Article

Chemical Properties of Heavy Metal-Contaminated Soils from a Korean Military Shooting Range: Evaluation of Pb Sources Using Pb Isotope Ratios

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Abstract: In this study, the geochemical properties of heavy metal-contaminated soils from a Korean military shooting range were analyzed. The chemical behavior of heavy metals was determined by analyzing the soil pH, heavy metal concentration, mineral composition, and Pb isotopes. In total, 24 soil samples were collected from a Korean military shooting range. The soil samples consist of quartz, albite, microcline, muscovite/illite, kaolinite, chlorite, and calcite. Lead minerals, such as hydrocerussite and anglesite, which are indicative of a transformation into secondary mineral phases, were not observed. All soils were strongly contaminated with Pb with minor concentrations of Cu, Ni, Cd, and Zn. Arsenic was rarely detected. The obtained results are indicated that the soils from the shooting range are contaminated with heavy metals and have evidences of different degree of anthropogenic Pb sources. This study is crucial for the evaluation of heavy metal-contaminated soils in shooting ranges and their environmental effect as well as for the establishment of management strategies for the mitigation of environmental risks.

Keywords: heavy metal; shooting range; contaminated soil; lead concentration; lead isotope; Korean military shooting range

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1. Introduction

Heavy metals (e.g., Pb, Cd, Cu, As, Sn, and Sb) are indicative of soil toxicity. They are potential sources of soil contamination and their mobility and availability affect the environment. In the previous studies, the effects of heavy metals on the environment, terrestrial biota, and human health were studied [1,2]. Heavy metals are transported via surface water and groundwater [3,4] and affect the surrounding area. Soils from military shooting ranges have attracted attention because they are contaminated with high concentrations of heavy metals [1,3], which do not decompose but remain in the environment [4]. Soil contamination in military shooting ranges has been investigated in numerous previous studies [1,3,5–11].

Ammunition, such as lead shots or lead bullets, is a source of the Pb pollution and soil toxicity in military shooting areas [5]. Bullets mainly consist of metallic lead (90%) and minor amounts of other heavy metals [6,12]. Lead is accumulated in the soil via the abrasion and weathering of the bullets [7]. After Pb bullets are fired, they come in contact with the soil and eventually are weathered. Fragmented and pulverized bullets lead to the Pb contamination of the soil [13]. Metallic Pb is converted into dissolved (soluble particle) and particulate Pb by oxidation, carbonation, and hydration reactions [6] and transported to the soil [14]. Dissolved and particulate Pb species are primarily incorporated into mineral phases such as cerussite (PbCO₃), hydrocerussite [Pb(CO₃)₂(OH)₂], anglesite (PbSO₄), and

massicot/plattnerite (PbO) [15]. The physicochemical conditions of the soil control the weathering and mobility of the contaminants [2]. Therefore, the physicochemical properties of heavy metal-contaminated soil from shooting ranges and the heavy metal distribution must be determined to effectively manage and restore the soil [2].

Worldwide, thousands of shooting ranges are utilized for recreational activities and military training [2]. Soils from shooting ranges that have been operated for many years are generally heavily contaminated [5]. In the United States, more than 3 million mg of metallic Pb were associated with hunting and recreational shooting in the 20th century; the Pb concentration is continuously increasing at a rate of ~60,000 mg per year [12,14–18]. In soils in the Netherlands, Denmark, Canada, and England, 200 to 6000 mg of metallic Pb has been detected [14]. In addition, it has been reported that metallic lead bullets in soils in Denmark can be preserved for 100–300 years [14]. In central Sweden, on average, 5% of metallic Pb in shooting range soil has been transformed into lead carbonate and lead sulfate over a period of 20 to 25 years [19]. In addition, 3400 to 5000 mg/kg of Pb has been reported in skeet shooting ranges in northern England and central Sweden [17,19]. However, heavy metal contaminated soils in shooting ranges have been rarely studied due to the limited accessibility [3]. In addition, the environmental effects of soil contamination are poorly understood and mitigation methods have yet to be established. In the Republic of Korea, 1400 active small arms firing ranges are in operation [20], but little information is available about the effects of heavy metals from Pb bullets on the soil in military shooting ranges [21].

