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공학석사학위논문

Effect of acid or alkali spills on physicochemical  
properties and pH buffering capacity of soil and its  
implication on soil vulnerability

산염기 유출이 토양의 물리화학적 특성 및 pH 완충능력에  
미치는 영향과 이를 이용한 토양 취약성 평가

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# Abstract

Effect of acid or alkali spills on physicochemical properties and pH buffering capacity of soil and its implication on soil vulnerability

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Acid or alkali spills occurs annually and accounts for around 50% of the total chemical accident in South Korea. Physicochemical properties of soils including organic matter content, cation exchange capacity (CEC), base saturation, and exchangeable cations changed as a result of acid or alkali spills. After these spills, as a part of the remediation, a neutralization, pouring neutralizing agents onto the acid- or alkali-spilled soil, has been performed, but it could not recover irreversible alteration of soil properties, such as dissolution of organic matter and structural modification of clay minerals. Due to the changes in soil properties, soil functions, particularly pH buffering capacity, might be altered despite

neutralization. In addition, since organic matter content decreased after acid or alkali spills, the clay minerals would play a significant role in pH buffering capacity of soils. Knowledge of the effect of acid or alkali spills on soils is essential in order to manage acid- or alkali-spilled sites properly; Thus, we investigated the effect of acid or alkali spills on soils and identified characteristics of soils which exhibit vulnerability to the spills. In addition, changes in surface properties of clay minerals as a result of the spills and its effect on pH buffering capacity of clay minerals were investigated.

Twenty field soils were collected and reacted with HCl and NaOH, respectively (i.e. one gram of soil received 30 mmol of HCl and NaOH, respectively), to simulate acid or alkali spills. The soils were neutralized to pH 6–8 and freeze-dried. Organic matter and clay content, and cation exchange capacity (CEC) of three different soils (untreated, acid-spilled, and alkali-spilled) were measured and pH buffering capacity, which is an indicator of soil function, was derived from titrations. In addition, statistical analyses including clustering analysis were conducted to identify characteristics of vulnerable soils. Acid or alkali spills significantly decreased organic matter from 3.25% to 1.55 and 1.00%, respectively, and decreased CEC from 13.29 cmol kg<sup>-1</sup> to 9.14 and 6.79 cmol kg<sup>-1</sup>, respectively. No change in clay content was detected. The pH buffering capacity decreased from 32.96 mmol kg<sup>-1</sup> pH unit<sup>-1</sup> to 20.26 and

18.48 mmol kg<sup>-1</sup> pH unit<sup>-1</sup>, respectively. The pH buffering capacity of untreated soils was strongly predicted (79%) by linear combination of organic matter and clay content, while that of acid- or alkali-spilled soils was well predicted by only clay content (61 and 80%, respectively) due to decrease in organic matter. Of the three clustered soil groups, the group of which pH buffering capacity is greater than 50 mmol kg<sup>-1</sup> pH unit<sup>-1</sup> was the most vulnerable to acid or alkali spills, and pH buffering capacity was decreased by 65%. This might be due to a greater organic matter content in this group, which increases vulnerability to the spills.

To investigate the effect of acid or alkali spills on clay minerals, kaolinite and montmorillonite were selected as 1:1 and 2:1 clay minerals, respectively. Because surface properties including site density of surface functional groups and their surface acidity constants (i.e. pK<sub>a1</sub> and pK<sub>a2</sub>) determined pH buffering capacity of clay minerals, the effect of acid or alkali spills on surface properties was investigated. Surface complexation modeling with potentiometric titrations and Fourier-transform infrared spectroscopy showed that acid or alkali spills did not significantly change the surface properties of kaolinite. In montmorillonite, however, acid spills decreased the basal site density from 832 to 737 mmol kg<sup>-1</sup> by dissolving substituted octahedral cations and decreased pK<sub>a2</sub> from 7.32 to 5.42 by dissolving SiOH. In response to alkali spills, the basal site density increased to 925 mmol kg<sup>-1</sup> through the isomorphic substitution, and the

edge site density increased from 84.8 to 253.2 mmol kg<sup>-1</sup> due to AlOH and SiOH formation; thus, pKa<sub>2</sub> decreased to 6.78. The pH buffering capacity of acid- or alkali-spilled kaolinite at pH 6 did not significantly change, while that of acid- or alkali-spilled montmorillonite increased from 30.33 to 35.89 and 56.03 mmol kg<sup>-1</sup> pH unit<sup>-1</sup>, respectively. Our results indicate that these spills greatly altered the surface properties of montmorillonite, but unexpectedly, increased the pH buffering capacity of montmorillonite.

This study clearly shows that acid or alkali spills did not have an adverse effect on pH buffering capacity of clay minerals, and that soil vulnerability to acid or alkali spills can be predicted based on soil properties, 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.

**Keyword: Acid or alkali spill, soil property, pH buffering capacity, clay mineral, surface complexation modeling**

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# Chapter 1. Introduction

## 1.1. Background

As the chemical industry develops, chemical accidents occur annually, and of them, acid or alkali spills are of great concern because of their high frequency and hazard (Kleindorfer et al., 2007). According to the Chemistry Safety Clearing-house database (Ministry of Environment, 2017), acid or alkali spills accounted for 46% of the chemical accidents in South Korea (Shin et al., 2014; National Institute of Environmental Research, 2013; Ministry of Environment, 2013). Regarding to the individual substances in the acid spills, hydrogen chloride (42%) was most frequently spilled, followed by sulfuric acid (26%), hydrogen fluoride (12%) and nitric acid (7%) (National Institute of Environmental Research, 2013).

Strong acid or strong alkali materials have acute hazards that have a negative effect on the human and the environment. Particularly, if strong acid or alkali materials are spilled onto soils, most of the physicochemical properties of the soils are altered, such as pH, soil texture, surface area, organic matter content, cation exchange capacity (CEC), and exchangeable cations (Jeon, Jung, and Nam,

2017). When strong acid is introduced to the soil, aluminum or iron oxide is dissolved, and the dissolved  $\text{Al}^{3+}$  or  $\text{Fe}^{2+}$  insolubilizes phosphorus used as a nutrient to the plants, and  $\text{Al}^{3+}$  replaces the exchangeable cations also used as a nutrient (Bohn, Myer, and O'Connor, 2002; Sposito, 2008; Ulrich and Sumner, 2012). 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 ( $\text{B}^{3+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Li}^+$ ) in the soil water (Bohn et al., 2002; Sposito, 2008). In addition, both humic acid and fulvic acid can be dissolved by strong alkali (Bohn et al., 2002).

Although neutralizers have been poured onto acid or alkali spilled soils for pH recovery (Kastman, Ghalib, and Zagula, 1992; Protopopov, Seredina, and Molokova, 2000), neutralization cannot recover nonreversible dissolution of organic matter or clay minerals and the change in CEC caused by the structural deterioration (Goulding, 2016). However, such neutralization cannot reverse changes such as a dissolution of organic matter or clay minerals and structural deterioration of soils (Goulding, 2016). 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. These effects of acid or alkali spills on physicochemical properties of soils should be further investigated because changes in these properties will alter soil ecological functions (Blum, 2005; Michael, Fitzpatrick, and Reid, 2015), particularly pH buffering capacity which determines soil productivity and the water quality of stream water (Jiang et al., 2016). The pH buffering is greatly related to the physicochemical properties of soils and it can be greatly altered by acid or alkali spills; Thus, studies of the change in pH buffering capacity of acid or alkali spilled soil after neutralization are needed.

For this purpose, the effects of acid or alkali spills on organic matter and clay minerals, the soil constituents that determine the pH buffering capacity of soils (Aitken, Moody, and McKinley, 1990), should be analyzed. In the case of organic matter, acid or alkali spills desorb or dissolve it (Chen, Koopal, Xiong, Avena, and Tan, 2017; Ulrich and Sumner, 2012; Weng, Van Riemsdijk, Koopal, and Hiemstra, 2006); thus, the pH buffering capacity decreases. However, the effect of these spills on clay minerals is unclear. Less attention

has been paid on changes in clay minerals' properties due to these spills. Only a few studies revealed that an acid or alkali treatment at room temperature over two weeks not only altered a crystal structure of clay minerals but also increased surface area (Jozefaciuk and Bowanko, 2002). Instead, many studies have focused on an acid or alkali activation treating clay minerals with high concentration of acid or alkali at high temperature, and its effect on clay minerals' surface area, porosity and surface acidity (Bhattacharyya and Gupta, 2008; Pálková, Hronský, Jankovič, and Madejová, 2013; Ravichandran and Sivasankar, 1997). However, this reaction condition is unrealistic in natural environment after acid or alkali spills. To predict the pH buffering capacity of acid- or alkali-spilled clay minerals, the site density and surface reaction constants of clay minerals should be determined. Previous studies have successfully identified the site density of surface functional groups in clay minerals and their surface reaction constants using surface complexation modeling (Bourg, Sposito, and Bourg, 2007; Tournassat, Davis, Chiaberge, Grangeon, and Bourg, 2016). Nevertheless, there have been no studies investigating alterations of surface properties of clay minerals at ambient temperature following intensive acid or alkali treatment, which is similar to acid or alkali spills. In addition, clay minerals play

a significant role in the pH buffering capacity of soils with low organic matter content resulting from acid or alkali spills; thus, knowledge of the changes in clay minerals' properties after these spills is essential to interpret the pH buffering capacity of the soils.

To manage acid- or alkali-spilled soils properly with regard to the recovery of soil function, the effect of acid or alkali spills on soil properties and pH buffering capacity should be investigated. In addition, soil properties to determine pH buffering capacity should be evaluated. They can be useful information to select vulnerable soils in advance, and to determine the extent of the damage after acid or alkali spills.

## 1.2. Objectives

The objective of this research is to investigate the effect of acid or alkali spills on physicochemical properties and pH buffering capacity of soils and to identify characteristics of vulnerable soils. The detailed research objectives are as follows:

- 1) To investigate the effect of acid or alkali spills on physicochemical properties and pH buffering capacity of soils, and to identify soil properties determining pH buffering capacity of soils
- 2) To identify characteristics of soils which are more highly vulnerable to acid or alkali spills
- 3) To investigate the effect of acid or alkali spills on surface properties and pH buffering capacity of clay minerals

## Chapter 2. Materials and Method

### 2.1. Materials

#### 2.1.1. 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 untreated soils were characterized for soil pH, organic matter content (OM) and 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 (Sparks, Helmke, and Page, 1996). Organic matter content was determined through using loss on ignition method (Heiri, Lotter, and Lemcke, 2001). Clay content was measured by using sedimentation method according to the Methods of Soil Analysis, Part 4–Physical Methods (Sparks et al., 1996). The CEC was determined using the sodium acetate method procedure following the US Environmental Protection Agency (US EPA) Method 9081 (USEPA, 1986). The

properties of soils used in this study are summarized in the Table 2.1, and all chemicals used in this study were of extra pure or reagent grade.

