

Sulfate adsorption properties of acid-sensitive soils in the Athabasca oil sands region in Alberta,  
Canada

Kangho JUNG <sup>a, †, 1</sup>, Yong Sik OK <sup>b, †</sup>, Scott X. CHANG <sup>a, \*</sup>

<sup>a</sup> Department of Renewable Resources, University of Alberta, Edmonton, AB T6G 2E3, Canada

<sup>b</sup> Department of Biological Environment, Kangwon National University, Chuncheon 200-701,  
Korea

†: Those two authors share co-first-authorship

Text pages: 21

Tables: 4

Figures: 2

Submitted to: Chemosphere

\*Corresponding author: [scott.chang@ualberta.ca](mailto:scott.chang@ualberta.ca), tel: 1-780-492-6375, fax: 1-780-492-1767

Address: Department of Renewable Resources, 442 Earth Sciences Building, University of  
Alberta, Edmonton, Alberta, Canada T6G 2E3

<sup>1</sup> Permanent address: Department of Agricultural Environment, National Academy of  
Agricultural Science, 150 Suinro, Kweonseonku, Suwon, Republic of Korea, 441-707

**This paper has been published as**

**Jung, K., Ok, Y. S., & Chang, S. X. (2011). Sulfate adsorption properties of acid-sensitive soils in the athabasca oil sands region in Alberta, Canada.**

**Chemosphere, 84(4), 457-463. doi:10.1016/j.chemosphere.2011.03.034**

**ABSTRACT:** The risk of soil acidification is high in the Athabasca oil sands region (AOSR) in Alberta, Canada, due to elevated SO<sub>2</sub> emission and the resultant acid deposition to sensitive, coarse-textured soils. Understanding the sulfate adsorption characteristics of soils sensitive to acidification will help establish critical loads of acid deposition in AOSR. Sulfate adsorption properties were evaluated and relationships between sulfate adsorption and soil properties were examined for soils in two contrasting watersheds (NE7 and SM8) in AOSR. The experimental data fitted well to both the Langmuir and the Freundlich models. The sulfate adsorption capacity was greater for soils in SM8 than in NE7 ( $p < 0.01$ ), even though it was relatively low in both watersheds as compared to other acid-sensitive soils in eastern North America. Based on the additional sulfate adsorbed when a soil was treated with 40 mL of 200 mg SO<sub>4</sub><sup>2-</sup> L<sup>-1</sup> solution, the weakly developed Podzolic B horizon (Bfj) in NE7 could adsorb more sulfate than the Ae horizon while no difference was found among other horizons. In SM8, the Bfj and illuviated B (Bt) horizons had greater ability to adsorb sulfate than the other horizons, likely caused by the presence of muscovite in the Bfj and Bt horizons. The additional sulfate adsorbed accounted for about 80% of the total sulfate adsorption capacity and was correlated with pH<sub>NaF</sub> (soil pH extracted with 1 M NaF) and ΔpH<sub>NaF</sub> (the difference between pH<sub>NaF</sub> and pH measured with deionized water), with the following relationships: sulfate adsorption (mg SO<sub>4</sub><sup>2-</sup> kg<sup>-1</sup>) = exp(2.03 pH<sub>NaF</sub> - 18.0) + 50.2 ( $R^2 = 0.63$ ,  $p < 0.001$ ) and sulfate adsorption (mg SO<sub>4</sub><sup>2-</sup> kg<sup>-1</sup>) = exp(1.83 ΔpH<sub>NaF</sub> - 6.57) + 48.9 ( $R^2 = 0.70$ ,  $p < 0.001$ ). The ΔpH<sub>NaF</sub> was likely a better indicator of the soil's sulfate adsorption capacity than pH<sub>NaF</sub> as the former excludes the effect of soil acidity. Our study indicates that the soil's capacity to adsorb sulfate should be considered in determining the critical load for acid deposition in AOSR in Alberta.

*Keywords:* sulfate adsorption, acid deposition, soil acidification, oil sands, Langmuir, Freundlich.

## 1. Introduction

Atmospheric emission of SO<sub>2</sub> has been clearly shown to accelerate soil acidification in industrialized regions when it is deposited as sulfuric acid (Ok et al., 2007a). When sulfate is deposited to the soil, it can be retained in the soil in a variety of forms, e.g., as sulfate ions in the soil solution, as adsorbed sulfate on soil particles, and as organic sulfur (S). It also can be lost from the soil through leaching. Leaching of sulfate ions would lead to the leaching of basic cationic elements from the soil, while sulfate adsorption by the soil is regarded as a major process of sulfate retention that can delay the loss of base cations through leaching with sulfate and thus counter the acidifying effect of atmospheric S deposition (Barton et al., 1999). This mechanism is especially important in reducing basic cation leaching loss from the deeper soil horizons (Cole and Johnson, 1977; MacDonald and Hart, 1990).

