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Feasibility of a Chemical Washing Method for Treating Soil Enriched with Fluorine Derived from Mica

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Abstract: High levels of fluorine in soil may pose health risks and require remediation. In this study, the feasibility of using a practical chemical washing method for the removal of fluorine from an enriched soil was evaluated. The chemical washing procedures were optimized through experimental analyses of various washing solutions and washing conditions (i.e., washing solution concentration, solid–liquid ratio, agitation speed, and reaction time). Additionally, the effects of techniques for improving the washing efficiency, such as ultrasonic washing, aeration, and multi-stage washing, were evaluated. Herein, among all applied methodologies, the maximum washing efficiency achieved for the total fluorine present in soil was only 6.2%, which indicated that chemical washing was inefficient in remediating this particular soil. Further sequential extraction analysis showed that the fluorine in this soil was present in a chemically stable form (residual fraction), possibly because of the presence of mica minerals. It was demonstrated that chemical washing may not be effective for remediating soils containing such chemically stable forms of fluorine. In these cases, other physical-based remediation technologies or risk management approaches may be more suitable.

Keywords: natural fluorine-enriched soil; natural sources; soil remediation; chemical extraction resistance; low washing efficiency

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1. Introduction

Fluorine, an element with atomic number 9, has high electronegativity and thus can readily react with other elements, such as Fe, Al, and Ca. Therefore, fluorine mostly exists as compounds in the natural state, and it is difficult to find fluorine in natural settings as a single element [1,2]. Human activities (e.g., fertilizer use, coal use, and aluminum and steel industrial activities) have resulted in the accumulation of fluorine in soil. Coal combustion releases hydrogen fluoride (HF), silicon tetrafluoride (SiF_4), and carbon tetrafluoride (CF_4), which can be accumulated in the soil environment [3,4]. Moreover, fluorine levels in soil can be elevated by fluorine-containing rocks (natural origin) [5,6]. Studies have shown that fluorine-containing mica, fluorite (CaF_2), and apatite can contribute to the accumulation of fluorine in soil and groundwater through weathering [5–12].

High intake of fluorine is known to cause dental fluorosis, skeletal fluorosis, and osteoporosis [13–15]. The World Health Organization (WHO) [16] has reported that the intake and inhalation of fluorine may cause cancer, such as osteosarcomas and bone tumors. Therefore, the concentration of fluorine in soil must be properly managed.

Chemical washing has been widely used as a treatment method for soil contaminated with metals and metalloids [17–24]. The chemical washing process can be implemented within a short period of time compared to solidification and stabilization technologies, and this means that it may be possible to reuse the site quickly. For soil contaminated with

As, Cd, Cu, Cr, Pb, and Zn, removal efficiencies between 56% and 100% were achieved with various washing solutions such as HCl, ethylenediaminetetraacetic acid (EDTA), phosphoric acid, sulfuric acid, and $FeCl_3$ (Table 1). Chemical washing with 3 M HCl was also performed on fluorine-contaminated soil near a chemical plant, and a removal efficiency of 97% was observed [17]. The application of the chemical washing technique to treat natural fluorine-enriched soil has not been previously studied.

Table 1. Chemical washing conditions and efficiencies for the metals, metalloids, and fluorine-contaminated soils reported in previous studies.