To evaluate the Pb contamination of soil, the Pb distribution has been commonly analyzed in previous studies [3,19,22–24]. The Pb concentrations and Pb isotopic compositions of the bullets, pellets, and soils have rarely been considered [6,10,11,25,26]. Therefore, the aims of this study were to understand spatial distribution of Pb contamination and to quantify the Pb input in soils from Korean military shooting ranges using both Pb concentration and Pb isotopic data, which are considered to be powerful indicators of the soil contamination in shooting ranges as well as the Pb sources.

2. Materials and Methods

2.1. Study Area and Sampling Site

Soil samples from a shooting range in the Gyeonggi-do Province, South Korea, which has been operated by the Korean military for training for many years, were chosen for this study because of the considerable Pb bullet weathering and preservation. The shooting range consists of eight firing lanes. The sampling locations are shown in Figure 1. Soil was also collected from the drainage ditch in the vicinity of the first shooting lane because it may be a migration pathway for heavy metals. For comparison, soil samples were collected from an off-target shooting range site, which are referred to as background soils. Background soils are not affected by Pb contamination. In total, 24 soil samples were collected from the beaten zones of the third and sixth lanes, drainage ditch, and background including targets at the 100, 200, and 250 m transects. The distance between the third and sixth lanes was 24 m, as indicated in Figure 1b. Samples were collected from surface (0–10 cm), subsurface (10–30 cm), and deeper (30–50 cm) soils (Figure 1).

Figure 1. (a) Geological map of the Korean military shooting range in South Korea. (b) Specific soil sampling locations in the third (A, C, E) and sixth (B, D, F) shooting lanes. (c) Altitude profile of studied shooting range [22].

2.2. Analytical Methods

The elemental concentrations of Cu, Ni, As, Cd, Pb, and Zn were determined at the Korea Military Academy using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Shelton, CT, USA). Powdered samples (3 g) were dissolved in a 1:3 mixture of HNO_3 to HCl. A reflux condenser and absorption container were attached to the mixture container and 15 mL of HNO_3 (0.5 M) was added to the absorption container over 16 h. The extraction was carried out by slowly increasing the temperature to 120 °C while circulating the coolant and heating it for 2 h at 120 °C. The temperature was then slowly lowered for 1 h to stop the coolant circulation. Subsequently, 10 mL of 0.5/L HNO_3 was poured into the absorption container and allowed to flow. Samples from the mixture container were filtered into a 100 mL volumetric flask using Whatman No. 40 filter paper. The flask was then filled to the marked line using 0.5 M HNO_3 . The samples were analyzed using ICP-OES. If the concentration exceeded the calibration range, the samples were diluted and reanalyzed to determine the exact concentration. The average values of three measurements were reported as results. The chemical properties of the soils are shown in Table 1.

The Pb isotope analyses were carried out on 15 samples at Activation Laboratories Ltd. (ActLabs, Ancaster, ON, Canada) using high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The Pb isotope ratios were calibrated using the USGS SRM BCR-2. The $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are presented in Table 2. The Pb isotope values were calibrated using the common lead NIST standard 981.

Table 1. The total Cu, Ni, As, Cd, Pb, and Zn concentration (ppm) and pH in soils of shooting ranges.