The ability of soils to adsorb sulfate has been determined with isothermal adsorption experiments using isothermal models such as Langmuir and Freundlich equations (e.g., Alves and Lavorenti, 2004) and with the additional sulfate adsorbed at a specific soil solution sulfate concentration (e.g., Bhatti et al., 1997), where the total adsorbed sulfate at a specific soil solution sulfate concentration includes initially adsorbed sulfate and additionally adsorbed sulfate. Sulfate adsorption has been shown to have large variations with soil type. Variable-charge soils such as Andosols have been reported to have a capacity of sulfate adsorption of more than several hundred mg SO<sub>4</sub><sup>2-</sup> kg<sup>-1</sup>, even greater than 1,000 mg SO<sub>4</sub><sup>2-</sup> kg<sup>-1</sup> in South America and Japan have been reported (Alves and Lavorenti, 2004; Mekar and Uehara, 1972) while some soils in Europe and North America have been reported to adsorb between 50 and 500 mg SO<sub>4</sub><sup>2-</sup> kg<sup>-1</sup> (Barton et al., 1999; Martinson et al., 2004; Bhatti et al., 1997; MacDonald and Hart, 1990;

Neary et al., 1987; Nodvin et al., 1986).

The soil's capacity to adsorb sulfate depends on numerous soil properties, including the concentrations of Al and Fe hydrous oxides, clay mineralogy, soil pH and organic matter content (Harrison et al., 1989; Xue and Harrison, 1991; Liu et al., 1999). Each of those parameters could be used as an indicator of the sulfate adsorption capacity if it has a significant relationship with sulfate adsorption. Sulfate adsorption is known to be positively correlated with Al- and Fe-hydrous oxide concentrations in the soil (Harrison et al., 1989). Soil pH is negatively correlated with sulfate adsorption (Elkins and Ensminger, 1971; Xue and Harrison, 1991) because positive surface charges that are able to adsorb sulfate increase with reducing soil pH. Organic matter can positively or negatively affect sulfate adsorption, as it may contribute to formation of Al- and Fe-humus complexes (Shoji and Fujiwara, 1984) and increase sulfate adsorption while organic anions may compete for adsorption sites with sulfate (Liu et al., 1999) and thus reduce sulfate adsorption. The effects of these properties are related to the soil type (Bhatti et al., 1997).

The Athabasca oil sands region (AOSR) is the largest area for open-pit oil sands mining in Alberta (Fung and Macyk, 2000). As a result, 289-359 Mg d<sup>-1</sup> of SO<sub>2</sub> was estimated to be released to the atmosphere and such emission rates may induce soil and water acidification in AOSR (NSMWG, 2004). Therefore, understanding the sulfate adsorption of forest soils in the AOSR is important for model and/or predict soil acidification and thus to inform policy making to control and reduce SO<sub>2</sub> emission in the AOSR. The objectives of this study were to assess the sulfate adsorption characteristics of forest soils sampled from two contrasting watersheds in the AOSR and to determine relationships between sulfate adsorption and soil physical, chemical and mineralogical properties.

## 2. Materials and Methods

### 2.1. Study sites

Soil samples used for this study were collected in 2005 from two watersheds, NE7 and SM8, selected for this study based on the work undertaken during 2003-2004 in the Acid Sensitive Lake Network in the oil sands region (Ok et al., 2007b). The two watersheds are of different distances from the main acid emission sources of oil sands open-pit mining and upgrading facilities. Watershed NE7 (57.15° N, 110.86° W) is located northeast of Fort McMurray, while SM8 (56.21° N, 111.20° W) is located south of Fort McMurray. Oil sands mining areas are located north of Fort McMurray and NE7 was expected to be affected more by anthropogenic emissions due to its closeness to the mining area. Climate conditions are similar in both watersheds. The mean annual temperature is 0.7 °C with a mean relative humidity of about 67%. The mean annual precipitation and evaporation are 456.0 to 456.8 and 485.8 to 486.8 mm, respectively (Ok et al., 2007b). Both watersheds (NE7 and SM8) are dominated by jack pine (*Pinus banksiana*) and aspen (*Populus tremuloides*) in upland forests and black spruce (*Picea mariana*) in low-lying areas and wetlands. The common soil types in upland forests of both watersheds NE7 and SM8 are eluviated Brunisolic soils and Luvisolic soils with Ae, Bfj, Bm, and/or Bt horizons in the Canadian system of soil classification (Soil Classification Working Group, 1998) or Boralf in US Soil Taxonomy (Soil Survey Staff, 1994).

