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A FREUNDLICH-BASED MODEL FOR PREDICTION OF pH-DEPENDENT SULFATE ADSORPTION IN FOREST SOIL

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SUMMARY IN SWEDISH

Den starka industrialiseringen i Europa efter andra världskriget medförde att stora mängder SO_2 och NO_x släpptes ut i samband med förbränning av fossila bränslen. De svenska skogsekosystemen påverkades av utsläpp av SO_2 följt av deposition av H_2SO_4 . Detta medförde att skogsmarkens förråd av sulfat (SO_4^{2-}) ökade. Denna masteruppsats studerar adsorptionen av SO_4^{2-} i podsolers Bs-horisonter i svensk skogsmark. Jordprov från fem olika provtagningspunkter studerades, och resultaten visar att jordarna förmår ackumulera varierande mängder av adsorberat SO_4^{2-} beroende på förändringar i jämviktskoncentration och pH-värde. Den här studien visar att mängden adsorberat SO_4^{2-} (mmol/kg jord) ökar med ökande jämviktskoncentration SO_4^{2-} (mmol/l) och med sjunkande pH-värde. Detta observerades i jämviktsexperiment på laboratoriet. För att beskriva resultaten utvecklades en modell för att kunna förutsäga förrådet adsorberat SO_4^{2-} (mmol/kg) i de olika jordproverna. En Freundlichbaserad modell användes, och mängden adsorberat SO_4^{2-} (mmol/kg) beräknades som funktion av pH och av jämviktskoncentrationen SO_4^{2-} (mmol/l) i marklösningen. Den utvidgade Freundlichmodellen optimerades på tre olika sätt: (1) genom obegränsad optimering då alla tre koefficienter K_f , m och y optimerades samtidigt, (2) genom begränsad optimering då värdet för y , som betecknade den mängd vätejoner (H^+) som bands till ytan för varje adsorberat sulfatjon, sattes till 2, och (3) genom en förenklad tvåpunktskalibrering, där en begränsad optimering gjordes för endast två prover från varje jord användes för varje jord. Determinationskoefficienten R^2 , samt värdena för de optimerade koefficienterna, var mycket likartade för obegränsad och begränsad optimering, beroende på att det optimerade värdet för y var nära 2 för 4 av 5 jordar. Värdet för R^2 översteg 0,96, och 0,99 för de två jordar (Risbergshöjden B och Kloten Bs) som hade högst kapacitet att adsorbera sulfat. Även den förenklade tvåpunktskalibreringen gav goda anpassningar med värden för de optimerade koefficienterna som låg nära de som fanns när hela mängden datapunkter användes i modellkalibreringen. Den förenklade tvåpunktskalibreringen ansågs vara den bästa optimeringsmetoden, eftersom den endast kräver två observationer för varje jord.

SUMMARY IN ENGLISH

The industrialization in Europe after World War II released the large amounts of SO_2 and NO_x during the combustion of fossil fuels. The Swedish forest ecosystems were affected by discharges of SO_2 followed by deposition of H_2SO_4 . This meant that the forest soil reservoir of SO_4^{2-} were increased. This master thesis study the adsorption of SO_4^{2-} in podzolic Bs horizons of Swedish forest land. The adsorption results of soil samples from five different sampling points show that the soils are able to accumulate varying amounts of adsorbed SO_4^{2-} by depending on the change in the equilibrium concentration and pH. This study shows that the amount of adsorbed SO_4^{2-} (mmol/kg soil) increases with increasing equilibrium concentration of SO_4^{2-} (mmol/l) and with decreasing pH. This was observed in equilibration experiments in the laboratory. To describe the results, developed a model to predict reservoirs of adsorbed SO_4^{2-} (mmol/kg) in the different soil samples. A Freundlich based model was used, and the amount of adsorbed SO_4^{2-} (mmol/kg) was calculated as a function of pH and the equilibrium concentration of SO_4^{2-} (mmol/l) in the soil solution. The extended Freundlich model was optimized in three different ways: (1) by unconstrained optimization when all three coefficients K_f , m and y were optimized simultaneously, (2) by constrained optimization when the value of y , which signifies the amount of hydrogen ions (H^+) bound to the surface together with each adsorbed sulfate ion, was set to 2, and (3) through a simplified two-point calibration, where a constrained optimization was made for only two samples from each soil. The coefficient of determination R^2 , and the values of the optimized coefficients were very similar for the unconstrained and constrained optimization, as the optimized value of y was close to 2 for 4 of 5 soils. The value of R^2 exceeded 0.96, and 0.99 for the two soils (Risbergshöjden B and Kloten Bs1) that had the highest capacity to adsorb SO_4^{2-} . The simplified two-point calibration produced the values of the optimized coefficients that were close to those obtained when the entire number of data points were used in the model calibration. Therefore the simplified two-point calibration was considered the best optimization method, since it requires only two observations for each soil.

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ABBREVIATIONS AND SYMBOLS

Al	Aluminum
Al ³⁺	Aluminum ion
Ca ⁺	Calcium ion
CaSO ₄ ·2H ₂ O	Calcium sulfate dihydrate (Gypsum)
DOC	Dissolved organic compound
Fe	Iron
H ⁺	Hydrogen ion
HNO ₃	Nitric Acid
IEAs	International environmental agreements
K ⁺	Potassium ion
K _f	Freundlich coefficient
M	Non-ideality parameter in Freundlich equation
MgSO ₄	Magnesium sulfate
Mg ⁺	Magnesium ion
N	Nitrogen
NO _x	Nitrogen oxide
Na ₂ SO ₄	Sodium sulfate
NO ₃ ²⁻	Nitrate ion
NH ₄	Ammonium
OH ⁻	Hydroxyl ion
R ²	Coefficient of determination in regression equation
SO ₂	Sulfur dioxide
SO ₄ ²⁻	Sulfate ion
USDA	United state department of agriculture
USEPA	United state environmental protection agency
WHO	World health organization
γ	The Proton co-adsorption stoichiometry

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ABSTRACT

The period of industrialization after the second World War in Europe released SO_2 and NO_x by combustion of fossil fuels and contributed the formation of S and N compounds in the forest ecosystem. The Swedish forest soil systems were influenced by emissions of SO_2 followed by H_2SO_4 deposition, consequently the pool of SO_4^{2-} had increased in the forest ecosystem. This thesis studied SO_4^{2-} adsorption in a podzolic Bs horizon soils taken from a Swedish forest soil system. The soil samples from five different sampling sites were collected and the results revealed different amounts of adsorbed SO_4^{2-} in response to changes in equilibrium concentration and pH. This study found that the amount of adsorbed SO_4^{2-} (mmol/kg) increased with an added equilibrium concentration of SO_4^{2-} (mmol/l) and with a decreasing pH. This was determined by equilibration experiments. Based on the results a Freundlich-based model was developed to predict the pool of adsorbed SO_4^{2-} in the soil samples. The model predicted the pool of adsorbed SO_4^{2-} (mmol/kg) as a function of pH and the equilibrium concentration of SO_4^{2-} (mmol/l) in the soil solution system. The extended Freundlich model was optimized in three different ways: by use of unconstrained, constrained and simplified two-point calibration. The results showed that the adsorption of sulfate in the Kloten Bs1 and Risbergshöjden B soils was higher as compared to the Tärnsjö B, Österström B, and Risfallet B soils. The coefficient of determination (R^2) determined from an unconstrained fit of the extended Freundlich model (with three adjustable parameters) for Risbergshöjden B and Kloten Bs1 were $R^2 = 0.998$ and $R^2 = 0.993$. Nearly as good fits were found in a constrained fit with two adjustable parameters when it was assumed that nearly 2 protons (2 H^+) are co-adsorbed with one SO_4^{2-} ion (Risbergshöjden B; $R^2 = 0.997$ and Kloten Bs; $R^2 = 0.992$). The simplified two-point calibration with two adjustable parameters showed similar parameter values for all most soils and was considered the best optimization method of extended Freundlich model, especially as it requires only limited input data.

Key Words : Sulfate; Spodosols; pH Dependent Sulfate Adsorption; Extended Freundlich Model.

1. INTRODUCTION

Acidic deposition which is mainly consists of sulfuric acid H_2SO_4 , nitric acid HNO_3 and ammonium NH_4^+ , are primarily derived from emissions of sulfur dioxide SO_2 , Nitrogen oxide NO_2 and ammonia NH_3 . These compounds are largely emitted to the atmosphere by fossil fuel combustion and some agriculture activities (USDA and WHO, 2000). The fossil fuels combustion which is largely for power generation, for industrial production process and by households, provide a significant contribution to air pollution in urban areas and on a regional or wider scale (Mitchel et al., 1998; van Stempvoort, 1992). These emissions lead to acidic deposition in the form of sulfuric acid H_2SO_4 , nitric acid HNO_3 and ammonium NH_4^+ to ecosystems. Once acid compounds enter sensitive ecosystems, they acidify soil and surface water by causing several ecological changes. In sensitive ecosystems, along with the acidification of soil and surface water, they affect nutrient cycling and impact the ecosystem services provided by forests. The atmospheric inputs of acidifying compounds derived from fossil fuel combustion hence disturb the soil ecosystem (Martinson et al., 2005). The long-term deposition of acidifying compounds on soil mainly results in three types of changes in soil: depletion of base cations, mobilization of dissolved inorganic aluminum and accumulation of sulfate and nitrogen (Krauskopf et al.; 1995; Schwartz et al., 2011).

The acidic emissions that contain compounds of sulfur (S) have oxidation states ranging from -2 (sulfide) to +6 (sulfate) (Prietz et al., 2009). In the unsaturated zone of forest soils, S is present as the dominant and stable form of inorganic sulfate. Lower oxidation-state inorganic compounds are also present but in negligible quantities. Concentrations of sulfate (SO_4^{2-}) in soils fluctuate throughout the year. Because of variations in the balance between atmospheric inputs, decomposition of plants, plant uptake, leaching and microbial activity change SO_4^{2-} concentration. In forest ecosystems, inorganic SO_4^{2-} exists in the form of soluble salts and adsorbed SO_4^{2-} on the surface of inorganic components of soil (Scherer, 2001; Eriksen, 2008).

Deposition of S and nitrogen (N) has led to acidification of soils and water in Europe. Different studies show that the soils are acidified by deposition of acidic emissions (Sverdrup et al., 1998). Deposition of S has however decreased substantially during the last decades and many acidified lakes show clear signs of recovery in eastern North America and Europe (Johnson, 1980). However, much of the problem with acidified soils and water still remains.

A decreased atmospheric deposition has altered the ecosystem of soils. The recovery of soil in response to decrease in deposition is delayed, a considerable time may be needed for recovery. The release of already adsorbed SO_4^{2-} is not completed until a new steady-state, with respect to current atmospheric inputs, is obtained. The delayed effect of SO_4^{2-} adsorption/desorption on the response of water systems to changes in the input acidity hence demands an accurate model to predict the recovery from acidification, and also to predict the delay of the soil chemical response to acidification due to altered forest management practices.

2. BACKGROUND

In forest ecosystems acid deposition occurs as wet deposition (rain and snow), dry deposition (gases and particulates), and as cloud and fog deposition (Fig. 1). During wet deposition nitrogen oxides (NO_x) and sulfur dioxide (SO_2) are converted to nitric acid (HNO_3) and sulfuric acid (H_2SO_4) and deposited to the forest ecosystem. Deposition of SO_4^{2-} and nitrate (NO_3^-) by wet deposition are considered roughly equivalent (Pirainen et al., 2002), whereas deposition of ammonium NH_4^+ in dry deposition form is higher. Dry deposition of SO_2 and NO_x leads to the deposition of acid after interacting with water in the forest ecosystem. NO_3^- and ammonium byproducts are used by forest vegetation to support growth.

