Soil vulnerability to acid or alkali spills: Identifying changes in physicochemical properties and pH buffering capacity in response to spills

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Abstract

Acid or alkali spills destroy physicochemical properties of soils and result in irreversible damages on soil ecological functions. This study examined changes in physicochemical properties (i.e., organic matter and clay content, and cation exchange capacity (CEC)) and pH buffering capacity (indicator of soil function) of twenty field soils as a result of acid or alkali spills, and identified characteristics of soils vulnerable to the spills. While both acid and alkali spills did not significantly change clay content, organic matter decreased about 40% and 60%, respectively, consequently resulting in 41% of decrease in pH buffering capacity. Unlike untreated soils whose pH buffering capacity was strongly predicted (R^2=0.79) by organic matter and clay content, the value of acid- and alkali-spilled soils was well predicted by the clay content alone (R^2=0.61 and 0.80, respectively). In addition, results of clustering analysis demonstrated that soils whose pH buffering capacity are higher than 50 mmol kg^{-1} pH $unit^{-1}$ are the most vulnerable to the spills due to high organic matter content. Our findings indicate that soil vulnerability to the spills can be evaluated from soil properties, and it can be potentially used to classify vulnerable soils in the areas with a high occurrence of spills.

Introduction

Acid or alkali spills are serious chemical accidents occurring with a high frequency annually, and account for 46% of the total chemical accidents in South Korea.[1–3] Change in soil pH as a result of strong acid or strong alkali materials exerts a negative impact on not only humans, but also the environment through increased chemical weathering of clay minerals and reaction with soil organic matter.[4–6] When strong acid is introduced to the soil, aluminum or iron oxide is dissolved and surface properties of clay minerals are changed.[7] Also, the dissolved Al^{3+} or Fe^{2+} insolubilizes phosphorus used as a nutrient to the plants, and Al^{3+} replaces the exchangeable cations also used as a nutrient.[8–10] On the other hand, when a strong alkali is introduced into the soil, the increase in the cation concentration increases the salinity, the electrical conductivity and the concentration of toxic ions (B^{3+}, Na^+, Cl^-, Li^+) in the soil water.[8,9] In addition, both humic acid and fulvic acid can be dissolved by strong alkali.[8]

Although neutralization is used as a remediation method for acid or alkali spills,[11,12] such neutralization cannot reverse changes such as a dissolution of organic matter or clay minerals and structural deterioration of soils.[13] While many fundamental acid-base reactions of soils are well-documented, there is a lack of research into the physicochemical properties of soils which have been neutralized after spills. Changes in physicochemical properties of soils, such as organic matter and clay content, and cation exchange capacity (CEC) in response to acid or alkali spills are still unclear. The outcomes of acid or alkali spills should be carefully evaluated because changes in physicochemical properties of soils will alter soil ecological functions,[14,15] which determine soil productivity and the water quality of stream water.[16]

The goals of this study are to investigate the effects of acid or alkali spills on the physicochemical properties, and pH buffering capacity of soils, which is a major indicator of soil function, and to identify characteristics of soils which are more highly vulnerable to acid or alkali spills. The organic matter and clay content, and CEC, which are known as major physicochemical properties determining pH buffering capacity of soils,[17–19] and pH buffering capacity before and after the spills were measured and statistically compared. Stepwise multiple linear regression (SMLR) analyses were performed to investigate the relationship between physicochemical properties and pH buffering capacity, while clustering analysis was conducted to classify soil groups and characteristics of vulnerable soils were analyzed by comparing the groups.

Results And Discussion

Characterization of properties of untreated, and acid- or alkali-spilled soils. Soil samples (n=20) were collected from rice paddy, field and forest sites in Gangwon, Chungcheong, and Jeolla Province and Seoul, South Korea. The samples were collected at a depth of 0-30 cm, and air-dried. The soils were passed through a 2-mm sieve, and these soils are referred to as untreated soils. The physicochemical properties of these untreated soils including soil pH, organic matter content (OM) and clay content, and CEC are summarized in the **Table S1.**

Considering the frequency of chemical accidents and frequency of use, HCl (35%, Daejung, Korea) and NaOH (98%, Daejung, Korea) were selected as the strong acid and alkali, respectively.[2,20] To simulate an extreme acid or alkali spill situation, ten grams of the untreated soil was placed in a 50-mL conical tube and 30 mL of 10 M HCl or NaOH was added. The reaction was conducted in a rotating shaker at 25°C and 40 rpm for two days, and then the suspension was centrifuged and the supernatant solutions were filtered through a 0.22-μm filter (Whatman, UK). Separated soils were washed with deionized water five times to remove excess salts and dissolved ions. Because excess H^+ and OH^- remaining after washing could affect the titration experiment, HNO_3 (60%, Daejung, Korea) or NaOH was added to the washed soils until the supernatant pH reached a range of pH 6-8. The suspensions were centrifuged and decanted, and the residual soils were washed five times with deionized water and freeze-dried. The physicochemical properties of acid- or alkali-spilled soils are summarized in **Table S2**. Finally, pH buffering capacity (pHBC) of three different soils (untreated, acid-spilled, and alkali-spilled) was determined by titration experiments, and titration curves and pH buffering capacity of soils are shown in **Fig. S1** and **Table S3**.