Soil	**Contaminant**	**Concentration (mg/kg)**	**Washing Conditions**		**Removal Efficiency (%)**	**Reference**
			Washing Agents	**Washing Conditions**		
Erie County, N.Y. (pH 5.5)	Pb	500–600	0.1 N HCl, 0.01 M EDTA, 1 M $CaCl_2$	900 g soil, acrylic column (upflow 10 mL/min, 24 h)	HCl—85 EDTA—100 $CaCl_2$—78	[19]
Lavrion Technology and Cultural Park (LTCP)—mine, refinery, industrial park (pH 7.0)	Fe Pb Zn As Mn Cu	223,600 64,195 55,900 7540 6500 4100	1 M HCl, 0.1 M Na_2EDTA	Soil/solution = 30 g/L, 150 rpm, 4 h for 1 M HCl, 1 h for 0.1 M Na_2EDTA	HCl Na_2EDTA 45 14 44 44 82 38 77 13 80 42 61 41	[20]
Ibaraki of Kuroboku, Japan—forest area soil (pH 5.94)	As	2830	9.4% H_3PO_4, 11% H_2SO_4	1 g soil: 25 mL solution, 20 °C, 2 h	H_3PO_4—97.9 H_2SO_4—87.7	[21]
Construction site in University Park, TX (pH 7.9)	Pb Cd Zn	742 603 624	0.01 M Na_2EDTA + 0.1 M $Na_2S_2O_5$	1 g soil: 12.5 mL solution, Shaker table operated at 175 rpm for 2 h	56.1 92.3 71.0	[22]
Burnley campus garden at Melbourne University, Australia (pH 6.14)	Pb Cd Cr	200 400 600	0.5 M $FeCl_3$	Shaker table operated at 180 rpm for 1 h	93.8 97.4 81.8	[23]
Fluoride contaminated soil from a chemical company in Changwon, Gyeongsangnam-do, Korea (pH 3.7)	F	740	3 M HCl 2 M NaOH 3 M HNO_3 3 M H_2SO_4 3 M $C_4H_6O_6$	5 g soil: 50 mL solution, Shaking incubator at 200 rpm, 20 °C for 1 h	97 71 91 88 64	[17]
Abandoned metallurgic plant located in Wubu, an old city district of Anhui Province, China (pH 6.7)	PAH Pb Cd Cr Ni F	352.8 839.7 23.7 622.4 432.8 2376.5	carboxymethyl-β-cyclodextrin (CMCD) carboxymethyl chitosan (CMC)	50 g/L CMCD + 5 g/L CMC solution Shaking at 100 rpm, 25 °C for 60 min and centrifugation at 1000 rpm for 30 min, multi-stage washing (3 cycle)	94.3 93.2 85.8 93.4 83.2 97.3	[24]
Fluorine-contaminated soil from Incheon City, South Korea (pH 6.4), No source information provided	F	488	1 M HNO_3 1 M H_2SO_4 1 M NaOH 2 M H_2SO_4	30 g soil: 270 mL solution, Shaking at 25 °C for 30 min	19.5 26.7 10.2 40.1	[25]

In this study, the feasibility of using a chemical washing method to remediate natural fluorine-enriched soil was evaluated. The soil at the target site requires specialized treatment because the fluorine concentration exceeds the soil contamination criterion of South Korea (Area 2: 400 mg/kg, "Area 2" refers to locations containing forests, warehouse sites, etc.) [18], and treatment needs to be completed within a relatively short period of time because the site is located in an urban area. The applicability of various washing solutions and washing conditions (i.e., washing solution concentration, solid–liquid ratio, agitation speed, and reaction time), which have been used previously for chemical washing of heavy metal-contaminated soil, was examined. In addition, the effects of techniques for improving the washing efficiency, such as ultrasonic washing, aeration, and multi-stage washing, were evaluated. X-ray diffraction (XRD) analysis and sequential extraction were performed on the target sample to obtain a better understanding of the nature of fluorine within the soil.

