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Research Article

Distribution of Available Silicon of Volcanic Ash Soils in Jeju Island

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In soils, dissolved silicon (Si) is adsorbed onto soil particles or is leached into groundwater through the soil profile. Andisols may play an important role in contributing to high dissolved Si concentrations in groundwater on Jeju Island, Korea. In this study, we evaluated the available Si content that potentially affects groundwater composition and investigated the relationship between the available Si content and chemical properties of volcanic ash soil on Jeju Island. We used the 1 M sodium acetate buffer (pH 4.0) to extract the available Si. Selected chemical properties were determined for 290 topsoil samples collected from different land sites throughout Jeju Island, and we analyzed the available Si content in the typifying pedons of Jeju Island and mainland Korea. The available Si content in Jeju Island topsoils ranged from 75 to 150 $mg \cdot kg^{-1}$, and the available Si content of Andisols in both orchards and grasslands was significantly higher than that of non-Andisols. The available Si content was highly correlated with the amounts of oxalate extractable Si, Al, and Fe in Andisols and was negatively related to the Al_p/Al_o ratio. With increasing elevation, we detected a decrease in the available Si and allophane content in Andisols, whereas Al-humus complexes increased with increasing elevation. The ratio of available Si in the lowest subsoil/topsoil increased to a value of 6.0, indicating that large amounts of available Si are present in the subsoil. The available Si content in the lowest subsoil of Andisols on Jeju Island was 10 times higher than that in the typifying pedons of the Korean mainland. In contrast, there were no differences in the available Si content between the topsoil and the subsoil of the typifying pedon series of Jeju and mainland non-Andisols because of differences in pedogenic processes. Collectively, our findings indicate that weathering of Andisols on Jeju Island potentially affects the Si concentration in groundwater.

1. Introduction

Jeju Island (latitude of 33°06′–34°00′ and longitude of 126°08′–126°58′) is located 450 km south of Seoul, the capital of South Korea. It is the largest volcanic island in South Korea (75 × 32 km) [1]. The volcanic activities of Jeju Island have progressed from 1.88 Ma to the Holocene. The island was formed from accumulated layers of lava flows and pyroclastic materials that erupted from polygenetic composite volcanoes around the body of Mount Hallasan and more than 360 monogenetic volcanoes [2–4]. The main parent material of the soils of Jeju Island is basalt, whereas some of the soils originated from trachyte and trachytic andesite [5].

The climate of Jeju Island is a mild oceanic climate, with an annual average temperature of 15°C. There is almost no difference in temperature between the eastern and western areas of the island, although with each 100 m increase in elevation, there is decrease in the average annual temperature of 0.6–0.8°C [6, 7]. The annual average precipitations of Seongsan on the eastern coast and Seogwipo in the southern coast are 1,967 mm and 1,923 mm, respectively, which are higher by 420–830 mm than the 1,143 mm and 1,498 mm received at Gosan on the western coast and Jeju on the northern coast, respectively [8]. Furthermore, with each 100 m increase in elevation, the annual average precipitation increases by 100–250 mm and the annual average precipitation on Mount Hallasan is over 4,000 mm [7].

Silicon (Si) is dissolved as monosilicic acid (H_4SiO_4) by mineral weathering [9]. The dissolved Si in soils is absorbed by plants and the leached Si is transported by rivers to the sea. However, Jeju Island does not have permanent streams or rivers because of the high permeability of the soils and rocks (basalt and trachyte) [3, 4]. Thus, the dissolved Si is readily leached into the groundwater through the pyroclastic materials. The median value of Si concentration in the groundwater of Jeju Island is 33.6 mg SiO_2 L^{-1} (maximum 63 mg SiO_2 L^{-1}), which is 1.8 times higher than the median value of 19.2 mg SiO_2 L^{-1} of bottled mineral water produced on the Korean mainland [10, 11]. High concentrations of Si in water, together with high concentrations of calcium and potassium, are considered to improve taste and have certain health benefits [12]. On Jeju Island, most of the drinking water is supplied from groundwater sources [4, 7], in which Si accounts for more than 80% of the constituents considered to contribute to its desirable taste [10]. Many researchers have reported that Si in drinking water not only is effective in preventing Alzheimer's disease by suppressing the absorption of aluminum in the body but also has antiarteriosclerosis effect, enhances bone formation, and reduces cholesterol [13–17]. Therefore, it is important to determine the source of Si flowing into the groundwater on Jeju Island.

Although the soils of Jeju Island are originated from basalt-based volcanic eruptions, the characteristics of the soil can vary depending on the climate, vegetation, topography, and generation age [18]. Approximately 80% of the soils on Jeju Island are Andisols. Along the western and northern coasts and in mid-mountainous areas on Jeju Island where there is relatively little precipitation, the soils are mainly of a non-Andisol type [19]. The main components of the Andisols are allophane and Al-humus complexes, whereas the main mineral comprising non-Andisol is silicate clays [20, 21].

Volcanic ash soils are characterized by a high solubility of Si, Al, and Fe, which is attributable to the rapid weathering of pyroclastic materials. Under a mild wet climate with abundant organic sources, Al initially combines with organic matter to form Al-humus complexes, which increases the dissolved Si concentration in the soil solution. Dissolved Si forms or leaches opaline silica, which combines with polymerized Al to form allophones [22, 23]. Dissolved Si that does not form allophanes with silicate clay minerals persists in weakly bonded complexes in soils or will be transported to groundwater by the downward movement of rainwater.