Soil	Distance from Firing Line (m)	Depth (cm)	pH	Cu	Ni	As	Cd	Pb	Zn
6th shooting range	250	0	8.78	1,073	27	0	27	28,040	267
		5–15	8.80	927	10	0	10	24,043	170
		15–30	8.77	463	10	0	7	19,763	63
	200	0	8.03	200	10	0	3	5127	0
		5–15	8.30	183	13	0	3	4147	0
		15–30	8.48	9	2	5	0	185	0
	100	0	8.02	400	7	13	7	11,137	0
		5–15	8.52	193	13	7	7	5297	0
		15–30	8.64	217	13	3	3	4293	0
3rd shooting range	250	0	8.94	643	10	0	3	20,030	90
		5–15	8.80	580	10	0	3	13,987	137
		15–30	8.76	623	10	0	3	17,303	60
	200	0	7.50	273	13	13	13	6203	0
		5–15	8.62	273	13	0	3	5313	0
		15–30	8.67	210	13	0	3	7557	0
	100	0	8.30	650	7	3	3	13,043	0
		5–15	8.52	533	7	0	3	11,093	10
		15–30	8.48	413	10	0	3	8140	3
Drain ditch	100	0	7.95	377	10	0	3	5417	3
		5–15	8.28	493	10	0	3	6977	23
		15–30	8.62	573	7	0	3	8740	63
Background	0	0	6.09	3	6	0	2	14	46
		5–15	6.04	3	5	0	2	21	45
		15–30	6.03	5	8	1	2	33	44

Table 2. The Pb isotope ratio of soils of 6th shooting lane with drain ditch and background.

Soil	Distance from Firing Line (m)	Depth (cm)	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb
6th shooting range	250	0	38.77	15.69	18.53	1.18	2.47
		5–15	38.21	15.45	18.26	1.18	2.47
		15–30	38.96	15.65	18.50	1.18	2.49
	200	0	38.09	15.53	18.46	1.19	2.45
		5–15	38.22	15.53	18.63	1.20	2.46
		15–30	39.08	15.77	18.62	1.18	2.48
	100	0	38.90	15.88	18.60	1.17	2.45
		5–15	35.98	15.11	15.14	1.00	2.38
		15–30	39.62	16.56	16.67	1.01	2.39
Drain ditch	100	0	37.97	15.53	15.77	1.02	2.44
		5–15	38.98	16.12	16.41	1.02	2.42
		15–30	38.79	16.03	16.26	1.01	2.42
Background	0	0	40.70	16.10	18.82	1.17	2.53
		5–15	38.73	15.55	18.21	1.17	2.49
		15–30	40.03	15.95	18.55	1.16	2.51

The mineralogy of selected soil samples was analyzed with X-ray diffraction (XRD). The XRD analyses were conducted at the Korea Institute of Geoscience and Mineral Resources (KIGAM) using an X'Pert MPD diffractometer (Philips, Eindhoven, The Netherlands). The X-ray patterns were obtained from 3° to 65° (2θ range) at a scan rate of 2° per minute.

The pH of the selected soils was determined following the standard method of APHA [27]. The soil samples were air-dried at room temperature, placed in a beaker

to which distilled water was added, left for 1 h while stirring occasionally with a glass rod, and read within 60 s using a calibrated pH meter (XL-20, Thermo Fisher Scientific, Fair Lawn, NJ, USA). The soil pH was measured using a suspension of 25 g of soil in 25 mL of water, that is, a soil/water ratio of 1:1.

The elements Cu, Ni, As, Cd, Pb, and Zn were mapped using an electron probe micro-analyzer (EPMA, EPMA-1600, Shimadzu, Tokyo, Japan) at the Korea Basic Science Institute (KBSI), Jeonju Center, South Korea, and a wavelength-dispersive X-ray (WDS) system.

3. Results and Discussion

3.1. Geochemical Properties of Soil

The transport and distribution of heavy metals in soil in the shooting area results in serious heavy metal contamination [24]. As mentioned above, Pb is considered to be the primary contaminant, accounting for the largest proportion of heavy metal contamination [12,14–18]. Lead is insoluble [28] and insignificantly affected by secondary effects [29]. The Pb mobility and solubility depend on the environmental conditions including the physicochemical properties of the soil, shooting range type, purpose of use, and vegetation (root exudates) [2,5,30].

