



# Use of clay and organic matter contents to predict soil pH vulnerability in response to acid or alkali spills

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## ABSTRACT

Acid or alkali spills destroy the physicochemical properties of soils and cause irreversible damage to their ecological functions. This study examined changes in physicochemical properties (*i.e.*, organic matter, clay content, and cation exchange capacity (CEC)) as well as pH buffering capacity (indicator of soil ecological function) of 20 field soils in response to the spills. Also, we identified the characteristics of soils vulnerable to the spills. Although the spills did not substantially change the clay content, organic matter decreased by approximately 50%, consequently resulting in a 41% decrease in pH buffering capacity. When we classified soils into three groups based on soil properties and pH buffering capacity, the extent of change in soil properties by spill differed by group. As the organic matter content increased or clay content decreased, the soil tended to be more vulnerable to spills in terms of the degree to which the soil function was changed. Considering that the protonation-deprotonation characteristics of clay sized fraction were not remarkably changed by the spills, this result was mainly attributed to the dissolution of organic matter. Together with the successful prediction of CEC and pH buffering capacity by multiple linear regression models using organic matter and clay content, our findings enable the easy classification of soils based on their vulnerability and site-specific management of areas with a high probability of spills.

## 1. Introduction

Acid or alkali spills are serious chemical accidents with a high annual frequency and account for 46% of the total chemical accidents in South Korea [1]. Change in soil pH as a result of strong acid or strong alkali materials increased chemical weathering of clay minerals and reaction with soil organic matter (OM) [2–4]. Also, it exerts a negative impact on not only humans but also the environment. When a strong acid is introduced to the soil, the surface properties of clay minerals are changed [5,6], and aluminum or iron oxide is dissolved. The dissolved  $\text{Al}^{3+}$  or  $\text{Fe}^{2+}$  reacts with phosphorus which is one of the major plant nutrients, and immobilizes phosphorus by forming less soluble compounds. It decreases the availability of plant nutrients, and aluminum toxicity is also one of the major factors inhibiting plant growth [7–9]. On the other hand, when a strong alkali is introduced into the soil, the increase in cation concentration from the alkali chemical augments the salinity, electrical conductivity, and concentration of toxic ions ( $\text{B}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Li}^+$ ) in the soil water [7,8].

Because the spills cause acute toxicity, mainly owing to a rapid pH change, neutralizers have been applied to the spilled area to

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recover the pH and prevent secondary leaching of acid or alkali chemicals [10,11]. However, neutralization cannot reverse changes, such as the dissolution of OM or clay minerals and structural deterioration of soils [12]. Although many fundamental acid-base reactions of soils are well-documented, research on the effects of the acid or alkali spills and neutralization has almost never been conducted so far. Particularly, changes in the physicochemical properties of soils, such as OM, clay content, and cation exchange capacity (CEC) in response to acid or alkali spills are still unclear. To our knowledge, we found only one study investigating the effect of acid shock and neutralization in the soil microbial community change [3]. Although they observed that the responses of soils varied depending on soil characteristics and the microbial community, the basic physicochemical properties of soils after neutralization were still limited. The outcomes of acid or alkali spills should be carefully evaluated because changes in the physicochemical properties of soils will alter soil ecological functions [13,14], which determine soil productivity and stream water quality [15].

Therefore, this study aimed to investigate the effects of acid or alkali spills on the physicochemical properties and pH buffering capacity of soils, which is one of the major indicators of ecological soil function, and to identify the characteristics of soils that are more vulnerable to acid or alkali spills. Clustering analysis was performed to group the soils based on their physicochemical and pH buffering capacity. The OM, clay content, and CEC, which are known as major physicochemical properties determining the pH buffering capacity of soils [16–18], and the pH buffering capacity before and after the spills were measured and statistically compared by group. To characterize soils vulnerable to the spills, we established a new indicator, soil pH vulnerability, which was defined as the degree to which the pH buffering capacity is decreased by acid or alkali spills. Moreover, we examined the change in the protonation-deprotonation characteristics of clay sized fraction in the soil before and after the spills. Finally, we performed stepwise multiple linear regression (SMLR) analyses to investigate the relationships between quantitative soil properties, including OM and clay content, CEC, and pH buffering capacity.

## 2. Materials and methods

### 2.1. Soil characterization

Soil samples ( $n = 20$ ) were collected from rice paddies, fields, and forest sites in Gangwon, Chungcheong, Jeolla Province (northern, central, and southern part of South Korea, respectively), and Seoul, South Korea. Samples were collected at a depth of 0–30 cm and air-dried. The soils were passed through a 2-mm sieve and were referred to as untreated soils. Untreated soils were characterized for soil pH, OM, clay content, and CEC. Soil pH was measured at a 1:5 ratio of soil to water according to the Methods of Soil Analysis, Part 3-Chemical Methods [19]. The OM was determined using the loss on ignition method [20]. Soil texture and clay content were measured using the sedimentation method according to the Methods of Soil Analysis, Part 4-Physical Methods [19]. The CEC was determined using the sodium acetate method following the US Environmental Protection Agency Method 9081 [21]. All used chemicals were of extra pure or reagent grade. The detailed procedure of soil sample collection and preparation was summarized in Text S1, and the properties of soils used in this study are summarized in Table S1.