According to Park [24], who performed fractional quantification of Si in the soils of Jeju Island using the Si sequential extraction method developed by Georgiadis et al. [25], Andisols contain a low proportion of Si in primary and secondary minerals but significantly higher proportions of Si comprising allophane, which is a poorly crystalline aluminosilicate, adsorbed Si, and soluble Si, compared with non-Andisol soils and soils on the Korean mainland. This tendency is more conspicuous in Andisols in areas characterized by high precipitation. Given that Andisols contain a high content or proportion of soluble Si or Si that can readily be solubilized, it is expected that soluble Si will be continuously leached in the future, thereby increasing the Si content in groundwater.

The Si adsorbed by soils is available Si, as it occurs in a soluble and exchangeable form that can be used by plants [26, 27]. As a critical element for plants, the availability of Si in paddy field soils is regularly analyzed and managed. In contrast, there are currently no analytical data relating to the available Si in the soils of Jeju Island. However, in the volcanic ash soils in upland areas of Japan [28] and forest soils in the Philippines [29], which originated from pyroclastic materials similar to the parent materials of Jeju Island soils, the available Si content has been found to be 150 mg·kg^{-1} or higher, which is higher than the content in soils originating from granite.

In this study, we sought to determine the factors contributing to the high Si content in the groundwater of Jeju Island. To this end, we collected 290 topsoil samples from upland, orchard, grassland, and forest sites on Jeju Island and examined the distribution patterns of available Si. In addition, using layer-by-layer samples, we compared the distribution characteristics of available Si in a 191 soil series of representative soils from the Korean mainland and a 27 soil series of representative soils from Jeju Island.

2. Materials and Methods

2.1. Soil Sampling. Topsoil (0–20 cm) samples were collected at 290 sites on Jeju Island (Figure 1). The sampling sites included 195 sites on cultivated land (144 samples of upland soils and 51 samples of citrus orchard soils) and 95 sites on uncultivated lands (75 samples of grassland soils and 20 samples of forestland soils). The samples were divided into Andisols and non-Andisols. Given that areas with Andisols account for more than 80% of Jeju Island, the number of Andisol samples was correspondingly larger than that of non-Andisol samples. We did not collect non-Andisols in forested areas as there are few examples of non-Andisols in these areas, which are located at high elevations on Jeju Island. The collected soils were air-dried and passed through 2-mm sieves prior to being used for analysis. To compare and analyze the layer-by-layer available Si content of representative soil series from Jeju Island and the Korean mainland, we prepared 20 soil series for Andisols and seven for non-Andisols (four for Mollisols and three for Alfisols) from the Jeju Island soils. For the Korean mainland soils, we prepared 34 soil series for Alfisols, 26 for Entisols, 97 for Inceptisols, and 34 for Ultisols. Thus, in total, we analyzed available Si from the layer-by-layer samples of 219 soil series, which represent more than 50% of the total 405 soil series of South Korea [18].

2.2. Soil Analysis. The silicate content that can potentially be readily transported to groundwater reserves in the soils of Jeju Island was evaluated in terms of the available Si in soils that can be used by plants, using the 1 N sodium acetate buffer extraction method. The available Si content was analyzed by extracting 5 g of soil with a 1 N sodium acetate (pH 4.0) buffer solution, and subsequently measuring the