**Table 2.1**

Physicochemical properties of soils used in this study

| Label   | Properties |         |                              |           |
|---------|------------|---------|------------------------------|-----------|
|         | pH         | OM<br>% | CEC<br>cmol kg <sup>-1</sup> | Clay<br>% |
| Soil 1  | 5.81       | 1.38    | 5.24                         | 2.24      |
| Soil 2  | 5.26       | 1.95    | 14.26                        | 12.37     |
| Soil 3  | 5.71       | 1.87    | 8.36                         | 8.94      |
| Soil 4  | 6.04       | 2.16    | 20.95                        | 17.60     |
| Soil 5  | 7.09       | 4.26    | 10.88                        | 17.65     |
| Soil 6  | 4.8        | 4.16    | 12.96                        | 17.71     |
| Soil 7  | 5.3        | 1.73    | 3.32                         | 2.71      |
| Soil 8  | 4.2        | 7.92    | 14.22                        | 19.31     |
| Soil 9  | 5.08       | 3.00    | 12.77                        | 10.14     |
| Soil 10 | 7.17       | 0.38    | 25.60                        | 25.64     |
| Soil 11 | 6.69       | 0.83    | 9.51                         | 9.29      |
| Soil 12 | 6.9        | 2.65    | 0.91                         | 2.74      |
| Soil 13 | 7.4        | 2.54    | 2.51                         | 2.55      |
| Soil 14 | 7.4        | 2.40    | 1.75                         | 2.97      |
| Soil 15 | 5.3        | 1.80    | 14.67                        | 13.51     |
| Soil 16 | 6.8        | 3.98    | 22.83                        | 16.85     |
| Soil 17 | 4.4        | 7.95    | 14.55                        | 21.06     |
| Soil 18 | 4.6        | 2.91    | 12.57                        | 11.91     |
| Soil 19 | 6.2        | 5.28    | 19.20                        | 24.33     |
| Soil 20 | 4.7        | 5.83    | 23.90                        | 26.29     |

### 2.1.2. Clay minerals

Kaolinite and montmorillonite were selected as 1:1 and 2:1 clay mineral, respectively. KGa-1b kaolinite (Georgia) and SWy-3 montmorillonite (Wyoming) were purchased from the Clay Minerals Society's Source Clays Repository. The clay minerals were prepared following a similar procedure to the best practices for analyzing surface properties of montmorillonite reviewed by Duc et al. (Chorover et al., 2003; M. Duc, F. Gaboriaud, and F. Thomas, 2005; Myriam Duc, Fabien Gaboriaud, and Fabien Thomas, 2005; Sarkar, Essington, and Misra, 2000). Thirty grams of kaolinite and montmorillonite was dispersed in 1 L of deionized water with a specific resistance of 18.2 M $\Omega$  m (Milipore, Bedford, Ma, USA) for 4 h. Prior to the size separation, the pH value of the kaolinite suspension was adjusted to 9.5 by adding NaOH (98%, Daejung, Korea) to facilitate a dispersion. The <2- $\mu$ m fraction of each clay mineral was collected via centrifugation (119 g, 5 min). This fraction was washed with 1 M NaNO<sub>3</sub> (99%, Daejung, Korea) and HNO<sub>3</sub> (60%, Daejung, Korea) solution at pH 3 and the supernatant was decanted after centrifugation. This decarbonating procedure was repeated until the supernatant pH reached 3. The clay minerals were then collected

via centrifugation and washed three times with 1 M NaNO<sub>3</sub> solution to change the clays to an Na<sup>+</sup> form. Excess salt was removed by washing five times with deionized water and the collected clay minerals were freeze-dried. These clay minerals are referred to as untreated clay minerals.

The CEC of untreated kaolinite and montmorillonite, measured using the ammonium acetate method (Schollenberger and Simon, 1945), was 44 and 832 mmol kg<sup>-1</sup>, respectively. The specific surface areas of the untreated kaolinite and montmorillonite, obtained using N<sub>2</sub>-Brunauer-Emmett-Teller (BET) analysis (ASAP2020, Micromeritics, USA) (Brunauer, Emmett, and Teller, 1938), were 12.10 and 33.75 m<sup>2</sup> g<sup>-1</sup>, respectively. These values were used as parameters for the surface complexation modeling.

## 2.2. Method

### 2.2.1. Acid or alkali spill and neutralization

HCl (35%, Daejung, Korea) and NaOH were selected as the strong acid and alkali, respectively, based on their frequency of chemical accidents and amount of use (Kleindorfer et al., 2007; Shin et al., 2014). Ten gram of the untreated soil was placed in a 50-mL conical tube and 30 mL of 10 M HCl or NaOH was added to simulate an extreme acid or alkali spill situation. Likewise, in the case of the untreated clay minerals, one gram of the untreated kaolinite or montmorillonite was placed in the conical tube and 45 mL of 5 M HCl or NaOH was added. Whole reactions were conducted in a rotating shaker at 25°C and 40 rpm for two days. The suspension was centrifuged and the supernatant solutions were filtered through a 0.22- $\mu\text{m}$  filter (Whatman, UK). The supernatant solutions of clay minerals were analyzed by using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7400, Thermo Fisher Scientific, USA) to determine the dissolution of the major constituents of kaolinite and montmorillonite such as Al, Si, Fe, and Mg.

Separated soils or clay minerals were washed with deionized water five times to remove excess salts and dissolved ions. A neutralization process was needed because excess  $H^+$  and  $OH^-$  remaining after washing and decanting could affect the titration experiment. Thus, the washed soils and clay minerals were neutralized by adding  $HNO_3$  or  $NaOH$  until the supernatant pH reached a neutral pH range. The suspensions were centrifuged and decanted. In the case of clay minerals, the residual clay minerals were washed three times with 1 M  $NaNO_3$  to make them homoionic, and then were washed five times with deionized water. The residual soils and clay minerals were freeze-dried. The CEC of acid- or alkali-spilled kaolinite was  $4.7 \text{ cmol kg}^{-1}$ , while that of acid- or alkali-spilled montmorillonite was 737 and 925  $\text{mmol kg}^{-1}$ , respectively. The specific surface area of the acid- or alkali-spilled kaolinite was 13.60 and  $14.14 \text{ m}^2 \text{ g}^{-1}$ , respectively, while that of the acid- or alkali-spilled montmorillonite was 34.88 and  $19.32 \text{ m}^2 \text{ g}^{-1}$ , respectively.

### 2.2.2. Titration experiment

The titration curves obtained through titration experiment are

normally used to compare the pH buffering capacity for different samples including soils (Xu, Zhao, Yuan, and Jiang, 2012b). In addition, the titration method has been used to quantify the density of active reaction sites of clay minerals and determine the surface acidity constants ( $K_a$ ) of those sites (Baeyens and Bradbury, 1997; Bourg et al., 2007; Bradbury and Baeyens, 1997; Brady, Cygan, and Nagy, 1996; M. Duc et al., 2005; Gu, Evans, and Barabash, 2010; Komarek, Koretsky, Stephen, Alessi, and Chrastny, 2015; Y. Liu et al., 2018; Schindler, Liechti, and Westall, 1987; Tertre, Castet, Berger, Loubet, and Giffaut, 2006; Tournassat et al., 2016; Tournassat, Greneche, Tisserand, and Charlet, 2004; Wanner et al., 1994).

#### 2.2.2.1. Discontinuous titration experiment for soils

Discontinuous titration was performed to measure pH buffering capacity of three different soils (untreated, acid-spilled, and alkali-spilled) (Aitken and Moody, 1994; Nelson and Su, 2010; Xu et al., 2012b). In discontinuous titration, titration curves were obtained by incremental input of titrants to soil suspension. Many studies have used the discontinuous titration method, which could

minimize unstable pH reading (Anda, Shamsuddin, Fauziah, and Omar, 2008), to measure the pH buffering capacity of soils (Nelson and Su, 2010; Xu, Zhao, Yuan, and Jiang, 2012a). 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<sub>3</sub> 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<sub>3</sub> (99%, Daejung, Korea) to minimize the effect of background electrolyte concentration on the titration experiment. The suspensions were then purged with N<sub>2</sub> 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.

#### 2.2.2.2. Continuous titration experiment for clay minerals

The protonation behaviors of three different kaolinite or montmorillonite (untreated, acid-spilled, and alkali-spilled) were investigated using an automatic potentiometric titrator (G10S, Mettler-Toledo, Switzerland). Due et al. recommended the best experimental conditions for the titrations to analyze the acid-base properties of montmorillonite (M. Duc et al., 2005; Myriam Duc et al.,

2005; Duc, Thomas, and Gaboriaud, 2006), and we adapted the procedure with some modifications as follows.

All titration experiments were performed within a pH range of 4–9 at  $25 \pm 1^\circ\text{C}$  under an  $\text{N}_2$ -purging condition. Kaolinite (0.1 g) or montmorillonite (0.05 g) was dispersed in 50 mL of background electrolyte ( $\text{NaNO}_3$ ) solution, and the suspensions were purged with  $\text{N}_2$  for 1 h to exclude  $\text{CO}_2$ . The suspensions were continuously stirred and purged with  $\text{N}_2$  during each titration. Titrations of each clay suspension were conducted at three different concentrations of  $\text{NaNO}_3$  (0.1, 0.01, and 0.001 M) to investigate the effect of the background electrolytic concentration. Titrant solutions (0.1 M  $\text{HNO}_3$  or  $\text{NaOH}$ ), also purged with  $\text{N}_2$ , were added to the suspensions as 5–10- $\mu\text{L}$  increments every 5 min, and the pH was automatically recorded. Previous research has demonstrated that a short time interval between successive increments of titrant, generally less than 10 min, is reasonable to minimize mineral dissolution (Brady et al., 1996; M. Duc et al., 2005; Rozalen, Brady, and Huertas, 2009; Tertre et al., 2006; Wanner et al., 1994). Drifts in the measured potential were less than  $1 \text{ mV min}^{-1}$  in all titration experiments. Two independent titrations of each clay suspension, from initial pH to pH 4 and from initial pH to pH 9, were conducted and combined to obtain

one titration curve ranging from pH 4 to 9. This pH range was selected because it is known that the dissolution of kaolinite and montmorillonite is negligible in this pH range (Baeyens and Bradbury, 1997; Gu et al., 2010; Tournassat et al., 2004).

### 2.2.3. Surface complexation modeling

A constant capacitance model with permanent negatively charged sites on basal plane and variable charged sites on the mineral edges was chosen to model the surface properties of the kaolinite and montmorillonite (Gu and Evans, 2008; Gu et al., 2010; X. Liu et al., 2013). The former was referred to as basal sites, while the latter as edge sites. A proton exchange reaction occurred on the basal sites of the clay minerals, while a protonation or deprotonation reaction occurred on the edge sites of them. The least square fitting program FITEQL 4.0 was used to optimize the site densities of the kaolinite and montmorillonite and their surface reaction constants from the titration experiment (Herbelin and Westall, 1999). The CEC of the kaolinite and montmorillonite was used as the total site density of the kaolinite and the basal site density of the montmorillonite, respectively (Bourg et al., 2007; Gu and Evans, 2008; Gu et al., 2010).

FITEQL failed to converge without fixing the equilibrium constant of the kaolinite's proton exchange reaction probably because the titration curves of the kaolinite could be well described without considering the basal sites' proton exchange reaction. Thus,  $pK_H$  of the kaolinite's proton exchange reaction constant was assumed to be  $-2.9$  (Table 2), which is an averaged value from references (Angove, Johnson, and Wells, 1997; Ikhsan, Johnson, and Wells, 1999; Schindler et al., 1987; Srivastava, Singh, and Angove, 2005)

A total of six parameters (surface acidity constants ( $K_{a1}$ ,  $K_{a2}$ ), proton exchange reaction constant ( $K_H$ ), edge and basal site density, and capacitance ( $\kappa$ )) were set as adjustable parameters for optimization. In the case of kaolinite, titration data under 0.1 and 0.01 M  $\text{NaNO}_3$  conditions were used to optimize  $K_{a1}$ ,  $K_{a2}$ , and the edge site density because the proton exchange reaction only slightly affected the titration curves under these conditions. The basal site density was calculated from the difference between the total site density and the averaged edge site density. Finally, all titration data were used to check the convergence with fixing all the averaged surface properties. This successive step was continued until a goodness-of-fit, indicated by the WSOS/DF value of the FITEQL, was between 0.1 and 20 (Herbelin and Westall, 1999). In the case of

montmorillonite, titration data under 0.1 and 0.01 M NaNO<sub>3</sub> conditions were used to optimize the K<sub>a1</sub>, K<sub>a2</sub>, and edge site density just as for kaolinite. In addition, titration data under a 0.001 M NaNO<sub>3</sub> condition was used to optimize K<sub>a1</sub>, K<sub>a2</sub>, edge site density, and K<sub>H</sub>. All titration data were used to check the convergence with fixing all averaged surface properties, and this successive step was also continued until the convergence was achieved. In this study,  $\kappa$  was treated as an adjustable parameter for convergence because it cannot be experimentally determined (Motta and Miranda, 1989). The  $\kappa$  of untreated, acid-spilled, and alkali-spilled kaolinite was 2.4 Farad m<sup>-2</sup>, and that of untreated, acid-spilled, and alkali-spilled montmorillonite was 2.8, 1.9, and 8.0 Farad m<sup>-2</sup>, respectively.

#### 2.2.4. Calculation of pH buffering capacity

The pH buffering capacity was calculated from the reciprocal of the slope of the titration curve.