### 2.2. Acid or alkali spill and neutralization

Considering the frequency of chemical accidents and frequency of use, HCl (35%, Daejung, Korea) and NaOH (98%, Daejung, Korea) were selected as strong acid and alkali, respectively [1,22]. We simulated an extreme but plausible acid or alkali spill situation that acid or alkali chemical was continuously spilled from a storage tank at a plant for a few days. For the experiment, 10 g of the untreated soil were placed in a 50-mL conical tube, and 30 mL of 10 M HCl or NaOH were added. The reaction was conducted in a rotating shaker at 25 °C and 40 rpm for two days, then the suspension was centrifuged, and the supernatant solutions were filtered through a 0.22- $\mu$ m filter (Whatman, UK). The 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 soil was washed five times with deionized water and freeze-dried. The physicochemical properties of the acid- and alkali-spilled soils are summarized in Table S2.

### 2.3. Measurement of the pH buffering capacity

Titration experiments were performed to measure the pH buffering capacity of three different soils (untreated, acid-spilled, and alkali-spilled) as follows [23–25]. Five grams of soil were 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 were added. The final volume of each tube was adjusted to 25 mL by adding deionized water, and the 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  $N_2$  gas for 30 min. All reactions were conducted in a rotating shaker at 25 °C and 40 rpm for four days. The pH of the suspension was measured after the reaction. In this study, the sigmoid function was used to approximate the shape of the titration curves of the soils [24], and the equation is as follows: Eq. (1):

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

where A is the amount of acid (negative) or alkali (positive) added to the soil suspension; a, b,  $A_0$  and  $pH_0$  are the fitting parameters. The adjustable parameters were optimized through a linear least-squares estimation procedure using SigmaPlot. By rearranging and differentiating Eq. (1), the pH buffering capacity of the soil was calculated using Eq. (2):

$$pH \text{ buffering capacity} = \frac{dA}{dpH} = \frac{ab}{(a + pH_0 - pH)(pH - pH_0)} \quad (2)$$

The titration curves and pH buffering capacities of the soils are shown in Fig. S1 and Table S3.

#### 2.4. Titration experiment of clay sized fraction

We evaluated protonation-deprotonation characteristics of clay sized fraction in response to acid or alkali spills by titration experiments. Clay sized fraction was separated from the soils using the sedimentation method. Prior to titration experiments, a small amount of NaOH was added to the suspension until the supernatant pH reached a range of pH 6–8, and the clay sized fraction was washed with deionized water several times. Then, clay suspension was prepared by adding 50 mg of clay sized fraction in 50 mL of 0.03 M of  $NaNO_3$  solution. The titration experiments of suspensions of clay sized fraction were performed within a pH range of 4–9 at 25 °C because the dissolution of clay minerals is negligible at this pH range [26].

#### 2.5. Soil pH vulnerability to acid or alkali spills

In this study, soil pH vulnerability to acid or alkali spills is defined as the degree to which the pH buffering capacity is decreased by acid or alkali spills. The pH buffering capacity is one of the most important soil ecological indicators, as it governs a capacity of soil to resist pH change and thus maintain good living conditions for plants and microorganisms [7]. Therefore, the pH buffering capacity is used to represent the soil function, the soil pH vulnerability to acid or alkali spills is calculated from Eq. (3):

$$\text{Soil vulnerability to acid or alkali spills} = -\frac{\Delta pHBC}{pHBC_0} \quad (3)$$

where  $\Delta pHBC$  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.

#### 2.6. Clustering analysis

A k-means clustering analysis was conducted to group 20 untreated soils based on OM and clay content, CEC, pH buffering capacity. Then the soil pH vulnerability of each group was compared to identify the characteristics of vulnerable soils. In brief, the clustering analysis found a local solution to minimize the Euclidean distance between observations and the cluster centers. The number of clusters (k) should be assigned a priori considering the characteristics of the data [27]. In this study, the within-group sum of squared errors (SSE) was used to find the optimal number of clusters. The SSE is the sum of the squared distance between each member of a cluster and its cluster centroid [28], and is calculated using Eq. (4):

$$SSE = \sum_{i=1}^k \sum_{x \in C_i} \text{distance}(c_i, x)^2 \quad (4)$$

where k is the number of clusters, x is the 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 for the number of clusters can be determined by plotting the SSE against a series of sequential cluster numbers. The point at which the decrease in SSE slows dramatically is defined as the solution.