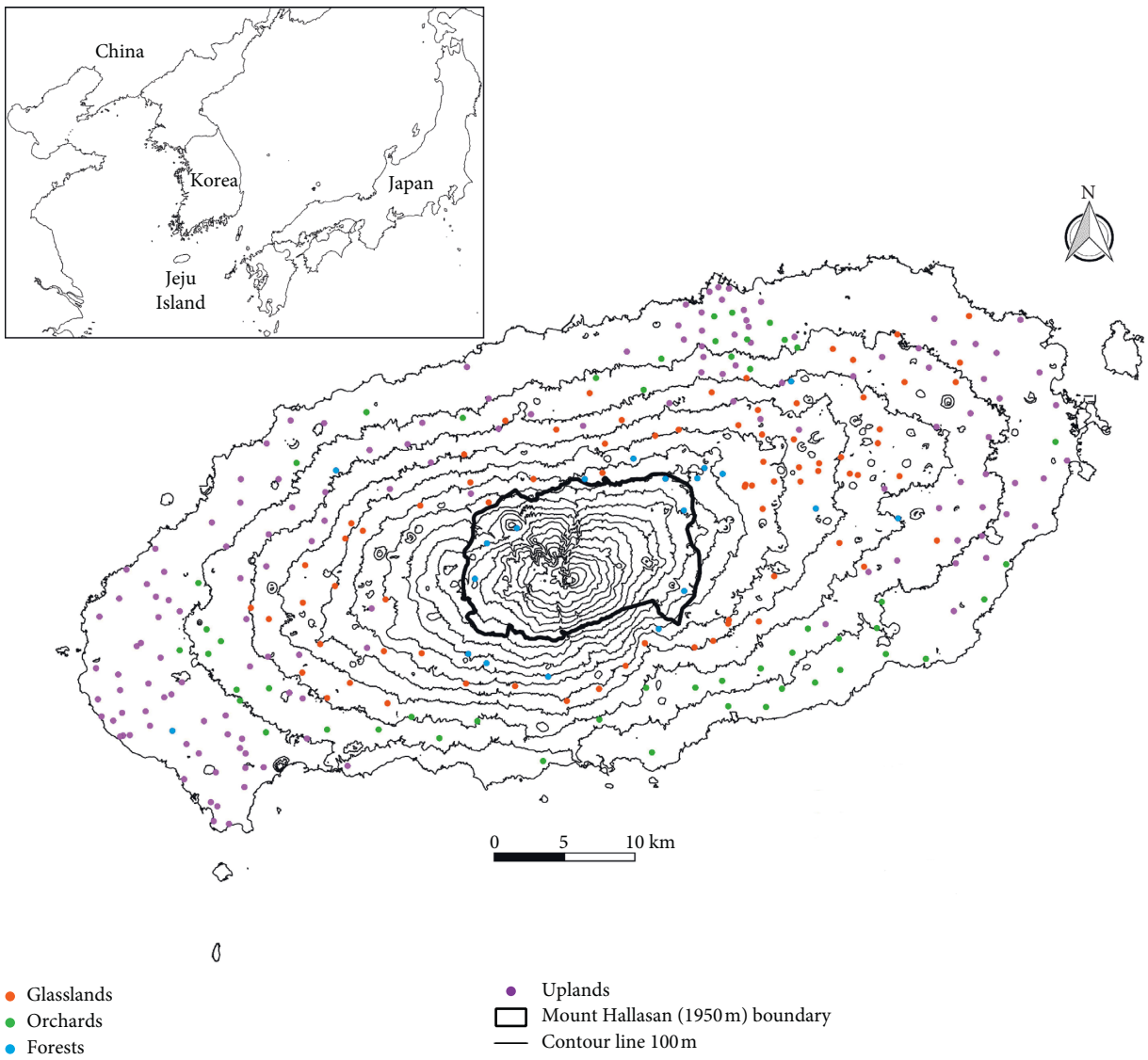

Figure 1: Soil sampling locations on Jeju Island.

absorbance of the leachate at 700 nm using a Lambda 25 UV/V is spectrometer (PerkinElmer, USA) [27].

Soil chemical analysis was performed to evaluate the correlation between the available Si content in soil and chemical properties. Soil pH was measured using an Orion Star A211 pH meter (Thermo Scientific, UK) after mixing the soil with distilled water at a 1 : 5 ratio and then shaking. The organic matter content was analyzed using the Walkley and Black method. Exchangeable cations were analyzed using the 1 M ammonium acetate (pH 7.0) method [27]. Determinations of sodium fluoride (NaF) pH and retained phosphate, and selective extraction were performed in accordance with the Soil Survey Laboratory Methods Manual [30]. For NaF pH, 50 mL of 1 N NaF solution was added to 1 g of soil and the sample was stirred with a pH electrode. The pH was measured after exactly 2 min. For the determination of retained phosphate, 25 mL of 1,000 mg·L^{-1} P solution was added to 5 g of soil, shaken for 24 h, and centrifuged. The P content of the supernatant was quantified using a Lambda 25 UV/Vis spectrometer (PerkinElmer, USA) and the amount adsorbed by soil was represented as a percentage. Al (Al_p) and Fe (Fe_p), which form complexes with organic matter, were extracted for 16 h using a 0.1 M sodium pyrophosphate solution (pH 10). The Si (Si_o), Al (Al_o), and Fe (Fe_o), which comprise Al (Fe)-humus complexes, the amorphous hydroxides of Al and Fe, and allophane and ferrihydrite, were extracted using a 0.2 M ammonium oxalate solution (pH 3.0) for 4 hours in the dark. All the extraction solutions were centrifuged, and having diluted filtrate solution with distilled water, measurements were performed using inductively coupled plasma optical emission spectroscopy (JY 138 Ultrace, Jobin Yvon). The allophane content was calculated using the following equation: $100 \times Si_o/\{-5.1[(Al_o - Al_p)/Si_o] + 23.4\}$ [31].

2.3. Data Analysis. As the results for the available Si content and Andic soil properties did not show normal distribution,

we analyzed the data using nonparametric methods. Differences in the available Si content in Andisols and non-Andisols according to land use were compared using the Mann–Whitney *U* test. Kruskal–Wallis one-way ANOVA of ranked data was performed for the available Si content according to elevation above sea level. For post hoc analysis of elevation-related differences, the data were converted to rank variables and the statistical significance was determined using Tukey's HSD test. Correlations between the available Si content and the major properties of the selected volcanic ash soils were evaluated using Spearman's rank correlation coefficient. All statistical analyses were performed using SPSS 18.0 (SPSS Inc. Chicago, USA) at the $p < 0.05$ level of significance.