In general, a large proportion of Pb in the soil from shooting ranges and their vicinity is considered to originate from Pb shots [6]. The soil physicochemical properties and distribution of heavy metals in soils from Korea military shooting ranges have been analyzed in several previous studies. Lee and Park [31] evaluated the heavy metal contamination of soils in Maehyang-ri in the Gyeonggi-do shooting range. The shooting range was operated for 50 years until 2005. The Maehyang-ri area has been contaminated with heavy metals from explosives (trinitrotoluene, TNT; hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX; and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane, HDX) associated with bombs, practice bullets, ammunition, and unexploded ammunition [31]. Lee and Park [31] compared the heavy metal concentration in Maehyang-ri with that in other shooting ranges in South Korea and identified the major heavy metal contaminants in the Maehyang-ri shooting range. Based on their research, the Cu concentration in the study area is 23 times higher than that of soils in South Korea and the Pb concentration is 1.2 times higher than the soil pollution standard [31]. Kim and Jeong [22] investigated the heavy metal concentrations and distribution in soils, plants, and water samples in the same shooting area. They reported that the heavy metal concentration is the highest near the targets and that the proportion of Pb is higher than that of other heavy metals. Based on their results, both surface and deeper soils are enriched in heavy metals because of adsorption; however, they did not evaluate the heavy metal leaching from soil by surface water [22]. Several researchers have suggested that the Pb concentrations in the surface water and plants in the shooting range are significantly affected by the Pb concentration of the soil [17,30,32].

The geochemical properties of the soils from the shooting range are presented in Table 1. The Pb concentration in the vertical soil profiles of the shooting range is heterogeneous. Figure 2 shows that the Pb concentration is high regardless of the soil depth, which is due to the discharge of bullets at all depths and diffusion/transport of Pb [11]. In some firing ranges, arsenic (As) was not detected due to its low concentration. The Pb concentrations of the surface soils from the third and sixth shooting lanes were 100 to 1000 times higher than that of the background soil, respectively. Heavy metals are generally enriched in the surface soil compared with deeper soil, indicating the preferential contamination of the surface soil and mobilization through the soil profile (Figure 2) [24]. However, in the drain ditch, the heavy metal contents were highest in the deeper soil. It can be assumed that the leaching of heavy metals from the surface soil by water at the drain ditch had occurred [24]. It seems that the heavy metal accumulation processes due to several controlling factors had occurred during the 30-year operation period of the shooting range. The total Pb concentration of soils from the shooting range determined in this study is as high as values reported in previous studies and higher than the Korean pollution standard [3]. In Korea, the standard concentration in shooting ranges is 700 ppm for Pb;

2000 ppm for Cu; 2000 ppm for Zn; 500 ppm for Ni; 200 ppm for As; and 60 ppm for Cd [22]. The Pb concentrations of soils in Cho-do and We-rye, Korea, exceeded $18,609 \pm 1202$ and 3918 ± 127 ppm, respectively [3]. Similar results were obtained for an outdoor shooting range in Michigan, which was also contaminated with heavy metals [24]. Murray et al. [24] reported that the Pb, Cu, Ni, Cd, and Zn concentrations are 10 to 100 times higher than those of the background soil. The Pb concentration in soils from shooting ranges worldwide ranges from ~10,000–70,000 mg/kg [2].

Figure 2. The Zn, Pb, Cd, As, Ni, and Cu concentration (ppm) of soils from (a,c,e) 3rd and (b,d,f) 6th shooting lane with (g) background and (h) drain ditch for each transect. The blue, green, red bars are indicative of vertical soil profiles of surface (0–10 cm), subsurface (10–30 cm), and the deeper soil (30–50 cm).

This heavy metal enrichment can also be observed in the element maps obtained by EPMA analysis. Heavy metals, such as Pb, As, Cd, Ni, and Zn, are distributed in certain

minerals (Figure 3). Based on the XRD analysis, the predominant minerals are quartz, albite, microcline, muscovite/illite, kaolinite, chlorite, and calcite (Figure 4). Note that Pb minerals were not detected in this study. It can be assumed that the heavy metals from bullets are adsorbed at the mineral surfaces.

Figure 3. Element maps for (a) BSE image, (b) Pb, (c) As, (d) Cd, (e) Ni, and (f) Zn in soils from the shooting range obtained from EPMA analysis.

Figure 4. Representative mineralogical composition of soils from the shooting range determined using X-ray diffraction (XRD).