#### 2.7. Statistical analysis

All statistical analyses were performed using SPSS version 24 (IBM, USA), and all statistical tests were two-tailed with a 5% significance level. To investigate the presence of a statistically meaningful difference in the properties before and after the spills, we first checked the distribution of the differences in the properties and the normality of the differences was assessed using Kolmogorov-Smirnov (KS) test. Then, pairwise t-tests or Wilcoxon signed-rank tests were performed to evaluate the statistically significant differences in the physicochemical properties and pH buffering capacity of the soils before and after acid or alkali spills. The physicochemical properties, pH buffering capacity, and soil pH vulnerability of each clustered soil group were compared using ANOVA or Kruskal-Wallis (KW) test. Homoscedasticity was analyzed using Levene's test. In case of ANOVA, post-hoc analysis was performed using Scheffe's or Dunnett's test, depending on whether the homoscedasticity was satisfied, whereas in case of KW test, Bonferroni correction method was used as the post-hoc analysis.

In addition, SMLR was used to determine the relationship between the physicochemical properties and pH buffering capacity. The pH buffering capacity was defined as a dependent variable, whereas OM and clay content were set as independent variables. ANOVA was used to assess the significance of the models. To validate the assumptions of the SMLR, the normal distribution, autocorrelation, independence, and homogeneity of residuals were checked using KS test, Durbin-Watson test, Q-Q plots, and standardized residual

**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 <sup>-1</sup>	mmol kg <sup>-1</sup> pH unit <sup>-1</sup>	%		cmol kg <sup>-1</sup>	mmol kg <sup>-1</sup> pH unit <sup>-1</sup>	%		cmol kg <sup>-1</sup>	mmol kg <sup>-1</sup> pH unit <sup>-1</sup>
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

plot. In addition, the variance inflation factor (VIF) was used to check the risk of multicollinearity [29]. If VIF was less than 10, no multicollinearity was detected among the independent variables.

### 3. Results and discussion

#### 3.1. Change in physicochemical properties and pH buffering capacity of soils due to acid or alkali spills

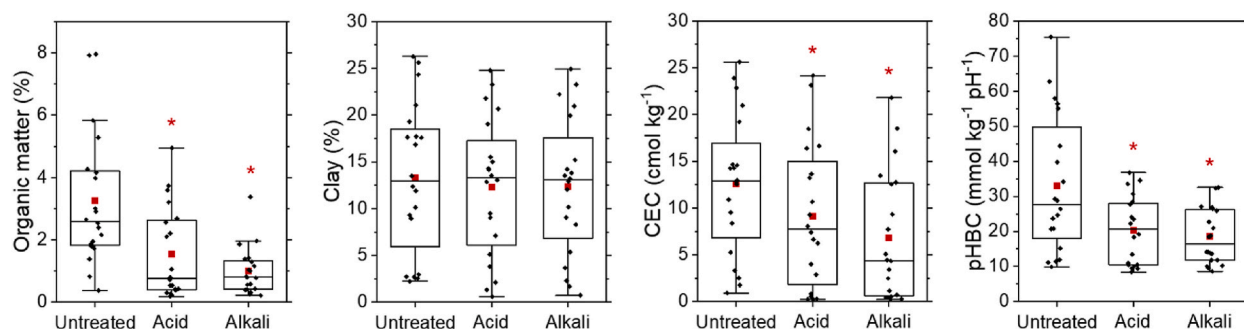
The mean, median, range, and standard deviation (SD) of physicochemical properties and pH buffering capacity of soils before and after acid or alkali spills are summarized in Table 1, and Fig. 1 shows box plots of the properties of the untreated, acid-spilled, and alkali-spilled soils. The differences in clay content as a result of both acid and alkali spills and CEC as a result of alkali spills were normally distributed, whereas in 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, whereas the differences in other properties were analyzed using Wilcoxon signed rank test. Results of the pairwise *t*-test and Wilcoxon signed-rank test are summarized in Table S5.