Change in physicochemical properties and pH buffering capacity of soils due to acid or alkali spills. The mean, median, range and standard deviation (SD) of physicochemical properties and pH buffering capacity of soils before and after acid or alkali spills are summarized in Table 1, and Fig. 1 shows the box plots of the properties of the untreated, acid-spilled, and alkali-spilled soils. The differences in clay content as a result of both acid and alkali spills and CEC as a result of alkali spills were normally distributed, while in the case of the other differences, the normal distribution was not satisfied (**Table S4**); Thus, the differences in clay content due to both spills and CEC due to alkali spills were analyzed by pairwise t-test, while the differences in the other properties were analyzed by Wilcoxon signed rank test. The results of pairwise t-test or Wilcoxon signed rank test are summarized in **Table S5**.

Table 1
Physicochemical properties and pH buffering capacity of untreated, acid-spilled, and alkali-spilled soils (n=20)

	Untreated soil				**Acid-spilled soil**				**Alkali-spilled soil**			
	OM	Clay	CEC	pHBC	OM	Clay	CEC	pHBC	OM	Clay	CEC	pHBC
	%		cmol kg^{-1}	mmol kg^{-1} pH $unit^{-1}$	%		cmol kg^{-1}	mmol kg^{-1} pH $unit^{-1}$		%	cmol kg^{-1}	mmol kg^{-1} pH $unit^{-1}$
Mean	3.25	12.55	13.29	32.96	1.55	12.33	9.14	20.26	1.00	12.38	6.79	18.48
Median	2.60	12.87	12.94	27.59	0.76	13.29	7.72	20.68	0.82	13.07	4.39	16.37
Range	0.38 – 7.95	0.91 – 25.60	2.24 – 26.29	9.89 – 75.42	0.19 – 4.94	0.59 – 24.80	0.26 – 24.15	8.42 – 36.77	0.22 – 3.38	0.75 – 24.93	0.23 – 21.80	8.62 – 32.51
SD	2.12	7.45	8.03	19.57	1.46	7.40	7.67	9.54	0.76	7.36	6.83	7.82

Acid or alkali spills did not significantly change the clay content, while organic matter content decreased from 3.25% to 1.55 and 1.00%, respectively ($p<0.05$), showing that the organic matter is more readily reduced by the spills compared to the clay. Decrease in organic matter content was probably due to the electrostatic repulsion between clay surfaces and soil organic matter or between adsorbed soil organic matter.[10,21,22] In addition, acid or alkali spills decreased the averaged CEC from 13.29 cmol kg^{-1} to 9.14 and 6.79 cmol kg^{-1}, respectively ($p<0.05$), and decreased the averaged pH buffering capacity from 32.98 mmol kg^{-1} pH $unit^{-1}$ to 20.26 and 18.48 mmol kg^{-1} pH $unit^{-1}$, respectively, ($p<0.05$). Because protonation or deprotonation reaction and cation exchange reaction of organic matter and clay minerals in soils determines the pH buffering capacity,[17] the change in physicochemical properties by acid or alkali spills is likely to decrease the pH buffering capacity of soils.

Effect of organic matter and clay content on CEC. The parameters derived from SMLR, in which the CEC is set as the dependent variable and organic matter and clay content are set as independent variables, are summarized in Table 2. All models (CEC of untreated soils, acid-spilled, and alkali-spilled soils) satisfied the assumptions of SMLR, and detailed information on checking the assumptions for multiple linear regression analysis is summarized in **Table S6** and **Fig. S2**. The normalized CEC models, i.e., CEC (untreated soils) = -1.58 + 0.82Clay + 0.30OM, CEC (acid-spilled soils) = -3.02 + 0.95Clay, CEC (alkali-spilled soils) = -3.63 + 0.91Clay, had adjusted R^2 of 0.89, 0.90, and 0.81, respectively, which suggested that each model could explain 89, 90 and 81% of CEC of untreated, acid-spilled, and alkali-spilled soils, respectively. According to Neter et al., the adjusted R^2 value can be used to evaluate the predictive ability.[23] Interestingly, without considering any qualitative properties of clay and organic matter, the overall CEC of all three types of soils was successfully predicted by linear combination of clay and organic matter content based on the predictive ability.