The pH values of the soils from the third and sixth shooting lanes and drainage ditch (pH = 7.50–8.94) are higher than that of the background soil (pH = ~6.00) at most targets in all transects, except for the 250 m transect in the third shooting lane (Figure 5, Table 1). This agrees with the results of a previous study [6] based on which the pH values of contaminated soils in shooting ranges in the Czech Republic (average pH = 5.9) are higher than those of the control sample (average pH = 4.6). The higher pH of the contaminated

soil leads to the weathering of Pb bullets and transformation of metallic Pb into oxidized species [5]. During these processes, the consumption of H^+ ions within soil leads to an increase in the soil pH [6]. These pH-dependent processes control the dissolution of Pb from bullets [6].

Figure 5. Depth profile of the pH of soils from the (a) third and (b) sixth shooting lanes of the shooting range.

Lead has four isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb) and the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios can be used as indicators of different sources [33]. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is used as an indicator of anthropogenic Pb sources [6]. The Pb isotopic signatures are commonly used in environmental studies [10,11,34–38]. However, they have been rarely applied for the analysis of heavy metal contamination in soils from shooting ranges [6]. The Pb isotopes of soils from the sixth shooting lane (B, D, and F in Figure 1) were analyzed and compared with those of drainage ditch and background samples. The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of the soils from the sixth shooting lane range from 1.171 to 1.199 and from 2.381 to 2.490, respectively. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the drainage ditch and background sample are 1.014–1.018 and 1.163–1.171, respectively (Table 2). Kelepertzis et al. [35] investigated the Pb isotopes of urban soils in Athens. The $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios displayed linear trends and plotted between the two endmembers of natural (high $^{206}\text{Pb}/^{207}\text{Pb}$) and anthropogenic (low $^{206}\text{Pb}/^{207}\text{Pb}$) sources [35]. This is consistent with our results. The $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the soils analyzed in this study exhibit a negative correlation and plot between the two endmembers (Figure 6a). Their linear trend might be explained by the mixing of two different sources, which might be geological and anthropogenic materials [36,39]. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of soils from the 200 and 250 m target lines of the sixth shooting lane were almost the same, indicating a similar Pb source [11]. Those soils were strongly contaminated with Pb, and their Pb isotopic ratios are indicative of anthropogenic sources. The background soils displayed similar $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, although their Pb concentrations were significantly lower (22 ppm on average). However, the subsurface soils, the deeper soils from the 100 m transect of the

sixth shooting lane, and all soils from the drainage ditch had different $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. This is related to the different sources of Pb contamination [40]. The lower Pb isotope values might be influenced by the background and geological factors [40]. As explained above, the heavy metal concentration in the drain ditch provides evidence of the influence of water on heavy metal diffusion and transport. Therefore, it can be assumed that the relatively lower Pb isotope values are indicative of a smaller contribution from anthropogenic sources. In other words, the values might represent a mixture of anthropogenic and geological Pb sources. Because no systematic trend between the Pb concentration or pH and Pb isotope ratios was observed in this study (Figure 6b), the correlations among pH, Pb concentration, and Pb isotopes require further study. In summary, the heavy metal concentrations and Pb isotopic data demonstrate that the soils in Korean military shooting ranges are strongly contaminated with heavy metals and originate from different degree of anthropogenic sources.

Figure 6. Plots of (a) $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ and (b) $^{206}\text{Pb}/^{207}\text{Pb}$ vs. Pb (mg/kg) for soils from 6th lane of shooting range with drain ditch and background.