Acid or alkali spills did not significantly change the clay content, whereas the OM decreased from 3.25% to 1.55% and 1.00%, respectively ( $p < 0.05$ ), indicating that the OM is more readily reduced by the spills than the clay. Decrease in OM was probably owing to the electrostatic repulsion between clay surfaces and soil OM or between adsorbed soil OM [9,30,31]. Considering that surface charge of soil components and OM was determined by the surrounding pH and  $pK_a$  of their surface functional groups, surface charge of soil components and OM became positive or negative during acid or alkali spills due to extremely low or high pH, respectively. As a result, the electrostatic repulsion between the same charged components could repel each other and decrease OM. In addition, acid or alkali spills decreased the averaged CEC from  $13.29 \text{ cmol kg}^{-1}$  to 9.14 and  $6.79 \text{ cmol kg}^{-1}$ , respectively, ( $p < 0.05$ ), and decreased the averaged pH buffering capacity from  $32.98 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  to 20.26 and  $18.48 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ , respectively, ( $p < 0.05$ ). It has been known that the pH buffering capacity is greatly determined by protonation or deprotonation reactions and cation exchange reactions of OM and clay minerals in soils [17]. Therefore, the change in the content of soil components (OM and clay) and their protonation-deprotonation characteristics by acid or alkali spills is likely to decrease the pH buffering capacity of the soils.

#### 3.2. Characteristics of clustered soil groups and changes in soil properties of each group after spills

Although acid or alkali spills changed the physicochemical properties of the soil and decreased the pH buffering capacity, the extent of the decrease widely varied depending on the type of soil. To identify the soils that were ecologically susceptible to acid and alkali spills, we conducted clustering analysis, and soils were classified into three groups based on OM and clay content, CEC, and pH buffering capacity (Fig. S2). The physicochemical properties and pH buffering capacity of each group before acid or alkali spills are summarized in Table 2, and all statistical test results are summarized in Table S6. Seven, eight, and five soils were classified into groups 1, 2, and 3, respectively. Soils in group 1 contained a small amount of OM and clay and consequently had a low CEC and pH buffering capacity. They were classified as sand or loamy sand according to the soil texture (Table S1). In contrast, soils in group 3 contained a large amount of OM and clay, and therefore had a high CEC and pH buffering capacity. Their soil textures were sandy loam or loam. The other soils were classified into group 2 and contained a small amount of OM but a high content of clay, which resulted in high CEC and moderate pH buffering capacity. Their soil textures were also classified as the loam type including sandy loam, sandy-clay loam, and loam. Therefore, soils in the order of groups 1, 2, and 3 were more fertile, with higher ecological values.

Fig. 2A shows box plots of the physicochemical properties and pH buffering capacity of the three clustered soil groups before and after acid or alkali spills. Acid spills decreased the OM of groups 1, 2, and 3 from 1.91%, 2.68%, and 6.02%–0.43%, 1.46%, and 3.24%, respectively, and alkali spills decreased the OM of groups 1, 2, and 3 to 0.50%, 1.24%, and 1.34%, respectively. Both acid and alkali spills did not result in a statistically significant change in the clay content of each group. The CEC of groups 1, 2, and 3 was decreased by acid spills from 4.49, 16.54, and  $20.40 \text{ cmol kg}^{-1}$ , respectively, to 1.29, 13.97, and  $12.42 \text{ cmol kg}^{-1}$ , respectively, and also