When sulfuric acid H_2SO_4 is deposited from the atmosphere into the soil system, each molecule splits into two hydrogen ions (H^+) and a negatively charged SO_4^{2-} ion (Alewell et al., 1995). Soil is acidified by the presence of H^+ ion to replace base cations by ion exchange process. Furthermore, removal of displaced base cations acidify the soil system (Harrison et al., 1989). Moreover, SO_4^{2-} is retained in the soil system. It is retained in a variety of forms, such as adsorbed SO_4^{2-} on soil particles and as organic S. It is also leached from the soil and accompanied by an equivalent amount of base cations (Ca^+ , Mg^+ and K^+). When SO_4^{2-} is retained by sulfate adsorption it delays the loss of base cations through leaching with SO_4^{2-} and thus counters the acidifying effect of atmospheric sulfur S deposition (Jung et al., 2011). Understanding the association between the inputs of S and forest soil ecosystem chemistry

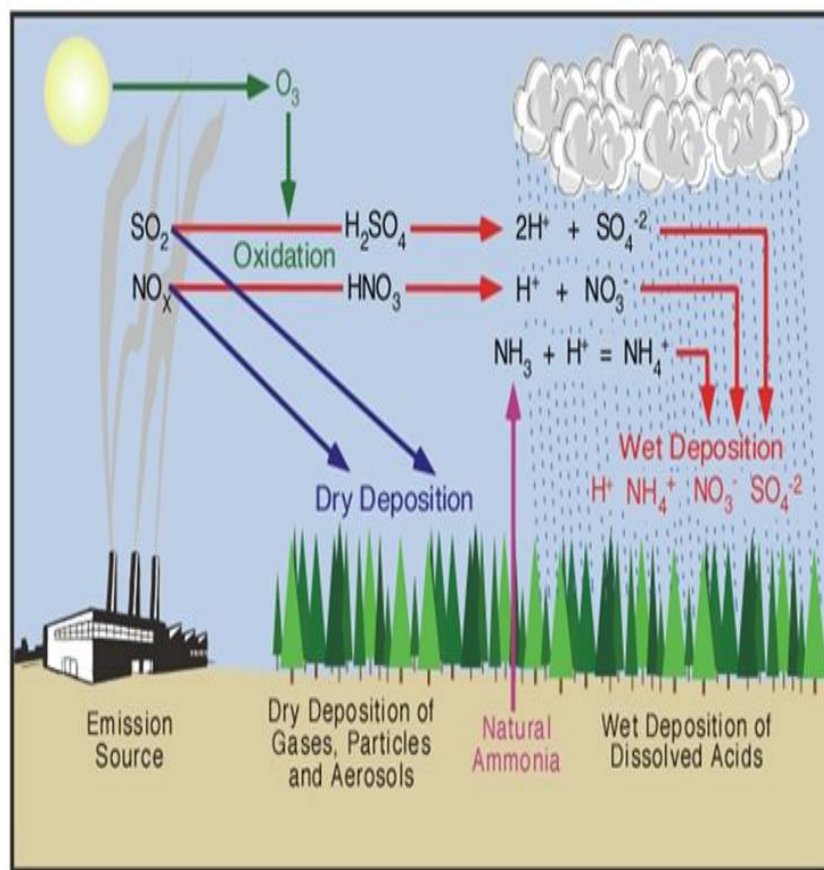


Fig.1. Emissions of sulfur dioxide SO₂ and nitrogen oxide compounds NO_x into the atmosphere as a source of dry and wet acid deposition in soil. Source: USDA Forest Service (<http://webcam.srs.fs.fed.us/pollutants/acidification>)

to appraise the response of forest ecosystem to acid inputs has been considered as critical (Mitchell et al., 1998; Barton et al., 1999).

Significant work has been done on the movement and reaction of SO₄²⁻ in soils. Some research has been performed to predict the adsorption of SO₄²⁻ in forest soil system. According to Gustafsson (1995) and Karlton (1997), the adsorption of SO₄²⁻ in forest soil is a proton-buffering process. This characteristic of SO₄²⁻ adsorption delays the soil water chemical response to changes in H⁺ and SO₄²⁻ ions concentration of the permeating solution. This may, for example, reduce the immediate impact of atmospherically deposited H₂SO₄ when the latter has been increased. This characteristic of sulfate adsorption is considered significant in reducing base cation losses (Gustafsson, 1995; Jung et al., 2011; Karlton, 1997). Base cations such as Ca⁺, K⁺ and Mg⁺ leach from the soil with SO₄²⁻ as a counter-ion. As a result of adsorption, SO₄²⁻ is retained in soil together with the base cations.

2.1. Forest soil system

The forest soil is a multifaceted heterogeneous medium consisting of solid phases that contain organic matter and different minerals (Gobran et al., 1998; Carlsson et al., 1999). The soils that are developed in sandy glacial tills with low weathering rates are the most vulnerable part of the forest ecosystem to atmospheric acidic inputs (Gustafsson and Jaks, 1993). The retention of SO₄²⁻ in soils is characterized by the particle surfaces which contribute to adsorption. Soil particles with clay minerals

and various oxide surfaces and solid phase humic substance usually possess large specific surface areas and reactive sites. Coarser particles such as sand possess very low surface area and hence are not important adsorbents (Gustafsson et al., 2007).

In humid regions the process of soil formation involves leaching of upper layer with accumulation of material in lower layers. In coarse textured glacial tills or sandy sediments, podzols are developed by the process of podzolisation. When organic matter present on the surface of soil releases abundant organic acids, the latter migrate downwards together with weathered Fe and Al in the soil profile (David et al.; 1983; Edwards, 1998; Alves et al., 2004; Gustafsson et al., 2007). During this process, organic acids form complexes with weathered Fe and Al and these are deposited in the subsoil horizon in the soil profile. In this subsoil horizon the complexes degrade, which leads to the formation of Fe and Al hydrous oxides.

Podzolised forest soils that contain Fe oxide and poorly crystalline aluminosilicate in the B horizon are important for SO_4^{2-} adsorption. The surfaces of these Fe and Al hydrous oxides serve as adsorbents for SO_4^{2-} especially under low pH conditions. SO_4^{2-} adsorption in forested soil systems is dependent on pH, quantity of Al and Fe hydroxide, organic matter and concentration of sulfate present in the soil system (Jung et al., 2011). In acidic soils, SO_4^{2-} is adsorbed to the surface of amorphous iron and aluminum oxide and hydrous oxide.

SO_4^{2-} in Swedish forest soils is adsorbed somewhat unevenly. The spodic B horizon has the maximum number of positive charges ions in the form of Fe and Al (hydr)oxides. Therefore in this horizon, and when organic carbon is low, SO_4^{2-} is adsorbed to a significant extent (Grerup et al.; 1987; Gustafsson, 1995).

2.2. Abatement in acid deposition

The abatement in acid deposition in various regions of the world as compared to Sweden can be seen as,

2.2.1. *North America, Europe and eastern Asia*

The SO_2 emissions have declined during the last decade in Europe and North America due to implementation of international laws, policies and agreements (i.e. IEAs) on the reduction of S (Finus et al., 2003), but instead a rapid increase have been observed in areas of world which have high economic growth such as south-east Asia (Akselsson et al., 2013). Since 1970, the deposition level has decreased by as much as two thirds in Europe (Akselsson et al., 2013; Martinson, 2003). Already in 1984, it was observed that emission of SO_2 and SO_4^{2-} deposition had declined by between 38 and 82 % in Europe and by 52 % in the United States (Johnson, 1984). Additionally, emissions of NO_x and nitrogen deposition show a slighter decline of 17 to 20 %. According to the literature, in Europe, in 1980 the SO_2 emissions was recorded as 55 Mt (million ton) but this level decreased to 41 Mt (million ton) in 1990. It is noticed that the mean annual pH of the precipitation in eastern North America and Europe is in the range of 3.0 to 4.7 (Chesworth, 2008; Johnson, 1984).

On the other hand in the Asian-Pacific region emissions in 1990 reached about 35 Mt and are expected to increase rapidly. The effect of widespread acid deposition due to sulfur emission may have decreased in Europe but it is highly likely to increase in the Asian developing countries (WHO, 2000).

Acid deposition in north-east Asia has increased hastily in the past decade because of industrial growth and will most likely exceed stages noticed previously in the most polluted area of central and eastern Europe (Cole et al., 1997; Zhang, 1996). Consequently, the increase in emissions is a threat to sustainable forest ecosystems and a question of concern to take account of reduction in emissions (Ishiguro et al.; 2011).

2.2.2 Sweden

In Sweden, the decrease in the deposition of SO_4^{2-} and H^+ due to the restriction (due to implementation of Environmental Protection Act 1969) of sulfur emissions started during the 1970s. They decreased considerably during the last decade (by following the targets of the Helsinki protocol in 1985 to reduce S emissions, the Oslo protocol in 1994 for further reduction S emissions, and the Gothenburg protocol in 1999 to abate acidification, eutrophication and ground level ozone) and now it is at level below that recorded in the mid-1950s. The continual decrease of the deposition resulted in an improved status of the water quality in forested catchments in Sweden (Fölster et al., 2002). However, the SO_4^{2-} concentration in the forest ecosystems and surface waters of south-west of Sweden has not decreased to the extent that could be expected from the decreased acid deposition. During the period of deposition decrease the desorption of already adsorbed sulfate acts as a buffering mechanism in forest soils. Depending on the soil properties, there may be a long delay between the decreased input of acid and the chemical recovery (Nömmik et al.; 1998; Jönsson et al.; 2003).

2.3. Adsorption

SO_4^{2-} and other anions such as phosphate, arsenate and molybdate adsorb on the surface of adsorbents present in the soil. These anions are adsorbed through a reaction between the adsorbate (anions) and the surface of a solid adsorbent (Fe and Al oxide in soils) that involves ligand exchange (Selim et al.; 2004; Belyazid et al.; 2006; Gustafsson et al., 2007; Sokolova et al.; 2008).

2.3.1 Factors affecting sulfate adsorption in soils

The pH and the equilibrium concentration are two important factors that govern the adsorption of SO_4^{2-} ions. The pH value is considered to be the most important parameter. The reason is that the surface of adsorbent usually possesses variable charge and therefore the electrostatic forces of attraction are also variable and depend on the pH value. For example, SO_4^{2-} is adsorbed more strongly at low pH on the variable positively charge surfaces of Fe and Al hydrous oxides in soils. At high pH a negative charge occurs on the surface, hence cations are adsorbed more strongly at high pH (Rao, et al.; 1984; Sharpley, 1990; Stanko et al.; 2008).

In certain cases, the adsorption of the ion itself affects the pH values in the surrounding environment. When one SO_4^{2-} ion is adsorbed to the surface of Fe oxide as a surface complex, it decreases the charge of oxide surface by a value of 2. To compensate for this large change in charge, H^+ ions and to some extent other cations are bound on the oxide surface (Gustafsson, 2007; Karlun, 1997; Gustafsson, 1995)

The effect of ionic strength changes the number of co-adsorbed monovalent cations during sulfate adsorption on the surface of oxide surfaces in soil. At high ionic strength i.e. under conditions of high salinity this value is about 1, because 1 H^+ is needed to protonate the surface for every sulfate ion being adsorbed. At low ionic strength, the number of co-adsorbed protons is nearly equal to 2 (Gustafsson, 1995).