3.2. Mineralogical Properties of Soil

The collected soils were examined using XRD (Figure 4, Table 3) to determine the major crystalline phases or Pb minerals in the soils and to identify the transformation of Pb minerals. The predominant mineral components are quartz, albite, microcline, muscovite/illite, kaolinite, chlorite, and calcite. Carbonate is known to be one of the crucial sources for anthropogenic Pb [35]. The soils in this study generally contain calcite, representing direct evidence of anthropogenic Pb contribution. Hematite only occurs in the surface soil of the 200 m transect of the sixth shooting lane. Minerals carry toxic elements. As shown in the element maps, the minerals in the soil are enriched in Pb, Cd, Ni, and Zn. However, although the soils have high Pb concentrations, Pb minerals, such as hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), massicot (PbO), hydroxypyromorphite ($\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$), cerussite (PbCO_3), and anglesite (PbSO_4), were not detected by XRD analysis in this study. This can be explained by the gradual transformation of Pb into secondary mineral phases in soils in shooting ranges [3]. The transformation processes are pH-dependent; Pb is soluble under acidic conditions and poorly soluble under neutral and alkaline conditions. In summary, transformation products of acidic soils have a high solubility and high mobility, whereas transformation products of basic soils have a low solubility and attach to the bullet surface or remain in the surface soil [14]. For example, cerussite dissolves at low pH [41] and cerussite and/or hydrocerussite in acidic soil (pH = 4.5) easily dissolves and transforms into ionic Pb^{2+} [9]. The soils in the study area are basic; therefore, the gradual transformation into Pb secondary minerals did occur.

Table 3. The representative mineral components in shooting ranges.

Soil	Distance from Firing Line (m)	Depth (cm)	Mineral Component
6th shooting range	250	0	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite, Calcite
		5–15	Quartz, Microcline, Albite, Muscovite/Illite, Kaolinite, Chlorite, Calcite
		15–30	Quartz, Microcline, Albite, Kaolinite, Muscovite/Illite, Chlorite, Calcite
	200	0	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite, Hematite
		5–15	Quartz, Microcline, Albite, Kaolinite, Muscovite/Illite, Chlorite, Calcite
		15–30	Quartz, Muscovite/Illite, Albite, Microcline, Kaolinite, Chlorite, Calcite
	100	0	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite
		5–15	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite
		15–30	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite, Calcite, Hematite
Drain ditch	100	0	Quartz, Microcline, Albite, Muscovite/Illite, Kaolinite, Chlorite, Calcite
		5–15	Quartz, Muscovite/Illite, Albite Microcline, Kaolinite, Chlorite, Calcite
		15–30	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite
Background	0	0	Quartz, Albite, Microcline, Muscovite/Illite, Kaolinite, Chlorite
		5–15	Quartz, Microcline, Albite, Muscovite/Illite, Kaolinite, Chlorite
		15–30	Quartz, Microcline, Albite, Muscovite/Illite, Kaolinite, Chlorite

3.3. Potential Pb Contamination

Shooting ranges are considered to be crucial sources of soil contamination with Pb [6]. In shooting ranges, Pb from bullets is accumulated and can be transferred into the soil as a major pollutant [12,14–18]. Soil contamination in the target area and its vicinity can result in serious environmental risks to groundwater, surface water, and plants [5,16]. Three migration pathways of Pb ammunition into the environment have been identified: (1) ingestion of bullets by wildlife and subsequent poisoning; (2) contamination of groundwater and wells; and (3) contamination of nearby aquatic ecosystems [42]. The mobility of water-soluble and exchangeable metals affects ecosystems [3]. The contamination of soils in shooting ranges and their vicinity represent an environmental hazard. Hence, contaminated soil must be managed to protect the environment [6].

4. Conclusions

In this study, the heavy metal (Cu, Ni, As, Cd, Pb, and Zn) contamination of soils in a Korean military shooting range was investigated by analyzing the heavy metal concentrations, pH, mineral composition, and Pb isotopes. The results demonstrate that Pb plays a critical role in the contamination of soils in the shooting range and its vicinity. The soils are characterized by high concentrations of Pb, which are representative heavy metal contaminants. The results suggest that heavy metals adhere to mineral surfaces. The soils are basic and composed of quartz, albite, microcline, muscovite/illite, kaolinite, chlorite, and calcite. Lead minerals were not observed in the soils because Pb was not transformed into secondary mineral phases. In addition, the Pb isotopic data are indicative of different

degree of anthropogenic Pb sources. Therefore, it is necessary to investigate soils from shooting ranges to evaluate their environmental effects and develop some management strategies for the mitigation of Pb contamination in shooting ranges.

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