### 2.2. Soil sampling

We selected five stands several hundred meters away from each other in upland forests in each watershed and dug a 1 m wide soil pit to 1 m depth in each stand in 2005. The soil had Ae, Bfj or Bm, Bm or Bt, and C horizons with increasing depth in the soil profiles (Table 1) with variable horizon thickness. Soil horizon samples were collected from a total of five soil profiles in each watershed to determine soil physical and chemical properties. One representative profile from the five soil profiles in each watershed was selected for the sulfate adsorption isotherm experiments. The selected soil profile in NE7 had the following horizons: Ae, Bfj1, Bfj2 and BC, while the selected soil profile in SM8 had the following horizons: Ae, Bfj, Bm1 and Bm2 (Table 2). Both soils selected for the isotherm experiments belong to Eluviated Dystric Brunisols in the Canadian system of soil classification (Soil Classification Working Group, 1998). Soil samples were air-dried and crushed to pass through a 2-mm sieve after removing coarse fragments, roots, and debris before analysis.

### *2.3. Soil physical, chemical, and mineralogical properties*

Soil texture was determined using the hydrometer method (Gee and Or, 2002). Soil pH was measured in deionized water ( $\text{pH}_{\text{water}}$ ) using 10 g of air-dried soil in 20 mL water. Soil pH was also measured using a 1:40 (w:v) ratio of soil to 1 M NaF solution ( $\text{pH}_{\text{NaF}}$ ) after shaking for 1 h at 25 °C (Alves and Lavorenti, 2004). The  $\Delta\text{pH}_{\text{NaF}}$  was calculated from the difference between  $\text{pH}_{\text{NaF}}$  and  $\text{pH}_{\text{water}}$  (Mekaru and Uehara, 1972). Each soil sample was further ground with a ball mill and used for determining total C concentration with a Carlo Erba NA 1500 elemental analyzer (Carlo Erba Instruments, Milano, Italy). Exchangeable cations including  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Mn}^{4+}$  were determined after extraction with 1 M  $\text{NH}_4\text{Cl}$  at a ratio

of 5 g soil to 100 mL extraction solution and shaking for 1 h. After filtration through a 0.45  $\mu\text{m}$  nylon membrane filter, the filtrates were analyzed using a Perkin Elmer Elan 6000 quadrupole ICP-MS (Perkin Elmer, Inc., Shelton, CT) equipped with an automated sampling system (Perkin-Elmer AS-91, USA). Cation exchange capacity (CEC) of each soil sample was calculated as the sum of the exchangeable cations (Ruan et al., 2004). Clay mineralogy was determined with the X-ray diffraction technique (Ultima IV, Rigaku, USA). Clay samples ( $< 2 \mu\text{m}$ ) were separated from bulk soil samples using an IEC MultiRF centrifuge (Thermo Electron Co., USA) following the method in Whittig and Allardice (1986). Total element concentrations of Al and Fe were determined for soils collected in the selected profiles for the sulfate isotherm experiments with a Shimadzu XRF-1700 Sequential X-ray Fluorescence Spectrometer (Shimadzu Corporation, Japan). Total Al and Fe concentration data will allow us to determine relationship between Al and Fe minerals and sulfate adsorption.

#### *2.4. Sulfate adsorption*

The sulfate adsorption isotherm was determined in a series of batch experiments. The adsorbed sulfate was calculated as the sum of initially adsorbed sulfate and additionally adsorbed sulfate at ten different sulfate concentrations: 5, 10, 20, 30, 40, 50, 60, 80, 125 and 200  $\text{mg SO}_4^{2-} \text{L}^{-1}$ . To determine the initially adsorbed sulfate, 4 g of soil was extracted with 40 mL of  $\text{Ca}(\text{H}_2\text{PO}_4)$  solution with 500  $\text{mg P L}^{-1}$ . After shaking for 24 h, the suspension was filtered with a 0.45  $\mu\text{m}$  membrane filter and then sulfate concentrations in filtrates were analyzed with an ion chromatography (DX 600, Dionex Corp., CA). To determine the additionally adsorbed sulfate, 40 mL of solution in each sulfate concentration was added to 4 g of soil. Solutions with different

sulfate concentrations were prepared by dissolving  $K_2SO_4$  in 0.01 M  $CaCl_2$  solutions. After shaking for 24 h, the suspension was filtered and sulfate concentrations in filtrates were determined as outlined above. The amount of additionally adsorbed sulfate at each sulfate concentration was calculated from the difference of sulfate concentrations between the initial solution and the filtrate.