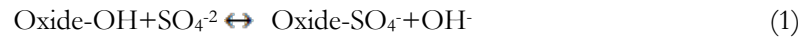
2.4. Mechanism of sulfate adsorption

Sulfate is retained in the soil system by varying mechanisms. The main adsorption mechanism is called ligand exchange. In this specific adsorption mechanism SO_4^{2-} is associated with metal (hydr) oxides of Fe and Al present in the soil system by displacing OH^- anions or H_2O . During specific adsorption, the surface also accepts or donates protons, for the reasons stated in the above section. During the adsorption of SO_4^{2-} on Fe and Al hydrous oxide surfaces, the sulfate anion accepts a proton from the positive site of Fe and Al hydrous oxide surface (M-OH_2^+ where $\text{M} = \text{Fe}$ or Al) and create monovalent HSO_4^- . This monovalent ion replaces a OH^- ion without creating additional negative charge on the surface (Sjöström, 1993; Gustafsson, 1995; Zhang et al., 1996; Karlun, 1997; van Hees et al.; 2000).

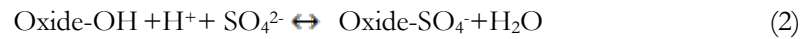
The adsorption process of sulfate removes the acidity of soil solution and during desorption process acidity is released. Due to this, the recovery of soil is also delayed.

2.4.1 Chemistry of sulfate adsorption

Adsorption of SO_4^{2-} results in the displacement of $-\text{OH}$ ligands from oxide:



When an $-\text{OH}$ from the metal (hydr)oxide is replaced, the surface charge decreases, which facilitates cation exchange. In reality, the replacement usually occurs in two steps: (i) H^+ ions are sorbed, and (ii) SO_4^{2-} ions bind by replacing $-\text{OH}_2^+$. Reaction (1) may therefore more accurately be written as follows:



The release of water changes the charge from positive to negative on the site. These equations show that SO_4^{2-} adsorption and the cation exchange capacity may increase at the same time (Gustafsson, 1995; Karlun, 1997; Martinson et al., 2003; Goldberg, 2005).

Another related way to understand SO_4^{2-} adsorption is by surface complex formation theory (Gustafsson, 1995). According to this theory, sulfate ions adsorb onto Fe and Al hydrous oxides as outer- and inner-sphere complexes. The adsorption of SO_4^{2-} as an inner-sphere surface complex means that adsorption of SO_4^{2-} changes the net charge on the oxide surface. The electrostatic non-specific type of adsorption creates outer-sphere surface complexes and it balances the positive charge surface of the metal oxides. On the other hand, adsorption of SO_4^{2-} as inner-sphere complexes is stronger.

2.5. Background of study

This thesis takes its starting point in the modeling approaches of Gustafsson (1993 and 1995), Karlun (1997), Martinson (2003), and Gobran et al. (1998).

Gustafsson (1995) modeled pH-dependent sulfate adsorption in the Bs horizons of podzolised soils. He assumed that $\sim 2 \text{ H}^+$ ions are consumed for every SO_4^{2-} ion during adsorption. It was accomplished by sequential leaching process with use of magnesium sulfate MgSO_4 . Use of acid until pH 4.4 was reached facilitated determination of the SO_4^{2-} adsorption capacity in soils.



The basic adsorption reaction of SO_4^{2-} (equation 3) was used to predict how the pH dependency of SO_4^{2-} adsorption can be incorporated in an

empirical model. This was tested in a Temkin isotherm approach in which the amount of adsorbed sulfate was assumed to be linearly related to log-transformed values of SO_4^{2-} and H^+ . Further it was assumed that the soil systems had very low ionic strength so that the value of γ (the proton co-adsorption stoichiometry, i.e. the number of H^+ that accompanies every SO_4^{2-} ion) is close to 2. This means that an extra H^+ is adsorbed in the basic reaction and that the sulfate adsorption reaction can be viewed as the adsorption of H_2SO_4 . Hence in this approach, the adsorption of sulfate ion SO_4^{2-} was assumed to be linearly related to the term $2\text{pH} + \text{pSO}_4$, where pSO_4 is the negative log of the dissolved sulfate concentration.

Similar studies were made by Karlton (1997), although he used a surface complexation model approach to describe his data. He compared the surface complexation of SO_4^{2-} and H^+ between goethite, gibbsite and a soil material from a podzol B horizon. He used the diffuse layer model and found that a model with only one SO_4^{2-} surface species and no H^+ ion explicitly take part in the adsorption reaction provided the best prediction of adsorption. He found that associated H^+ co-adsorption occurs during SO_4^{2-} adsorption and by this the neutralization in the inner layer the surface potential is decreased. He also performed his experiments under different pH, ionic strength and SO_4^{2-} concentrations to determine the γ value, which was found to vary with pH and SO_4^{2-} concentration and with the ionic strength. His experimental work determined the γ as being close to 1 at high ionic strength (0.1 M) but at low ionic strength (0.001 M) γ was in the range of 1.5 to 1.7.

Courchesne & Hendershot (1989) measured the adsorption and desorption of SO_4^{2-} to/from some podzolic soils of the southern Laurentians in Canada as a function of pH and used six podzolic soils (Hermine B, Coniferous B, Laflamme 1 B1, Laflamme 1 B2, Laflamme 2 B1 and Laflamme 2 B2) of two forested watersheds of southern Laurentians. The effect of soil solution pH on SO_4^{2-} of podzolic soils was determined. They used four simple adsorption equations i.e. the Gurney equation, Freundlich equation, Langmuir equation and Temkin equations and observed SO_4^{2-} adsorption and desorption as a function of pH and initial sulfate concentration. They observed an increase in SO_4^{2-} adsorption with decreasing pH to a maximum adsorption at pH 3.8 to 4.2. They could also relate the amount of adsorbed SO_4^{2-} and total native SO_4^{2-} to the total oxalate extractable Al contents of soils. They found the Gurney equation to produce the best fits to the soil data ($R^2=0.999$, $R^2=0.995$, $R^2=0.993$, $R^2=0.999$, $R^2=0.994$ and $R^2=0.999$ respectively) of each six soils as compared to Freundlich equation ($R^2=0.983$, $R^2=0.977$, $R^2=0.987$, $R^2=0.972$, $R^2=0.980$, and $R^2=0.948$ respectively).

Martinsson et al., (2003; 2005) parameterized, evaluated and modeled the adsorption of SO_4^{2-} by an isotherm in which it was assumed that SO_4^{2-} adsorption is fully reversible and depends on the concentration of SO_4^{2-} as well as the soil solution pH. The isotherm they used was in fact an extended Freundlich equation, which is described in detail below in chapter 4. The adsorption model was implemented in the dynamic multilayer soil chemistry model SAFE. The batch experimental work was performed at different pH and SO_4^{2-} concentrations. In this research the model was evaluated by applying to the roof covered catchment at Lake Gårdsjön in the south west of Sweden.

2.6. Scope and objective

2.6.1 Importance of study

As the increased deposition of acidic compound in soil after WW II in Europe increased the acidity and the amount of adsorbed SO_4^{2-} in forest soil. After the implementation of S emission abatement practices, the deposition of acidic compounds in soil is decreased. The response of reduction in emissions and acid deposition in soil is not the same. There is a lag of time to recover from acidity in soil. The adsorbed SO_4^{2-} under reduced acid deposition conditions will continuously release acidity (H^+) and leachable SO_4^{2-} to the soil solution. This action of desorption has delayed the soil water chemical response to changes in the H^+ and SO_4^{2-} ion concentrations of the permeating solution.

To facilitate correct dynamic models for acidification recovery it is important to develop a robust model for the prediction of the adsorbed pool of SO_4^{2-} . In this thesis work different experiments have been performed to investigate the extent of adsorption in five different soil samples from Swedish Podzols. The results of the equilibration experiments were used to optimize the model. Ultimately, the following questions will be answered:

1. Can the extended form of Freundlich equation predict the adsorbed pool of SO_4^{2-} in forest soil?
2. Which optimization approach is the best considering the requirement to use as few samples as possible to bring down analysis costs?

2.6.2 Scope

This thesis presents an attempt to develop a model to predict the pool of adsorbed SO_4^{2-} in the Bs horizons of podzolic Swedish forest soils. Such a model is of interest due to the delayed effect sulfate adsorption/desorption has on the response of water systems to changes in the input acidity. Hence an accurate model is needed to be able to predict the recovery from acidification, and also to predict the delay of the soil chemical response to acidification due to altered forest management practices.

2.6.3 Objective

The objective of this study is therefore to calibrate a Freundlich equation for the prediction of SO_4^{2-} adsorption using experiments data in which the adsorption of SO_4^{2-} is studied as a function of pH and dissolved equilibrium concentrations of SO_4^{2-} . In the calibration, five soil samples were selected from well-developed spodic B horizons in five different locations from Swedish forest soils.

3. MATERIALS AND METHODS

3.1. Site and soil description

The soil samples used in the investigation were sampled from five different locations. The four soil samples (Tärnsjö B, Risfallet B, Risbergshöjden B and Kloten Bs1) were sampled from the Bergslagen area which is situated west of Uppsala, and one soil (Österström B) was from Holm, to the west of Sundsvall (Fig. 2). The samples were collected in May and July 2012. All sampled soils are Podzols (Table 1) and the samples were collected from the upper part of the B horizons (Bs1). The exact sampling depth of each soil was different (Table 2) and varied between the locations.

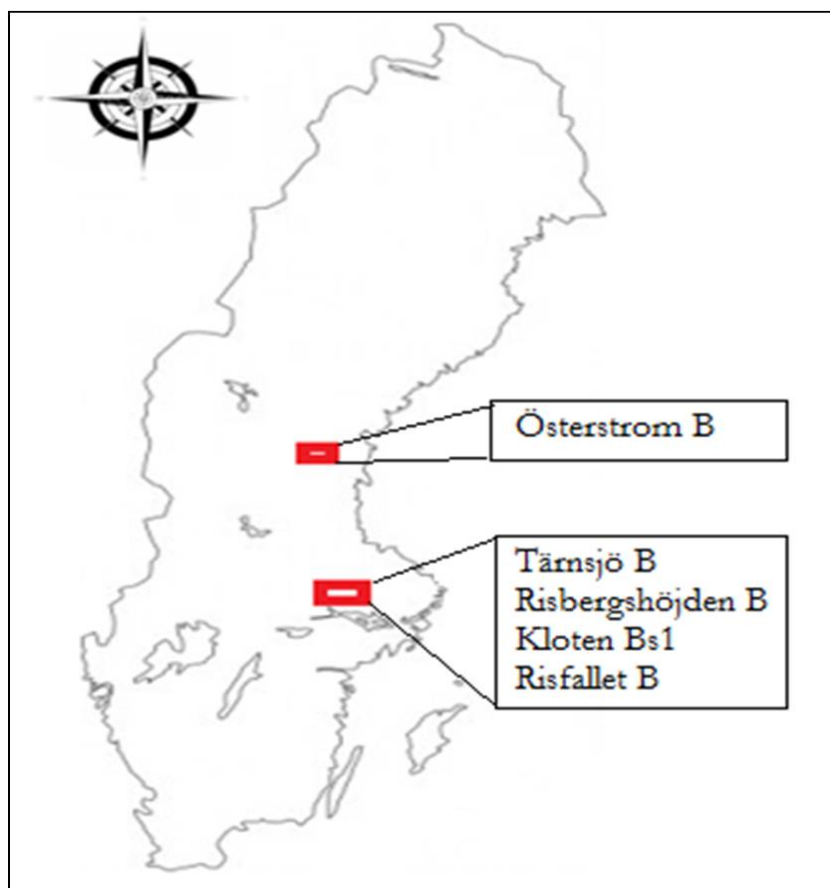


Fig. 2. Map to indicate the location of sampling sites of Tärnsjö B, Risbergshöjden B, Kloten Bs1, Risfallet B and Österström B soils.