3. Results and Discussion

3.1. Available Si Content in the Soils of Jeju Island. Figure 2 shows the frequency and regional distributions of the available Si content in 290 topsoil samples collected from volcanic ash soils on Jeju Island. The average and range of the available Si content were 149 mg·kg^{-1} and 28.6–720 mg·kg^{-1}, respectively. When the distribution was examined by dividing the available Si content by 25 mg·kg^{-1}, we found that 46% of all soils were distributed within the range of 75–150 mg·kg^{-1} (Figure 2(a)). When the available Si content was analyzed according to the region, the western and eastern coast areas showed values that were on average 325 mg·kg^{-1} higher than those in other areas (Figure 2(b)). Soils under garlic cultivation in the west and under radish cultivation in the east showed particularly high available Si content. We suspect that these high levels are attributable to the use of silicate fertilizer, which contains available silicate (25%) and alkali powder (40%) and is used as an effective corrector of soil pH [32–34]. Among the study soils, the pH of soils under garlic and radish cultivation with high available Si content ranged from 6.6 to 7.8, which is higher than that of citrus orchard, grassland, and forest soils (data not shown). Previously, it has been demonstrated that the average available Si content in paddy field soils collected from 2,070 sites in Korea (excluding Jeju Island) was 68.2 mg·kg^{-1} [34], whereas the average available Si content in upland soils under melon cultivation in the Gyeongsangbuk-do region of Korea was found to be 96.7 mg·kg^{-1} [35], which are lower than the available Si content in the soils of Jeju Island. However, Yanai et al. [28] reported that the average available Si content in the upland soils of Japan is 148 mg·kg^{-1}, which is similar to the volcanic ash soils of Jeju Island. The available Si content in soils originating from basalt and volcanic ash has been shown to be higher than that in soils originating from granite, quartz porphyry, and peat [36]. Similarly, Klotzbücher et al. [29] reported that soils in the Philippines originating from andesitic-basaltic lavas and pyroclastics formed by volcanic activities had higher available Si content than Vietnamese soils that developed from granite, gneiss, schist, sandstone, and limestone.

Figure 3 shows a comparison of the available Si content of soils according to land use and elevation above sea level after classifying the study soils into Andisols [37] and non-Andisols based on values of NaF pH above 9.4 and values of $Al_o + 1/2Fe_o$ higher than 2%, which are extracted by 0.2 M ammonium oxalate (pH 3.0). When samples were compared according to land use, we found that the available Si content was the highest in the upland Andisols and non-Andisols, and that the difference between these two soils was not statistically significant. This similarity can again be explained by the fact that silicate fertilizers are applied to some upland soils, resulting in a very high available Si content. In contrast, however, we found that Andisols collected from citrus orchards ($p = 0.016$) and grasslands ($p = 0.002$) contained significantly higher available Si content than non-Andisols (Figure 3(a)). These differences appear to be related to differences in soil properties that emerge as soils develop into Andisols or non-Andisols during the weathering process rather than due to soil pH management.

Given that we suspected the application of silicate fertilizers in some upland soils, we excluded upland soils from the data analysis. Thus, we only compared the available Si content in orchard, grassland, and forest soils classified according to elevation (Figure 3(b)). We accordingly found that the available Si content of Andisols increased with an increase in elevation up to 600 m, but tended to decrease at higher elevations. The highest content of available Si (150 mg·kg^{-1}) was measured within an elevation range of 200–400 m. In contrast, the available Si content of non-Andisols ranged from 62.4 to 69.2 mg·kg^{-1} and showed no elevation-related differences (Figure 3(b)).

3.2. Relationships between Available Si Content and Selected Chemical Properties of Soils. Table 1 shows the correlation coefficients between the available Si content and selected chemical properties of soils. The available Si content for all 290 topsoil samples showed positive correlations with pH, exchangeable Ca and Mg, Si_o, Al_o, Fe_o, $Al_o + 1/2Fe_o$, and allophane ($p < 0.01$) and a negative correlation with the Al_p/Al_o ratio. Furthermore, we found that the correlation coefficients between the available Si content and pH for cultivated soils were higher than those for uncultivated soils.

For uncultivated soils, the available Si content showed no obvious correlation with exchangeable Ca and Mg, whereas for other factors, correlations in uncultivated soils tended to be higher than those recorded for cultivated soils, which appear to associate with the use of silicate fertilizers and are not directly related to the properties of cultivated soils.

Most uncultivated soils are Andisols with Andic properties, and in these soils, the available Si content showed high correlations with Si_o, Al_o, and Fe_o. These observations are consistent with the findings of studies conducted by Makabe et al. [38] and Yanai et al. [28], who found that the available Si content is correlated with the oxides and hydroxides of Al and Fe and amorphous minerals such as allophane and imogolite. Furthermore, we found that the available Si content in Andisols showed an increasing tendency as the Al_p/Al_o ratio decreased or the allophane content increased. Moreover, we observed that with increasing elevation, Al-humus complexes become