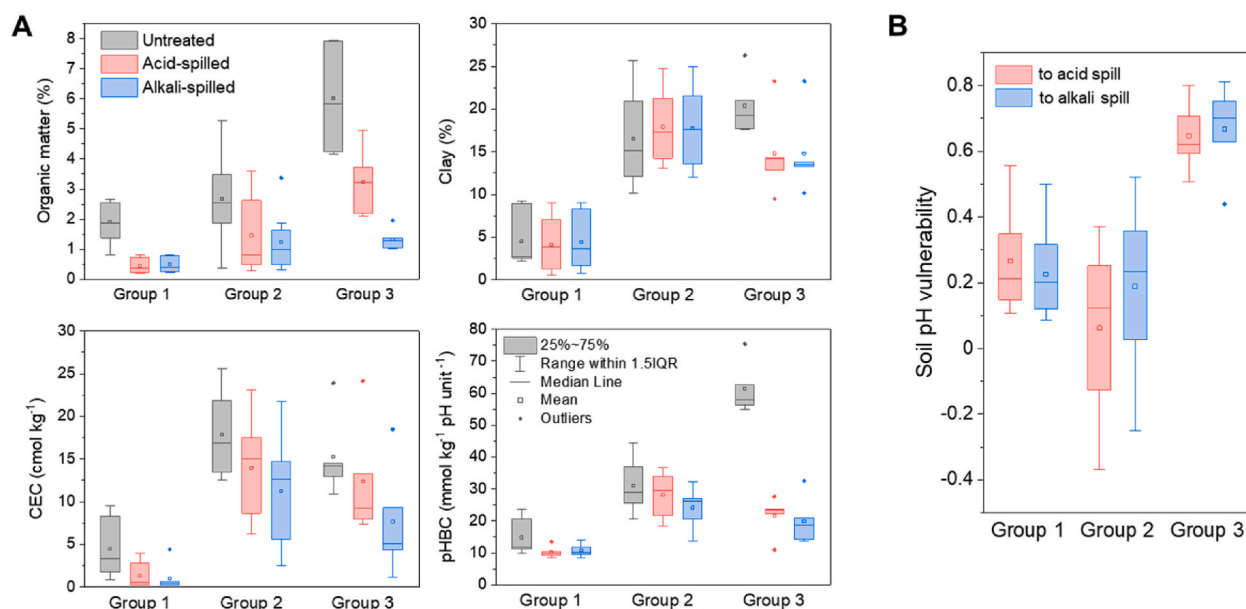


**Fig. 1.** Box plots of organic matter content, clay content, CEC, and pH buffering capacity of untreated, acid-spilled, and alkali-spilled soils. Black dots represent actual data points, whereas red dots represent the mean values. Asterisk represents the significant difference in properties before and after acid or alkali spills ( $p < 0.05$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 2**  
Physicochemical properties of three clustered soil groups and their 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 <sup>-1</sup> )	4.49 ± 3.17	16.54 ± 5.78	20.40 ± 3.57
pHBC (mmol kg <sup>-1</sup> )	14.85 ± 5.30	30.99 ± 7.92	61.49 ± 8.32
Characteristics <sup>a</sup>	Low OM Low Clay Low CEC Low pHBC	Low OM High Clay High CEC Moderate pHBC	High OM High Clay High CEC High pHBC

<sup>a</sup> Group 1 had the lowest organic matter and clay content, CEC, and pH buffering capacity among the three groups, whereas group 3 had the highest organic matter content, CEC, and pH buffering capacity. The organic matter content of group 2 was greater than that of group 1 (without statistical significance) but significantly lower than that of group 3. The 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 but lower than that of group 3 (without statistical significance). The pH buffering capacity of group 2 was significantly greater than that of group 1 but significantly lower than that of group 3.



**Fig. 2.** Box plots of the properties of three clustered soil groups: (A) physicochemical properties (*i.e.*, organic matter content, clay content, and CEC) and pH buffering capacity before and after acid or alkali spills and (B) soil pH vulnerability to acid or alkali spills.

decreased by alkali spills to 1.01, 11.28, and 7.68 cmol kg<sup>-1</sup>, respectively. The OM and CEC were more drastically reduced by alkali spills because soil OM, such as humic and fulvic acids, is possibly desorbed and dissolved in alkali solutions [7].

Particularly, acid and alkali spills caused the most significant decrease in the OM and CEC of soils in group 3. The OM was decreased by 46% and 78%, respectively, and the CEC was decreased by 39% and 62%, respectively. Likewise, acid or alkali spills decreased the pH buffering capacity of groups 1 and 2 by less than 30% and 20%, respectively. However, acid or alkali spills significantly reduced the pH buffering capacity of group 3 by more than 65%, from 61.49 mmol kg<sup>-1</sup> pH unit<sup>-1</sup> to 21.62 or 20.00 mmol kg<sup>-1</sup> pH unit<sup>-1</sup>, respectively. This shows that although the tendency of changes in physicochemical and pH buffering capacity was consistent between groups, the degree of the changes due to acid or alkali spills varied by the type of group, and interestingly, the most fertile soils (group 3) were found to be the most affected by the spills.

### 3.3. Characteristics of vulnerable soils

By using the relative change in pH buffering capacity after acid or alkali spills, soil pH vulnerability to spills was calculated using Eq. (3) to evaluate the characteristics of soils that are vulnerable to spills in terms of their ecological function (Fig. 2B). Soil pH vulnerability to acid spills in groups 1, 2, and 3 was 0.27, 0.06, and 0.65, respectively, which means that 27%, 6%, and 65% of soil functions decreased by acid spills, respectively. For alkali spills, soil pH vulnerabilities were 0.23, 0.19, and 0.67, respectively,

indicating that alkali spills decreased the soil function by 23%, 19%, and 67%, respectively. Among the three groups, group 3 had the highest soil pH vulnerability to acid or alkali spills. We found a positive relationship between OM and soil pH vulnerability to acid or alkali spills, and Spearman's rank correlation coefficients of OM and soil pH vulnerability were 0.49 ( $p = 0.03$ ) and 0.74 ( $p = 0.00$ ), respectively. This indicates that an increase in OM is correlated with an increase in soil pH vulnerability to acid or alkali spills. Although OM is the most important factor determining the pH buffering capacity of soils, it is susceptible to acid or alkali spills; therefore, soils with a pH buffering capacity of  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  or more (group 3), owing to the high OM, are highly vulnerable to acid or alkali spills. However, the group 3 soils were still most fertile among the three groups based on the CEC and pH buffering capacity after acid or alkali spills.