Table 2
Parameters derived from multiple linear regression analysis

Dependent variable	Classification	N	Independent variable	Constant	Unstandardized coefficients	Standardized coefficients	Adjusted R^2	t	Sig
CEC	Untreated	20	Clay, OM	-1.58	0.88, 1.16	0.82, 0.30	0.89	10.32, 3.86	0.00
	Acid-spilled	20	Clay	-3.02	0.99	0.95	0.90	13.17	0.00
	Alkali-spilled	20	Clay	-3.63	0.84	0.91	0.81	9.08	0.00
pHBC	Untreated	19[a]	Clay, OM	-2.30	0.88, 7.71	0.35, 0.74	0.79	3.07, 6.59	0.00
	Acid-spilled	20	Clay	7.67	1.02	0.79	0.61	5.51	0.00
	Alkali-spilled	20	Clay	6.68	0.95	0.90	0.80	8.63	0.00

[a]The most outlying data (soil No. 17) was excluded to satisfy the normal distribution

In all SMLR of three different soils, clay content was selected as the independent variable, and the standardized coefficient of clay content is higher than that of organic matter. Because the standardized coefficient indicates the relative strength of the explanatory variables affecting CEC, clay content played the most significant role in determining CEC of soils used in this study. In addition, the standardized coefficient of clay content was even higher in the acid-spilled or alkali-spilled soils, increasing from 0.82 to 0.95 and 0.91, respectively, while the organic matter content was not selected as the independent variable in both acid-spilled and alkali-spilled soils. This was because organic matter, which also has a great influence on CEC before the spills, was removed through desorption or dissolution. As a result, the models of both acid-spilled and alkali-spilled soils could successfully account for more than 90% of CEC with only considering clay content.

Effect of physicochemical properties of soils on pH buffering capacity. The parameters of SMLR, in which the pH buffering capacity is set as the dependent variable and organic matter and clay content are set as independent variables, are summarized in Table 2. The models of pH buffering capacity of acid-spilled and alkali-spilled soils met the assumptions of SMLR, while that of untreated soils (n=20) did not satisfy the assumption of normal distribution. Therefore, data of untreated soils, excluding the most outlying data (soil 17), was analyzed to do SMLR and to satisfy the assumptions (**Table S6** and **Fig. S2**).

The models of normalized pH buffering capacity, i.e., pHBC (untreated soils) = -2.30 + 0.35Clay + 0.74OM, pHBC (acid-spilled soils) = 7.67 + 0.79Clay, pHBC (alkali-spilled soils) = 6.68 + 0.90Clay, had adjusted R^2 of 0.79, 0.61, and 0.80, respectively, and shows that each model from SMLR could describe 79, 61, and 80% of the pH buffering capacity of untreated, acid-spilled, and alkali-spilled soils, respectively. In the case of the untreated soils, pH buffering capacity was strongly predicted by linear combination of organic matter and clay content, corresponding to the result of literature.[24] Both organic matter and clay content were selected as independent variables, and a standardized coefficient of organic matter content (0.74) was higher than that of clay content (0.35). It is also consistent with the result of previous studies that the organic matter content was more important factor in determining pH buffering capacity of untreated soils than clay content.[17,25] On the other hand, in the case of both acid-spilled and alkali-spilled soils, the selected independent variable is only clay content due to decrease in organic matter content. Nevertheless, the models of both acid-spilled and alkali-spilled soils could predict pH buffering capacity well by only using clay content. It emphasizes that the impact of soil components on pH buffering capacity is determined by both qualitative and quantitative characteristics.

Figure 2 shows that the plot of pH buffering capacity predicted by using SMLR against the measured pH buffering capacity. According to the Fig. 2, pH buffering capacities of all three types of soils were successfully predicted by using SMLR model of untreated soils in which both organic matter and clay content were selected as independent variables (Fig. 2A). Although SMLR models of acid-spilled and alkali-spilled soils considering only clay content accurately predicted the pH buffering capacity less than 50 mmol kg^{-1} pH $unit^{-1}$, they underestimated the pH buffering capacity of the soils (No.5, 6, 8, 17, and 20) greater than 50 mmol

kg^{-1} pH $unit^{-1}$ (Fig. 2B and 2C). It might be because they originally contain relatively higher amount of organic matter (6%) compared to the others, and the remaining organic matter content after acid or alkali spills is still not negligible (**Table S2**).