3.2. Physical characteristics of soil samples

The physical characteristics of soil samples were determined. The soils varied in texture, particle size, moisture and color (Fig. 3). As these soil samples were taken from the spodic B horizons, they had reddish-brown color due to the presence of Fe, Al and humic substances.

The Tärnsjö B soil sample was dark brown, less moist and a little coarser in texture. In physical appearance, the Risfallet B soil was dark and more moist than Tärnsjö B. Risbergshöjden B and Österström B were more fine, dark and with much moisture present in soils. The Kloten Bs1 soil was mixed with clay and was much moist and sticky in nature.

The suspension of soil samples were prepared according to the recipe (Appendix I) by adding 2 g of soil, then adding volume of water as per the recipe, then adding 0.10 mM MgCl_2 as background electrolyte and lastly SO_4^{2-} (using the appropriate amount of Mg^{2+} and H^+ as counter ions) was added at the amounts specified in the recipe. Each suspension was prepared in duplicate. After that the lid was tightly attached to all centrifuge bottles and placed in a rack. The rack with 40 centrifuge bottles was inserted in the end-over-end shaker and was fixed tightly. The rack along with bottles was shaken for 6 days to reach equilibration at room temperature (21°C). After 6 days of shaking, the bottles were removed from the end-over-end shaker and placed in the centrifuge for centrifugation at 3500 rpm for 15 minutes to separate the soil and solution phases. After centrifugation, the bottles were removed from the centrifuge carefully to avoid phase mixing and placed at room temperature to cool down for a while.

3.2.1 Phase separation and pH measurement

The bottles were transferred to the pH meter. A Radiometer PHM 93, Copenhagen pH meter was used. 40 scintillation bottles (20 ml) were prepared and marked to store the filtrate of each equilibrium suspension accordingly. The pH meter was calibrated according to standard procedures. After this, 5 ml of the supernatant was taken by using a Biohit pipette, transferred to the pH measurement bottle and the pH measurement was started (the results of the pH measurements for each series are shown in Appendix II). The remaining phase-separated supernatant (15-20 ml) was filtered using an Acrodisc PF 32 mm 0.8/0.2 μm membrane syringe filter (Pall Corp., Washington, NY, USA) and the filtrate was transferred into a scintillation bottle marked with the appropriate sample number.

3.3. Extraction of initially adsorbed SO_4^{2-}

To be able to know the amount of adsorbed SO_4^{2-} in equilibrium with a certain dissolved SO_4^{2-} concentration, the amount of adsorbed SO_4^{2-} is determined by calculating initially adsorbed SO_4^{2-} and additionally adsorbed SO_4^{2-} .

For the data treatment it was required to quantify the initially adsorbed amount of SO_4^{2-} in the soil samples. This was done in two ways: by the phosphate and by bicarbonate extraction.

3.3.1 Extraction of initially adsorbed SO_4^{2-} by phosphate

For the purpose of determining initially adsorbed SO_4^{2-} in soil, an initial solution of 20 mM NaH_2PO_4 was prepared. Extraction of initially adsorbed SO_4^{2-} was done to all five soil samples individually. For each soil the extractions were carried out in duplicate. For this purpose, 10 centrifuge bottles were prepared by washing with acid and deionized water, and then dried. All centrifuge bottles were marked according to the soil samples consequently. After this, 2 g of moist soil was added to a centrifuge bottle. Then 20 ml of 20 mM NaH_2PO_4 was added. The lid was attached to the bottle and placed into the rack. The rack was adjusted tightly to the end-over-end shaker and shaken for 24 hours at

Table 1. General properties of Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet B sampling sites.

Site	Land use	Vegetation	Topography	Ground-water table	Drainage
Risfallet	Forestry	Coniferous forest, birch. Moss, grass	Hilly	> 80 cm	Rather well drained
Tärnsjö	Forestry	Coniferous forest (pine). Moss, lichen	Flat	> 80 cm	Well drained
Risbergs-höjden	Forestry	Coniferous forest. Lichen, lingon/blueberry	Hilly	> 80 cm	Well drained
Kloten	Forestry	Coniferous forest. Grass, heather, moss	Slightly sloping	> 80 cm	Well drained
Österström	Forestry	Coniferous forest. Lichen, lingon/blueberry	Hilly	> 80 cm	Well drained

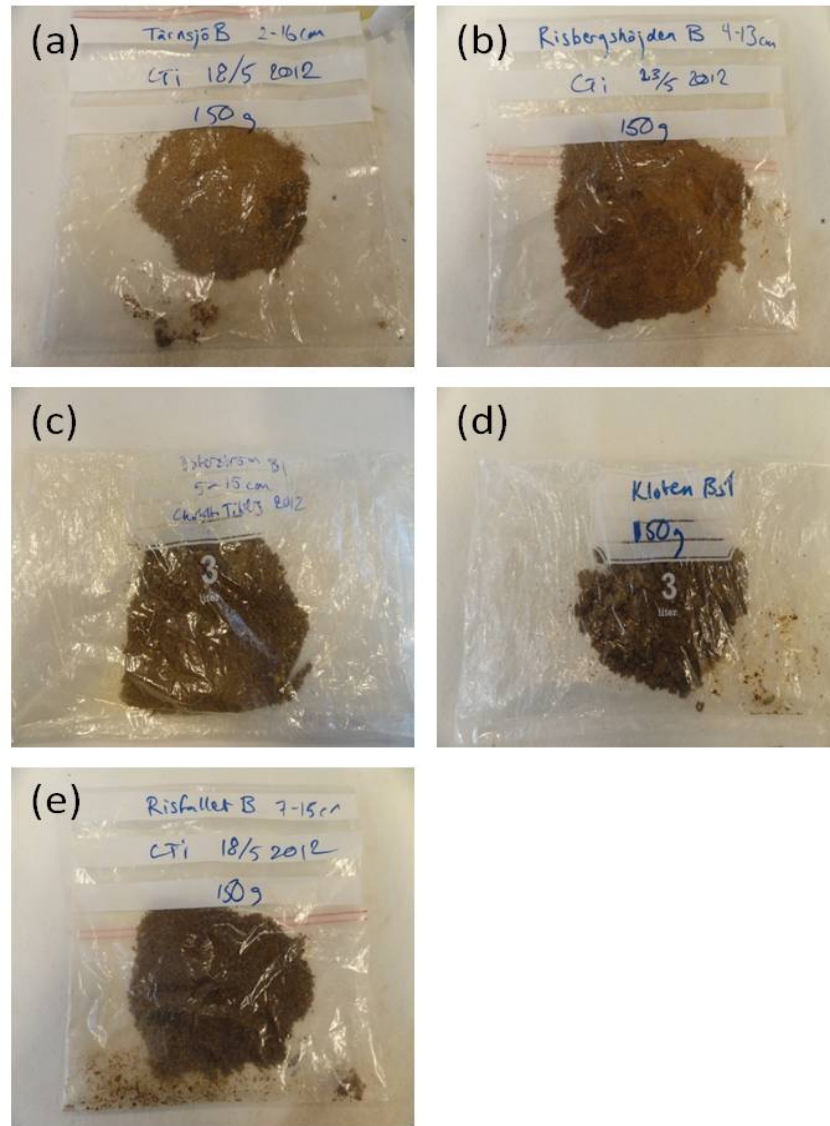


Fig. 3. Images of (a) Tärnsjö B; (b) Risbergshöjden B; (c) Österström B; (d) Kloten Bs1 and (e) Risfallet B soil samples before equilibration experiments.

Table 2. General properties of Tärnsjö B, Risfallet B, Risbergshöjden B, Österström B and Kloten Bs1 soils.

Soil	Horizon	Depth (cm below surface)	pH (0.01 M CaCl ₂)	Oxalate-Fe (mmol /kg)	Oxalate -Al (mmol /kg)
Tärnsjö	Bs1	2-16	4.88	45	118
Risfallet	Bs1	7-15	4.24	151	265
Risbergshöjden	Bs1	4-13	4.39	119	534
Österström	Bs1	5-15	4.13	85	166
Kloten	Bs1	14-24	4.73	114	647

room temperature. After shaking, bottles were removed and placed in the centrifuge. The centrifugation was at 3500 rpm for 15 minutes. After centrifugation bottles were removed carefully to avoid phase mixing. After this, filtration of the extracts was done by using Acrodisc PF 32 mm 0.8/0.2 μm membrane syringe filters attached to a plastic syringe. The filtered extract of each soil solution was stored in 20 ml scintillation bottles.

3.3.2 *Extraction of initially adsorbed SO_4^{2-} by bicarbonate*

For the extraction of initially adsorbed SO_4^{2-} by bicarbonate, 40 mM NaHCO_3 was prepared. The same five moist soils were used to extract initially adsorbed SO_4^{2-} . The same procedural steps were followed as for extraction by phosphate to prepare suspensions, shaking, centrifugation and filtration.

3.4. Measurement of the soil moisture content

The results for SO_4^{2-} adsorption were reported in terms of sulfate adsorbed per gram weight of dry soil. For this reason it was required to measure the moisture content of soil samples. The moisture content of each soil sample was measured as follows: First the oven was set at 105°C. Five clean and dry porcelain crucibles were weighted and was noted as the initial weight of the crucible. 3 to 5 g of soil sample was added to the porcelain crucible and placed again on a balance, the weight of moist soil and crucible was noted (up to 3 decimals). After this, the crucible with soil sample was placed in the oven to dry for 24 hours. After drying for 24 hours the crucible was removed from the oven and was transferred carefully and immediately to an excicator to let it cool down for 20 minutes. After this, the sample was taken out from the excicator and weighed exactly (three decimals). This same procedure was adopted for each soil, the results of soil moisture content are in Appendix IV.

3.5. SO_4^{2-} measurement

The filtrates stored in the scintillation bottles were analysed for SO_4^{2-} using ion chromatography. A Dionex DX-120 instrument (Dionex Corp., Sunnyvale, CA, USA) was used to measure the amount of dissolved SO_4^{2-} (mg/l) for all samples from the batch equilibrations and from the extractions.

3.5.1 *Calculation of added concentration of SO_4^{2-} - C_{added}*

The concentration of added SO_4^{2-} was calculated by using the recipe for each suspension preparation. However, it needed to be corrected for (a) a slight deviation of 7 % between the nominal concentration and the final one, as found after repeated IC analysis of the stock solution, and (b) the amount of water present in the field-moist soil (which causes a slight dilution). The resulting value of C_{added} was expressed in $\mu\text{mol/l}$.

3.5.2 *Calculation of initial concentration of SO_4^{2-} present in soil- C_{init}*

The calculation of initial concentration of SO_4^{2-} present already in the soil was done with the help of phosphate extraction. During extraction of initial SO_4^{2-} by phosphate the filtrate extract was analysed by ion chromatography. The L/S (liquid to solid ratio) was calculated with the help of the moisture content of each sample. The calculated L/S value was used to calculate the experimental SO_4^{2-} (mmol/kg of SO_4^{2-}). After this these values given in mmol/kg were converted to initial concentration C_{init} of SO_4^{2-} $\mu\text{mol/l}$ present in the samples.