##### 2.2.4.1. Soils

A linear approximation has successfully explained the

titration curve of soils in the pH 4.5–6.5 range (Aitken et al., 1990; Magdoff and Bartlett, 1985). However, considering the dramatic increase with decreasing or increasing pH, the titration curve is generally modeled as a sigmoidal curve (Nelson and Su, 2010). In this study, the sigmoid function was used to approximate the shape of titration curves of soils (Nelson and Su, 2010), and the equation is as follows Eq. (1):

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

in which A is the amount of acid (negative) or alkali (positive) added to the soil suspension, and a, b, A<sub>0</sub> and pH<sub>0</sub> were fitting parameters. The adjustable parameters were optimized through a linear least squares estimation procedure by using SigmaPlot®. By rearranging and differentiating Eq. (1), the pH buffering capacity of soils were calculated from Eq. (2):

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

#### 2.2.4.2. Clay minerals

The pH buffering capacity of clay minerals was the reciprocal of the slope of the titration curve, and it was calculated from the following Eq. (3):

$$\text{pH buffering capacity at pH } x = - (\text{TOT}_{\text{H}_{\text{pH}x+0.1}} - \text{TOT}_{\text{H}_{\text{pH}x}}) / 0.1 \quad (3)$$

where,  $\text{TOT}_{\text{H}_{\text{pH}x}}$  ( $\text{mol L}^{-1}$ ) is the total amount of proton added to the suspension of clay minerals during the titration until the suspension pH reaches a value of x. Because the initial pH of the suspension of all the clay minerals ranged from 5.5 to 6.5, the pH buffering capacity at pH 5.5, 6.0 and 6.5 was calculated from the titration curves predicted by using surface complexation modeling under 0.001 M  $\text{NaNO}_3$  condition.

#### 2.2.5. Soil vulnerability to acid or alkali spills

Soil vulnerability to acid or alkali spills is defined 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. (4):

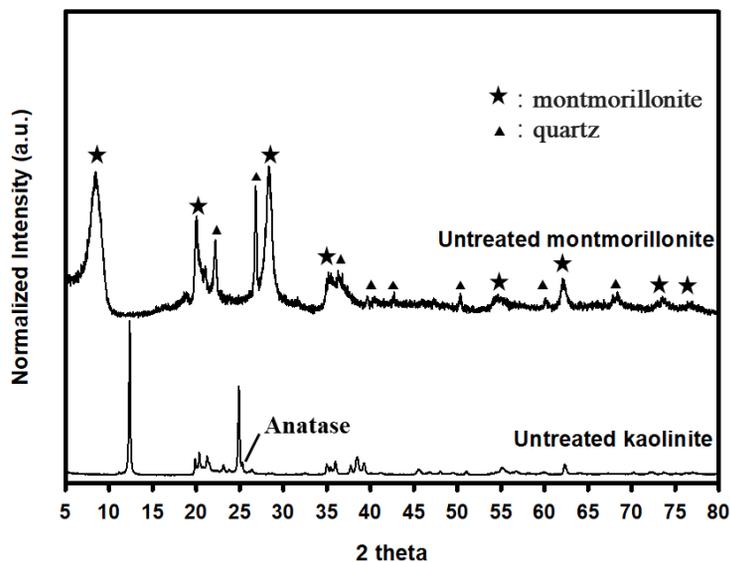
$$\text{Soil vulnerability to the acid or alkali spills} = -\frac{\Delta\text{pHBC}}{\text{pHBC}_0} \quad (4)$$

where  $\Delta\text{pHBC}$  is the change in pH buffering capacity as a result of acid or alkali spills, and  $\text{pHBC}_0$  is the pH buffering capacity of untreated soils.

## 2.2.6. Surface characterization for clay minerals

### 2.2.6.1. X-ray diffraction analysis

The mineral identity of clay samples was confirmed by X-ray diffraction analysis (XRD, D8 Advance, Bruker, Germany) using Cu K $\alpha$  radiation. The XRD patterns showed that the untreated kaolinite and montmorillonite were mainly composed of pure kaolinite and montmorillonite with some impurities such as an anatase and a quartz, respectively (Fig. 2.1). The results are consistent with the previous baseline study on the XRD patterns of KGa-1b kaolinite and Swy-2 montmorillonite (Chipera and Bish, 2001).



**Fig. 2.1.** XRD patterns of untreated kaolinite and montmorillonite. Kaolinite and montmorillonite contained an anatase and a quartz as an impurity, respectively, which is consistent with the previous baseline study on the XRD patterns of KGa-1b kaolinite and Swy-2 montmorillonite (Chipera and Bish, 2001).

#### 2.2.6.2. Fourier-transform infrared spectroscopy

Fourier-transform infrared (FT-IR) spectroscopy was used to investigate the mineralogical and chemical structure and active surface sites of clay minerals for surface acidity (Madejová, 2003; Madejova and Komadel, 2001). Clay samples were dried at 110°C

overnight to minimize water adsorption. KBr pellets were prepared by mixing kaolinite (1.5 mg) or montmorillonite (1 mg) with 240 mg of KBr powder at a pressure of 10 tons. The FT-IR spectra of the pellets with kaolinite or montmorillonite were recorded using an FT-IR spectrometer (Nicolet 6700, Thermo Scientific, USA) with 32 scans at a resolution of  $4\text{ cm}^{-1}$  within the range of  $400\text{--}4,000\text{ cm}^{-1}$ .

#### 2.2.7. Statistical analysis

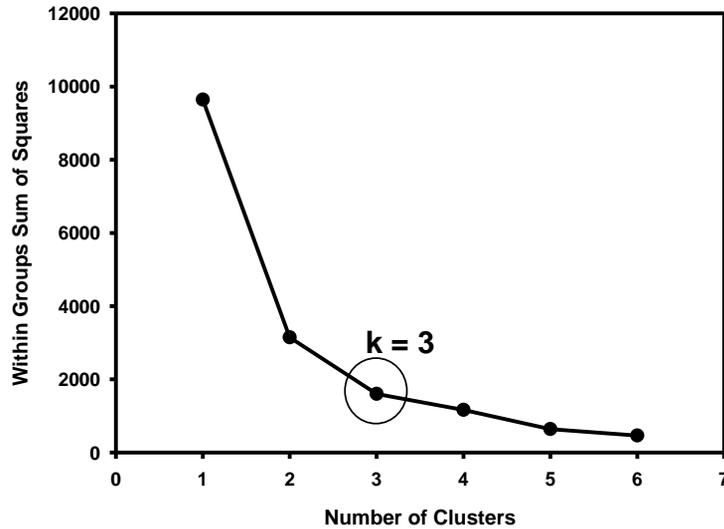
All statistical analyses were performed using SPSS 24 (IBM, USA), and all statistical tests were two-tailed with 5% significance level. Pairwise t-test or Wilcoxon signed rank test was performed to evaluate the statistically significant difference in physicochemical properties and pH buffering capacity of soils before and after acid or alkali spills. The normality of the differences was assessed using the Kolomogorov-Smirnov (KS) test. In addition, stepwise multiple linear regression analyses (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 (Montgomery, Peck, and Vining, 2012). If VIF is less than 10, there is no multicollinearity among independent variables.

In addition, 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 (Baxter and Sacks, 2014). 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 (Kaufman and Rousseeuw, 2009), and is calculated as following Eq. (5):

$$SSE = \sum_{i=1}^k \sum_{x \in C_i} distance(c_i, x)^2 \quad (5)$$

where  $k$  is the number of clusters;  $x$  is an untreated soil;  $C_i$  is the  $i$ th 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. Fig. 2.2 shows the within groups SSE for a number of clusters ranging from 1 to 6, and the within groups SSE is similar if  $k$  is greater than three; Thus, three clusters were selected as the solution.



**Fig. 2.2.** Number of clusters against within groups sum of squared errors (SSE) based on organic matter and clay content, CEC, and pH buffering capacity.

The physicochemical properties, pH buffering capacity, and soil vulnerability of each 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.

## Chapter 3. Results and Discussions

### 3.1. Effect of acid or alkali spills on physicochemical properties and pH buffering capacity of soils

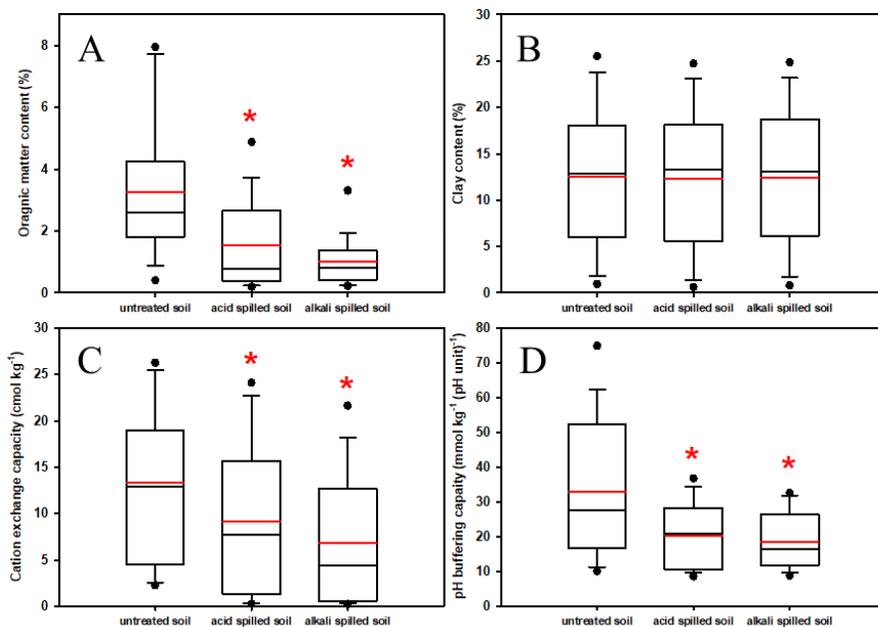
#### 3.1.1. Change in physicochemical properties and pH buffering capacity of soils due to acid or alkali spills

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 3.1, and Fig. 3.1 shows the box plot of the properties of the untreated, acid-spilled, and alkali-spilled soils. Titration curves and pH buffering capacity of three different soils are shown in Fig. 3.2 and Table 3.2.

**Table 3.1**

The 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><br>pH unit <sup>-1</sup> | %                 |                 | cmol kg <sup>-1</sup> | mmol kg <sup>-1</sup><br>pH unit <sup>-1</sup> | %                   |                 | cmol kg <sup>-1</sup> | mmol kg <sup>-1</sup><br>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<br>- 7.95 | 0.91<br>- 25.60 | 2.24<br>- 26.29       | 9.89<br>- 75.42                                | 0.19<br>- 4.94    | 0.59<br>- 24.80 | 0.26<br>- 24.15       | 8.42<br>- 36.77                                | 0.22<br>- 3.38      | 0.75<br>- 24.93 | 0.23<br>- 21.80       | 8.62<br>- 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   |



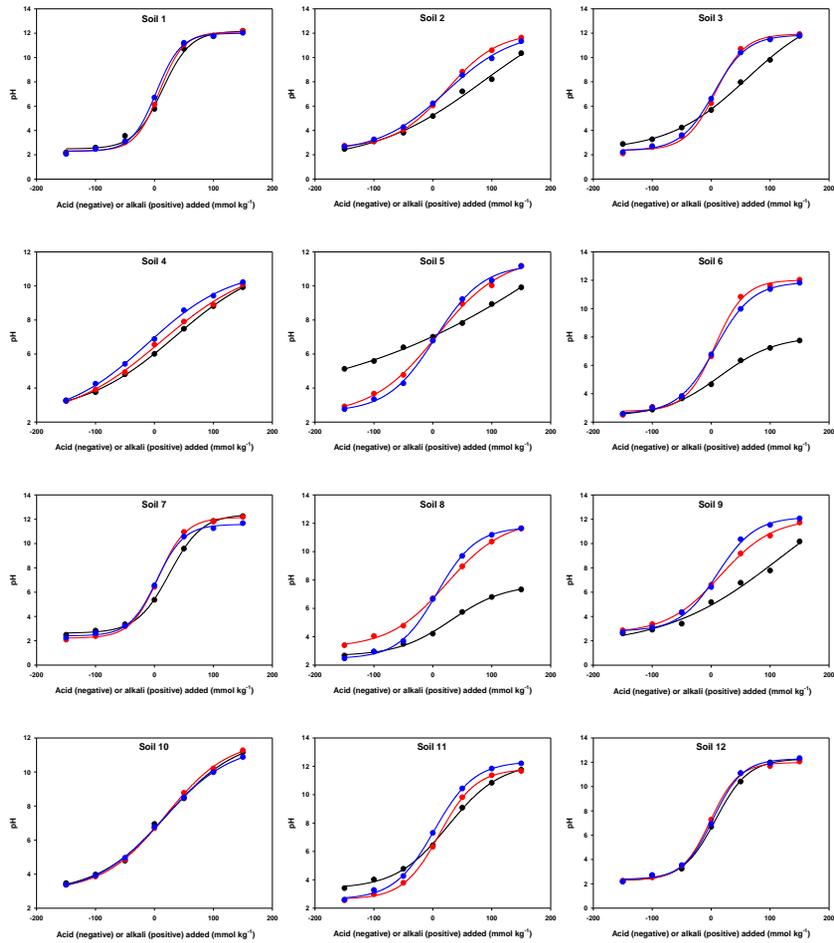
**Fig. 3.1.** Box plots of (A) organic matter content, (B) clay content, (C) CEC, and (D) pH buffering capacity of untreated, acid-spilled, and alkali-spilled soils. Red line represents the mean value. Asterisk represents the significant difference in properties before and after acid or alkali spills ( $p < 0.05$ ).