Change in physicochemical properties and pH buffering capacity of clustered soil groups before and after spills. Based on a clustering analysis, soils are classified into three groups based on organic matter and clay content, CEC, and pH buffering capacity (**Fig. S3**). The physicochemical properties and pH buffering capacity of each group before acid or alkali spills are summarized in Table 3, and all results of statistical tests in this section are summarized in **Table S7**. Seven, eight, and five soils were classified as group 1, 2, and 3, respectively. Soils in a group 1 contain a small amount of organic matter and clay, and consequently have a low CEC and pH buffering capacity. In contrast, soils in a group 3 contain a large amount of organic matter and clay, and therefore they have a high CEC and pH buffering capacity. The other soils are classified into a group 2, and they have a small amount of organic matter, but containing high content of clay, which results in high CEC and moderate pH buffering capacity. More descriptions on comparison among the groups are described in Table 3.

Table 3
Three clustered soil groups' physicochemical properties and pH buffering capacity before acid or alkali spills

Properties	Group 1	Group 2	Group 3
No. of sample	7	8	5
OM (%)	1.91±0.67	2.68±1.49	6.02±1.87
Clay (%)	4.52±3.32	17.86±4.97	15.30±5.02
CEC ($cmol\ kg^{-1}$)	4.49±3.17	16.54±5.78	20.40±3.57
pHBC ($mmol\ kg^{-1}$)	14.85±5.30	30.99±7.92	61.49±8.32
Characteristics[a]	Low OM Low Clay Low CEC Low pHBC	Low OM High Clay High CEC Moderate pHBC	High OM High Clay High CEC High pHBC

[a]Group 1 had the lowest organic matter and clay content, CEC and pH buffering capacity among the three groups, while group 3 had the highest organic matter content, CEC and pH buffering capacity. Organic matter content of group 2 was greater than that of group 1 (without statistical significance) while significantly lower than that of group 3. Clay content of group 2 was significantly higher than that of group 1, and higher than that of group 3 (without statistical significance). The CEC of group 2 was significantly greater than that of group 1, while lower than that of group 3 (without statistical significance). The pH buffering capacity of group 2 was significantly greater than that of group 1, while significantly lower than that of group 3.

Figure 3 shows three clustered soil groups' physicochemical properties and pH buffering capacity of before and after acid or alkali spills. Acid spills decreased the organic matter content of group 1, 2, and 3 from 1.91, 2.68, and 6.02%, respectively, to 0.43, 1.46, and 3.24%, respectively, and alkali spills decreased that of group 1, 2, and 3 to 0.50, 1.24, and 1.34%, respectively. Both acid and alkali spills did not result in meaningful change in clay content of each group. The CEC of group 1, 2, and 3 was decreased by acid spills from 4.49, 16.54, and 20.40 cmol kg^{-1}, respectively, to 1.29, 13.97, and 12.42 cmol kg^{-1}, respectively, and also decreased by alkali spills to 1.01, 11.28, and 7.68 cmol kg^{-1}, respectively. Alkali spills reduced the organic matter content and CEC more than acid spills, as soil organic matter is possibly not only desorbed, but also dissolved in alkali solutions.[8] In addition, acid and alkali spills decreased organic matter content of group 3 most significantly to 46 and 78%, respectively, and CEC to 39 and 62%, respectively.

In the case of the pH buffering capacity, acid or alkali spills decreased that of group 1 less than 30% from 14.85 mmol kg^{-1} pH $unit^{-1}$ to 10.25 or 10.88 mmol kg^{-1} pH $unit^{-1}$, respectively, and decreased that of group 2 less than 20% from 30.99 mmol kg^{-1} pH $unit^{-1}$ to 28.18 or 24.19 mmol kg^{-1} pH $unit^{-1}$, respectively. However, acid or alkali spills significantly reduced pH buffering capacity of group 3 more than 65%, from 61.49 mmol kg^{-1} pH $unit^{-1}$ to 21.62 or 20.00 mmol kg^{-1} pH $unit^{-1}$, respectively. Because organic matter and clay content determine pH buffering capacity (Table 2), the biggest drop in pH buffering capacity of soils in group 3 was ascribed to the largest decrease in organic matter content. Interestingly, all soils of which pH buffering capacity was greater than 50 mmol kg^{-1} pH $unit^{-1}$, whose pH buffering capacity was poorly predicted by using only clay content (Fig. 2), were classified into group 3 (**Table S3**). It means that although both spills substantially reduce the organic matter content of soils which originally contain a great amount of clay and organic matter (group 3), remaining organic matter content after acid or alkali spills still plays a significant role in determining pH buffering capacities.