3.5.3. Calculation of dissolved concentration of SO_4^{2-} - C_{aq}

The calculation of dissolved concentration of SO_4^{2-} was done by taking the average of SO_4^{2-} dissolved (mg/l) in duplicate samples measured by ion chromatography for each soils, divided with the average value of dissolved SO_4^{2-} (mg/l) with the molecular weight of SO_4^{2-} (96.06 g/mol). Then this value was multiplied by 1000 to obtain the units of C_{aq} in $\mu\text{mol/l}$.

3.5.4. Calculation of sorbed concentration of SO_4^{2-} - C_{sorbed}

The concentration of sorbed SO_4^{2-} was calculated by using the values of C_{init} , C_{added} and C_{aq} . For this, first the general calculations were done by using the relationship of these above mentioned concentrations as, $C_{init} + (C_{added} - C_{aq}) \mu\text{mol/l}$. The result obtained was in $\mu\text{mol/l}$, it was converted to $\mu\text{mol/kg}$ by multiplying L/S derived by using soil in equilibration experiments.

4. MODELING APPROACH

4.1. The Freundlich equation

The basic Freundlich equation is the derived form of linear K_D model with adjustable parameters m and Freundlich coefficient K_f .

The general form of Freundlich equation is as:

$$Q = K_f \times C^m \quad (4)$$

The non linear relationship between adsorbed concentration of solute (sulfate) Q (mol/kg) and dissolved concentration C (mol/l) gives a slope less than 1.

4.1.1. Limitations

This simple form of Freundlich equation is useful to fit the adsorption data only at fixed pH. In addition it cannot explain the competition of ions.

As we are interested in simulating pH-dependent SO_4^{2-} adsorption, there is a need to extend the simple Freundlich equation. Through the extended Freundlich equation, the major drawbacks of the simplistic equation can be resolved.

4.2. Extended Freundlich equation

To overcome the limitations of simple Freundlich equation, it can be extended by including extra terms of activity of H^+ i.e. $\{H^+\}$ and concentration of competing ions with adjustable parameters. The version of the extended Freundlich equation to be used in this thesis can be expressed as:

$$Q = K_f \times C^m \times \{H^+\}^n \quad (5)$$

The logarithmic form of the equation can be written as

$$\log Q = \log K_f + m \times \log C + n \times \log \{H^+\} \quad (6)$$

$$\log Q = \log K_f + m \times \log C - n \times \text{pH} \quad (7)$$

where Q represents the amount of adsorbed sulfate in mol/kg, C is the equilibration concentration of sulfate measured in mol/l, K_f is the Freundlich coefficient measured as the y-intercept in Freundlich equation, and m is the slope.

Equation (7) implies that we can plot (Fig. 4) adsorbed SO_4^{2-} as $\log Q$ (mol/kg) on the y axis against dissolved SO_4^{2-} as $\log C$ (mol/l) and pH on the x axis.

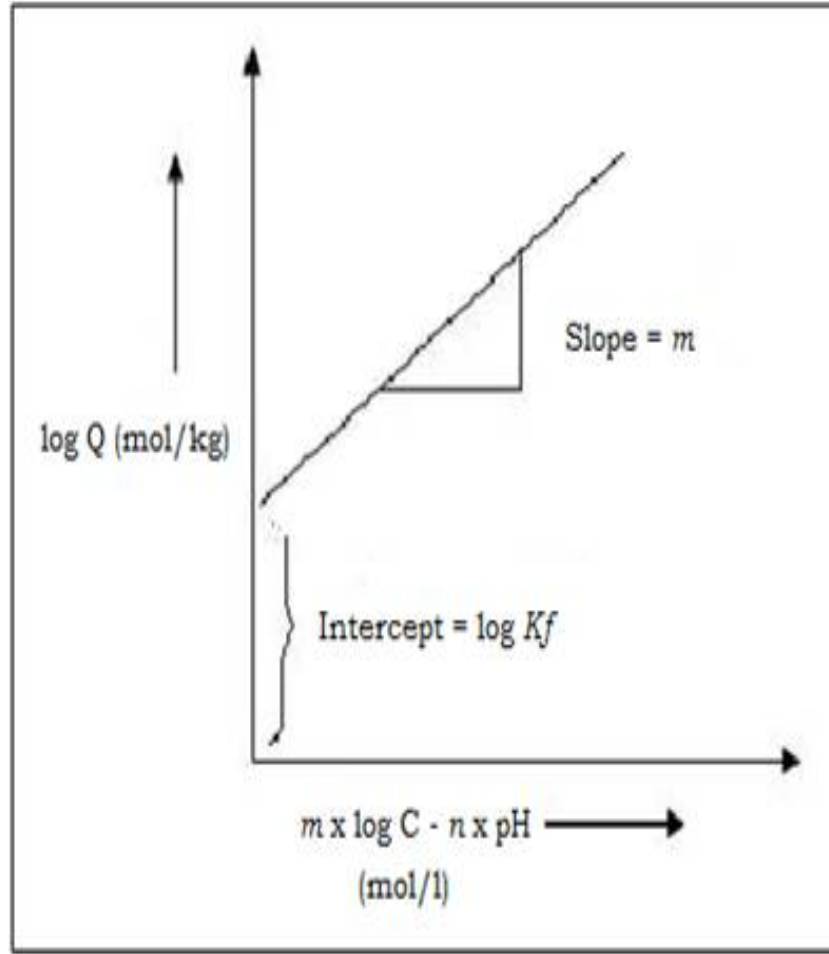


Fig. 4. Freundlich equation isotherm expressing the amount of adsorbed sulfate $\log Q$ (mol/kg) as a function of equilibrium concentration $\log C$ (mol/l).

Fitting the extended Freundlich equation for SO_4^{2-} adsorption:

During SO_4^{2-} adsorption onto hydrous oxides of Fe and Al, a certain number of H^+ ions is co-adsorbed (i.e. the number of H^+ ions that accompany each SO_4^{2-} ion during adsorption) to prevent excess charge development on the surface of minerals (hydrous) oxide. Hence, we can write the SO_4^{2-} adsorption reaction as follows:



where y is the number of protons e.g. number of H^+ co-adsorbed to prevent excess charge development. It varies depending on the ionic strength. At high ionic strength, i.e. when the salinity is high, the number of co-adsorbed H^+ needed to protonate the mineral surface for SO_4^{2-} to adsorb is close to 1. With a decrease in salt content at low ionic strength the number of co-adsorbed proton H^+ is close to 2. We may derive the hypothetical equilibrium constant of the above equation as:

$$\frac{[\text{ads-SO}_4]}{[\text{SO}_4^{2-}][\text{H}^+]^y} = K \quad (9)$$

We may then express this in terms of the extended Freundlich equation, in which the exponent m describes the non-ideality of the dissolved components. Furthermore, the SO_4^{2-} ion activity $\{\text{SO}_4^{2-}\}$ is replaced with the term total dissolved SO_4^{2-} i.e. $[\text{SO}_4^{2-}]_t$ as is customarily the case in the Freundlich equation, and we get,

$$\text{ads-SO}_4 = K_f \times ([\text{SO}_4^{2-}]_t \{H^+\}^y)^m \quad (10)$$

where ads-SO₄ is expressed in mol/kg and represents all adsorbed SO₄²⁻. It includes the amount of SO₄²⁻ sorbed during the experiment and initially present adsorbed SO₄²⁻. The sorbed SO₄²⁻ is calculated by subtracting the concentration of dissolved SO₄²⁻ from the added SO₄²⁻ (mmol/kg). K_f and m are the coefficients of the Freundlich equation (the y intercept and slope respectively after log-log transformation). The total dissolved sulfate $[\text{SO}_4^{2-}]_t$ is expressed in mol/l.

Equation (10) can be written in the logarithmic form as:

$$\log \text{ads-SO}_4 = \log K_f + m (\log [\text{SO}_4^{2-}]_t + y \log \{H^+\}) \quad (11)$$

as we know $\text{pH} = -\log \{H^+\}$

$$\log \text{ads-SO}_4 = \log K_f + m (\log [\text{SO}_4^{2-}]_t - y(\text{pH})) \quad (12)$$

The plot of $\log \text{ads-SO}_4$ on the y axis against $\log [\text{SO}_4^{2-}]_t - y(\text{pH})$ on the x axis should provide a straight line according to the extended Freundlich equation, after adjustment of the value of y to an optimum value. In practice during the calculations, the trendline tool in the Microsoft Excel was used to provide the best fit using linear regression. For the unconstrained fit (section 4.4.2), a trial-and-error method was used to simultaneously arrive at optimum values of y , K_f and m .

4.3. Optimization strategy

The optimization of extended Freundlich equation (12) was done in three different ways:

- *Unconstrained fit.* In this method, the values of y , K_f and m were optimized simultaneously without any constraints on their values.
- *Constrained fit.* A constant value of y was assumed, which means that only K_f and m were optimized.
- *Simplified two-point calibration.* This method also used a constant value of y , but only two data points with different pH and $[\text{SO}_4^{2-}]_t$ were used in the optimization.

During optimization, the data of each soil was processed individually.

4.3.1. Unconstrained fit

By definition, the unconstrained fit function is the fit of data by means of all three adjustable parameters y , K_f and m . To optimize the extended Freundlich equation (Equation 12) the unconstrained fit requires a wide range of pH values and dissolved sulfate concentrations to be successful, because otherwise different combinations of y , K_f and m can equally well describe the data.

4.3.2. Procedure of optimization

During optimization the following procedural steps were adopted,

- Calculation of the term $\log [\text{SO}_4^{2-}]_t$ (mol/l) from the data set for each individual soil.
- Calculation of $\log \text{ads-SO}_4$ (mol/kg).
- The use of relationship $\log [\text{SO}_4^{2-}]_t - y(\text{pH})$.
- Optimization of the value of y by the trial-and-error method.
- $\log \text{ads-SO}_4$ was plotted as a function of $\log [\text{SO}_4^{2-}]_t - y(\text{pH})$.
- The trendline (linear) tool was used to produce the regression equation and R^2 values (five decimal points).
- The value of y was again optimized by the trial-and-error method to obtain a new value of R^2 , and the steps above were repeated until the optimum combination of y and R^2 values were found.

- At this point the values of the slope (m) and the y-intercept ($\log K_f$) were collected from the graph.
- The Freundlich coefficient K_f was calculated from $\log K_f$.

4.3.3 *Constrained fit*

In the constrained fit the adjustable parameter y is selected as common value of 2. The value of 2 was chosen because it was thought to represent low-ionic-strength conditions as found in the forest soils acceptably well (Background section). The constrained fit has the advantage that optimization of only two parameters results in more robust estimates and thus it does not require such a large variation in pH and dissolved sulfate concentrations.

4.3.4 *Procedure of optimization*

During optimization following procedural steps were adopted,

- Calculation of the term $\log [\text{SO}_4^{2-}]_t$ (mol/l) from the data set for each individual soil.
- Calculation of the term $\log \text{ads-SO}_4$ (mol/kg).
- The relationship of $\log [\text{SO}_4^{2-}]_t - 2\text{pH}$ was used.
- $\log \text{ads-SO}_4$ was plotted as a function of $\log [\text{SO}_4^{2-}]_t - 2\text{pH}$.
- The trendline (linear) tool was used to produce the regression equation and R^2 values.
- The slope m and the y intercept $\log K_f$ were taken from the regression equation.
- The Freundlich coefficient K_f was calculated from $\log K_f$.

4.3.5 *Simplified two-point calibration*

In the simplified two-point calibration only two data points were selected from the data set and used in the optimization. By this method it was tested whether it was possible to select only two points from the data set and still be able to produce a reliable model. By using the simplified two-point calibration, the use of the extended Freundlich model will be much easier, because large sets of soils can be optimized with a limited number of observations.