**Table 3.2**

The pH buffering capacity of twenty soils before and after acid or alkali spills

| Label      | pH buffering capacity ( $\text{mmol kg}^{-1} (\text{pH unit})^{-1}$ ) |                   |                     |
|------------|---|-------------------|---------------------|
|            | Before the spills   | After acid spills | After alkali spills |
| Soil No.1  | 9.89  | 8.42              | 8.62                |
| Soil No.2  | 29.21   | 18.38             | 22.76               |
| Soil No.3  | 23.60   | 10.49             | 11.81               |
| Soil No.4  | 34.12   | 34.52             | 32.29               |
| Soil No.5  | 62.74   | 23.83             | 18.74               |
| Soil No.6  | 55.02   | 10.94             | 13.62               |
| Soil No.7  | 11.46   | 9.47              | 10.08               |
| Soil No.8  | 75.42   | 22.18             | 14.21               |
| Soil No.9  | 28.77   | 19.18             | 13.79               |
| Soil No.10 | 26.41   | 24.08             | 26.44               |
| Soil No.11 | 20.66   | 13.47             | 14.13               |
| Soil No.12 | 11.17   | 9.97              | 10.23               |
| Soil No.13 | 11.94   | 9.42              | 9.55                |
| Soil No.14 | 15.22   | 10.49             | 11.74               |
| Soil No.15 | 20.72   | 28.38             | 25.88               |
| Soil No.16 | 39.73   | 33.52             | 26.96               |
| Soil No.17 | 56.34   | 27.66             | 20.91               |
| Soil No.18 | 24.63   | 30.60             | 18.52               |
| Soil No.19 | 44.32   | 36.77             | 26.90               |
| Soil No.20 | 57.91   | 23.49             | 32.51               |

The adjustable parameters in Eq. (1) were optimized through a linear least squares estimation procedure, and the pH buffering capacities were calculated from Eq. (2).



**Fig. 3.2.** Titration curves of twenty soils (untreated, acid–spilled, and alkali–spilled). Symbols are experimental data and lines are fitted sigmoidal curve derived from optimized adjustable parameters in Eq. (2). Black, red, and blue symbols or lines represent data of untreated, acid–spilled, and alkali–spilled soils, respectively. All experimental data fitted well within predicted titration curves.

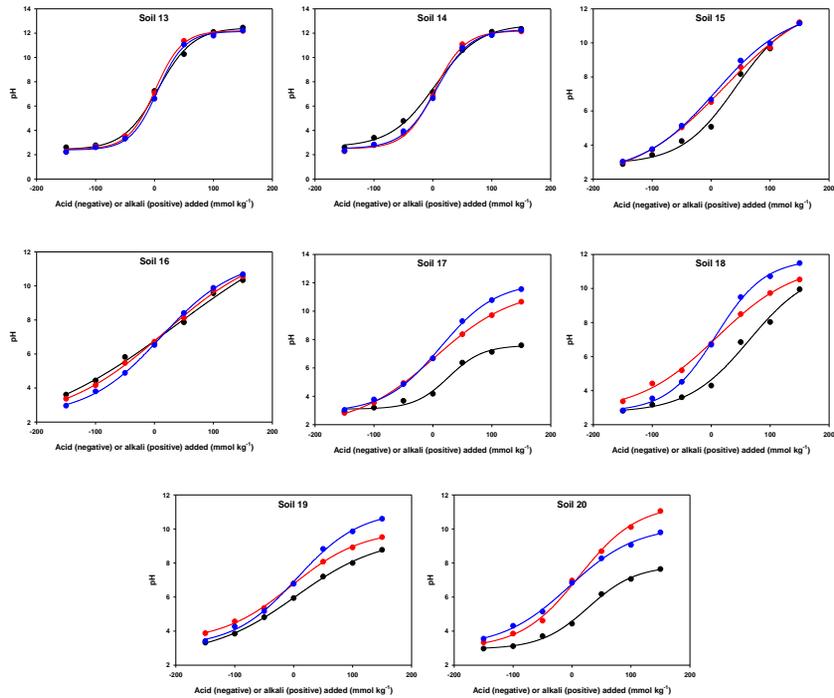


Fig. 3.2. (Continued)

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 3.3); Thus, the differences in clay content due to both acid and alkali spills and CEC due to alkali spills were analyzed by pairwise *t*-test, while those 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 3.4.

**Table 3.3**

The results of Kolmogorov–Smirnov test to check normality assumption of the differences in physicochemical properties and pH buffering capacity of soils before and after acid or alkali spills

| Difference    |      | Kolmogorov–Smirnov |                   |                     |
|---------------|------|--------------------|-------------------|---------------------|
|               |      | Statistic          | Degree of freedom | p value             |
| Acid spills   | OM   | .200               | 20                | .036                |
|               | Clay | .128               | 20                | .200 <sup>a,b</sup> |
|               | CEC  | .220               | 20                | .012                |
|               | pHBC | .243               | 20                | .003                |
| Alkali spills | OM   | .222               | 20                | .011                |
|               | Clay | .140               | 20                | .200 <sup>a,b</sup> |
|               | CEC  | .183               | 20                | .077 <sup>b</sup>   |
|               | pHBC | .221               | 20                | .011                |

<sup>a</sup>This is a lower bound of the true significance.

<sup>b</sup>Because a p value was greater than the 0.05, pairwise t–test was conducted. Otherwise, Wilcoxon signed rank test was conducted.

**Table 3.4**

The pairwise t-test or Wilcoxon signed rank test results of the differences in the physicochemical properties and pH buffering capacity of soils before and after acid or alkali spills

|               | Difference | Method                          | p value           |
|---------------|------------|---------------------------------|-------------------|
| Acid spills   | OM         | Wilcoxon<br>signed rank<br>test | .000              |
|               | Clay       | Pairwise t-<br>test             | .149 <sup>a</sup> |
|               | CEC        | Wilcoxon<br>signed rank<br>test | .000              |
|               | pHBC       | Wilcoxon<br>signed rank<br>test | .002              |
| Alkali spills | OM         | Wilcoxon<br>signed rank<br>test | .000              |
|               | Clay       | Pairwise t-<br>test             | .109 <sup>a</sup> |
|               | CEC        | Pairwise t-<br>test             | .000              |
|               | pHBC       | Wilcoxon<br>signed rank<br>test | .000              |

<sup>a</sup>There was no significant difference before and after acid or alkali spills.

Acid or alkali spills decreased the averaged organic matter content from 3.25% to 1.55 and 1.00%, respectively ( $p < 0.05$ ), but did not change the averaged clay content significantly. Decrease in organic matter content as a result of acid or alkali spills was probably

due to the electrostatic repulsion between clay surfaces and soil organic matter or between adsorbed soil organic matter (Chen et al., 2017; Ulrich and Sumner, 2012; Weng et al., 2006). This result showed that the organic matter content decreased more readily as a result of acid or alkali spills than the clay content. 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, ( $p < 0.05$ ). Because protonation or deprotonation reaction and cation exchange reaction of organic matter and clay in soils determines the pH buffering capacity (Aitken et al., 1990), the change in physicochemical properties by acid or alkali spills is likely to decrease the pH buffering capacity of soils.

### 3.1.2. Effect of organic matter and clay content on CEC

The parameters of 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 3.5. All models (CEC of untreated soils, acid-spilled, and alkali-spilled soils) satisfied the

assumptions of SMLR (Table 3.6 and Fig. 3.3). The normalized CEC models, i.e.  $CEC \text{ (untreated soils)} = -1.58 + 0.82\text{Clay} + 0.30\text{OM}$ ,  $CEC \text{ (acid-spilled soils)} = -3.02 + 0.95\text{Clay}$ ,  $CEC \text{ (alkali-spilled soils)} = -3.63 + 0.91\text{Clay}$ , 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. (1996), the adjusted  $R^2$  value can be used to evaluate the predictive ability. Without considering properties of clay and organic matter, the overall CEC was strongly predicted by linear combination of clay and organic matter content according to the predictive ability (Neter, Kutner, Nachtsheim, and Wasserman, 1996).

**Table 3.5**

Parameters derived from multiple linear regression analysis

| Dependent variable | Classification | N               | Independent variable | Constant | Unstandardized coefficients | Standardized coefficients | Adjusted R <sup>2</sup> | t           | Sig  |
|--------------------|----------------|-----------------|----------------------|----------|-----------------------------|---------------------------|-------------------------|-------------|------|
|                    | Untreated      | 20              | Clay, OM             | -1.58    | 0.88, 1.16                  | 0.82, 0.30                | 0.89                    | 10.32, 3.86 | 0.00 |
| CEC                | 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 |
|                    | Untreated      | 19 <sup>a</sup> | Clay, OM             | -2.30    | 0.88, 7.71                  | 0.35, 0.74                | 0.79                    | 3.07, 6.59  | 0.00 |
| pHBC               | 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 |

<sup>a</sup>The most outlying data (soil 17) was excluded to satisfy the normal distribution.

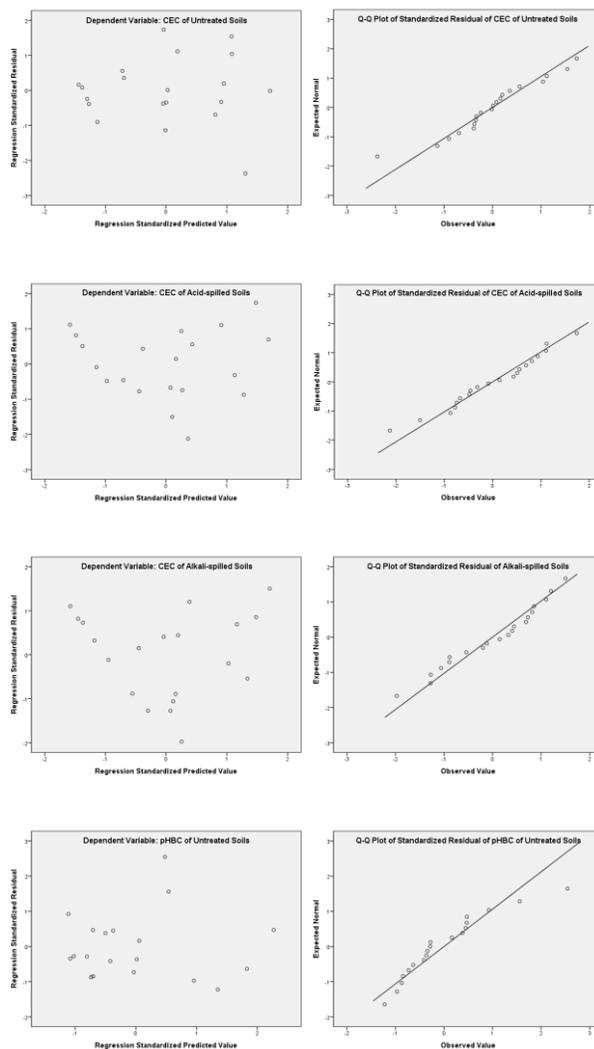
**Table 3.6**

The results of tests to check the normality, autocorrelation, and multicollinearity assumptions for multiple linear regression analysis