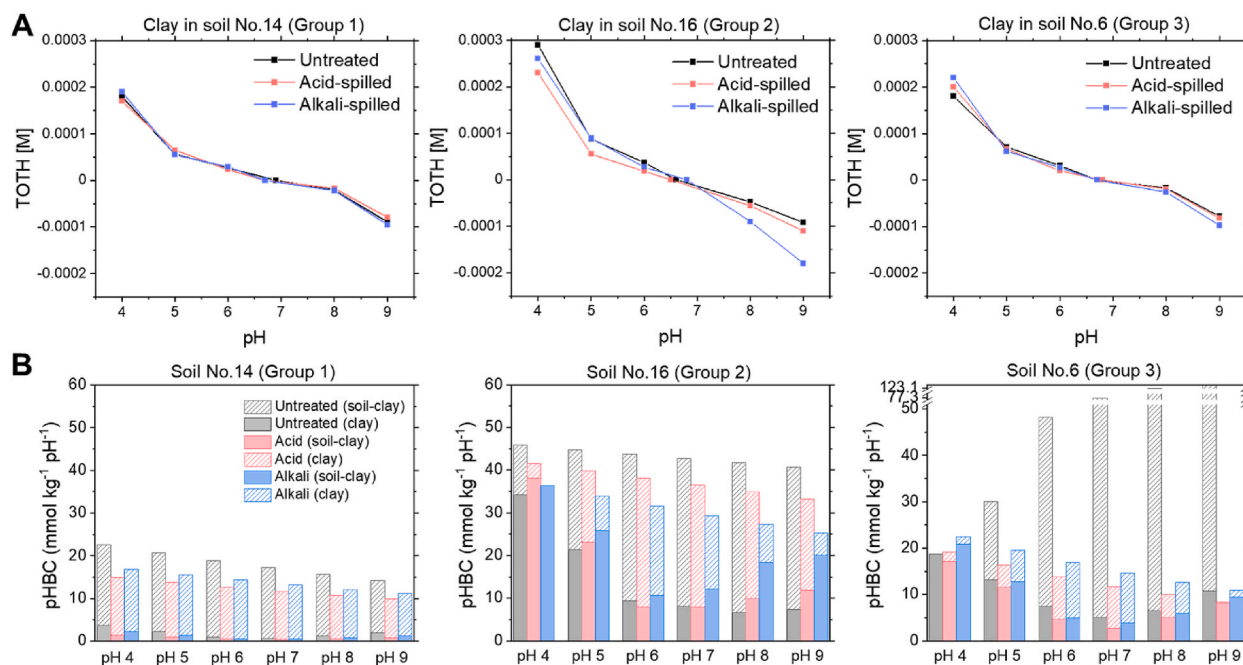
In contrast to OM, clay is resistant to acid or alkali spills. Thus, soil pH vulnerability decreases with an increase in clay content. In addition, since clay minerals have a high resistance to acid or alkali attack, and their surface properties do not substantially change [6]. This may explain why group 2 was less vulnerable than group 1, although no significant difference was present in OM. The correlations between OM or clay content and soil pH vulnerability can be utilized to predict soil pH vulnerability to acid or alkali spills based on soil properties, particularly by quantitative quality, and can also be used to classify vulnerable soils in areas with a high probability of spills and to manage these spilled areas on a site-specific basis.

### 3.4. Effect of acid or alkali spills on protonation-deprotonation characteristics of clay minerals in the soil

Clay minerals and OM are the most important components that determine the soil pH buffering capacity. Considering that the spills significantly reduced the amount of OM and did not change that of clay minerals, it is reasonable to hypothesize that the decrease in pH buffering capacity by the spills was mostly attributed to the dissolution of OM. To verify this hypothesis, we further investigated the qualitative change in the protonation-deprotonation characteristics of clay sized fraction as a result of acid or alkali spills by titration experiments. We selected one representative soil for each clustered group (soils No. 14, 16, and 6 for groups 1, 2, and 3, respectively).

The titration curves of three clay sized fractions before and after acid or alkali spills under 0.03 M of  $\text{NaNO}_3$  (50 mg of clay sized fraction in 50 mL of solution) are shown in Fig. 3A, and the y-axis represents the total molar concentration of added protons to the suspension (TOTM). As shown in Fig. 3A, acid or alkali spills had a limited effect on the acid-base properties of the clay sized fraction in groups 1 and 3. In group 2, alkali spills slightly increased the pH buffering capacity under basic conditions, which corresponds to our previous study showing that alkali spills generate  $\text{AlOH}$  and  $\text{SiOH}$  at the basal and edge sites of montmorillonite; thereby, increasing the pH buffering capacity [6]. Nevertheless, neither spill remarkably changed the protonation-deprotonation characteristics of clay sized fraction at acidic and neutral pH.