Langmuir and Freundlich equations were fitted to the data. The Langmuir equation is expressed as:

$$q = k_l C b / (1 + k_l C) \dots\dots\dots (1)$$

where  $C$  = equilibrium concentration of sulfate,  $mg L^{-1}$ ;  $q$  = adsorbed sulfate,  $g kg^{-1}$ ;  $b$  = sulfate adsorption capacity,  $mg kg^{-1}$ ; and  $k_l$  = a parameter related to the affinity of the soil by sulfate,  $L mg^{-1}$ .

The Freundlich equation is expressed as:

$$q = k_f C^{1/n} \dots\dots\dots (2)$$

where  $q$  = adsorbed sulfate,  $mg kg^{-1}$ ;  $k_f$  = a constant,  $mg^{(1-1/n)} kg^{-1} L^{1/n}$ ;  $C$  = equilibrium concentration of sulfate,  $mg L^{-1}$ ; and  $n$  = a dimensionless constant.

The affinity factor ( $k_l$ ) and sulfate adsorption capacity ( $b$ ) in the Langmuir equation can be compared among different soils while the adsorption index ( $k_f$ ) in the Freundlich equation is not

valid for comparing different soils due to inconsistency of units; the unit for  $k_f$  changes with  $n$  (Chen et al., 1999). For this reason, a unified adsorption variable ( $k_u$ ) was proposed as an alternative for comparing sulfate adsorption characteristics using the Freundlich equation (Chen et al., 1999).

$$k_u = k_f / C^{(n-1)/n} \dots\dots\dots (3)$$

where  $k_u$  = unified adsorption variable for the Freundlich equation, L mg<sup>-1</sup>; and  $C$ ,  $k_f$  and  $n$  are parameters in the Freundlich equation. This index is used to compare sulfate adsorption of different soils in this study.

In addition, to assess the ability of soils to retain additional sulfate, 4 g of soil was weighed for all horizon samples for all five soil profiles in each watershed and shaken for 24 h at 20 °C with 40 mL of 0.01 M CaCl<sub>2</sub> containing 200 mg SO<sub>4</sub><sup>2-</sup> L<sup>-1</sup> solution as K<sub>2</sub>SO<sub>4</sub>. Sulfate concentration and additional sulfate adsorbed was determined as outlined above. The additional sulfate adsorbed was used to indicate the potential of sulfate adsorption (Bhatti et al., 1997; MacDonald and Hart, 1990).

*2.5. Statistical analysis*

Nonlinear regression analysis was employed to find the best fit curve for both Langmuir and Freundlich models for the sulfate adsorption isotherm. Correlation analysis was performed among parameters of adsorption isotherm equations and soil properties. Nonlinear regression analysis was used to determine regression equations for sulfate adsorption using soil properties.

All statistical analyses were performed using version 9.01 of SAS (SAS Institute Inc., Cary, NC)

### 3. Results

#### 3.1. Soil properties

The basic physicochemical properties of horizon soils from the studied soil profiles are listed in Table 1. The surface mineral soil horizon (Ae) had the lowest  $\text{pH}_{\text{NaF}}$  in each watershed ( $p < 0.001$  in each case) while the highest values were found in the Bfj horizon in both watersheds ( $p < 0.05$ ). The  $\text{pH}_{\text{water}}$  was also the lowest in the Ae horizon in both watersheds ( $p < 0.01$ ). Soils in both watersheds had the coarsest texture in the topsoil and had relatively finer texture in the subsoil. Clay contents of Ae ranged from 9.6 to 47.1  $\text{g kg}^{-1}$  in NE7 and from 23.2 to 68.7  $\text{g kg}^{-1}$  in SM8 based on Ae horizons from five profiles in each watershed while those of Bt ranged from 220.8 to 231.7  $\text{g kg}^{-1}$  in NE7 and from 313.4 to 442.5  $\text{g kg}^{-1}$  in SM8 based on three Bt horizons in each watershed. In both watersheds, the Bm and Bt horizons had greater exchangeable  $\text{Ca}^{2+}$  and CEC than the parent material ( $p < 0.01$  in all cases). Exchangeable  $\text{Al}^{3+}$  concentrations in the Ae horizon were greater than that in the C horizon in SM8 but not in NE7. The major clay minerals in the solum in both watersheds were quartz, kaolinite, and orthoclase. Montmorillonite was found in all horizons in NE7 while it was found only in the Bm and Bt horizons in SM8. Muscovite ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$ ) was found in the Ae horizon in both watersheds and in the Bfj and Bt horizons in SM8. The C horizon included clay minerals such as clinocllore and anorthoclase that were not found in the solum.