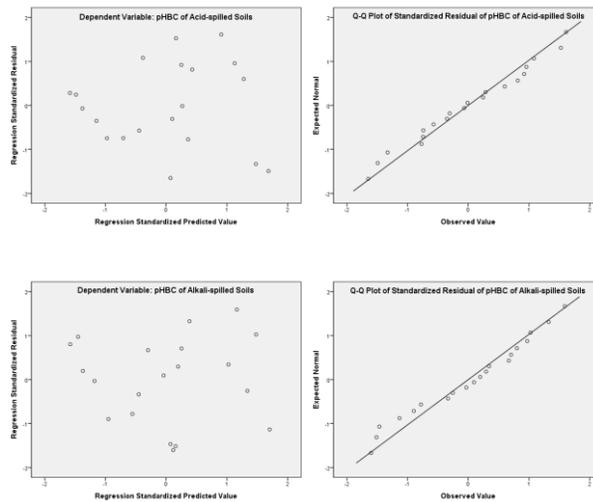
| Dependent variable | Classification | N               | Independent variable | SMLR assumption                   |  |                          |
|--------------------|----------------|-----------------|----------------------|-----------------------------------|--|--------------------------|
|                    |                |                 |                      | Normality<br>p value<br>(KS test) | Autocorrelation<br>Durbin-Watson<br>statistics | Multicollinearity<br>VIF |
| CEC                | Untreated      | 20              | Clay, OM             | 0.200 <sup>a</sup>                | 2.07<br>(No autocorrelation)                   | 1.07                     |
|                    | Acid-spilled   | 20              | Clay                 | 0.200 <sup>a</sup>                | 1.50<br>(No autocorrelation)                   | –                        |
|                    | Alkali-spilled | 20              | Clay                 | 0.200 <sup>a</sup>                | 1.71<br>(No autocorrelation)                   | –                        |
| pHBC               | Untreated      | 19 <sup>b</sup> | Clay, OM             | 0.054                             | 1.09<br>(Inconclusive)                         | 1.08                     |
|                    | Acid-spilled   | 20              | Clay                 | 0.200 <sup>a</sup>                | 1.39<br>(Inconclusive)                         | –                        |
|                    | Alkali-spilled | 20              | Clay                 | 0.200 <sup>a</sup>                | 1.53<br>(No autocorrelation)                   | –                        |

<sup>a</sup>This is a lower bound of the true significance.

<sup>b</sup>The most outlying data (soil 17) was excluded to satisfy the normal distribution.



**Fig. 3.3.** (Left) standardized residual plots and (right) Q–Q plots of CEC and pH buffering capacity of three different soils (untreated, acid–spilled, and alkali–spilled).



**Fig. 3.3.** (Continued)

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 of both acid-spilled and alkali-spilled soils. The models of both acid-spilled and alkali-spilled soils,

considering only clay content, could successfully account for more than 90% of CEC, and this was because organic matter, which also has a great influence on CEC before the spills, was removed through desorption or dissolution.

### 3.1.3. Effect of physicochemical properties of soils on pH buffering capacity

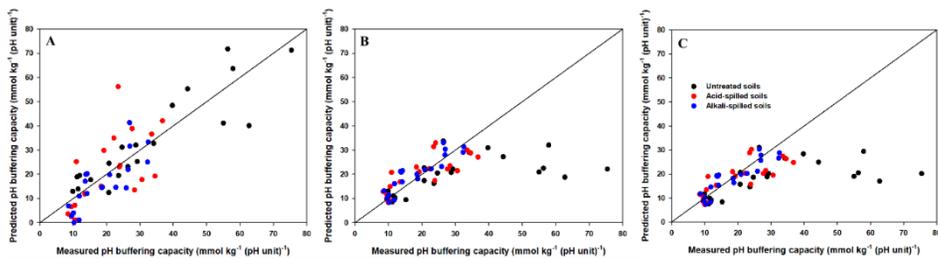
The parameters of SMLR, in which the pH buffering capacity is set as the dependent variable and organic matter and clay content are set as independent variables, are summarized in Table 3.5. The models of pH buffering capacity of acid-spilled and alkali-spilled soils met the assumptions of SMLR, while that of untreated soils (n=20) did not satisfy the assumption of normal distribution; Untreated soils, excluding the most outlying data (soil No.17), was analyzed to satisfy the assumptions (Table 3.6 and Fig. 3.3).

The models of normalized pH buffering capacity, i.e. pHBC (untreated soils) =  $-2.30 + 0.35\text{Clay} + 0.74\text{OM}$ , pHBC (acid-spilled soils) =  $7.67 + 0.79\text{Clay}$ , pHBC (alkali-spilled soils) =  $6.68 + 0.90\text{Clay}$ , 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 (Neter et al., 1996). 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 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 (Aitken et al., 1990; Magdoff and Bartlett, 1985). On the other hand, the selected independent variable is clay content in terms of the pH buffering capacity of both acid-spilled and alkali-spilled soils due to decrease in organic matter content, which is similar with the result of SMLR model of CEC. Nevertheless, the models of both acid-spilled and alkali-spilled soils could predict pH buffering capacity well by only using clay content.

Fig. 3.4 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 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. 3.4A). Although SMLR models of acid-spilled and alkali-spilled soils considering only clay content accurately predicted the pH buffering capacity less than  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ , they underestimated the pH buffering capacity of soils greater than  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  (Fig. 3.4B and 3.4C). It indicated that the high pH buffering capacity cannot be predicted by clay content only.



**Fig. 3.4.** 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.

## 3.2. Identification of characteristics of soils vulnerable to acid or alkali spills

### 3.2.1. Physicochemical properties and pH buffering capacity of clustered soil groups

The physicochemical properties and pH buffering capacity of each group before acid or alkali spills are summarized in Table 3.7. Seven, eight, and five soils were classified as group 1, 2, and 3, respectively. 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 (Table 3.8). Clay content of group 2 was significantly higher than that of group 1, and higher than that of group 3 (without statistical significance) (Table 3.8). The CEC of group 2 was significantly greater than that of group 1, while lower than that of group 3 (without statistical significance) (Table 3.8). The pH buffering capacity of group 2 was significantly greater than that of group 1, while significantly lower than that of group 3 (Table 3.8).

Particularly, all soils of which pH buffering capacity was greater than 50 mmol kg<sup>-1</sup> pH unit<sup>-1</sup>, were classified into group 3.

**Table 3.7**

The average values of three clustered soil groups' physicochemical properties and pH buffering capacity before acid or alkali spills

| Properties   | Group 1      | Group 2      | Group 3      |
|--|--------------|--------------|--------------|
| # 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<br>(mmol kg <sup>-1</sup> (pH unit) <sup>-1</sup> ) | 14.85 ± 5.30 | 30.99 ± 7.92 | 61.49 ± 8.32 |

<sup>a</sup>The comparison among groups is summarized in Table 3.8.

**Table 3.8**

The results of statistical tests (i.e. KS, ANOVA, KW, and Levene' s test, and post-hoc analysis) of three clustered groups' physicochemical properties and pH buffering capacity

|                            | OM                 | Clay               | CEC                | pHBC               | Soil vulnerability (acid, alkali)       |
|----------------------------|--------------------|--------------------|--------------------|--------------------|---|
| Kolmogorov–Smirnov p value |                    |                    |                    |                    |   |
| Group 1                    | 0.200 <sup>a</sup> | 0.200 <sup>a</sup> | 0.010              | 0.104              | 0.200 <sup>a</sup> , 0.200 <sup>a</sup> |
| Group 2                    | 0.200 <sup>a</sup> | 0.199              | 0.200 <sup>a</sup> | 0.200 <sup>a</sup> | 0.200 <sup>a</sup> , 0.200 <sup>a</sup> |
| Group 3                    | 0.200 <sup>a</sup> | 0.033              | 0.200 <sup>a</sup> | 0.200 <sup>a</sup> | 0.200 <sup>a</sup> , 0.200 <sup>a</sup> |
| ANOVA                      |                    |                    |                    |                    |   |
| p value <sup>b</sup>       | 0.000              | 0.001              | 0.001              | 0.000              | 0.000, 0.001                            |
| Levene' s test             |                    |                    |                    |                    |   |
| p value                    | 0.075              | –                  | –                  | 0.570              | 0.162, 0.263                            |
| Post-hoc analysis          |                    |                    |                    |                    |   |
|                            | Scheffe            | Bonferroni         | Bonferroni         | Scheffe            | Scheffe                                 |
| 1–2 <sup>c</sup>           | 0.568              | 0.033              | 0.017              | 0.002              | 0.171, 0.933                            |
| 1–3                        | 0.000              | 0.001              | 0.001              | 0.000              | 0.015, 0.004                            |
| 2–3                        | 0.002              | 1.000              | 0.743              | 0.000              | 0.000, 0.002                            |
| Rank <sup>d</sup>          | <u>1&lt;2&lt;3</u> | <u>1&lt;3&lt;2</u> | <u>1&lt;2&lt;3</u> | 2<1<3              | <u>2&lt;1&lt;3</u> , <u>2&lt;1&lt;3</u> |

<sup>a</sup>This is a lower bound of the true significance.

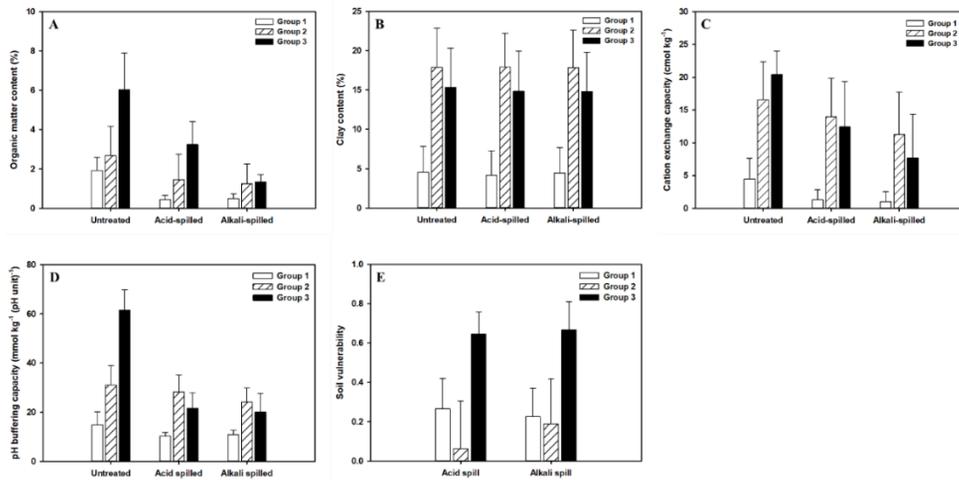
<sup>b</sup>If a p value is lower than 0.05, reject the null hypothesis that the distribution of physicochemical properties or pH buffering capacity is the same across clustered soil groups.

<sup>c</sup>1–2: Difference in group 1 and 2.

<sup>d</sup>A<B: A is significantly less than B, A<B: A is less than B, but there is no statistical significance.

### 3.2.2. Characteristics of vulnerable soils

Fig. 3.5 shows three clustered soil groups' physicochemical properties and pH buffering capacity of before and after acid or alkali spills and soil vulnerability to the 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  $\text{cmol kg}^{-1}$ , respectively, to 1.29, 13.97, and 12.42  $\text{cmol kg}^{-1}$ , respectively, and also decreased by alkali spills to 1.01, 11.28, and 7.68  $\text{cmol kg}^{-1}$ , 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 (Bohn et al., 2002). 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.



**Fig. 3.5.** 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.

In the case of the pH buffering capacity, acid or alkali spills decreased that of group 1 less than 30% from  $14.85 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  to  $10.25$  or  $10.88 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ , respectively, and decreased that of group 2 less than 20% from  $30.99 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  to  $28.18$  or  $24.19 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ , respectively. However, acid or alkali spills significantly reduced pH buffering capacity of group 3 more than 65%, from  $61.49 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  to  $21.62$  or

20.00 mmol kg<sup>-1</sup> pH unit<sup>-1</sup>, 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 a decrease in organic matter.