Characteristics of vulnerable soils. Soil vulnerability to acid or alkali spills is defined in this study as the degree to which soil function is decreased by acid or alkali spills. Because the pH buffering capacity is used to represent the soil function, soil vulnerability to the acid or alkali spills is calculated from Eq. (1):

$$Soilvulnerabilitytotheacidoralkalispills = -\frac{\Delta pHBC}{pHBC_0}$$

1

where ΔpHBC is the change in pH buffering capacity as a result of acid or alkali spills, and $pHBC_0$ is the pH buffering capacity of untreated soils. By using the relative change in pH buffering capacity after acid or alkali spills, soil vulnerability to the spills was used to evaluate characteristics of soils which are vulnerable in terms of soil ecological function (Fig. 3E).

Soil vulnerability to acid spills in group 1, 2, and 3 were 0.27, 0.06, and 0.65, respectively, and it represented that 27, 6, and 65% of soil functions decreased by acid spills, respectively. For alkali spills, soil vulnerabilities were 0.23, 0.19, and 0.67, respectively, which indicated that alkali spills decreased soil function by 23, 19, 67%, respectively. Group 3 had the highest soil vulnerability to acid or alkali spills among three groups. It could be explained by Spearman's rank correlation coefficient of organic matter and soil vulnerability to acid or alkali spills, which were 0.49 ($p=0.03$) or 0.74 ($p=0.00$), respectively. It indicates that an increase in organic matter content was correlated with an increase in soil vulnerability to acid or alkali spills. Although organic matter is the most important factor determining pH buffering capacity in the untreated soils (Table 2), since it is susceptible to acid or alkali spills, soils with pH buffering capacity of 50 mmol kg^{-1} pH $unit^{-1}$ or more, due to the high organic content, are highly vulnerable to the acid or alkali spills. Contrary to organic matter, clay is resistant to acid or alkali spills, and, as such, soil vulnerability decreases with an increase in clay content. In addition, it has been known that clay minerals have a high resistance on acid or alkali attack and their surface properties did not substantially change.[7] This may explain why group 2 is less vulnerable than group 1 although there is not a significant difference in organic matter content. A relationship between organic matter and clay content and soil vulnerability to the spills is also clearly observed in **Fig. S4**. These results indicate that soil vulnerability to acid or alkali spills can be predicted based on soil properties, particularly by the quantitative quality, and it is useful to classify vulnerable soils in the areas with a high probability of spills, and to manage these spilled areas on a site-specific basis.

Conclusions

In this study, we investigated changes in physicochemical properties and pH buffering capacity of soils in response to acid or alkali spills and identified those characteristics of soils which exhibit vulnerability to the spills. Acid or alkali spills greatly decreased organic matter content and CEC, but did not cause a significant change in clay content. As a result of a decrease in organic matter content, the pH buffering capacity is significantly decreased after acid or alkali spills. The pH buffering capacity of untreated soils was strongly predicted by the linear combination of both organic matter and clay content, while that of acid-spilled and alkali-spilled soils was successfully predicted by only clay content. Although SMLR models of pH buffering capacity considering only clay content successfully predict pH buffering capacity less than 50 mmol kg^{-1} pH $unit^{-1}$, the models were likely to underestimate pH buffering capacity of soils greater than 50 mmol kg^{-1} pH unit $^{-1}$ because organic matter remaining after the spills is not negligible. These findings and the cluster analysis indicate that soils containing greater organic matter content are more vulnerable to acid or alkali spills because organic matter is susceptible to the spills, while soils containing higher amount of clay are more resistant to the spills. It highlights that the quantitative properties (*i.e.*, organic matter and clay content) can be used to classify soil vulnerability on the spills in the areas with a high probability of the spills.

Materials And Methods

Soil characterization. Soil pH was measured at a 1:5 ratio of soil to water according to the Methods of Soil Analysis, Part 3-Chemical Methods.[26] Organic matter content was determined through using loss on ignition method.[27] Clay content was measured by using sedimentation method according to the Methods of Soil Analysis, Part 4-Physical Methods.[26] The CEC was determined using the sodium acetate method procedure following the US Environmental Protection Agency (US EPA) Method 9081.[28] All chemicals used in this study were of extra pure or reagent grade.