Using titration curves of clay sized fraction and clay content, we evaluated the pH buffering capacity of the clay sized fraction



**Fig. 3.** (A) Titration curves of clay minerals in untreated, acid-spilled, and alkali-spilled soils (Nos. 14, 16, and 6 for groups 1, 2, and 3, respectively) under 0.03 M of  $\text{NaNO}_3$ . The Y-axis is the molar concentration of total proton added to the solution. (B) Contribution of clay minerals and the other components to pH buffering capacity soils (Nos. 14, 16, and 6 for group 1, 2, and 3, respectively) at different pH values. Filled bars represent pH buffering capacity of clay minerals, whereas cross-hatched bars are obtained by subtracting the pH buffering capacity of clay minerals from that of the soil, which is mainly attributed to organic matter.

(Fig. 3B). In soil No. 14 in group 1, the contribution of clay to the pH buffering capacity of the untreated soil was originally marginal owing to its low clay content, and the acid-base characteristics of clay sized fraction did not change with either acid or alkali spills (Fig. 3A). In contrast, soil No. 16 in group 2 and soil No.6 in group 3 had a moderate amount of clay minerals; therefore, clay sized fraction had a higher contribution to the pH buffering capacity of the untreated soils throughout the entire pH range. Nevertheless, the change in the pH buffering capacity at neutral pH after the spills, which is the actual pH after neutralization, was negligible in all groups. Although the contribution of clay sized fraction to the pH buffering capacity of soils at neutral pH increased after the spills in all cases, it was mainly owing to a decrease in the contribution of other soil components, not because of the change in the protonation-deprotonation of clay sized fraction. This supports our claim that an increase in clay content correlates with a decrease in soil pH vulnerability because clay content did not remarkably change after either spills, and clay sized fractions were resistant to acid or alkali spills. These results also highlight that the primary reason for the decrease in pH buffering capacity by the spills is the dissolution of OM rather than a change in the surface chemistry of clay sized fraction.

### 3.5. Implication: using clay and organic matter contents to predict soil pH vulnerability

We found that quantitative soil properties play a substantial role in determining soil pH vulnerability to acid or alkali spills, and there are numerous soil databases of these basic properties, including OM and clay content. For example, the Global Soil Information System provides a global soil organic carbon map and the NASA Land Data Assimilation System provides a global soil texture map including a fraction of clay [32,33]. However, it is more difficult to obtain databases for CEC and pH buffering capacity, which are the other two soil properties used to cluster soils in this study. Therefore, a simple and effective method to predict these properties is required to cluster soils and predict their vulnerability. One way to predict those properties is developing multiple linear regression model, and several studies developed multiple linear regression models to predict CEC or pH buffering capacity, which reveals that it is possible to predict the pH buffering capacity or CEC by soil OM and mineral contents [17,34,35].

To further verify whether the multiple linear regression model based on OM and clay content can predict CEC and pH buffering capacity of untreated, acid-spilled, and alkali-spilled soils, we performed SMLR, in which the CEC or pH buffering capacity were set as dependent variables, and OM and clay content were set as independent variables. The results are summarized in Table S7. In the case of CEC, all models (CEC of untreated, acid-spilled, and alkali-spilled soils) satisfied the assumptions of SMLR. For pH buffering capacity, the models of pH buffering capacity of acid-spilled and alkali-spilled soils met the assumptions of SMLR, whereas those 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), were analyzed to perform SMLR and satisfy the assumptions. Detailed information on checking the assumptions for the SMLR is summarized in Table S7 and Fig. S3.

The normalized CEC models (*i.e.*,  $CEC(\text{untreated soils}) = -1.58 + 0.82\text{Clay} + 0.30\text{OM}$ ,  $CEC(\text{acid-spilled soils}) = -3.02 + 0.95\text{Clay}$ , and  $CEC(\text{alkali-spilled soils}) = -3.63 + 0.91\text{Clay}$ ) had adjusted  $R^2$  values of 0.89, 0.90, and 0.81, respectively, suggesting that each model could explain 89%, 90%, and 81% of CEC, respectively. In the case of pH buffering capacity, the models of normalized pH buffering capacity (*i.e.*,  $\text{pHBC}(\text{untreated soils}) = -2.30 + 0.35\text{Clay} + 0.74\text{OM}$ ,  $\text{pHBC}(\text{acid-spilled soils}) = 7.67 + 0.79\text{Clay}$ , and  $\text{pHBC}(\text{alkali-spilled soils}) = 6.68 + 0.90\text{Clay}$ ) had adjusted  $R^2$  values of 0.79, 0.61, and 0.80, respectively. It indicates 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. According to Neter et al. the adjusted  $R^2$  value can be used to evaluate the predictive ability [36]. Based on the predictive ability, the overall CEC and pH buffering capacity of all three types of soils was successfully predicted by a linear combination of clay and OM content without considering any qualitative properties of clay and OM, as previously described [35]. Interestingly, clay content was selected as the independent variable for both CEC and pHBC models of all three types of soils, whereas OM was only selected for the models of untreated soils. Nevertheless, the models of both acid- and alkali-spilled soils could accurately predict CEC and pH buffering capacity using only clay content. This result is likely because OM, which has a great influence on CEC or pH buffering capacity, was removed through desorption or dissolution, which also corresponds to our results showing that the relative contribution of clay minerals to the pH buffering capacity of soil increases after the spills owing to a decrease in OM (Fig. 3B).