4.3.6 *Procedure of optimization*

- From each soil data set, the duplicate samples according to the recipe with 0.1 mM MgCl_2 only were selected. For example, for Tärnsjö B, sample A1 and A2, for Risbergshöjden B, sample B1 and B2, for Österström B, sample C1 and C2, for Risfallet B, sample A27 and A28, and for soil Kloten Bs1, sample D1 and D2 were selected (Appendix V), and the average value of each duplicate sample were calculated.
- Selection of the pH value of each respective soil samples and calculation of average of each duplicate pH value.
- Similarly, selection of the dissolved sulfate value $[\text{SO}_4^{2-}]_t$ (mmol/l) and adsorbed sulfate values (mmol/kg) for each respective soil samples and calculation of the average and log of each duplicate dissolved sulfate and adsorbed sulfate values.
- In the same manner, the duplicate sample with the addition of highest amount of SA solution according to the recipe (resulting in 0.05 mM $\text{MgSO}_4 + 0.05$ mM H_2SO_4) was used, since these samples differed significantly in both pH and dissolved sulfate compared to the 0.10 mM MgCl_2 samples. For example, for Tärnsjö B, sample A25 and A26, for Risbergshöjden B, sample B25 and B26, for Österström

B, sample C25 and C26, for Risfallet B, sample A39 and A40, and for Kloten Bs1, sample D25 and D26 from the data set were selected (Appendix V), and the average of each sample values were calculated.

- Again the average of pH values for each respective sample of highest SA solution were calculated.
- The dissolved SO_4^{2-} value $[\text{SO}_4^{2-}]_t$ (mol/l) and adsorbed SO_4^{2-} (mol/kg) for each respective soil samples were selected and the average and the logs of each duplicate dissolved SO_4^{2-} and adsorbed SO_4^{2-} were calculated.
- The term $\log [\text{SO}_4^{2-}]_t - 2\text{pH}$ was used.
- A graph between $\log [\text{SO}_4^{2-}]_t - 2\text{pH}$ on the x axis vs $\log \text{ads-SO}_4$ on the y axis was plotted.
- The trendline (linear) tool was used to the data of each soil to display the regression equation and R^2 .
- The values of the slope m and the y intercept $\log K_f$ were taken from regression equation.
- The Freundlich coefficient K_f was calculated from $\log K_f$.

5. RESULTS AND DISCUSSION

Firstly, in this section the initially extractable adsorbed SO_4^{2-} present in each soil samples and correlation between initially adsorbed SO_4^{2-} with the amount of Fe and Al hydrous oxide as determined by oxalate extraction can be expressed as,

5.1. Initial extractable SO_4^{2-} present in soils

The initially adsorbed SO_4^{2-} present in the soils extracted by phosphate extraction is different in each soil. It may depend on the location of the sampling sites, depth, soil type, the nature of sampling site, and the type of forest ecosystem (Table 2). The initially adsorbed SO_4^{2-} (Fig. 5) present in the soil samples extracted by phosphate (sodium phosphate, NaH_2PO_4) shows that the extracted amount of SO_4^{2-} in Risbergshöjden B soil is high (4.55 mmol/kg) as compared to other soils. The second largest amount of SO_4^{2-} initially adsorbed is in Kloten Bs1, 4.17 mmol/kg. Similarly, in Risfallet B, Tärnsjö B and Österström B, initially adsorbed SO_4^{2-} extracted by NaH_2PO_4 is 1.30 mmol/kg, 0.78 mmol/kg and 0.61 mmol/kg respectively.

The high value of initially bound sulfate in Risbergshöjden B and Kloten Bs1 is well correlated (Fig. 6) with the amount of Fe and Al hydrous oxide as determined by oxalate extraction. The high amount of oxalate extractable Fe in Kloten Bs1 (114 mmol/kg) and oxalate extractable Al (647 mmol/kg) and in Risbergshöjden B (119 mmol/kg and 534 mmol/kg Fe and Al respectively) as compared to other soil provide evidence (Fig. 6) that Risbergshöjden B and Kloten Bs1 soils have high value of initially bound sulfate.

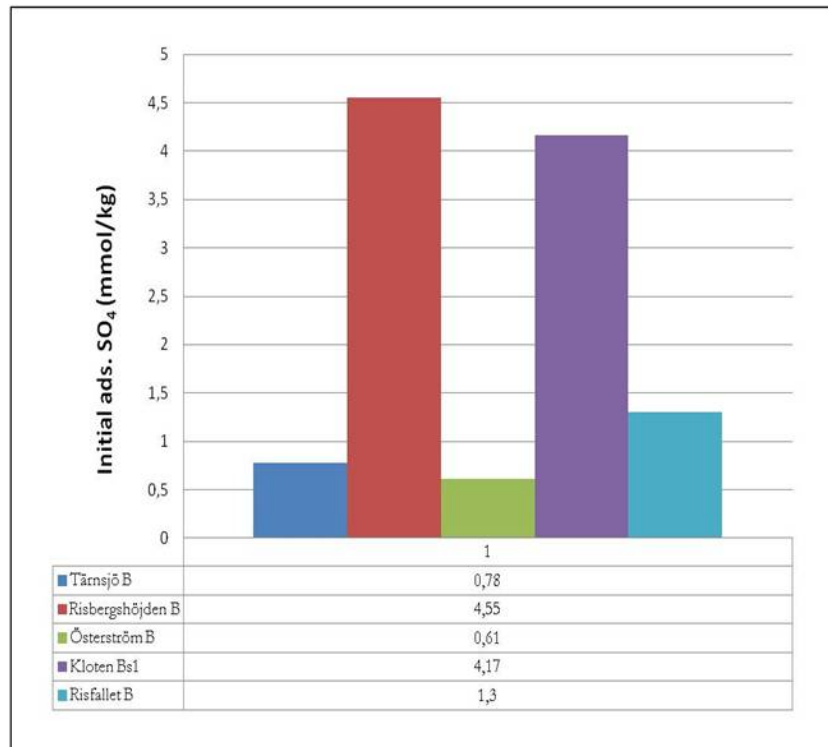


Fig. 5. The amount of initially adsorbed SO_4^{2-} (mmol/kg) in the Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1, and Risfallet B soils.

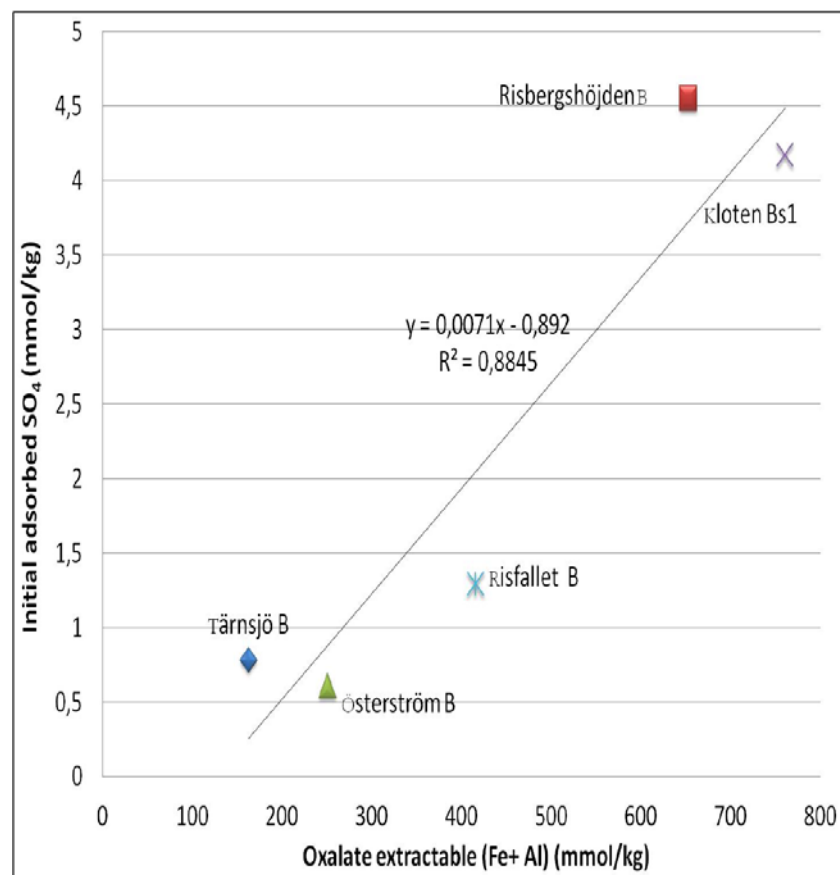


Fig. 6. Plot to represent the effect of oxalate extractable Fe and Al on initially adsorbed SO_4^{2-}

5.2. Sulfate adsorption isotherms

The sulfate adsorption isotherms (Fig. 7) of Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1, and Risfallet B soils used in the study were determined by plotting the equilibrium concentration of sulfate (mmol/l) against the amount of SO_4^{2-} adsorbed (mmol/kg) in soil. Comparing the highest amount of SO_4^{2-} adsorbed (mmol/kg) in each soil, it is evident that the soils differ in terms of their SO_4^{2-} adsorption capacity. The results for adsorption of SO_4^{2-} (Table 3) show that the maximum concentration of SO_4^{2-} adsorbed in Tärnsjö B soil is 3.93 mmol/kg when the pH was 4.71 and the dissolved SO_4^{2-} concentration was 0.348 mmol/l.

The soil data plotted in Fig. 7 are the mean values of duplicate samples. The pattern of SO_4^{2-} adsorption as a function of equilibrium concentration for all levels of sulfate addition is the same for all soils.

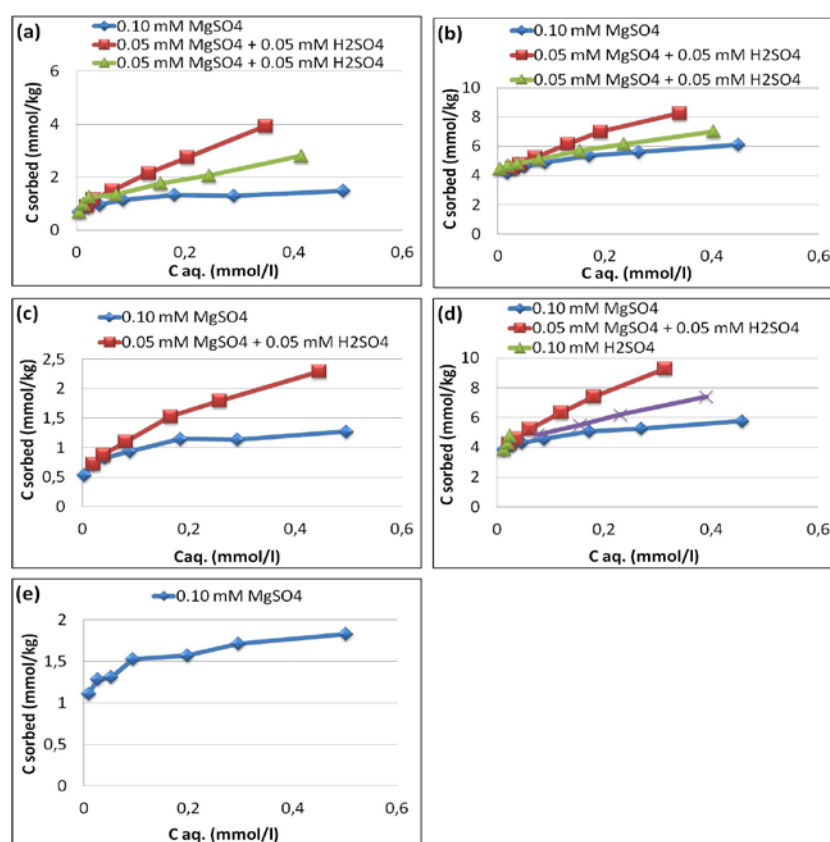


Fig. 7. Adsorbed SO_4^{2-} (mmol/kg) during the experiment as a function of equilibrium concentration of SO_4^{2-} (mmol/l) for (a) Tärnsjö B; (b) Risbergshöjden B; (c) Österström B; (d) Kloten Bs1; (e) Risfallet B.