### 3.2. Sulfate adsorption

The sulfate adsorption data fitted very well to both the Freundlich (Fig. 1, Table 2) and Langmuir equations (Table 2). The Freundlich equation was a better fit than the Langmuir equation for B horizon soil samples while the opposite was true for Ae horizon soil samples (Table 2). However, both models sufficiently explained sulfate adsorption in most of our data (Table 2). The sulfate adsorption capacity,  $b$ , in the Langmuir equation and unified adsorption variable,  $k_u$ , in the Freundlich equation were greater in SM8 than in NE7 while  $k_f$  values in both watersheds were similar. The  $b$  values ranged from 29.7 to 98.5 mg kg<sup>-1</sup> in NE7 and from 80.8 to 158.8 mg kg<sup>-1</sup> in SM8. The  $k_u$  values ranged from 0.33 to 0.59 L mg<sup>-1</sup> in NE7 and from 0.49 to 1.99 L mg<sup>-1</sup> in SM8. The Ae horizons had the lowest  $b$  and  $k_u$  in each profile. Among the soil horizons, the Bfj horizon had greater sulfate adsorption ( $p < 0.05$ ) than the other horizons (Table 2).

Based on additional sulfate adsorption with 40 mL of 200 mg SO<sub>4</sub><sup>2-</sup> L<sup>-1</sup> solution, the ability of soils to retain additional sulfate was greater ( $p < 0.01$ ) in SM8 than in NE7 (Table 1). In NE7, the weakly developed Podzolic B horizon (Bfj) could adsorb more added sulfate ( $p < 0.05$ ) than the Ae horizon while no difference was found among other horizons. In SM8, the Bfj and illuviated B (Bt) horizons had greater ability to adsorb sulfate than the other horizons ( $p < 0.001$ ). Soils in SM8 had greater additionally adsorbed sulfate than those in NE7 ( $p < 0.05$ ). The Ae was the horizon with the lowest additionally adsorbed sulfate in both watersheds. The Bfj and Bt horizons in SM8 had greater ( $p < 0.05$ ) additionally adsorbed sulfate than other soil horizons. In addition, the additional sulfate adsorption accounted for 80% of the sulfate adsorption capacity.

### *3.3. Relationships between sulfate adsorption and other soil properties*

The additional sulfate adsorption was significantly correlated with  $b$  ( $p < 0.01$ ) and  $k_u$  ( $p < 0.001$ ) (Table 3). The  $k_u$  was positively correlated with  $\text{pH}_{\text{NaF}}$  and  $\Delta\text{pH}_{\text{NaF}}$  ( $p < 0.05$ ) while no significant correlation was found between the parameters from the Freundlich and Langmuir equations and other soil properties such as total concentrations of Al and Fe (Table 3). Most soil properties were correlated with total carbon and clay contents (Table 4). However,  $\text{pH}_{\text{water}}$ ,  $\text{pH}_{\text{NaF}}$  and  $\Delta\text{pH}_{\text{NaF}}$  were not correlated with clay content. The additional sulfate adsorption was positively correlated with clay content ( $p < 0.01$ ), exchangeable  $\text{Al}^{3+}$  ( $p < 0.001$ ), CEC ( $p < 0.01$ ),  $\text{pH}_{\text{NaF}}$  ( $p < 0.001$ ), and  $\Delta\text{pH}_{\text{NaF}}$  ( $p < 0.001$ ). Analyzing the data by horizon, however, we found that the clay content was not correlated with additional sulfate adsorption while  $\text{pH}_{\text{NaF}}$  and  $\Delta\text{pH}_{\text{NaF}}$  were correlated with additional sulfate adsorption in the Bfj and Bt horizons, respectively ( $p < 0.05$ ). Both regression curves of  $\text{pH}_{\text{NaF}}$  and  $\Delta\text{pH}_{\text{NaF}}$  with additional sulfate adsorption were exponential (Fig. 2). The regression equation between sulfate adsorption and  $\Delta\text{pH}_{\text{NaF}}$  ( $R^2 = 0.70$ ,  $p < 0.001$ ) was a better fit than that between adsorption capacity and  $\text{pH}_{\text{NaF}}$  ( $R^2 = 0.63$ ,  $p < 0.001$ ) (Fig. 2).

## **4. Discussion**

### *4.1. Sulfate adsorption capacity is soil type specific*

With sulfate adsorption capacity ranged from 50 to 500  $\text{mg SO}_4^{2-} \text{ kg}^{-1}$ , the ability of soils in the AOSR to retain sulfate was relatively low (Table 1 and 2) as compared to other soils in

North America such as glaciated acid-sensitive soils in northeastern United States (MacDonald and Hart, 1990; Nodvin et al., 1986) and eastern Canada (Bhatti et al., 1997; Neary et al, 1987), and in northern Europe (Barton et al., 1999; Martinson and Alveteg, 2004). As sulfate is one of the major anions in atmospheric deposition in AOSR (Jung et al., 2011) and one of the major processes retaining sulfate in forest ecosystems is sulfate adsorption by soil particles (Reuss and Johnson, 1986), the low sulfate adsorption capacity of soils in AOSR implies that forest soils in AOSR have high risk of cationic nutrient leaching that could be caused by excessive sulfate deposition. Reduction of cationic nutrient by sulfate leaching can lead to soil acidification and subsequently forest decline caused by detrimental effects, such as Al toxicity and Ca deficiency, associated with soil acidification (Clark and Baligar, 1995). In addition, forest ecosystems in NE7 may be exposed to a greater risk of soil acidification caused by greater rates of S deposition but lower sulfate adsorption capacity; as is described in section 2.1, NE7 is closer to emission sources such as mining areas and upgrading facilities.