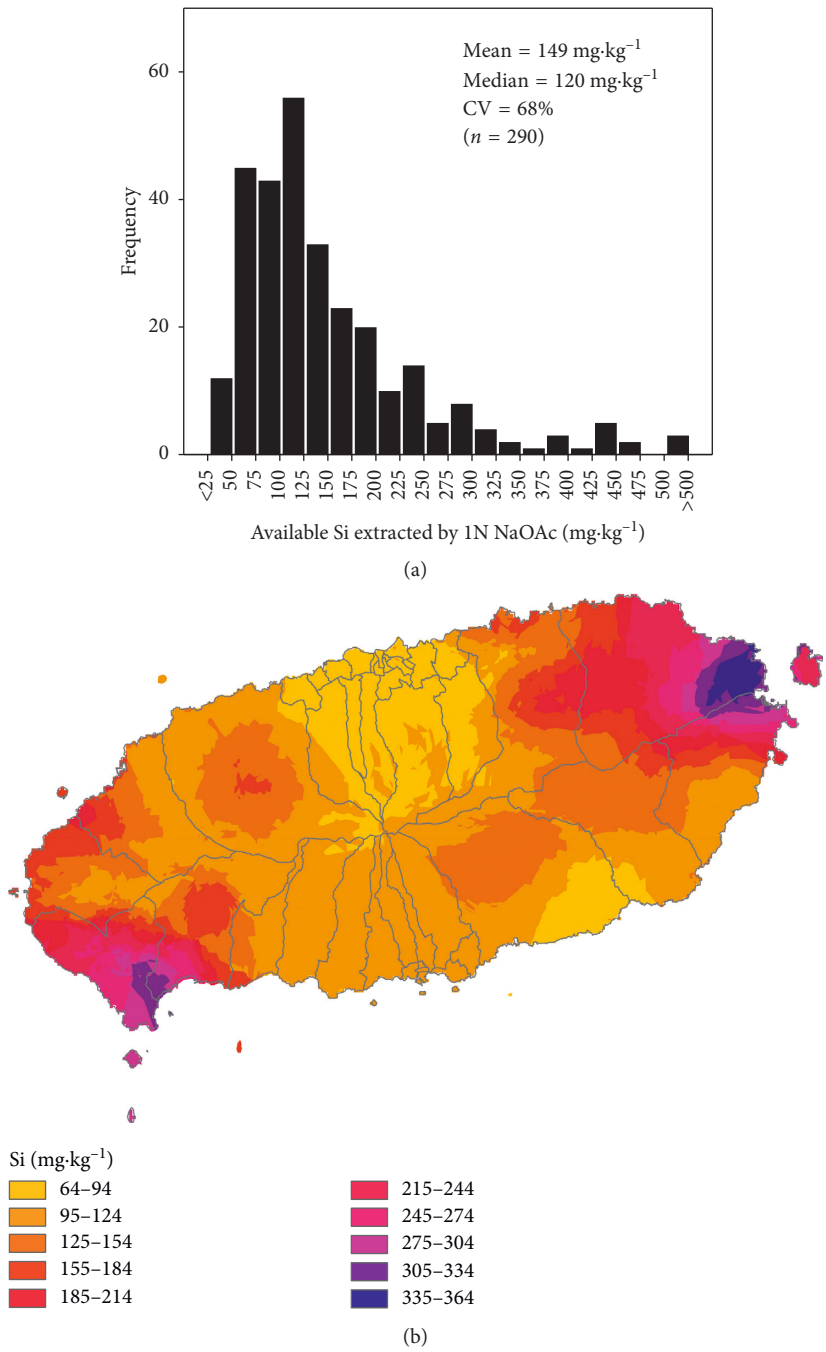

Figure 2: Frequency (a) and regional distribution (b) of available Si in topsoils on Jeju Island extracted using 1 N sodium acetate buffer (NaOAc) solution.

dominant and the allophane content decreases. As Al initially bonds with organic matter, the amount of Al that becomes bonded to Si decreases, resulting in large quantities of Si in the topsoils. However, with an increase in elevation, there is a concomitant increase precipitation. Thus, it is conceivable that large quantities of dissolved Si are leached from soils in upland areas, resulting in a decrease in the content of available Si, as shown in Figure 3(b). Accordingly, we assume that the available Si content will be high in the deep layers of these upland soils.

3.3. Comparison of the Available Si Content of Typifying Pedons according to Elevation. The typifying pedons of Jeju Island were divided into Andisols and non-Andisols, and the available Si content was compared with respect to elevation (Table 2). At elevations less than 400 m, the available Si content in the A layer of Andisols ranged from 97.4 to 459 mg·kg^{-1} and tended to decrease in the range of 77.2 to 146 mg·kg^{-1} at elevations greater than 400 m. As the soil depth increased, the available Si content tended to increase. At elevations of 335 m or higher, the available Si content in