2. Materials and Methods

2.1. Soil Preparation and the Determination of Its Characteristics

In this study, natural fluorine-enriched soil was collected from Seoul (latitude: 37°29′23″, longitude: 127°00′03″), a mega city. Topsoil with a depth of 30 cm or less was collected, air-dried at room temperature, and sifted through a 2-mm sieve; then, the pH, organic matter content (Walkley–Black method), cation exchange capacity (ammonium acetate method), and iron/aluminum/manganese oxide content (dithionite–citrate system buffered with sodium bicarbonate (DCB) method) of the soil were measured [26–29]. Additionally, pellets with a diameter of 34 mm (prepared by compressing soil samples to enable X-ray analysis on a flat surface) were fabricated and subjected to X-ray fluorescence analysis (S8 Tiger, Bruker, Billerica, MA, USA) under vacuum conditions at an output of 40 mA and 40 V. Based on these data, the main components (Si, Al, Fe, Ca, Na, K, Mg, Ti, P, and S) of the soil samples were determined. The types of crystalline minerals in the soil samples were identified through XRD analysis (D8 ADVANCE, Bruker, Billerica, MA, USA). This analysis was conducted with a 2theta range of 3–90°, step of 0.02, scan speed of 0.5 s/step, and wavelength of Cu kα1 = 1.5418 Å at a generator output of 40 kV and 40 mA.

Meanwhile, wet sieving was also performed for soil samples of 2 mm or less to analyze the fluorine concentration by particle size. The sizes of the sieves used were 0.5, 0.15, and 0.075 mm, and the composition ratio was calculated by measuring the dry weight after sieving.

Finally, mica, which was estimated to be the main fluorine-containing mineral in the target soil, was manually collected from the gravel (>2 mm). Then, it was pulverized and the fluorine content was measured using the alkali fusion method described in Section 2.3.

2.2. Chemical Washing Procedures for Natural Fluorine-Enriched Soil

To determine optimal conditions for the chemical washing method used on the natural fluorine-enriched soil, experiments were performed by varying the washing solution type, washing solution concentration, ratio between the soil sample and the washing solution (g:mL), agitation speed, and reaction time. Furthermore, changes in washing efficiency due to aeration, ultrasonic irradiation, and multi-stage washing were also evaluated. First, to determine the optimal washing solution, 1 M solutions of sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH), oxalic acid ($H_2C_2O_4$), nitric acid (HNO_3), perchloric acid ($HClO_4$), and hydrochloric acid (HCl) were mixed with the soil samples at a solid–liquid ratio of 1:5 (g:mL), and the amount of fluorine eluted was evaluated after a reaction time of 60 min at an agitation speed of 200 rpm. Washing experiments were performed while the washing solution concentration was varied from 1 to 2 and 2.5 M, solid–liquid ratio (g:mL) from 1:2 to 1:3 and 1:5, agitation speed from 100 to 150 and 200 rpm, and reaction time from 10 to 30, 60, 120, and 240 min. In addition, the amount of fluorine eluted was evaluated after aeration and ultrasonic irradiation for 10, 30, and 60 min and two to four cycles of multi-stage (repeated) washing. After chemical washing experiments were carried out under each condition, solid–liquid separation was performed using a 0.45-µm Gelman hydrophilic polypropylene (GHP) syringe filter (Pall, Port Washington, NY, USA). The fluorine concentration in the filtrate was then measured using a fluoride ion electrode (F001502, ISTEK, Seoul, Korea) after mixing the filtrate with total ionic strength adjustment buffer (TISAB) at a 1:1 ratio. The washing efficiency was calculated as the ratio of the fluorine concentration in the washing solution (i.e., the filtrate) (unit: mg/kg) to the total fluorine concentration in soil (unit: mg/kg).

2.3. Determination of the Total Fluorine Concentration in Soil

The alkali fusion method was used to measure the total fluorine concentration in soil [30]. For this procedure, 0.5 g of the dried soil sample was placed in a nickel crucible, and 6 mL of 16 M NaOH was injected. The crucible was placed in a dryer at 150 °C for 1 h and then in a furnace at 300 °C. The temperature was increased to 600 °C, and the reaction was allowed to proceed for 30 min. Approximately 10 mL of distilled water was then added to the residue in the nickel crucible, and the pH was adjusted between 8 and 9 with concentrated HCl. After transferring the sample to a volumetric flask and adding distilled water to reach 100 mL, the solution was filtered through Whatman No. 40 filter paper. After mixing the filtrate and TISAB at a ratio of 1:1, the concentration of fluoride ions in the filtrate was measured using the fluoride ion electrode, and these data were used to determine the fluorine concentration in soil.