pH buffering capacity measurement. Titration experiments were performed to measure pH buffering capacity of three different soils (untreated, acid-spilled, and alkali-spilled).[29−31] Five grams of soils was placed into 50-mL conical tubes with 10 mL of deionized water, and 0, 2.5, 5.0, and 7.5 mL of 0.1 M HNO_3 or NaOH was added. A final volume of each tube was adjusted to 25 mL with addition of deionized water and ionic strength was adjusted to 0.03 M by adding 1 M $NaNO_3$ (99%, Daejung, Korea) to minimize the effect of background electrolyte concentration on the titration experiment. The suspensions were then purged with N_2 for 30 min. Whole reactions were conducted in a rotating shaker at 25°C and 40 rpm for four days. After reaction, a pH value of the suspension was measured. In this study, the sigmoid function was used to approximate the shape of titration curves of soils,[29] and the equation is as follows Eq. (2):

$$pH = pH_0 + \frac{a}{1 + e^{-\frac{(A - A_0)}{b}}}$$

2

in which A is the amount of acid (negative) or alkali (positive) added to the soil suspension, and a, b, A_0 and pH_0 were fitting parameters. The adjustable parameters were optimized through a linear least squares estimation procedure by using SigmaPlot®. By rearranging and differentiating Eq. (2), the pH buffering capacity of soils were calculated from Eq. (3):

$$pHbufferingcapacity = \frac{dA}{dpH} = \frac{ab}{(a + pH_0 - pH)(pH - pH_0)}$$

3

Clustering analysis. A k-means clustering analysis was conducted to group twenty untreated soils based on organic matter and clay content, CEC, and pH buffering capacity, and soil vulnerability of each group was compared to identify characteristics of vulnerable soils. In brief, the clustering analysis found a local solution to minimize the Euclidean distance between observations and the cluster centers, and the number of clusters (k) should be assigned a priori considering the characteristics of data.[32] In this study, the within groups sum of squared errors (SSE) was used to find the optimal number of clusters. SSE is the sum of the squared distance between each member of a cluster and its cluster centroid,[33] and is calculated as following Eq. (4):

$$SSE = \sum_{i=1}^{k} \sum_{x \in C_i} distance(c_i, x)^2$$

4

where k is the number of clusters; x is an untreated soil; C_i is the ith cluster; distance is the Euclidean distance between two objects; and c_i is the centroid of cluster C_i. The most appropriate solution to the number of clusters can be found by a plot of the SSE against a series of sequential cluster numbers. The point at which the decrease in SSE slows dramatically is defined as the solution.

Statistical analysis. All statistical analyses were performed using SPSS 24 (IBM, USA), and all statistical tests were two-tailed with 5% significance level. Pairwise t-test or Wilcoxon signed rank test was performed to evaluate the statistically significant difference in physicochemical properties and pH buffering capacity of soils before and after acid or alkali spills. The normality of the differences was assessed using the Kolomogorov-Smirnov (KS) test. In addition, SMLR were used to find the relationship between physicochemical properties and pH buffering capacity. Two different SMLR were conducted; 1) the CEC was defined as a dependent variable while the organic matter and clay content were set as independent variables, 2) the pH buffering capacity was defined as a dependent variable while organic matter and clay content were set as independent variables. The ANOVA was used to assess the significance of the models. To validate assumptions of SMLR, the normal distribution, autocorrelation, independence, and homogeneity of residuals were checked through KS test, Durbin-Watson test, Q-Q plots, and standardized residual plot. In addition, the variance inflation factor (VIF) was used to check the risk of multicollinearity.[34] If VIF is less than 10, there is no multicollinearity among independent variables.

The physicochemical properties, pH buffering capacity, and soil vulnerability of each clustered soil group were compared by using the ANOVA or Kruskal Wallis H (KW) test. The homoscedasticity was analyzed by Levene's test. In the case of ANOVA, post-hoc analysis was performed by Scheffe test or Dunnet T3 test depending on satisfying the homoscedasticity or not, while in the case of KW test, Bonferroni correction method was used as the post-hoc analysis.

Declarations

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Author contributions statement

K. Nam directed this research and was the overall in-charge. I. Jeon and K. Nam planned and designed the experiments. I. Jeon performed the experiments and I. Jeon, H. Chung, and S.H. Kim analyzed the data. All authors wrote and reviewed the manuscript.

Competing interests statement

The authors declare no competing interests.

Data availability statement

Authors can confirm that all relevant data are included in the article and its supplementary information files.