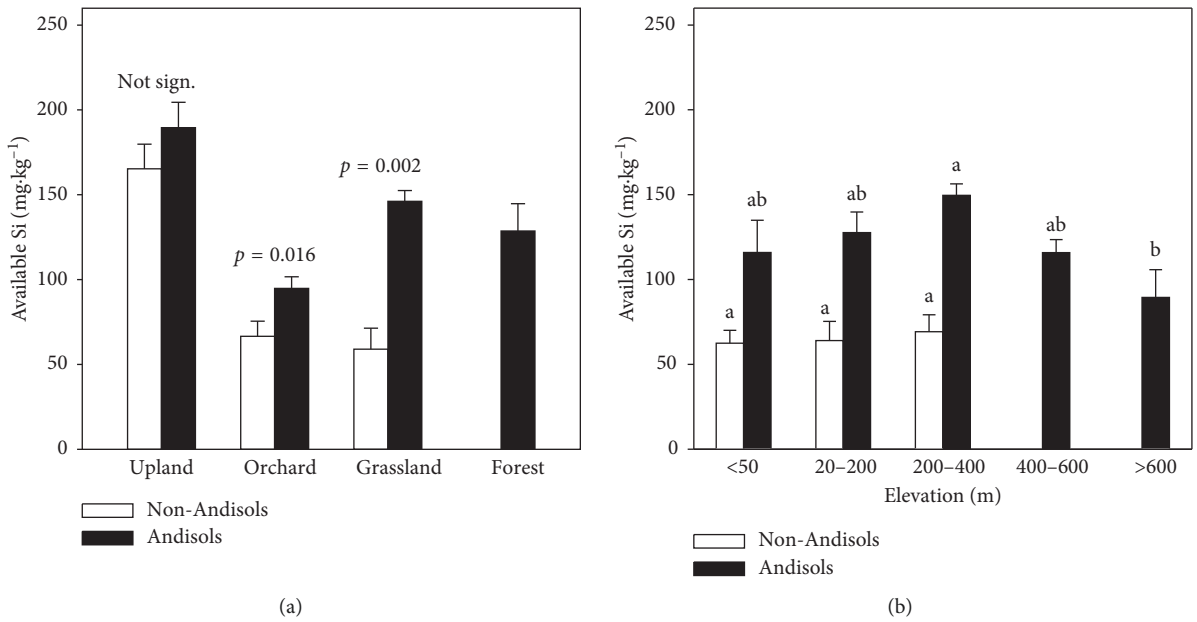

Figure 3: Comparison of available Si content in topsoils of non-Andisols and Andisols on Jeju Island according to land use types (a) and elevation (excluding upland soils) (b). Error bars indicate the standard error. Shown are the p values of Mann–Whitney U test analyses. Different letters above bars within the same soil type indicate significant differences among the elevations, as determined by Tukey's HSD test computed with ranks after Kruskal–Wallis one-way ANOVA on ranks. For all analyses, a p value of 0.05 was considered significant.

Table 1: Spearman rank correlation coefficients between the available Si content and the selected chemical properties of analyzed soils.

	Total ($n = 290$)	Land use		Soil type	
		Cultivated ($n = 195$)	Uncultivated ($n = 95$)	Andisols ($n = 204$)	Non-Andisols ($n = 86$)
pH H_2O	0.468**	0.563**	0.368**	0.519**	0.834**
Organic C	−0.017	−0.045	−0.216*	−0.116	−0.420**
Exch. Ca	0.312**	0.497**	0.140	0.267**	0.643**
Exch. Mg	0.262**	0.392**	0.102	0.254**	0.532**
Si_o	0.451**	0.303**	0.834**	0.693**	0.102
Al_o	0.721**	0.103	0.720**	0.490**	−0.357**
Fe_o	0.264**	0.186**	0.393**	0.409**	−0.123
$Al_o + 1/2Fe_o$	0.279**	0.128	0.660**	0.483**	−0.266*
Al_p/Al_o	−0.588**	−0.652**	−0.647**	−0.608**	−0.617**
P retention	−0.006	0.093	0.443**	0.292**	−0.225
Allophane	0.427**	0.283**	0.443**	0.670**	0.079

*, **Significant difference at the 0.05 and 0.01 probability levels, respectively.

the Bw2 or BC layer of all typifying pedons was 510 mg·kg^{-1} or higher.

Being derived from pyroclastic materials, the soils of Jeju Island are typically characterized by rapid weathering. Furthermore, as precipitation increases at higher elevations, the soil may contain excessive amounts of Si, as under these conditions Al forms humus complexes in the presence of abundant sources of organic matter [5, 21–23]. However, as a large proportion of rainwater move down through the soil, large quantities of dissolved Si are leached to the lower soil layers, and thus the content of available Si tend to be relatively low in the topsoils of upland soils. Deep soils are characterized by continual weathering, resulting in the continual accumulation of weathered Si. Thus, although the topsoil layers receive large quantities of leached Si, these layers are mainly associated with the generation of allophones with a relatively low Si content. Consequently, the available Si content tends to be very high in the deep soils of highlands.

In contrast to Andisols, we found that non-Andisol soils did not show large changes in the available Si content with changes in soil depth. The non-Andisols of Jeju Island also undergo rapid weathering, as they are also derived from pyroclastic materials. However, relatively low precipitation has resulted in the generation of layered silicate clay minerals, and consequently relatively little dissolved Si has been leached.

Figure 4 shows the ratio of available Si in the topsoil and the lowest subsoil at different elevations. In Andisols, we observed that the ratio of available Si in the subsoil and topsoil increased to 6.0 or higher with an increase in

Table 2: Comparison of the available Si content of typifying pedons at different elevations on Jeju Island.

