53	37:02:54
80	GB	Bonghwa-gun	Gakhui (Geumjeong3)	Au, Ag, Pb	128:47:14	37:02:55
81	GB	Sangju-si	Gongsung	Au, Ag, Cu, Pb	128.01.53.7	36.20.14.5
82	GB	Sangju-si	Sangju, Daeneung, Daeyu	Au, Ag	128.12.58.7	36.22.40.12
83	GB	Sunsan-gun	Okbong	Au, Ag	128.15.45.9	36.19.22.8
84	GB	Andong-si	Andong, Sundaek	Pb, Zn, Fe	128:53:08	36:24:48
85	GB	Yeongduk-gun	Daenam	Fe	129:23:56.2	36:39:36.7
86	GB	Yeongduk-gun	Yeongduk, Sambo (Seojeom A,B)	Mn	129.17.16.4	36.22.07.2
87	GB	Yeongduk-gun	Munmyeong	Au, Ag	129:18:39.5	36:25:11.0
88	GB	Yeongduk-gun	Chilbo, Eunjeom	Au, Ag, Cu, Pb, Zn	127:07:41.9	36:48:37.1
89	GB	Cheongsong-gun	Jangja	Ag, Zn, Cu, Pb	129.02.34.1	36.15.49.5
90	GB	Chilgok-gun	Gukil	Au, Ag	128.37.05.3	36.00.24.7
91	GB	Pohang-si	Duma	Au, Ag	129.01.00.1	36.10.17.9
92	GB	Pohang-si	Yucheon, Cheongha	Au, Ag, Cu, Pb, Bi	129.17.43.3	36.12.20.1
93	JN	Goheung-gun	Heungsin	Cu, Bi	127:17:55	34:35:32
94	JN	Goksung-gun	Gokseong	Au, Ag	127:20:09	35:15:02
95	JN	Yeosu-si	Bonghwang	Au, Ag, Cu, Zn, Bi	127:46:30	34:37:07
96	JN	Yeongam-gun	Eunjeok	Au, Ag	126:32:49	34:47:50
97	JB	Gimje-si	Moak	Au, Ag	127:03:28	35:44:44
98	JB	Muju-gun	Geumryeong	Au, Ag	127:45:04	35:54:25
99	JB	Muju-gun	Sechang	Au	127:40:36	35:57:03
100	JB	Jangsu-gun	Yeongdae	Au	127:23:21	35:35:35

[a] Two-letter acronyms for each province should be referred to Fig. A1 for their full name and specific geographical locations in Korea.

properly utilize the land–water resources surrounding the mine sites.

3.4. The distribution of As in the sediment layers

In Table 6, the concentration data of As in sediment samples beneath the bodies of surface water systems are summarized along with the concurrently measured pH data. The measured As levels in sediments ranged from 0.01 to 493 mg kg^{-1} with a mean of 8.11 ($n = 322$), none of which were limited by instrumental detectability. It is possible to infer that sediments affected by mine wastes or mine effluents (253 mg kg^{-1}, $n = 2$) should be significantly enriched with As relative to those from streambed (6.73 mg kg^{-1}, $n = 311$) and reservoir/pools (1.30 mg kg^{-1}, $n = 9$), as the latter types should be affected less significantly by mine wastes. Interestingly, sediment As levels affected by our mine tailings are quite comparable to those determined from surface sediments with diverse source activities (smelters, arsenical herbicides, and mine tailings: 198–3500 mg kg^{-1}) in certain locations such as New Zealand and Hawaii ([23] and references therein). Although sediment samples generally maintained near neutral pH values (a mean of 6.72), the values in MW sediments (5.75) were more acidic than those of RP (6.45) or SW (6.73). This observed pattern thus coincides with that described earlier, e.g., high As levels at low pH values. As a result, sediment fauna populations are not likely to be damaged directly by pH conditions in the sediments that are maintained near neutrality.

3.5. Correlation between As levels in soil, water, and sediments and the relevant parameters

The Pearson correlation (ρ) analysis was conducted to investigate the relationship between soil As level and the associated key variables (such as soil pH and the distance from mine sites), as shown in Table 7. For this analysis, TA samples ($n = 74$) were treated separately because of their eccentricity. Based on the correlation analysis, the following patterns are apparent: (1) As concentrations generally display an inverse correlation with dis-

tance from mine sites ($p < 0.05$), (2) soil pH shows a declining pattern with increasing As levels ($p < 0.01$), (3) soil pH tends to rise with increasing distance from mine sites ($p < 0.01$), (4) As in surface soils is positively correlated with its subsurface counterpart ($p < 0.01$), and (5) the mean pH values in each mine site tend to be strongly correlated between CS and TS samples ($p < 0.01$).

The observed correlation patterns indicate that As levels in soils tend to diffuse with increasing distance from the mine sites, which in turn coincides with decreasing soil acidity [31]. Hence, the relationship between these two variables appears to be bound to each other to a large extent. Maximum As levels in soil layers were typically found within close distance from mining areas (e.g., <100–200 m); consequently, such values tend to decrease with the increasing distance. In case of tailings, however, this distance effect is fairly unpredictable because of their irregular occurrence. It is not easy to explain the presence of sporadically high As values in distant locations (e.g., 4100 m from the mines), although such phenomenon is suspected to come from the transport of mine waste materials (and tailings). Moreover, as As levels are not significantly correlated between CS and TS samples, the notably enhanced As levels in TS samples are unlikely to be explained without considering the effect of previous mining activities.