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Figures

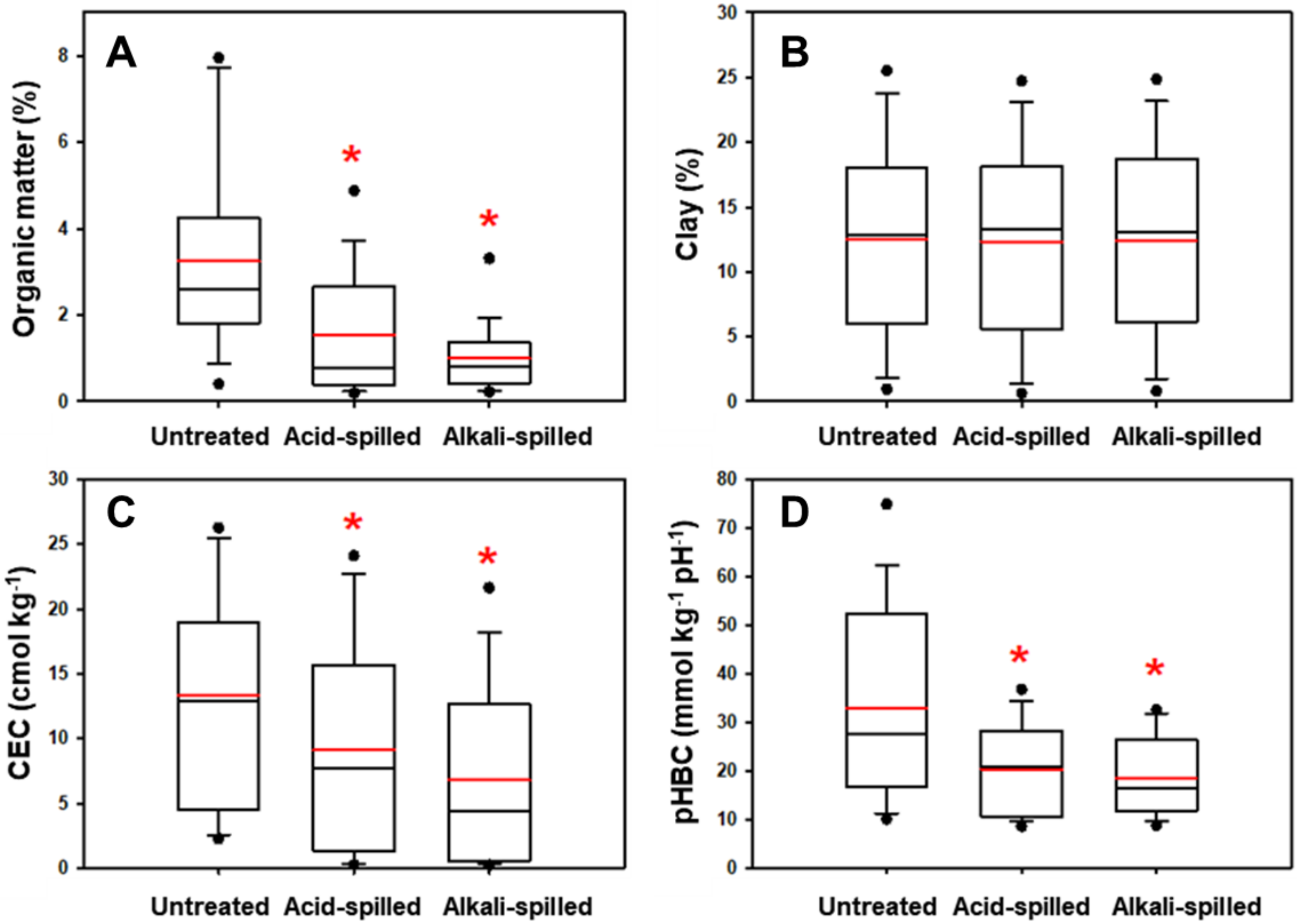

Figure 1

Box plots of (A) organic matter content, (B) clay content, (C) CEC, and (D) pH buffering capacity of untreated, acid-spilled, and alkali-spilled soils. Red line represents the mean value. Asterisk represents the significant difference in properties before and after acid or alkali spills ($p<0.05$).