Sulfate adsorption has been reported to increase with soil depth likely due to increases in Al and Fe oxide concentrations and decreases in organic anion concentrations (Cole and Johnson, 1977; MacDonald and Hart, 1990). The top mineral soil horizon in the AOSR is normally an Ae horizon that developed by eluviation of clay, Fe, Al, or organic matter alone or in combination (Soil Classification Working Group, 1998), resulting in coarser textured soils with less Fe, Al, and organic matter contents than underlying B horizons. Although both watersheds had less organic matter and greater clay content in the deeper soil horizons than in the Ae horizon, sulfate adsorption was similar between horizons in NE7 while the Bfj and Bt horizons in SM8 had the ability to retain two times as much sulfate as the Ae horizon (Table 1). Such differences between the two watersheds might be related to differences in clay mineralogy among the soil profiles

studied. Unlike soils in NE7, soils in SM8 contained muscovite that have gibbsite layers sandwiched between two silica layers (Hamer and Hamer, 2004) and they are thus more effective in adsorbing sulfate than other clay minerals such as quartz and kaolinite that were also found in the studied soils.

Differences in the sulfate adsorption between the studied soil profiles would indicate that the impact of acid deposition would vary with local conditions such as soil type and clay mineralogy as well as the rate of acid deposition (Maitat et al., 2000; Yang et al., 2009). Based on our results, small differences in clay mineralogy between soil profiles could affect the capacity of soils to adsorb sulfate, which may subsequently influence soil acidification. Therefore, understanding the spatial variation in soil properties would help to determine the risk for soil acidification and establishment of the critical load for S deposition in the AOSR.

#### *4.2. Relationships between sulfate adsorption and soil properties*

There are many factors that influence sulphate adsorption by soils, including mineralogical composition, content and nature of organic matter, pH and the presence of other ions (Alves and Lavorenti, 2004). Adsorption of sulfate occurs mostly at the outer-sphere of sorbents such as Al and Fe oxides (Zhang and Sparks, 1990) although sulfate can also be adsorbed as an inner-sphere complex (Peak et al., 1999). In this study, both  $\text{pH}_{\text{NaF}}$  and  $\Delta\text{pH}_{\text{NaF}}$  were positively correlated with sulfate adsorption (Table 3 and 4). Such relationships may allow indices such as  $\text{pH}_{\text{NaF}}$  that measure the anion exchange capacity of the soil to reflect sulfate adsorption capacity, because  $\text{F}^-$  can effectively replace the exposed hydroxyl ions on soil particle surfaces (Bolland et al., 1996; Perrott et al., 1976). Therefore,  $\text{pH}_{\text{NaF}}$  and  $\Delta\text{pH}_{\text{NaF}}$  could be used

as an indirect measure of sulfate adsorption capacity. However, there are limitations with using  $\text{pH}_{\text{NaF}}$  to assess sulfate adsorption as  $\text{pH}_{\text{NaF}}$  is affected by soil acidity as well as sulfate adsorption. For example, the Ae horizon soil samples showed lower  $\text{pH}_{\text{NaF}}$  than samples from Bm and C horizons although they could adsorb similar amounts of added sulfate (Fig. 2). As  $\text{pH}_{\text{NaF}}$  is affected by soil acidity,  $\text{pH}_{\text{NaF}}$  may erroneously indicate lower sulfate adsorption capacities in acidic soils than in less acidic soils. Therefore, the sulfate adsorption capacity of acidic soils may be underestimated if  $\text{pH}_{\text{NaF}}$  is used to assess the soil's potential for sulfate adsorption. The potential effect of soil acidity on  $\text{pH}_{\text{NaF}}$  could be excluded when  $\Delta\text{pH}_{\text{NaF}}$  was used, which likely resulted in a greater determination of coefficient for  $\Delta\text{pH}_{\text{NaF}}$  than that for  $\text{pH}_{\text{NaF}}$  (Fig. 2). Using soil properties such as  $\Delta\text{pH}_{\text{NaF}}$  that can be easily determined to estimate sulfate adsorption capacity may save time and cost as compared with determining sulfate adsorption capacity by conducting conventional adsorption isotherm experiments.