Table 3. Amount of adsorbed SO_4^{2-} after addition of 0.5 mM SO_4^{2-} .

Soil	Maximum SO_4^{2-} adsorbed (mmol/kg)	pH at maximum SO_4^{2-} adsorption
Tärnsjö B	3.93	4.71
Risbergshöjden B	8.25	4.45
Österström B	2.29	4.22
Kloten Bs1	9.26	4.65
Risfallet B	1.83	4.82

The values for adsorbed SO_4^{2-} include the initial sulfate adsorbed in each soil. The difference in the amounts of adsorbed SO_4^{2-} in each soil is well correlated with the amount of sulfate that was initially adsorbed, and maximum adsorbed SO_4^{2-} with oxalate-extractable Fe+Al (Fig. 6). It is evident from Fig. 6 that SO_4^{2-} adsorption increased with the increase in the concentration of SO_4^{2-} , but also that the equilibrium pH had a strong effect on the result. There is illustrated that the amount of sulfate adsorbed (mmol/kg) is increasing with the increase in amount of sulfate in equilibrium solution at any given equilibrium pH value.

The trends of the isotherm of each soil (Fig. 7) explain the concept of adsorption of SO_4^{2-} . The general tendency of an increase in sulfate adsorption with a decrease in pH is understandable. At low pH, the soils possess more positive surface charge. The different sulfate adsorption behavior of different soils can be attributed partly to differences in competitive adsorption of other anions and organic compounds in the soil.

5.3. Fitting the extended Freundlich model for sulfate adsorption.

The fitting of the extended Freundlich model for SO_4^{2-} adsorption can be expressed by Unconstrained, Constrained and Simplified Two point fits as;

5.3.1. The proton co-adsorption stoichiometry - unconstrained fit

When the sorption data for all five soils sample were plotted between $\log [\text{SO}_4^{2-}]_i - y(\text{pH})$ on the x axis and $\log \text{ads-SO}_4$ on y axis by using unconstrained fit Freundlich equation (Fig. 8), it showed that the adsorption data were well described for all soils. The co-adsorbed number of proton y during SO_4^{2-} adsorption in each soil (Table 4) was different but ideally it should be close to 2, because of the low ionic strength in these systems.

From Fig. 8 it seems that the extended Freundlich model showed an excellent fit to the data particularly at lower concentration.

From the unconstrained fit (Table 4) it seems that Risbergshöjden B and

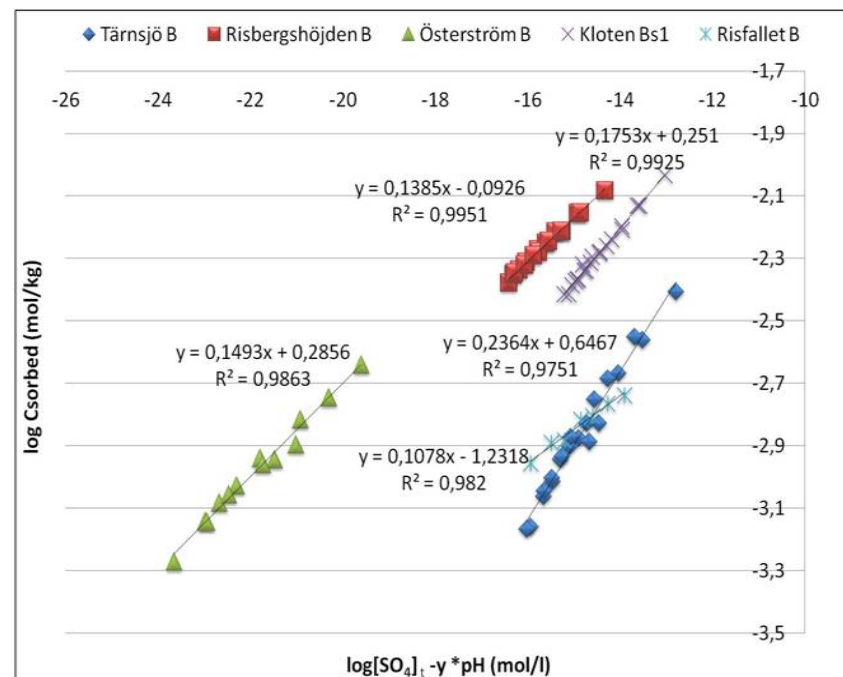


Fig. 8. Unconstrained fits of extended Freundlich model for Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1, and Risfallet B soil samples.

Table 4. Co-adsorbed stoichiometry (γ), Coefficient of determination (R^2), slope (m), and Freundlich coefficient (K_f) for soil samples – unconstrained fit.

Soil	γ	Equation	m	$\log K_f$	K_f	R^2
Tärnsjö B	1.98	$y = 0.2364x + 0.6467$	0.236	0.646	4.425	0.975
Risbergshöjden B	2.44	$y = 0.1385x - 0.0926$	0.138	-0.092	0.809	0.995
Österström B	3.85	$y = 0.1493x + 0.2856$	0.149	0.285	1.927	0.986
Kloten B	2.05	$y = 0.1753x + 0.251$	0.175	0.251	1.782	0.993
Risfallet B	2.20	$y = 0.1078x - 1.2318$	0.107	-1.231	0.058	0.982

Kloten Bs1 showed the best fit ($\gamma = 2.44$, $R^2 = 0.995$, and $\gamma = 2.05$, $R^2 = 0.993$ respectively) followed by Österström B, Risfallet B and Tärnsjö B.

5.3.1 The proton co-adsorption stoichiometry - constrained fit

In the constrained fit γ is set to 2, and hence Fig. 9 was constructed with $\log [\text{SO}_4^{2-}]_t - 2(\text{pH})$ on the x axis and $\log \text{ads SO}_4$ on the y axis. In the constrained fit of the extended Freundlich model Risbergshöjden B showed the best fit ($m = 0.148$ and $R^2 = 0.997$). The values of the slope m , the coefficient of determination R^2 and the y-intercept $\log K_f$ are shown in Table 5.

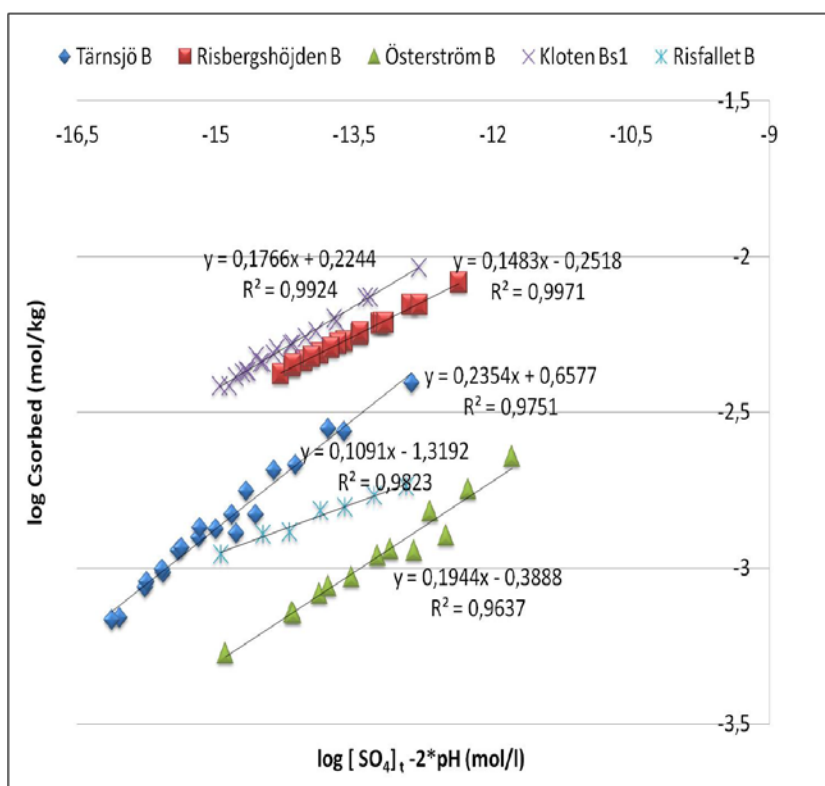


Fig. 9. Constrained fits of extended Freundlich model for Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1, and Risfallet B soil samples.

Table 5. Co-adsorbed stoichiometry (y), Coefficient of determination (R^2), slope (m), and Freundlich coefficient (K_f) for soil samples – Constrained fit.

Soil	y	Equation	m	$\log K_f$	K_f	R^2
Tärnsjö B	2	$y = 0.2354x + 0.6577$	0.235	0.658	4.54	0.975
Risbergs-höjden B	2	$y = 0.1483x - 0.2518$	0.148	-0.252	0.56	0.997
Österström	2	$y = 0.1944x - 0.3888$	0.194	-0.389	0.41	0.964
Kloten B	2	$y = 0.1786x + 0.2244$	0.177	0.224	1.67	0.993
Risfallet B	2	$y = 0.1091x - 1.3192$	0.109	-1.319	0.04	0.982

5.3.2 The proton co-adsorption stoichiometry- simplified two-point calibration

The simplified two-point calibration is in fact a simplified version of the constrained fit, where only two data points were selected. The plot of $\log [\text{SO}_4^{2-}]_t - 2\text{pH}$ on the x axis and $\log \text{ads-SO}_4$ on the y axis (Fig. 9) gives the extended Freundlich model parameters (Table 6) for Tärnsjö B, Risbergshöjden B, Österstrom B, Kloten Bs1 and Risfallet B soil.

To get R^2 values that were comparable to those obtained for the other fits, the R^2 values shown in Table 6 are those obtained when using the optimized coefficients for the whole data set (not just the two data

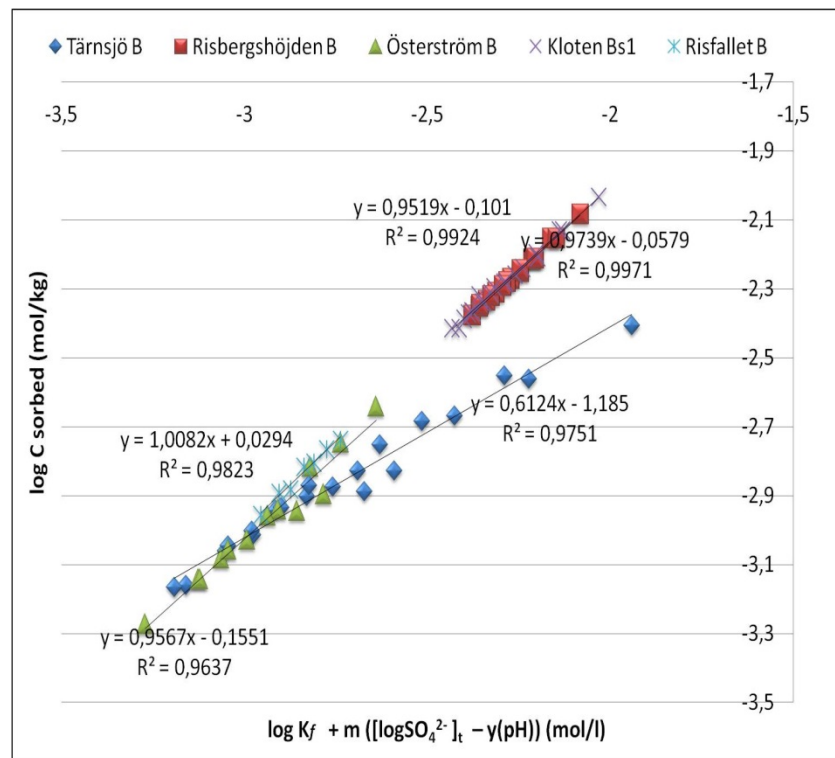


Fig. 10. Plot between predicted amount of adsorbed sulfate ($\log C$ sorbed, mol/kg) and observed amount of adsorbed sulfate ($\log K_f + m([\log \text{SO}_4^{2-}]_t - y(\text{pH}))$) for Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet B soil.