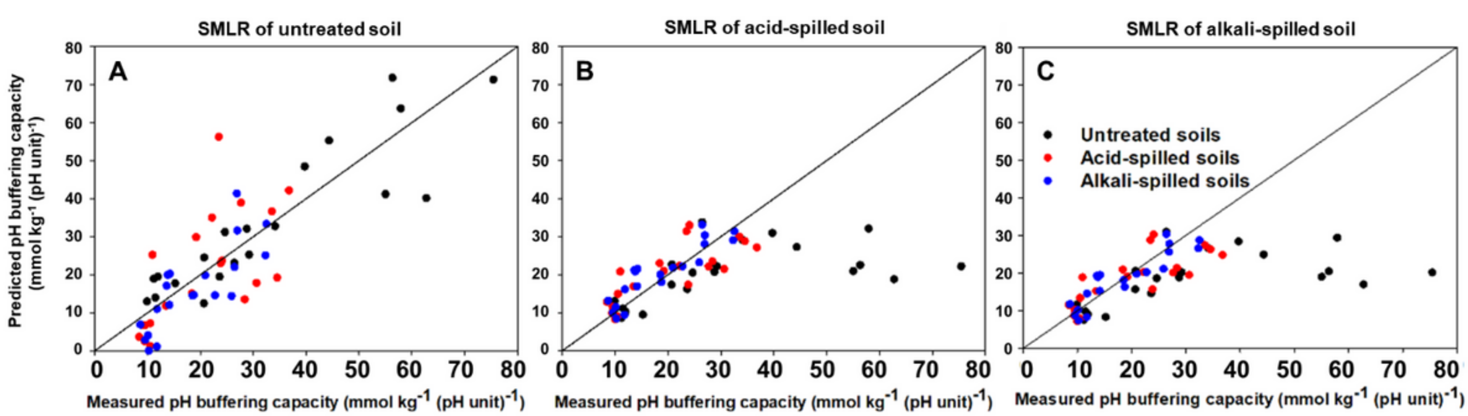

Figure 2

Plots of pH buffering capacity predicted by SMLR model in (A) untreated soils, (B) acid-spilled soils, and (C) alkali-spilled soils, compared with the measured pH buffering capacity. Black, red, and blue symbols represent untreated, acid-spilled and alkali-spilled soils, respectively.

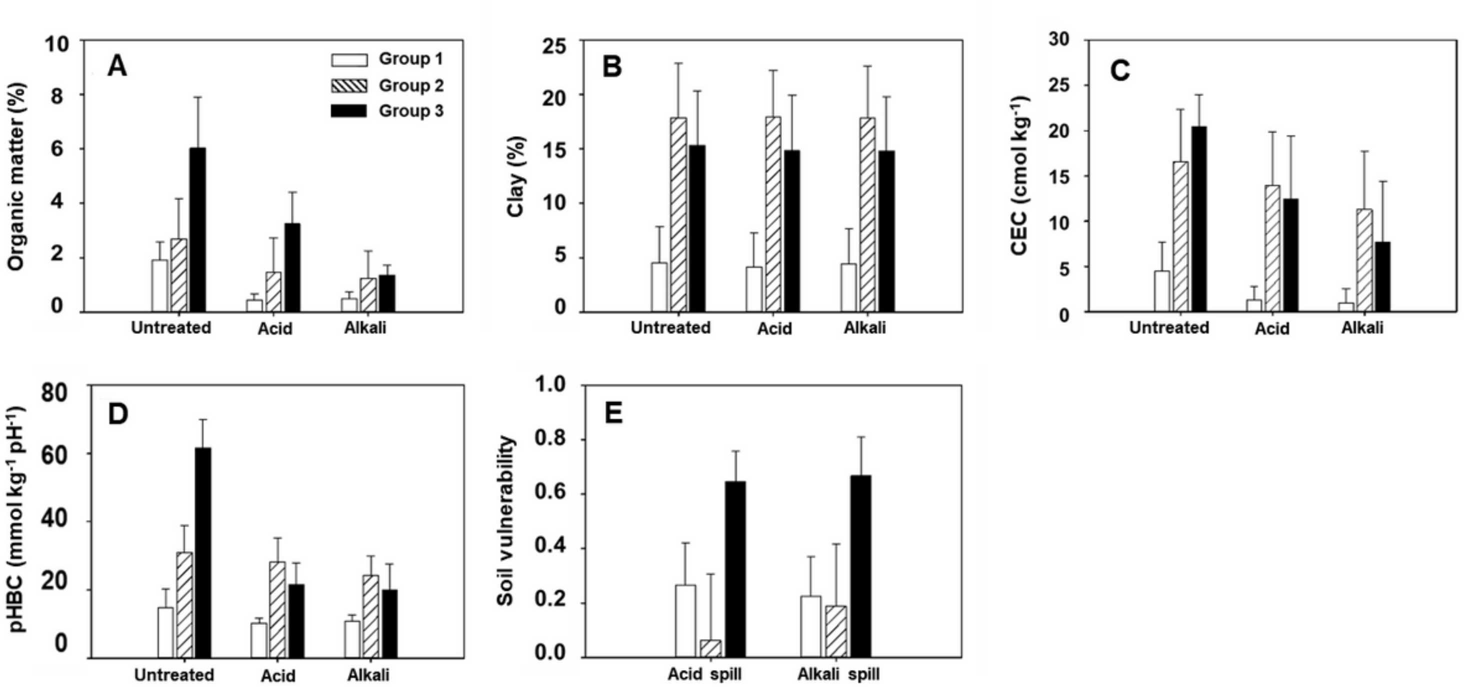

Figure 3

Three clustered soil groups' physicochemical properties (i.e. (A) organic matter content, (B) clay content, and (C) CEC) and (D) pH buffering capacity of before and after acid or alkali spills and (E) soil vulnerability to the spills. Open, cross-hatched, and filled bars represent group 1, 2, and 3, respectively.

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