## 5. Conclusions

Coarse-textured soils in the AOSR are sensitive to acidification because of their low cation exchange capacity and thus low buffering capacity. Horizon samples of the two studied soils had low capacities of sulfate adsorption; therefore, such soils will have low capacities to retain sulfate deposited from the atmosphere and that will increase the risk of cation leaching that accompanies sulfate leaching. Risk for soil acidification would be greater in NE7 than in SM8 due to the lower sulfate adsorption capacity of soils in NE7. In both watersheds, the Ae horizon in the profile was most susceptible to acidification because of its lowest ability to adsorb additional sulfate. Significant differences in sulfate adsorption capacity between horizon samples indicate that differences in the thickness and configuration of the various horizons in a soil

profile can have marked impact on the soil's sensitivity to cation leaching and therefore acidification. The sulfate adsorption capacity appeared to be mainly related to clay mineralogy rather than clay content, and Al and Fe concentrations within the soils we have studied. The  $pH_{NaF}$  and  $\Delta pH_{NaF}$  were significantly correlated with sulfate adsorption and conventional parameters of isotherm equations; therefore  $pH_{NaF}$  and  $\Delta pH_{NaF}$  can be used to estimate sulfate adsorption capacity for the studied soils in the AOSR, with the latter parameter being preferred due to the fact that the relationship between sulfate adsorption capacity and  $\Delta pH_{NaF}$  is not affected by soil acidity. To avoid soil acidification in AOSR, the low capacity of soils to retain sulfate should be considered in determining the critical load for acid deposition in the AOSR in Alberta. As soil acidification is of concern particularly for coarse-textured soils in AOSR, assessment of sulfate adsorption capacity should be focused on acid-sensitive, coarse-textured soils.

### **Acknowledgements**

This study was conducted with financial support from the  $NO_x$  and  $SO_2$  Management Working Group (NSMWG) in the Cumulative Environmental Management Association (CEMA), Alberta Environment and the University of Alberta.

### **References**

- Alves, M.E., Lavorenti, A., 2004. Sulfate adsorption and its relationships with properties of representative soils of the São Paulo State, Brazil. *Geoderma* 118, 89-99.
- Barton, D., Gammack, S.M., Billet, M.F., Cresser, M.S., 1999. Sulphate adsorption and

- acidification of *Calluna* heathland and scots pine forest podzol soils in north-east Scotland. For. Ecol. Manage. 114,151-164.
- Bhatti, J.S., Foster, N.W., Evans, L.J., 1997. Sulphate sorption in relation to properties of podzolic and brunisolic soils in northeastern Ontario. Can. J. Soil Sci. 77, 397–404.
- Bolland, M.D.A., Gilkes, R.J., Brennan, R.F., Allen, D.G., 1996. Comparison of seven phosphorus sorption indices. Aust. J. Soil Res. 34, 81-89.
- Chen, Z., Xing, B., McGill, W.B. 1999., A unified sorption variable for environmental applications of the Freundlich equation. J. Environ. Qual. 28:1422-1428.
- Clark, R.B., Baligar, V.C., 1995. Acidic and alkaline soil constrains on plant mineral, in: Wilinon, R.E. (Ed.), 2 ed. Marcel Dekker, Inc., New York, pp. 133-177.
- Cole, D.W., Johnson, D.W., 1977. Atmospheric sulfate additions and cation leaching in a Douglas-fir ecosystem. Water Resour. Res. 13, 313-317.
- Elkins, D.M., Ensminger, L.E., 1971. Effect of soil pH on the availability of adsorbed sulfate. Soil Sci. Soc. Am. Pro. 35, 931-934.
- Fung, M.Y.P., Macyk, T.M., 2000. Reclamation of oil sands mining areas, in: Barnhisel, R.I., Darmody, R.G., Daniels, W.L. (Eds.), Reclamation of Drastically Disturbed lands. ASA, CSSA and SSSA, Agronomy Monograph 41, Madison. pp. 755-774.
- Gee, G.W., Or, D., 2002. Particle size analysis, in: Dane, J. H., Topp, C. (Eds.), Methods of Soil Analysis, Part 4 Physical Methods. ASA, Wisconsin, pp. 255-293.
- Harrison, R.B., Johnson, D.W., Todd, D.E., 1989. Sulfate adsorption and desorption reversibility in a variety of forest soils. J. Environ. Qual. 18, 419-426.
- Hamer, F., Hamer, J., 2004. The Potter's Dictionary of Materials and Techniques, fifth ed. A&C Black, London.