Furthermore, the accuracy of the method for analyzing the fluorine concentration in soil was assessed using GSP-2 and NIM-G, which are certified reference materials (CRMs). The fluorine content was 3000 mg-F/kg-soil for GSP-2 and 4200 mg-F/kg-soil for NIM-G.

2.4. Sequential Extraction Procedures for Fluorine in Soil

Sequential extraction was performed to understand the binding pattern between soil components and fluorine. Fluorine was divided into a water-soluble fraction (F1), exchangeable fraction (F2), Mn and Fe oxide bound fraction (F3), organic matter bound fraction (F4), and residual fraction (F5) (Table 2). In step 1, 2.5 g of the dried soil sample and 25 mL of the extractant were mixed [31,32]. After centrifugation, the precipitates and 25 mL of each extractant were mixed in steps 2 to 4. For the analysis in step 5, the alkali fusion method described in Section 2.3 was used. For the separation of the extractant and the soil sample, centrifugation (1580R, Labogene, Seoul, Korea) was performed for 15 min at 2357 *g* [33].

Table 2. Sequential extraction procedures for fluorine-enriched soil (following Yi et al. [32] with some modifications).

Fraction of Fluorine in Soil	Extractant	Experimental Conditions		
		Temperature (°C)	**Incubation time (h)**	**Agitation speed (rpm)**
Water soluble (F1)	Deionized water	70	0.5	30–40 [a]
Exchangeable (F2)	1 mol/L $MgCl_2$ (pH 7)	25	1	
Bound to Mn and Fe oxides (F3)	0.04 mol/L $NH_2OH{\cdot}HCl$ dissolved in 20% acetic acid	60	1	
Bound to organic matter (F4)	0.02 mol/L HNO_3 + 30% H_2O_2 + 3.2 mol/L and ammonium acetate [b]	25	0.5	
Residual (F5)	Alkali fusion with NaOH	600	1.5	None

[a] Cited from Davison et al. [34]. [b] 0.02 M HNO_3 3 mL + 30% H_2O_2 10 mL and ammonium acetate 12 mL [35].

3. Results

3.1. Characteristics of Fluorine-Natural Enriched Soil

Table 3 shows the fluorine concentration for various soil particle sizes. The properties of the natural fluorine-enriched soil used in this study are presented in Tables A1 and A2. The total fluorine concentration in the soil samples (<2 mm) was found to be 1078 ± 178 mg/kg, which exceeds the soil contamination criterion of Korea (Area 2: 400 mg/kg) [25]. Thus, these data confirmed that an appropriate remediation technique was required for this natural fluorine-enriched soil. The soil sample with a particle size of 0.15 mm or less exhibited 1.5 times higher fluorine concentration than the total soil sample (i.e., particle size of 2 mm or less). Because pollutants introduced to soil from external sources are easily adsorbed on the surface of silt or clay particles with a large specific surface area, the concentration of heavy metals increases as the particle size of soil decreases [36,37]. Despite the above finding, the distribution of fluorine concentrations was relatively homogeneous in this study (i.e., no significant differences were observed for the different soil particle sizes). This indicated that the pollutants adsorbed on soil particles were not introduced from the outside but were possibly of natural origin (from minerals).

Table 3. Particle size distribution of the soil sample and the corresponding total fluorine concentrations.

Particle Size (mm)	Weight Composition (%)	Total Fluorine Concentration (mg/kg)
<2	100	1078 ± 178
0.5–2	26.3	1126 ± 272
0.15–0.5	26.8	1036 ± 34
0.075–0.15	10.2	1564 ± 159
<0.075	36.7	1594 ± 42

3.2. Chemical Washing Efficiency

The soil samples were mixed with 1 M solutions of H_2SO_4, H_3PO_4, NaOH, KOH, $H_2C_2O_4$, HNO_3, $HClO_4$, and HCl at a solid–liquid ratio of 1:5 (g:mL). For each mixture, the reaction was allowed to proceed for 1 h at an agitation speed of 200 rpm, but the washing efficiency remained as low as 0.6–3.0% (Table 4).