When the correlation analysis was extended to cover different environmental reservoirs of As (soil, water, and sediments (Table 7)), the following relationships can be drawn based on this analysis: (1) As in TS increases in relation to As levels in tailings and (2) As levels in sediments rise with increasing As values in TS samples. However, there were no distinct relationships in As levels between soil and water or between water and sediment. Knowing that mining disperses metals and metalloids across a landscape through erosion into streams and rivers, it may be valid to hypothesize that large fractions of As leached from the TS systems must have been deposited on sediment layers through the years [32]. Although the Pearson correlation analysis was conducted to examine such possibility, it was difficult to extract direct evidence based on such analysis.
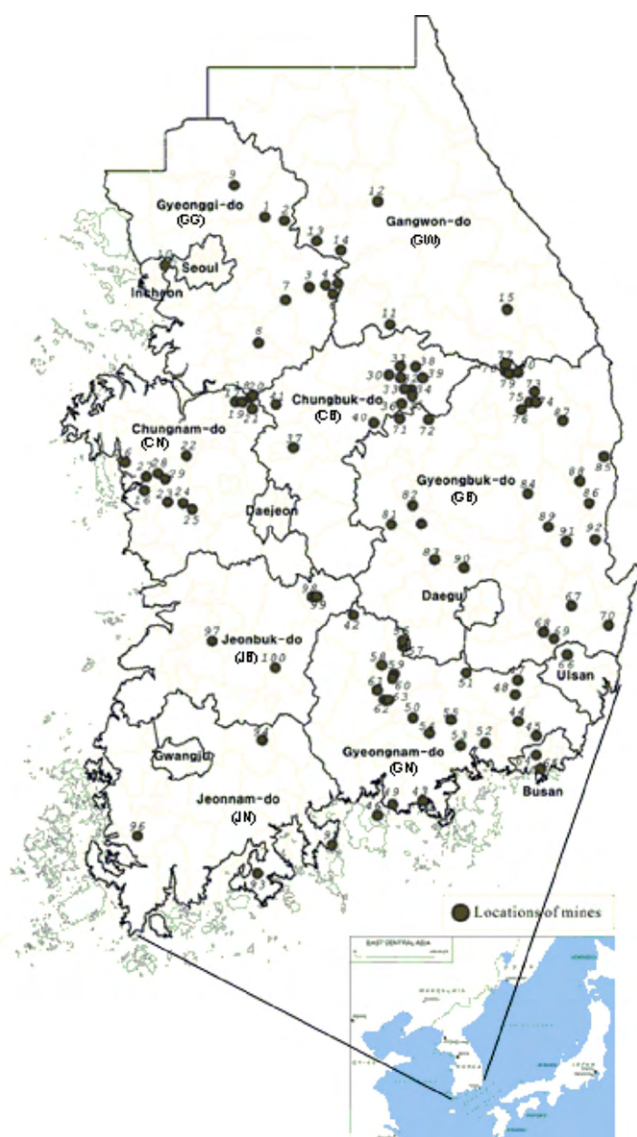
drinking water. Moreover, water bodies of 21 (21%) mines are not suitable for rice production and other agricultural use.

According to our study, most of our study sites need an immediate remedy, i.e., removal of tailings/mine wastes from soil surfaces and from near water systems. Soil-topping method appears to be an effective strategy to treat much of the excess As on the subsurface soil horizon by minimizing its dispersal. Liming was also beneficial in raising pH levels to a more desirable, neutral range for the protection of plant populations. The suitability of current land use types in areas exceeding various guidelines should be further assessed, as such considerations should be properly reflected in both present and future land use planning and area developments. It is also desirable to consider tightening the maximum permissible level of As in drinking water (e.g., $10\,\mu g\,L^{-1}$ in Korea) in accordance with a more strict guideline (e.g., WHO or US EPA) as protective measure. Proper evaluation of the water resources affected by mining activities should also be made on a routine basis to learn more about the pollution level of toxic pollutants (including As) and various important water parameters (prior to actual usage). Consequently, future efforts on abandoned mines should be directed to account for the mechanism of As dispersal across various ecosystems along with the simultaneous collection of quantitative information, i.e., the contents of As in various environmental reservoirs.

Acknowledgements

Appendix A.

Table A1 and Fig. A1.

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Fig. A1. Location of 100 mining sites investigated in this study. Refer to Table A1 for specific site information.

4. Conclusion

A comprehensive field monitoring study was conducted to measure As contamination in relation with abandoned mine sites or mine waste materials. The results of our study indicate great implications on As dispersal in the surrounding soil and water systems. Soil As levels increased significantly in TS relative to CS in both surface and subsurface soil horizons, suggesting widespread contamination of As via mining activities. The observed increase in As concentrations in soils can lead to the reduction of pH levels, as manifested by the inverse relationship between these two factors. Note that such relationship is also observed between distance and As levels. The application of soil-topping method is found to be successful in trapping much of the As on the subsurface soil layers and in reducing As levels in the surface soils. Liming treatment also increased pH levels to near neutrality. This finding suggests that agricultural activities in the study areas should be safe, as there is low risk of As contamination in crop plants or endangering plant life due to soil acidity. Nonetheless, comparison of our As data in water system with a number of As guideline limits indicate that water bodies from as many as 50 mines (50%) are not suitable for

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