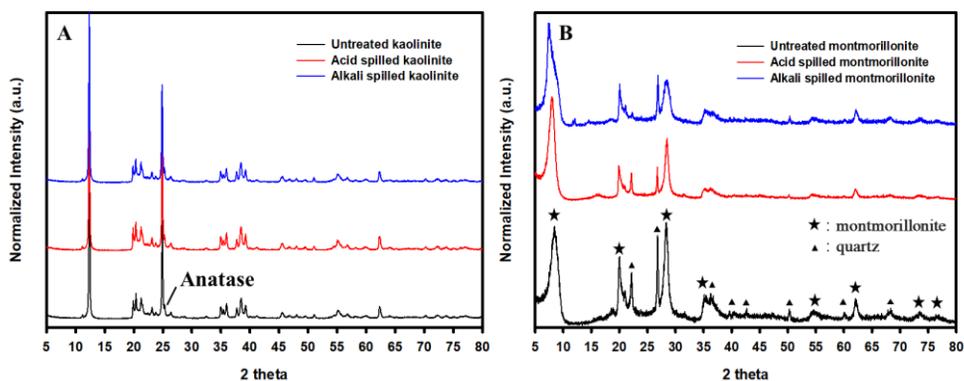
Soil vulnerability to acid spills in group 1, 2, and 3 were 0.27, 0.06, and 0.65, respectively, and it represented that 27, 6, and 65% of soil functions decreased by acid spills, respectively. For alkali spills, soil vulnerabilities were 0.23, 0.19, and 0.67, respectively, which indicated that alkali spills decreased soil function by 23, 19, 67%, respectively. Group 3 had the highest soil vulnerability to acid or alkali spills among three groups, and 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. 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 3.5), since it is susceptible to acid or alkali spills, soils with pH buffering capacity of 50 mmol kg<sup>-1</sup> pH unit<sup>-1</sup> 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. This may explain why group 2 is less vulnerable than group 1 although there is not a significant difference in organic matter content. These results indicate that soil vulnerability to acid or alkali spills can be predicted based on soil properties, 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.

### 3.3. Effect of acid or alkali spills on surface properties and pH buffering capacity of clay minerals

#### 3.3.1. XRD characterization and dissolution of major elements due to acid or alkali spills

The XRD patterns of three different kaolinite and montmorillonite samples are shown in Fig. 3.6. The XRD analysis showed that while acid or alkali spills had little effect on the crystalline structure and the mineral identity of kaolinite, they had some effects on those of montmorillonite. According to Fig. 3.6, the acid- or alkali-spilled montmorillonite had broader XRD patterns than the untreated montmorillonite, and the intensity of the quartz peak decreased. Nevertheless, the XRD patterns clearly indicated that acid- or alkali-spilled montmorillonite also included some impurities including the quartz and amorphous silica.



**Fig. 3.6.** XRD patterns of three different (A) kaolinite and (B) montmorillonite samples. Black, red, and blue lines represent the XRD patterns of untreated, acid-spilled, and alkali-spilled clay minerals, respectively. Kaolinite and montmorillonite contained an anatase and a quartz as an impurity, respectively, which is consistent with the previous baseline study on the XRD patterns of KGa-1b kaolinite and Swy-2 montmorillonite (Chipera and Bish, 2001).

The concentrations of dissolved elements of kaolinite and montmorillonite are summarized in the Table 3.9. The dissolved Al and Si concentrations of kaolinite after acid spill were 2.673 mg-Al g<sup>-1</sup> and 0.737 mg-Si g<sup>-1</sup>, respectively, and those after alkali spill were 21.799 mg-Al g<sup>-1</sup> and 25.020 mg-Si g<sup>-1</sup>, respectively. Kaolinite was more susceptible to alkali spill than to acid spill. In the

case of montmorillonite, while the dissolved Al and Si concentrations after acid spill were 9.090 mg-Al g<sup>-1</sup> and 18.793 mg-Si g<sup>-1</sup>, respectively, those after alkali spill were 1.243 mg-Al g<sup>-1</sup> and 103.797 mg-Si g<sup>-1</sup>, respectively. While more than five times of the octahedral cations such as Al, Fe and Mg were dissolved by acid spill than by alkali spill, the tetrahedral cation Si dissolved five times more by alkali spill than by acid spill. The high dissolution of octahedral cations as a result of acid spill was probably because protons preferentially attack the isomorphic substituted elements in octahedral sheet during acid treatment (Theng, Lagaly, and Bergaya, 2006).

**Table 3.9**

Dissolution of the clay minerals' constituent elements by acid or alkali spills measured by ICP–OES.

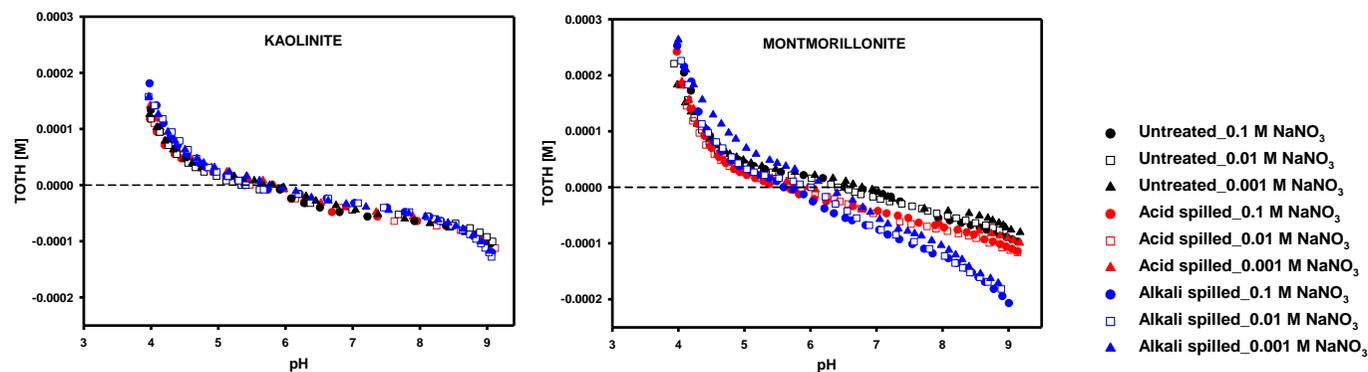
| Clay minerals   | Condition | Concentration of Dissolved Constituent Elements |              |             |            |
|-----------------|-----------|---|--------------|-------------|------------|
|                 |           | Al  | Si           | Fe          | Mg         |
|                 |           | mg (g clay minerals) <sup>-1</sup>              |              |             |            |
| Kaolinite       | Acid      | 2.67±0.15                                       | 0.74±0.04    | 0.249±0.01  | 0.03±0.00  |
|                 | Alkali    | 21.80±1.0                                       | 25.02±2.30   | 0.483±0.14  | 0.018±0.00 |
| Montmorillonite | Acid      | 9.09±1.56                                       | 18.79±6.22   | 11.281±1.19 | 1.99±0.34  |
|                 | Alkali    | 1.24±0.28                                       | 103.79±11.51 | 2.606±0.16  | 0.11±0.06  |

The concentration of dissolved elements are the average values of triplicate experiment.

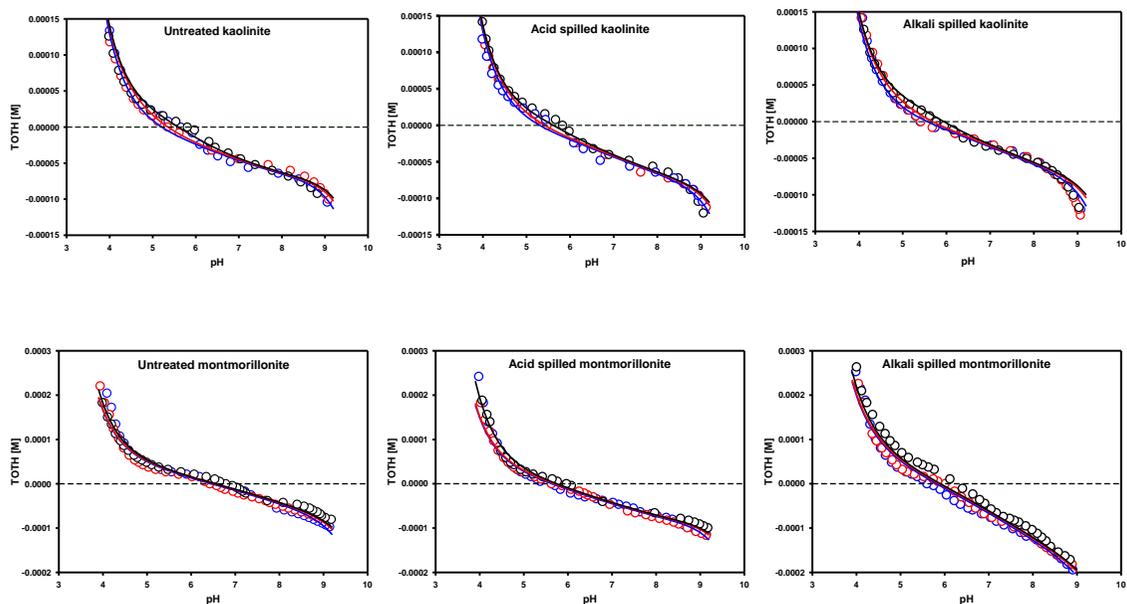
### 3.3.2. Irreversible alteration on surface properties resulting from acid or alkali spills

The titration curves of three different kaolinite and montmorillonite samples under different NaNO<sub>3</sub> concentration are shown in Fig. 3.7. As shown, acid or alkali spills have a greater effect on the titration curves of montmorillonite than those of kaolinite, and the titration curves of montmorillonite were grouped depending on the treatments. The background electrolytic concentration had a

limited effect on the titration curves of both kaolinite and montmorillonite at experimental pH values of 4–9 (Fig. 3.7). The optimized values of the surface properties obtained from FITEQL are summarized in Table 3.10.



**Fig. 3.7.** Titration curves of three different (left) kaolinite and (right) montmorillonite samples obtained from potentiometric titrations. The Y-axis is the molar concentration of the total added proton in the solution. The black, red, and blue symbols represent untreated, acid-spilled, and alkali-spilled kaolinite or montmorillonite, respectively, and the circle-, rectangle-, and triangle-shaped symbols represent a 0.1, 0.01, and 0.001 M NaNO<sub>3</sub> condition, respectively. All experimental data were well fitted with predicted titration curves using SCM; these curves are found in the in Fig. 3.8)



**Fig. 3.8.** Titration curves of three different (up) kaolinite and (down) montmorillonite samples under three different concentrations of NaNO<sub>3</sub>. Symbols are experimental data and lines are fitted data calculated using SCM. Black, red, and blue symbols or lines are those under a 0.001, 0.01, and 0.1 M NaNO<sub>3</sub> condition, respectively.

**Table 3.10**

Optimized surface properties of three different kaolinite and montmorillonite samples using FITEQL.

|   | Kaolinite          |                    |                    | Montmorillonite |                  |                    |
|---|--------------------|--------------------|--------------------|-----------------|------------------|--------------------|
|   | Untreated          | Acid<br>-spilled   | Alkali<br>-spilled | Untreated       | Acid<br>-spilled | Alkali<br>-spilled |
| <b>Surface reaction constants (pK)</b>  |                    |                    |                    |                 |                  |                    |
| $\equiv \text{SOH}_2^+ \leftrightarrow \equiv \text{SOH} + \text{H}^+$ (pKa1)   | -4.55              | -4.38              | -4.72              | -5.79           | -5.93            | -5.00              |
| $\equiv \text{SOH} \leftrightarrow \equiv \text{SO}^- + \text{H}^+$ (pKa2)  | 5.49               | 5.94               | 6.34               | 7.32            | 5.42             | 6.78               |
| $\equiv \text{X}^- \cdot \text{Na}^+ + \text{H}^+ \leftrightarrow \equiv \text{X}^- \cdot \text{H}^+ + \text{Na}^+$ (pKH) | -2.90 <sup>a</sup> | -2.90 <sup>a</sup> | -2.90 <sup>a</sup> | 1.51            | 0.72             | 1.85               |
| <b>Functional group density</b>   |                    |                    |                    |                 |                  |                    |
| edge site density (mmol kg <sup>-1</sup> )  | 35.8               | 40.6               | 38.6               | 84.8            | 85.3             | 253.2              |
| basal site density (mmol kg <sup>-1</sup> )   | 8.3                | 5.9                | 8.2                | 832.0           | 737.0            | 925.0              |

<sup>a</sup>Not determined by optimization, but the average value of other research (Angove et al., 1997; Ikhsan et al., 1999; Schindler et al., 1987; Srivastava et al., 2005)