Table 4. Chemical washing efficiencies when using various washing solutions.

Washing Reagent (1 M)	Extracted Fluorine Concentration (mg/kg)	Washing Efficiency (%)
H_2SO_4	16.2 ± 1.5	1.5
H_3PO_4	6.8 ± 0.6	0.6
NaOH	20.3 ± 1.9	1.9
KOH	20.2 ± 1.9	1.9
$H_2C_2O_4$	6.2 ± 0.6	0.6
HNO_3	30.3 ± 2.8	2.8
$HClO_4$	27.2 ± 2.5	2.5
HCl	32.7 ± 3.0	3.0

To improve the washing efficiency, various conditions (i.e., washing solution fixed to HCl, washing solution concentration (1–2.5 M), solid–liquid ratio (1:2–1:5), agitation speed (100–200 rpm), reaction time (10–240 min), aeration (10–60 min), ultrasonic washing (10–60 min), and multi-stage washing (1–4 times)) were tested. The washing efficiency, however, did not exceed 6.2% (Table 5).

According to a previous study [17], a 97% removal efficiency was achieved when chemical washing was performed for 1 h under conditions of 200 rpm and 20 °C at a solid–liquid ratio of 1:5 (g:mL) using 3 M HCl (Table 1); these results are markedly different from the results of this study.

3.3. Origin of Fluorine in Soil

To analyze the causes of the significantly low washing efficiency obtained in this research, even though chemical washing conditions similar to those applied in previous research on soil contaminated with heavy metals and fluorine of an artificial origin were maintained (Table 1), XRD analysis and sequential extraction were performed on the target sample.

Table 5. Chemical washing efficiencies when applying various washing conditions.

Washing Conditions		Extracted Fluorine Concentration (mg/kg)	Washing Efficiency (%)
Solid–liquid ratio (g:mL)	1:2	18.2 ± 1.1	1.7
	1:3	24.4 ± 1.8	2.3
	1:5	32.8 ± 1.1	3.0
Reaction time (min)	10	58.7 ± 2.5	5.4
	30	36.8 ± 0.6	3.4
	60	32.8 ± 1.1	3.0
	120	30.3 ± 1.6	2.8
	240	24.9 ± 0.0	2.3
Agitation speed (rpm)	100	34.5 ± 0.3	3.2
	150	36.6 ± 0.9	3.4
	200	58.7 ± 2.5	5.4
Concentration of HCl (mol/L)	0	1.5 ± 0.0	0.1
	1	32.8 ± 1.1	3.0
	2	26.8 ± 0.2	2.5
	2.5	24.8 ± 1.8	2.3
Aeration time (min)	10	49.6 ± 4.1	4.6
	30	62.3 ± 0.3	5.8
	60	66.7 ± 5.3	6.2
Ultrasonicating time (min)	10	37.7 ± 0.3	3.5
	30	43.4 ± 0.7	4.0
	60	41.9 ± 0.7	3.9
Multi-stage washing (cycle)	1	35.3 ± 2.1	3.3
	2	14.3 ± 1.1	1.3
	3	6.1 ± 0.3	0.6
	4	2.8 ± 0.4	0.3

3.3.1. X-Ray Diffraction Analysis

Figure 1 shows the XRD analysis results. Peaks of biotite, phlogopite, muscovite, and lepidolite, which belong to mica, were detected in the soil sample data. It is known that mica can contain fluorine as a result of the substitution of hydroxide ions (OH^-) and fluoride ions (F^-) [4–11]. Based on the XRD analysis results, gravel-sized fragments rich in mica were manually collected from the > 2 mm sifted soil sample in which a large amount of mica was detected. Then, the mineral samples obtained were pulverized and subjected to fluorine concentration analysis and XRD analysis.