Order	Series	Elevation (m)	Available Si ($mg \cdot kg^{-1}$)				
			A	AB	Bw1	Bw2	BC
Andisols	Wolryeong	24	433	308	367	321	398
	Gamsan	75	123	93.4	132	161	169
	Euigwi	88	136	210	336	363	—
	Bongseong	95	100	219	237	250	228
	Jeongbang	150	243	408	679	636	—
	Ara	172	283	312	325	—	—
	Pyoseon	198	459	459	454	506	637
	Hoesu	250	236	241	255	314	271
	Topyeong	269	102	114	130	252	—
	Namwon	285	97.3	87.7	140	236	395
	Haengwon	325	136	200	253	—	323
	Minag	335	119	112	283	542	—
	Pyeongdae	366	390	433	620	516	—
	Songdang	373	339	309	460	867	852
	Hanrim	406	77.2	405	511	810	—
	Noro	646	173	360	730	788	—
	Nongo	684	71.4	563	332	488	—
	Jeogag	704	146	322	516	585	—
	Tosan	914	102	123	549	608	—
	Heugag	938	86.7	143	515	517	—
Order	Series	Elevation (m)	Available Si ($mg \cdot kg^{-1}$)				
			Ap	BA	Bt1	Bt2	Bt3
Non-Andisols	Gueom	6	392	385	261	—	—
	Gangjeong	8	86.6	65.5	91.8	145	157
	Onpyeong	10	345	310	390	428	—
	Yongsu	14	147	168	213	185	—
	Daejeong	21	110	164	113	140	—
	Mureung	22	211	148	197	154	108
	Donggong	30	208	209	164	156	150

elevation ($R^2 = 0.6875$, $p < 0.001$), indicating the presence of large quantities of available Si in the subsoil. In non-Andisols, however, the ratio of available Si in the subsoil and topsoil layers was approximately 1.0, thereby indicating little or no difference in the Si content of the topsoil and subsoil.

Figure 5 shows the available Si content among soil orders in the typifying pedons of Korea. The average available Si content in the A horizons of Alfisols of Korean mainland soils was the highest at 94.3 $mg \cdot kg^{-1}$, and approximately 50 $mg \cdot kg^{-1}$ for Ultisols (57.1 $mg \cdot kg^{-1}$), Inceptisols (70.9 $mg \cdot kg^{-1}$), and Entisols (45.5 $mg \cdot kg^{-1}$). The average available Si content in the A horizons of Jeju soils was higher than 198 $mg \cdot kg^{-1}$, which is two to three times higher than that in Korean mainland soils. The average available Si content in the A horizons of non-Andisol Jeju soils was 214 $mg \cdot kg^{-1}$, and there was virtually no difference in amounts at different soil depths. The average available Si content in the A horizons of Jeju Andisols was 192 $mg \cdot kg^{-1}$, and increased with increasing soil depth, whereas in the in Bw2 and BC horizons, the average available Si content increased to 494 $mg \cdot kg^{-1}$. Notably, the available Si content in the deep layers of Jeju soils was 10 times higher than that in Korean mainland soils.

Some researchers have reported that analyses based on the 1 N sodium acetate buffer extraction method could overestimate the amounts of available Si in soils because, in addition to available Si adsorbed by soils, it also extracts Si in silicate minerals that cannot be used by plants [25, 28, 39]. However, in the Si fractions of soils, soluble Si (mobile Si extracted by $CaCl_2$) and available and exchangeable Si (adsorbed Si extracted by acetic acid) can move readily, and amorphous Si can represent a potential source of mobile Si [40], as amorphous Si is more readily dissolved than crystalline minerals [38]. Therefore, when quantifying the available Si content, it is appropriate to include some amorphous Si as well as the Si in silicate minerals and allophanes.

The fact that the amount of the available Si content in the deep layers of Jeju Andisols that can readily dissolve in the soil solutions and move to groundwater is 10 times higher than that in the general Korean mainland soils probably explains why the average dissolved Si content in the groundwater on Jeju Island is nearly twice as high as that in the bottled mineral water produced on the Korean mainland.

4. Conclusions

In order to determine the factors contributing to the high dissolved Si content in the groundwater in Jeju Island, we used a sodium acetate (pH 4.0)-based extraction method to analyze the available Si content in 290 samples from topsoils (uplands, orchard, grassland, and forest) collected on Jeju Island and layer-by-layer samples from the typifying pedons collected from the Korean mainland (191 samples) and Jeju Island (27 samples). The Andisols of Jeju Island contained large quantities of available Si that can readily dissolve in soil solutions, among which grassland topsoils collected at elevations of 200 to 400 m had the highest average available Si content of 150 $mg \cdot kg^{-1}$. Among the Andisols examined, those consisting primarily of Al-humus complexes had a low available Si content. With an increase in the allophone content of soils, we detected a concomitant increase in the content of available Si. With regard to the available Si content in the layer-by-layer samples of the typifying pedons collected from the Korean mainland soils, the A horizons of Alfisols showed the highest average available Si content of 94.3 $mg \cdot kg^{-1}$, whereas the available Si content in other soils was approximately 50 $mg \cdot kg^{-1}$. In A horizons of the typifying pedons among Jeju soils, we found that the available Si content was two to four times higher than that in the A horizons of the typifying pedons in Korean mainland soils. The non-Andisols among the typifying pedons in Jeju and Korean mainland soils showed little or no variation in available Si w at different soil depths. In contrast, we observed that the available Si content of Andisols increased with soil depth, being 494 $mg \cdot kg^{-1}$ on average in the Bw2 and BC horizons. Thus, the available Si content in the deep layer of Jeju soils was 10 times higher than that in the typifying pedons of Korean mainland soils. These results accordingly help to explain why the dissolved Si content of the groundwater in Jeju Island is nearly twice as high as that in bottled mineral