We also investigated whether the SMLR models obtained for one type of soil can be used to predict the CEC and pH buffering capacity of the other two types. Fig. S4 shows the plot of CEC and pH buffering capacity predicted using the SMLR against the measured CEC and pH buffering capacity. It should be noted that the SMLR models of pH buffering capacity obtained from either acid- or alkali-spilled soil cannot accurately predict some untreated soils (Soil Nos. 5, 6, 8, 17, and 20) whose pH buffering capacity was greater than  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ , all of which belong to group 3. This might be because they originally contained relatively higher amounts of OM (6%) compared to those of other soils, and the remaining OM after acid or alkali spills was still not negligible (Table S2). Therefore, SMLR models that do not consider OM are prone to substantially underestimating the pH buffering capacity of fertile soils. However, the pH buffering capacity of all three types of soils was successfully predicted by the SMLR model obtained from untreated soils, which had both OM and clay content as independent variables for the model. Similarly, the SMLR model of CEC obtained from untreated soil could predict the CEC of all three types of soil. Even neutralized soils after acid or alkali spills nearly followed multiple linear regression models that were established by the untreated soils before the spills. This can be explained by the small difference in the unstandardized coefficient of clay between the three SMLR models (Table S7) and the decrease in the OM of the acid- or alkali-spilled soils. Because clay content did not remarkably change by the spills, the SMLR model obtained from the untreated soils predicted the CEC or pH buffering capacity of acid- or alkali-spilled soils as well.

Our results showed that multiple linear regression models using OM and clay content as independent variables can successfully estimate the CEC and pH buffering capacity of various soils. Therefore, together with available maps of soil OM and clay content, we can easily classify areas based on soil pH vulnerability to acid or alkali spills, and this information will be beneficial for site-specific



management of areas with a high incidence of acid or alkali spills. Based on the purpose of land use where spills occur, the addition of OM should be considered after neutralization. However, it should be noted that the SMLR models obtained in this study were not the universal models for the CEC and pH buffering capacity, and they were the examples of showcasing the potential implication. This implication does not discount the importance of CEC and pH buffering capacity in determining soil pH vulnerability, and it is always better to have soil physicochemical properties as well as pH buffering capacity to accurately investigate soil pH vulnerability. Therefore, more conservative and universal SMLR models of CEC and pH buffering capacity from numerous datasets of OM and clay content should be further investigated, and the validation of the models should be conducted as well.

#### 4. Conclusions

In this study, we investigated changes in the physicochemical properties and pH buffering capacity of soils in response to acid or alkali spills and identified the characteristics of soils that are vulnerable to spills. Acid or alkali spills greatly decreased the OM, CEC, and pH buffering capacity but did not cause a remarkable change in clay content. However, the extent of change in the physicochemical and pH buffering capacity of the soils differed according to the clustered soil groups. A positive correlation was detected between the clay content and soil pH vulnerability, whereas a negative correlation was detected between the OM and soil pH vulnerability. This is mainly because clay was resistant to spills and both the protonation-deprotonation properties and the content of clay were not meaningfully changed, whereas OM was susceptible to both spills because of dissolution. As a result, soils with a pH buffering capacity greater than 50 mmol kg<sup>-1</sup> pH unit<sup>-1</sup> owing to their high organic content were the most vulnerable to acid or alkali spills, although these soils were the most fertile with the highest CEC and pH buffering capacity before and after the spills. We also confirmed that CEC and pH buffering capacity could be predicted by SMLR using OM and clay content. This highlights that by using the quantitative soil properties with a number of available databases, we can easily estimate soil ecological function, and eventually it is possible to classify soils in regions with a high probability of spills by soil pH vulnerability to the spills and manage them site-specifically.

#### Author contribution statement

**Inhyeong Jeon:** Conceptualization, Methodology, Data curation, Investigation, Software, Formal analysis, Visualization, Writing – original draft. **Hyeonyong Chung:** Investigation, Validation. **Sang Hyun Kim:** Validation, Data curation. **Kyoungphile Nam:** Conceptualization, Project administration, Resources, Writing – review & editing, Supervision.

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#### Data availability statement

Data will be made available on request.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e17044>.

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