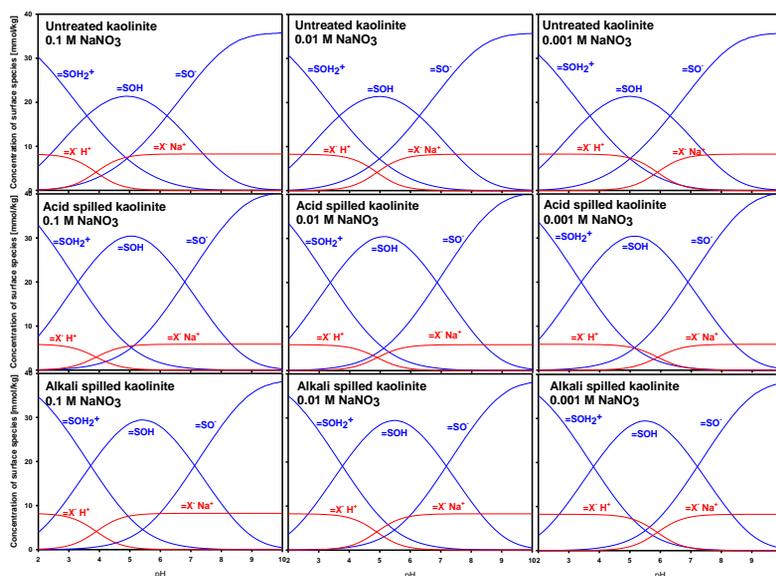
Table 3.10 shows that an acid or alkali spill did not significantly change the edge and basal site density of kaolinite (i.e. less than 5 mmol kg<sup>-1</sup>). An acid or alkali spill increased the edge site density of kaolinite from 35.8 to 40.6 and 38.6 mmol kg<sup>-1</sup>, respectively, and changed the basal site density of kaolinite from 8.3 to 5.9 and 8.2 mmol kg<sup>-1</sup>, respectively. In the case of montmorillonite, an acid or alkali spill significantly changed the edge and basal site density (i.e. greater than 100 mmol kg<sup>-1</sup>) except for the edge site density of the acid-spilled montmorillonite. An alkali spill greatly increased the edge site density from 84.8 to 253.2 mmol kg<sup>-1</sup>. In addition, an acid or alkali spill changed the basal site density from 832 to 737 and 925 mmol kg<sup>-1</sup>, respectively.

Regarding the surface acidity constants (i.e. pK<sub>a1</sub> and pK<sub>a2</sub>), an acid or alkali spill did not cause meaningful changes in the kaolinite (i.e. less than a 0.5 pKa value) except the pK<sub>a2</sub> of the alkali-spilled kaolinite increased from 5.49 to 6.34. In the case of montmorillonite, the pKa values greatly changed compared to those of the kaolinite (i.e. greater than a 0.5 pKa value) except for the pK<sub>a1</sub> value of the acid-spilled montmorillonite. The pK<sub>a1</sub> value of the alkali-spilled montmorillonite increased from -5.79 to -5.00, while the pK<sub>a2</sub> value of the acid-spilled montmorillonite greatly decreased from 7.32 to

5.42 and that of the alkali-spilled montmorillonite decreased to 6.78. In addition, the proton exchange reaction constant of montmorillonite ( $pK_H$ ) changed from 1.51 to 0.72 and 1.85 as a result of an acid or alkali spill, respectively.

According to the Fig. 3.7, titration curves of the kaolinite and montmorillonite only slightly changed under the different concentrations of background electrolyte. In the case of kaolinite, this was probably because the edge site density was approximately five times higher than the basal site density, which was consistent with previous studies (Gu and Evans, 2008; Sposito, 2008). Thus, the effect of the proton exchange reaction of the kaolinite's basal sites on the titration curve was relatively small in a range of pH 4–9 (Fig. 3.9). In contrast to the kaolinite, the basal site density of montmorillonite was approximately 5–10 times higher than its edge site density, which was consistent with previous research summarized in Bourg et al. (Bourg et al., 2007). However, the concentration of the electrolyte also had a slight effect on the titration curves of montmorillonite, and this might be because montmorillonite used in this study has a high affinity to  $Na^+$ . Basal sites were saturated with  $Na^+$  at pH values of 4–9; thus, the proton exchange reaction could be negligible within this pH range (Fig. 3.9). This

indicated that the pH buffering of both kaolinite and montmorillonite was largely determined by the edge site reactions rather than those of the basal sites at pH 4–9. Thus, it is reasonable that the larger change in the titration curves of the montmorillonite compared to that of the kaolinite resulting from acid or alkali spills was probably because of the greater alterations on the edge sites' properties in the montmorillonite.



**Fig. 3.9.** Predicted surface speciation diagrams of three different kaolinite and montmorillonite samples at three concentrations of  $\text{NaNO}_3$ . Blue lines represent the edge sites' species (i.e.  $\equiv \text{SOH}_2^+$ ,  $\equiv \text{SOH}$  and  $\equiv \text{SO}^-$ ) and red lines represent the basal sites' species (i.e.  $\equiv \text{X}^- \cdot \text{Na}^+$  and  $\equiv \text{X}^- \cdot \text{H}^+$ )

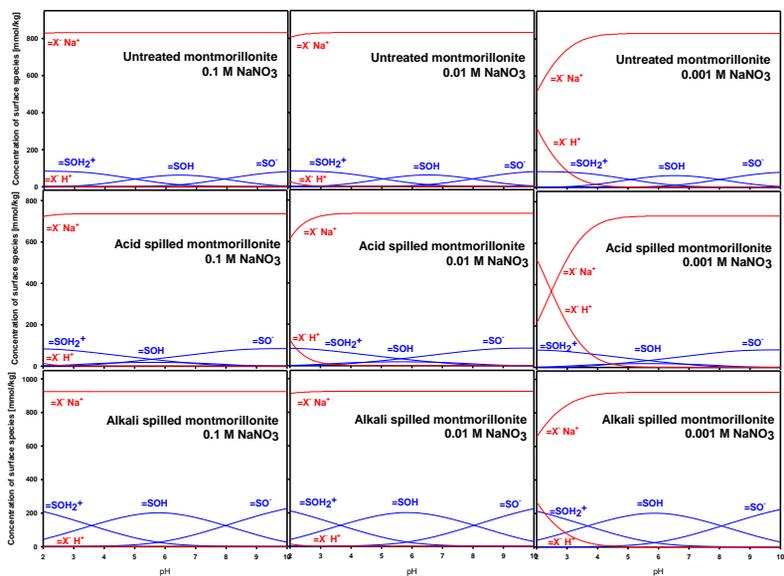
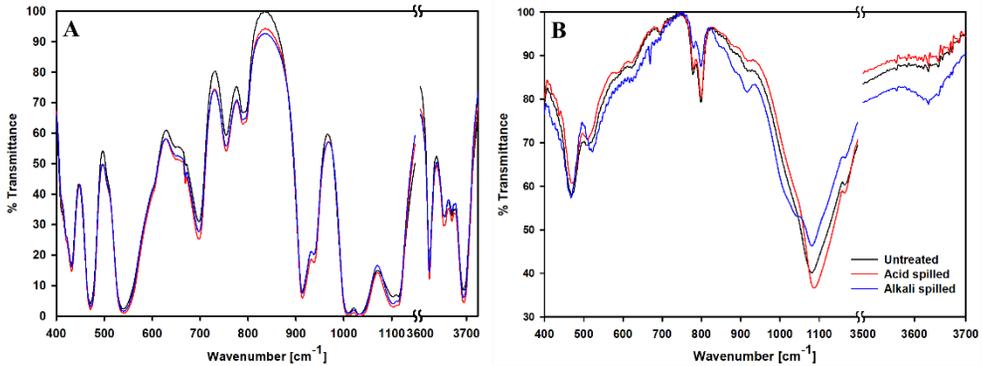


Fig. 3.9. (Continued)

### 3.3.3. Structural modification due to acid or alkali spills

FT-IR spectra of the three different kaolinite and montmorillonite samples are shown in Fig. 3.10.; the band assignments of the Clay Minerals Society's source clay (KGa-1b kaolinite, Swy-2 montmorillonite) were used in this study (Madejová, 2003; Madejova and Komadel, 2001). All absorption bands, particularly the Si-O of the tetrahedral sheet at  $400\text{--}1100\text{ cm}^{-1}$ , Si-O-Si at  $472\text{ cm}^{-1}$ , Al-O-Si of the octahedral sheet at  $541\text{ cm}^{-1}$ , and the OH hydroxyl groups at  $915, 938, \text{ and } 3600\text{--}3700\text{ cm}^{-1}$ , of the

untreated kaolinite were observed and the positions of the bands were nearly the same as the reference. However, the untreated montmorillonite (Swy-3) used in this study had a similar but slightly different shape and position of bands compared to the Swy-2 montmorillonite in the reference. The absorption band assigned for Al-O-Si, found in Swy-2 at  $524\text{ cm}^{-1}$ , was observed near  $512\text{ cm}^{-1}$ , and the band assigned for the Si-O of the tetrahedral sheet, found in Swy-2 montmorillonite at  $1041\text{ cm}^{-1}$ , disappeared in the untreated montmorillonite. Instead, the prominent band at  $1080\text{ cm}^{-1}$ , assigned to the Si-O of amorphous silica (Farmer, 1974; Madejová, 2003), was observed. This indicated that the untreated montmorillonite naturally had some amorphous silica as an impurity. The other bands were similar to those of the Swy-2 montmorillonite. Absorption bands at  $842$ ,  $885$ , and  $917\text{ cm}^{-1}$  were assigned to octahedral sites where isomorphic substitution occurred, and the band at  $3627\text{ cm}^{-1}$  was assigned to the hydroxyl groups of octahedral cations, particularly  $\text{Al}^{3+}$  (Vicente-Rodríguez, Suarez, Bañares-Muñoz, and de Dios Lopez-Gonzalez, 1996). In addition, adsorption bands at  $778$  and  $798\text{ cm}^{-1}$ , the Si-O of quartz and silica, showed that the untreated montmorillonite contained some quartz and silica, which is consistent with the result of XRD analysis (Fig. 3.6).



**Fig. 3.10.** FT-IR spectra of (left) kaolinite and (right) montmorillonite. Black, red, and blue lines represent untreated, acid-spilled, and alkali-spilled kaolinite or montmorillonite.

Acid or alkali spills did not significantly change the FT-IR spectra of the kaolinite. All the absorption bands were in the same position and the intensity of the bands was minimally altered. This indicated that limited structural alteration occurred. This is consistent with little changes in XRD patterns of kaolinite after an acid or alkali spill (Fig. 3.6), and the results of the titration experiment in which surface reaction constants and site density did not appreciably change as a result of an acid or alkali spill (Table 3.10). In addition, previous studies revealed the similar result that kaolinite, which is one of the non-swelling minerals, is the most resistant clay mineral to acid or alkali attacks (Jozefaciuk, 2002;

Jozefaciuk and Bowanko, 2002).

The acid- or alkali-spilled montmorillonite showed different FT-IR spectra compared to those of the untreated montmorillonite (Fig. 3.10). As a result of acid spill, the intensity of the isomorphically substituted octahedral cation sites (i.e., Al-(Mg, Fe, Al)-OH) decreased. This result was probably because of the great amount of dissolution of Fe and Mg in montmorillonite after acid spill (Table 3.9). It implies that the decrease in the basal site density of the acid-spilled montmorillonite was due to the dissolution of isomorphically substituted octahedral cation sites. In addition, acid spill decreased the intensity of the Si-O-Si sites, while increased that of the amorphous silica's Si-O. It indicates that, during acid spill, the dissolved Si from montmorillonite formed the amorphous silica and Madejová also observed the similar trend in smectite that the amorphous silica was formed after acid treatment {Madejová, 2003 #40}.

In contrast to acid spill, alkali spill increased the intensity of the isomorphically substituted octahedral cation sites of montmorillonite. The possible reason for the increase can be ascribed to the substitution of dissolved Al for Si in the tetrahedral site in montmorillonite during alkali spill. Thus, the isomorphic substitution

during alkali spill might have increased the basal site density of the alkali-spilled montmorillonite. In addition, the increase in the intensity of hydroxyl group at  $3627\text{ cm}^{-1}$  represented that the new hydroxyl groups were formed during alkali spill, and it could account for the increase in the edge site density of alkali-spilled montmorillonite from titration experiment (Table 3.10). Regarding the Si environment in montmorillonite, alkali spill decreased the intensity of Si-O of quartz, silica, and amorphous silica at 778, 798, and  $1080\text{ cm}^{-1}$ , respectively. Also, the adsorption band assigned to the Si-O of the tetrahedral sheet, which was not observed in the untreated or acid-spilled montmorillonite, appeared in the alkali-spilled montmorillonite at  $1041\text{ cm}^{-1}$ . This indicates that, during alkali spills, impurities including quartz and silica dissolved and new tetrahedral Si-O in montmorillonite was formed.