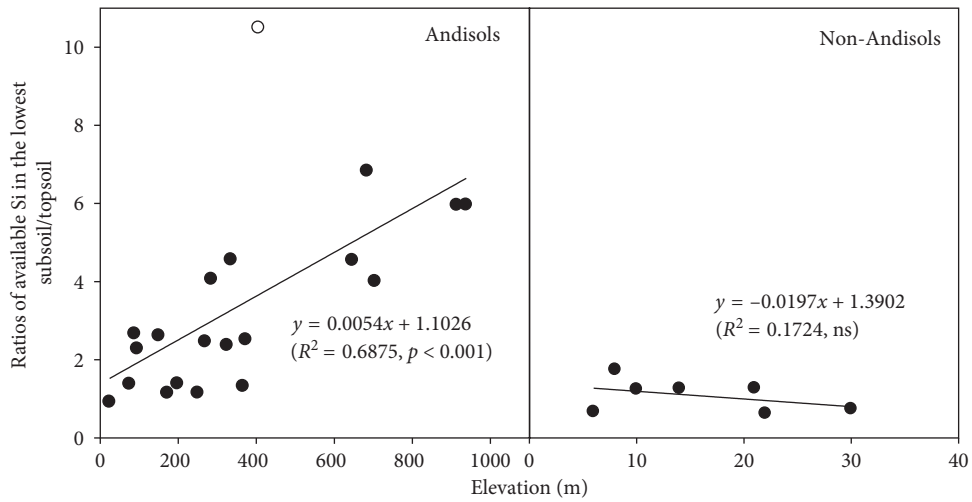

Figure 4: Correlation analysis of the relationship between elevation and ratio of available Si in the lowest subsoil/topsoil in the typifying pedons on Jeju Island. The open circle is excluded from the fitting.

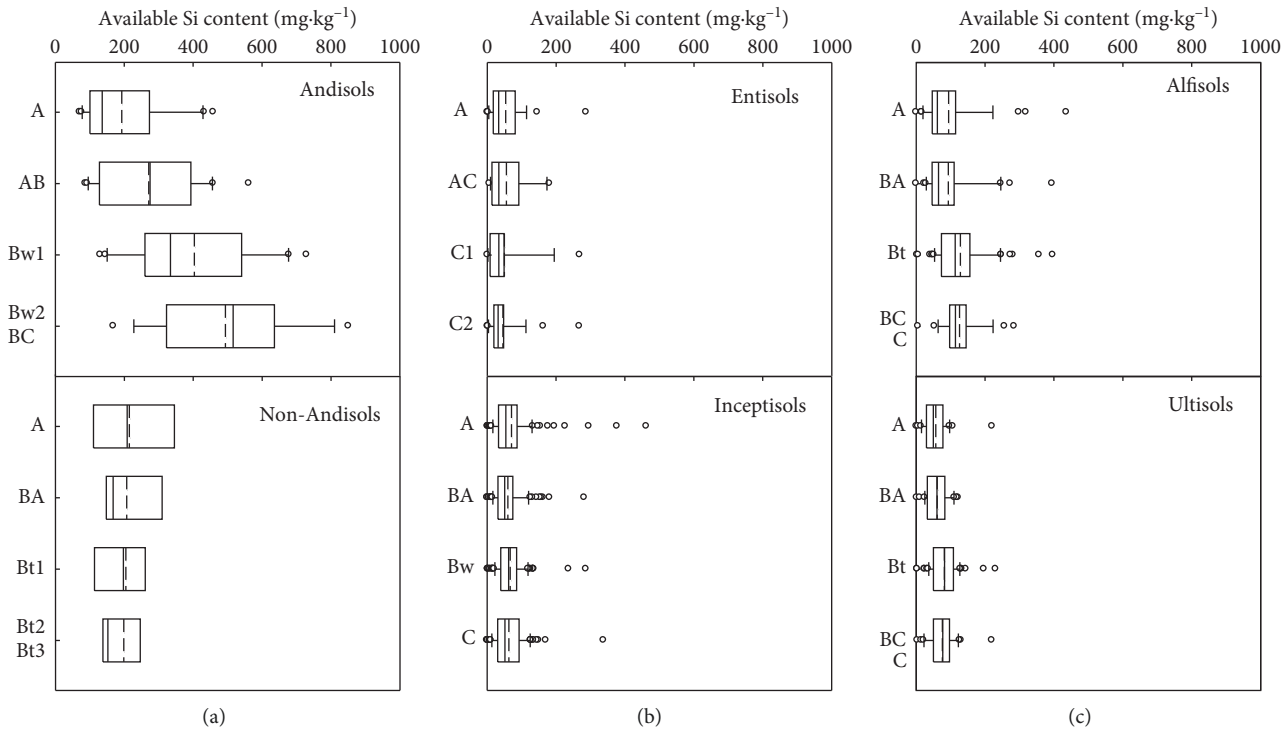

Figure 5: Comparison of available Si content among soil orders in typifying pedons of Jeju soils (Andisols and non-Andisols) and Korean mainland soils (Alfisols, Ultisols, Entisols, and Inceptisols). Boxes represent 25th, 50th (median), and 75th percentiles, and the whiskers indicate the minimum and maximum values. Mean values (dashed line); outliers (*o*).

water produced on the Korean mainland. Therefore, the high available Si content in Andisols can be a potential source that contributes to the Si content in the groundwater on Jeju Island.

Data Availability

The research data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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