- Jung, K.H., Chang, S.X., Arshad, M.A., 2011. Effects of canopy-deposition interaction on H<sup>+</sup> supply to soils in *Pinus banksiana* and *Populus tremuloides* ecosystems in the Athabasca oil sands region in Alberta, Canada. Environ. Poll. in press.
- Liu, F., He, J., Colombo, C., Violante, A., 1999. Competitive adsorption of sulfate and oxalate on goethite in the absence or presence of phosphate. Soil Sci. 164, 180–189.
- MacDonald, N.W., Hart, J.B., 1990. Relating sulfate adsorption to soil properties in Michigan forest soils. Soil Sci. Soc. Am. J. 54, 238-245.
- Maitat, O., Boudot, J.P., Merlet, D., Rouiller, J., 2000. Aluminum chemistry in two contrasted acid forest soils and headwater streams impacted by acid deposition, Vosges Mountains, N.E. France. Water Air Soil Poll. 117, 217–243.
- Martinson, L., Alveteg, M., 2004. The importance of including the pH dependence of sulfate adsorption in a dynamic soil chemistry model. Water Air Soil Poll. 154, 349-356.
- Mekaru, T., Uehara, G., 1972. Anion adsorption in ferruginous tropical soils. Soil Sci. Soc. Am. Pro. 36, 296–300.
- Neary, A.J., Mistry, E., Vanderstar, L., 1987. Sulphate relationships in some central Ontario Forest soils. Can. J. Soil Sci. 67, 341–352.
- Nodvin, S.C., Driscoll, C.T., Likens, G.E., 1986. Simple partitioning of anions and dissolved organic carbon in a forest soil. Soil Sci. 142, 27–35.
- NOx-SO<sub>2</sub> Management Working Group (NSMWG), 2004. A Summary of Work for the Management of Acid Emissions in the Oil Sands: Background Information for the Dynamic Modeling of Acid Emissions. Workshop 2. Cumulative Environmental Management Association, Alberta.
- Ok, Y.S., Chang, S.X., Feng, Y.S., 2007a. The role of atmospheric N deposition in soil

- acidification in forest ecosystems, in: Munoz, S.I. (Ed.), Ecological Research Progress. Nova Science Publishers. USA. pp. 47-77.
- Ok, Y.S., Chang, S.X., Feng, Y.S., 2007b. Sensitivity to acidification of forest soils in tow watersheds with contrasting hydrological regimes in the oil sands region of Alberta. *Pedosphere* 17, 747-757.
- Peak, J.D., Ford, R.G., Sparks, D.L., 1999. An *in situ* ATR-FTIR investigation of sulfate bonding mechanisms on goethite. *J. Colloid Interf. Sci.* 218, 289-299.
- Perrot, K.W., Smith, B.F. L., Inkson, R.H.E., 1976. The reaction of fluoride with soils and soil minerals. *J. Soil Sci.* 27, 58-67.
- Reuss, J.O., Johnson, D.W., 1986. Acid deposition and the acidification of soils and waters. Springer-Verlag. New York.
- Ruan, J.Y., Ma, L.F., Zhang, F.S., 2004. Effects of litter incorporation and nitrogen fertilization on the contents of extractable aluminum in the rhizosphere soil of tea plant (*Camellia sinensis* (L.) O. Kuntze). *Plant Soil* 263, 283-296.
- Shoji, S., Fujiwara, Y., 1984. Active aluminum and iron in the humus horizons of Andosols from North eastern Japan: their forms, properties, and significance in clay weathering. *Soil Sci.* 137, 216– 226.
- Soil Classification Working Group, 1998. The Canadian System of Soil Classification, third ed. NRC Research Press, Ottawa.
- Soil Survey Staff, 1994. Keys to Soil Taxonomy, sixth ed. NRCS, Washington, D.C.
- Whittig, L.D., Allardice, W.R., 1986. X-ray diffraction techniques, in: Klute, A. (Ed.), Methods of Soil Analysis, Part 1 Physical and Mineralogical Methods, second ed. ASA, Wisconsin, pp. 331-362.

- Xue, D.S., Harrison, R.B., 1991. Sulfate, aluminum, iron and pH relationships in four Pacific-Northwest forest subsoil horizons. *Soil Sci. Soc. Am. J.* 55, 837-840.
- Yang, J.E., Lee, W.Y., Ok, Y.S., Skousen, J., 2009. Soil nutrient bioavailability and nutrient content of pine trees (*Pinus thunbergii*) in areas impacted by acid deposition in Korea. *Environ. Monit. Assess.* 157, 43-50.
- Zhang, P.C., Sparks, D.L., 1990. Kinetics and mechanisms of sulfate adsorption/desorption on goethite using pressure-jump relaxation. *Soil Sci. Soc. Am. J.* 54, 1266–1273.