The XRD analysis results for the minerals that were estimated to be mica exhibited peaks of biotite, phlogopite, lepidolite, and muscovite (Figure 1) that were more prominent than those in the above results [38,39], and a fluorine concentration of 2647 mg/kg was measured (the fluorine concentration in the soil sample with a size of 2 mm or less from the same soil was 1078 mg/kg). This finding indicated that fluorine was possibly present in the soil sample (with a size of 2 mm or less) as result of the fragmentation of mica minerals.

3.3.2. Sequential Extraction Results

Table 6 shows the fluorine sequential extraction results for the target soil sample. The residual fraction (F5) amounted to 99.2–99.6%, thus confirming that most of the fluorine was present in soil in a chemically stable form. When the sample, obtained by manually collecting mica minerals with a size of 2 mm or higher and pulverizing them, was subjected to fluorine sequential extraction using the same method, the residual fraction (F5) was found to be 99.8%, which was similar to the value obtained for the soil sample.

As confirmed in Section 3.3.1, the target soil sample represents a case in which fluorine of a natural origin (mica) is present and has accumulated above the soil environmental criterion. In such a case, fluorine is present in a chemically stable form because it exists as minerals. This appears to have contributed to the significantly low efficiencies for the chemical washing procedures tested.

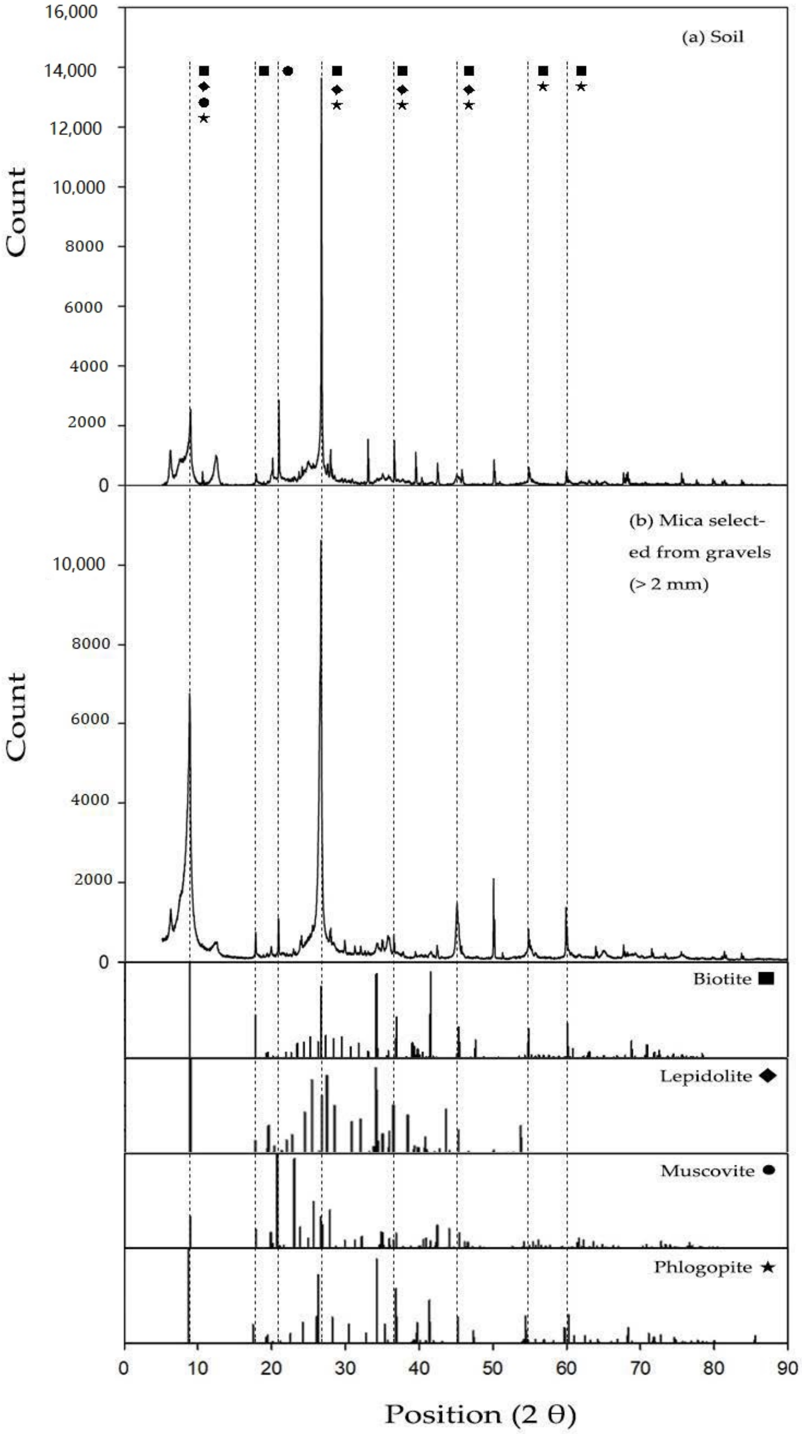

Figure 1. X-ray diffraction analysis results for (**a**) the soil sample and (**b**) mica selected manually from the gravel (>2 mm).

Table 6. Sequential extraction results for the soil sample and mica selected from gravel.

Fraction of Fluorine in Soil	**Soil Sample (<2 mm)**		**Sample of Crushed Mica Selected by Hand from Gravel (>2 mm)**	
	Extracted Fluorine Concentration (mg/kg)	**Extraction Efficiency (%)**	**Extracted Fluorine Concentration (mg/kg)**	**Extraction Efficiency (%)**
Water soluble (F1)	7.19 ± 0.17	0.57	2.31 ± 0.01	0.09
Exchangeable (F2)	0.58 ± 0.04	0.05	0.34 ± 0.34	0.01
Bound to Mn and Fe oxides (F3)	0.09 ± 0.01	0.01	0.08 ± 0.01	0.00