FT-IR spectra demonstrated that montmorillonite was more vulnerable to acid or alkali spills compared to kaolinite, similarly to the titration experiment, and had good agreement with the optimized site density (Table 3.10). This is probably because  $\text{H}^+$  and  $\text{OH}^-$  could attack not only the edges but also the swollen interlayer spaces of the montmorillonite (Jozefaciuk, 2002; Jozefaciuk and Bowanko, 2002). The results indicated that the extent of change in the surface

properties resulting from an acid or alkali spill varied with the type of clay mineral, and especially, an expandability should be carefully considered.

#### 3.3.4. Effect of acid or alkali spills on pH buffering capacity

Fig. 3.11 shows the predicted pH buffering capacity of the three different kaolinite and montmorillonite samples at pH 5.5, 6.0, and 6.5 calculated from Eq. (3) under a 0.001 M  $\text{NaNO}_3$  condition. Acid or alkali spills slightly decreased the pH buffering capacity of the kaolinite at pH 5.5, 6.0, and 6.5 from 19.24, 17.56, and 14.56  $\text{mmol kg}^{-1}$  to 17.58 or 18.17, 15.80 or 16.62, and 14.19 or 14.60  $\text{mmol kg}^{-1}$ , respectively. In the case of montmorillonite, these spills increased the pH buffering capacity at pH 5.5, 6.0 and 6.5 from 37.67, 30.33 and 27.91  $\text{mmol kg}^{-1}$  to 44.54 or 63.24, 35.89 or 56.03, and 32.71 or 55.79  $\text{mmol kg}^{-1}$ , respectively. Because the surface reaction constants and site density determined the pH buffering capacity, the pH buffering capacity of montmorillonite, of which the surface properties were greatly altered by the acid or alkali spills compared to those of kaolinite, was more affected by these spills than kaolinite.

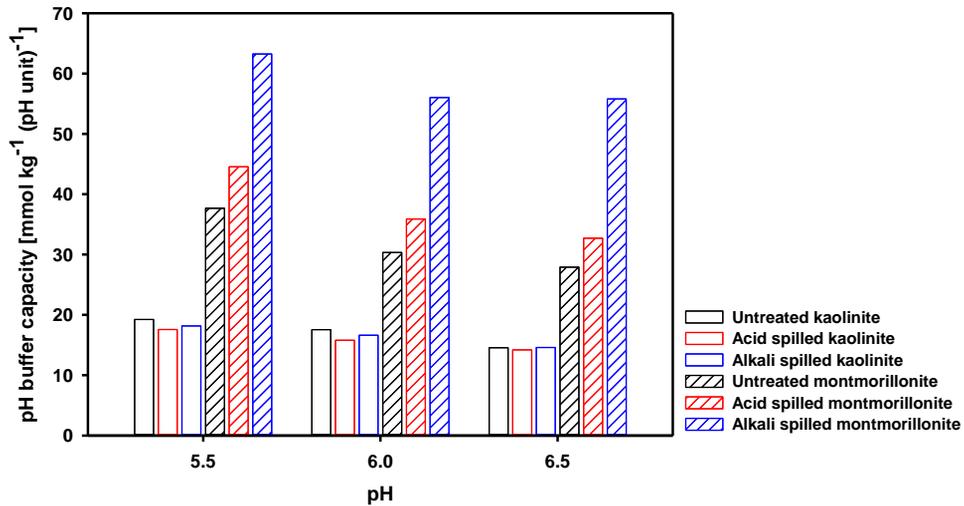


Fig. 3.11. pH buffering capacity of three different kaolinite and montmorillonite samples at pH 5.5, 6.0, and 6.5. Open and cross-hatched bars represent kaolinite and montmorillonite, respectively, and black, red, and blue bars represent untreated, acid-spilled, and alkali-spilled kaolinite or montmorillonite, respectively.

Despite the change in surface properties of clay minerals, the results of the clay minerals' pH buffering capacity clearly show that the pH buffering capacity was not deteriorated, but rather increased in montmorillonite after acid or alkali spills. It indicated that clay minerals are highly resistant to the acid or alkali spills in terms of pH buffering capacity, which was consistent with the result (Table 3.1, Fig. 3.1 and Fig. 3.5). These results support the idea that soil

vulnerability can be successfully predicted by physicochemical properties of soils, particularly organic matter and clay content.

## Chapter 4. Conclusions

In this study, the effect of acid or alkali spills on physicochemical properties and pH buffering capacity of soils was investigated, and characteristics of soils which exhibit vulnerability to the spills were identified. In addition, the change in surface properties of clay minerals due to the spills and its effect on pH buffering capacity were investigated. The results of this study are as follows.

1) Acid or alkali spills greatly decreased organic matter content and CEC, but did not cause significant changes in clay content. The CEC of untreated soils was determined by the clay and organic matter content. In acid-spilled and alkali-spilled soils, CEC was determined by clay content due to dissolution or desorption of organic matter. As a result of a decrease in organic matter content, the pH buffering capacity is significantly decreased in 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 corresponded well with pH buffering capacity less than  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ , the models were likely to underestimate pH buffering capacity of soils greater than  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  due to high organic matter content. These findings indicate that soils with high organic matter content are most vulnerable to acid or alkali spills because organic matter is susceptible to the spills.

2) Surface complexation modeling indicated that acid or alkali spills did not significantly change the site density of surface functional groups and their surface acidity constants in kaolinite. In contrast, acid or alkali spills greatly changed the site density and surface acidity constants of montmorillonite. Acid spills dissolved isomorphically substituted octahedral cations and SiOH sites, from which the dissolved Si formed amorphous silica. In addition, alkali spills dissolved the amorphous silica and edge sites such as AlOH and SiOH sites were newly formed in montmorillonite. Regarding the pH buffering capacity of clay minerals, acid or alkali spills did not have an adverse effect on it, but rather increased in montmorillonite.

3) These results indicate that soil vulnerability to acid or alkali spills

can be predicted based on soil properties, 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.

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# 초 록

## 산염기 유출이 토양의 물리화학적 특성 및 pH 완충능력에 미치는 영향과 이를 이용한 토양 취약성 평가

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산염기 유출 사고는 해마다 발생하고 있으며 한국에서 발생하는 전체 화학사고의 대략 50%를 차지할 정도로 매우 빈번하게 발생하고 있다. 산염기 유출로 인하여 토양의 특성인 유기물 함량, 양이온교환능력, 염기 포화도, 그리고 치환성 양이온이 변할 수 있다. 현재는 산염기 유출이 발생한 이후에 정화 작업의 일환으로서 중화제를 유출 토양에 살포하는 중화 작업이 수행되고 있지만, 이는 유기물의 용해 혹은 점토광물의 구조적 변화와 같은 비가역적 변화를 회복시키지 못한다. 이러한 토양 특성의 변화로 인하여 산염기 유출 이후 중화를 하더라도 토양 기능 중 특히 pH 완충능력이 변할 수 있다. 또한 유기물 함량은 산염기 유출로 인하여 감소하기 때문에 점토광물이 산염기 유출

토양의 pH 완충능력을 결정하는 주요한 매질이 될 것이다. 산염기 유출이 토양 및 점토광물에 미치는 영향을 파악하는 것은 산 혹은 염기 유출 토양을 적절히 관리하기 위하여 매우 중요한 실정이다. 따라서 본 연구에서는 산염기 유출이 토양에 미치는 영향과 산염기 유출에 취약한 토양의 특성을 규명해보았다.

20개의 현장 토양을 채취하여 각각 HCl 및 NaOH와 반응시키고 (즉, 토양 1 g 당 30 mmol의 HCl 및 NaOH가 유입), pH를 6-8로 중화한 후 동결 건조하여 산 혹은 염기 유출 토양을 제조하였다. 산염기 유출 전후 토양의 물리화학적 특성 및 pH 완충능력의 변화는 통계학적으로 분석되었으며 pH 완충능력을 결정하는 토양 특성을 규명하기 위하여 다중 회귀 분석을 수행하였다. 또한 군집 분석으로 산염기 유출에 취약한 토양의 특성을 그룹화하여 평가하였다. 산 혹은 염기 유출은 유기물 함량을 3.25%에서 각각 1.55 및 1.00%로 유의하게 감소시켰으며 양이온교환능력을  $13.29 \text{ cmol kg}^{-1}$ 에서 각각  $9.14$  및  $6.79 \text{ cmol kg}^{-1}$ 으로 감소시켰다. 점토 함량은 산 혹은 염기 유출로 인하여 변하지 않았다. pH 완충능력은 산 혹은 염기 유출로 인하여  $32.96 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ 에서 각각  $20.26$  및  $18.48 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$ 으로 감소하였다. 기존 토양의 pH 완충능력은 유기물 및 점토 함량의 선형 결합 모델로 79%가 예측됐지만, 산 혹은 염기 유출 토양의 경우에는 유기물의 감소로 인하여 점토 함량만으로도 각각 61 및 80%가 설명되었다. 토양의 물리화학적 특성 및 pH 완충능력을

기준으로 균집화된 세 그룹 중에서, pH 완충능력이  $50 \text{ mmol kg}^{-1} \text{ pH unit}^{-1}$  이상인 그룹이 산 혹은 염기 유출에 가장 취약했으며 pH 완충능력은 65% 감소하였다. 이는 이 그룹이 산 혹은 염기 유출에 취약한 유기물을 많이 함유하고 있기 때문이라고 사료된다.

또한 산염기 유출이 점토광물의 특성에 미치는 영향을 분석하기 위하여 카올리나이트와 몬모릴로나이트가 각각 1:1 및 2:1 점토광물로 선정되었다. 점토광물의 표면 작용기 밀도와 표면 산해리상수 (i.e.  $\text{pKa}_1$  와  $\text{pKa}_2$ ) 가 점토광물의 pH 완충능력을 결정하기 때문에 산염기 유출이 표면 특성에 미치는 영향을 분석하였다. 전위차 적정을 통한 surface complexation modeling과 Fourier-transform infrared spectroscopy (FT-IR) 의 실험 결과, 카올리나이트는 산염기 유출로 표면 특성이 크게 변하지 않았다. 이에 반해 몬모릴로나이트의 경우에는 산 유출로 인하여 동형치환된 양이온들이 용해되어 basal site 밀도가  $832 \text{ mmol kg}^{-1}$ 에서  $737 \text{ mmol kg}^{-1}$ 으로 감소하였고 SiOH기의 용해로 인하여  $\text{pKa}_2$ 가 7.32에서 5.42로 감소하였다. 염기 유출은 동형 치환을 증가시켜 몬모릴로나이트의 basal site 밀도를  $925 \text{ mmol kg}^{-1}$ 으로 증가시켰고 AlOH와 SiOH가 새롭게 형성되어 edge site 밀도가  $84.8 \text{ mmol kg}^{-1}$ 에서  $253.2 \text{ mmol kg}^{-1}$ 으로 크게 증가하였다. 이로 인하여  $\text{pKa}_2$ 는 6.78로 감소하였다. 산 혹은 염기가 유출된 카올리나이트의 pH 6에서의 pH 완충능력은 유출 전 카올리나이트의 값과 크게 변하지 않았지만, 몬모릴로나이트의 pH 완충능력은 산염기 유출로 인하여 기존  $30.33 \text{ kg}^{-1} \text{ pH unit}^{-1}$

<sup>1</sup>에서 각각 35.89 및 56.03 mmol kg<sup>-1</sup> pH unit<sup>-1</sup>로 증가하였다. 이 결과는 산염기 유출이 몬모릴로나이트의 표면 특성을 크게 변화시키지만, 작용기 밀도의 증가 등으로 인하여 pH 완충능력이 유출 전보다 오히려 더 증가하는 것을 의미한다. 본 연구 결과는 산염기 유출될 가능성이 높은 지역에서 취약한 토양을 분류하거나, 산염기 물질에 유출된 토양을 부지특이적으로 관리하는 방안을 모색할 시 활용될 수 있을 것이라 사료된다.

**주요어:** 산염기 유출, 토양 특성, pH 완충능력, 점토광물, surface complexation modeling

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