Bound to organic matter (F4)	1.99 ± 0.30	0.16	1.86 ± 0.12	0.07
Residual fraction (F5)	1253 ± 85	99.21	2647 ± 11.55	99.84

4. Conclusions

In this study, the applicability of chemical washing was evaluated for the treatment of a soil containing high levels of fluorine that originated from mica. This soil exceeded the soil environmental criterion for the region. Various conditions (washing solution type, washing solution concentration, solid–liquid ratio, agitation speed, reaction time, aeration, ultrasonic washing, and multi-stage washing), similar to those of the general washing method for soil contaminated with heavy metals and the washing method previously applied to soil contaminated with fluorine of an artificial origin (near a chemical plant, where a 97% washing efficiency was achieved) [17], were tested; however, from all methodologies applied, the maximum washing efficiency achieved in our study for natural fluorine-enriched soil was 6.2%. The sequential extraction results showed that approximately 99% of the fluorine was present as a residual fraction, thus indicating that it occurred in the soil in a chemically stable form, possibly because of the presence of the fragmented mica minerals. This may have contributed to the low washing efficiency. Consequently, treating this soil enriched with fluorine of a natural origin (mica) using general chemical washing methods is not feasible. Therefore, it is recommended that physical separation technology be applied or other approaches be used to manage potential human health and/or ecological risks.

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Data Availability Statement: Data is contained within the article and Appendix A.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Composition of the major elements in the soil samples determined using an X-ray fluorescence spectrometer.

Major Element	Composition (%)
SiO_2	52.85
Al_2O_3	24.63
Fe_2O_3	11.03
K_2O	4.25
MgO	2.41
TiO_2	1.85
CaO	1.55
Na_2O	0.44
P_2O_5	0.43
SO_3	0.14

Table A2. Characteristics of the soil samples used in this study.

pH	Organic Matter Content (%)	CEC (cmol/kg)	Fe Oxides (mg/kg)	Al Oxides (mg/kg)	Mn Oxides (mg/kg)
7.4	0.6	11.8	26,655	2584	374

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