Table 6. Co-adsorbed stoichiometry (y), Coefficient of determination (R^2), slope (m), and Freundlich coefficient (K_f) for soil samples – two-point calibration

Soil	y	Equation	m	$\log K_f$	K_f	R^2
Tärnsjö B	2	$y = 0.3844x + 3.0087$	0.384	3.009	1018	0.975
Risbergs-höjden B	2	$y = 0.1523x - 0.1991$	0.152	-0.199	0.63	0.997
Österström B	2	$y = 0.2032x - 0.2442$	0.203	-0.244	0.57	0.964
Kloten B	2	$y = 0.1855x + 0.3419$	0.186	0.342	2.20	0.992
Risfallet B	2	$y = 0.1082x - 1.3376$	0.108	-1.338	0.045	0.982

points used during calibration). The simplified two-point calibration with two adjustable parameters of the extended Freundlich model of each soil data set (Table 6) shows that each soil data set has a similar coefficient of determination R^2 as obtained by the constrained fit (Table 5). This shows that the two-point calibration method resulted in surprisingly good fits despite the small number of data points used.

5.4. Discussion

The results obtained by modeling the data set of all five soils show that the optimization strategy of the extended Freundlich model in three different ways i.e. unconstrained, constrained and simplified two-point calibration is promising. The unconstrained fit of the extended version of Freundlich model gives an y value of close to 2 for Risberghöjden B and Kloten Bs1 soil data set; it supports the presumption that $y = 2$ at low ionic strength I . It also validates the assumption that the unconstrained fit of extended Freundlich model is virtually equal to that of the constrained fit model (e.g. for Kloten Bs1, $R^2 = 0.993$ and $R^2 = 0.992$ by using unconstrained and constrained fit at $y = 1.98$ and $y = 2$, respectively). By this, it is validated that the assumption of common stoichiometry $y = 2$ is the optimum value to calibrate the model by using different soil data sets. It implies that it is advantageous to optimize only two parameters m and K_f of the extended Freundlich equation to calibrate the soil data set. Consequently, the real power of the constrained fit is proved, it allows us to calibrate the model with much less data available. Moreover, the optimization using the simplified two point calibration procedure shows results that are usually in close agreement with those of the constrained fit (e.g. for Kloten Bs1 by using constrained fit and simplified two-point fit it obtained $m = 0.177$ and $m = 0.186$, $K_f = 1.6$ and $K_f = 2.19$ respectively). However, a slight variation in optimization parameters values were observed especially in case of the Tärnsjö B and Österström B soil data. The reason for this is not known at present. Due to the selection of only two points, it has a significant advantage over the unconstrained and constrained fits, i.e. it is more suitable to measure only pH and dissolved sulfate concentration for two points when there are large soil data sets available to calibrate. These benefits show the suitability to use simplified two-point extended Freundlich model calibration.

When comparing the simplified two-point calibration of the extended Freundlich model with the modeling approach used by Martinsson et al. (2003), the latter authors calibrated the isotherms at a co-adsorbed proton stoichiometry $y = 1.7$ by using three variables m , n and q . However, a more robust calibration method is to optimize only two variables (m and K_f) instead of three variables, since this leads to a better

constrained model when limited data are available. Hence, the extended version of Freundlich model by use of the simplified two-point calibration at $y=2$ is more appropriate to use for large sets of soil data.

5.5. Conclusion

The extended Freundlich model proposed in this study is a promising tool for predicting SO_4^{2-} adsorption in soils that adsorb and desorb SO_4^{2-} . The simplified two-point optimization strategy is the best option when using the extended version of Freundlich model for soil data. The suggested model is less complex and needs a smaller number of optimized parameters (only m and K_f) compared to earlier attempts. Still, the model is able to predict pH-dependent adsorption effects. Moreover, all extended Freundlich model calculations and fitting is executed within a simple Microsoft Excel worksheet, since it does not need any advanced numerical geochemical tool.

5.6. Practical significance of the model

Practically, the extended form of Freundlich model is of great significance to estimate the adsorption of sulfate under different amounts of atmospheric sulfate input to the soil system, because it is estimated that nearly 2 H^+ are accompanied for every SO_4^{2-} ion during adsorption and desorption. This form of model is able to predict the amount of adsorbed SO_4^{2-} at associated equilibrium concentration of sulfate and pH. It is especially well adapted for use in dynamic soil chemistry models, where large amounts of soil data are needed for predictions on a regional or national basis.

5.7. Future recommendation

The present study did not explicitly incorporate the competitive reaction of other anions (e.g. P) and dissolved organic carbon (DOC) during SO_4^{2-} adsorption, although it may be argued that competition is indirectly accounted for with the adjustable parameters K_f and m . The absence of any direct account for competition effects may be a weakness in long-term scenarios in which the levels of competitors (i.e. DOC and P, phosphate) are subject to change. In future development it is recommended to acknowledge the influential presence of DOC and other competitors that may play a decisive role in the mobility of sulfate in the soil profile and may act as a negatively charged ion. This may be done by using, e.g, more mechanistically based surface complexation models.

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APPENDIX I

Initial solution and recipes of equilibration experiments used in Series A to Series D for all five soil samples.

Initial solutions used in sample preparation for equilibration experiments.

Initial solution	Strength
C	0.01 M MgCl ₂
E	0.01 M Ca(OH) ₂
S	0.01 M MgSO ₄
SA	0.005 M MgSO ₄ + 0.005 M H ₂ SO ₄
A	0.01 M H ₂ SO ₄
SL	1 mM MgSO ₄
SAL	0.5 mM MgSO ₄ + 0.5 mM H ₂ SO ₄
AL	1 mM H ₂ SO ₄

Recipe of Series A to D for soil Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet B for equilibration experiments.

Series A. Tärnsjö B and Risfallet B soils.

2 g of Tärnsjö B							
Sample No.	Solution C (ml)	H ₂ O (ml)	Solution S (ml)	Solution SA (ml)	Solution A (ml)	Solution SL (ml)	Sol. SAL(ml)
1,2	0.32	31.68	-	-	-	-	-
3,4	0.32	30.88	-	-	-	0.8	-
5,6	0.32	30.08	-	-	-	1.6	-
7,8	0.32	31.36	0.32	-	-	-	-
9,10	0.32	31.04	0.64	-	-	-	-
11,12	0.32	30.72	0.96	-	-	-	-
13,14	0.32	30.08	1.6	-	-	-	-
15,16	0.32	30.88	-	-	-	-	0.8
17,18	0.32	30.08	-	-	-	-	1.6
19,20	0.32	31.36	-	0.32	-	-	-
21,22	0.32	31.04	-	0.64	-	-	-
23,24	0.32	30.72	-	0.96	-	-	-
25,26	0.32	30.08	-	1.6	-	-	-
2 g of Risfallet B							
27,28	0.32	31.68	-	-	-	-	-
29,30	0.32	30.88	-	-	-	0.8	-
31,32	0.32	30.08	-	-	-	1.6	-
33,34	0.32	31.36	0.32	-	-	-	-
35,36	0.32	31.04	0.64	-	-	-	-
37,38	0.32	30.72	0.96	-	-	-	-
39,40	0.32	30.08	1.6	-	-	-	-

Series B. Risbergshöjden B and Tärnsjö B soils.

2 g of Risbergshöjden B								
Sample No.	Solution C (ml)	H ₂ O (ml)	Solution S (ml)	Solution SA (ml)	Solution A (ml)	Sol. SL (ml)	Sol. SAL(ml)	Sol. Al (ml)
1,2	0.32	31.68	-	-	-	-	-	-
3,4	0.32	30.88	-	-	-	0.8	-	-
5,6	0.32	30.08	-	-	-	1.6	-	-
7,8	0.32	31.36	0.32	-	-	-	-	-
9,10	0.32	31.04	0.64	-	-	-	-	-
11,12	0.32	30.72	0.96	-	-	-	-	-
13,14	0.32	30.08	1.6	-	-	-	-	-
15,16	0.32	30.88	-	-	-	-	0.8	-
17,18	0.32	30.08	-	-	-	-	1.6	-
19,20	0.32	31.36	-	0.32	-	-	-	-
21,22	0.32	31.04	-	0.64	-	-	-	-
23,24	0.32	30.72	-	0.96	-	-	-	-
25,26	0.32	30.08	-	1.6	-	-	-	-

2 g of Tämsjö B								
27,28	0.32	31.68	-	-	-	-	-	-
29,30	0.32	30.88	-	-	-	-	-	0.8
31,32	0.32	30.08	-	-	-	-	-	1.6
33,34	0.32	28.48	-	-	-	1.6	1.6	-
35,36	0.32	31.04	0.32	0.32	-	-	-	-
37,38	0.32	30.72	0.48	0.48	-	-	-	-
39,40	0.32	30.08	0.8	0.8	-	-	-	-

<i>Series C Österström B and Risbergshöjden B soils</i>								
2 g of Österström B								
Sample No.	Sol. C (ml)	H ₂ O (ml)	Sol. S (ml)	Solution SA (ml)	Solution A (ml)	Sol. SL (ml)	Solution SAL(ml)	Solution Al (ml)
1,2	0.32	31.68	-	-	-	-	-	-
3,4	0.32	30.88	-	-	-	0.8	-	-
5,6	0.32	30.08	-	-	-	1.6	-	-
7,8	0.32	31.36	0.32	-	-	-	-	-
9,10	0.32	31.04	0.64	-	-	-	-	-
11,12	0.32	30.72	0.96	-	-	-	-	-
13,14	0.32	30.08	1.6	-	-	-	-	-
15,16	0.32	30.88	-	-	-	-	0.8	-
17,18	0.32	30.08	-	-	-	-	1.6	-
19,20	0.32	31.36	-	0.32	-	-	-	-
21,22	0.32	31.04	-	0.64	-	-	-	-
23,24	0.32	30.72	-	0.96	-	-	-	-
25,26	0.32	30.08	-	1.6	-	-	-	-
2 g of Risbergshöjden B								
27,28	0.32	31.68	-	-	-	-	-	-
29,30	0.32	30.88	-	-	-	-	-	0.8
31,32	0.32	30.08	-	-	-	-	-	1.6
33,34	0.32	28.48	-	-	-	-	1.6	1.6
35,36	0.32	31.04	0.32	0.32	-	-	-	-
37,38	0.32	30.72	0.48	0.48	-	-	-	-
39,40	0.32	30.08	0.8	0.8	-	-	-	-

<i>Series D Kloten Bs1</i>								
2 g of Kloten Bs1								
Sample No.	Sol. C (ml)	H ₂ O (ml)	Solution S (ml)	Solution SA (ml)	Sol. A (ml)	Solution SL (ml)	Sol. SAL(ml)	Solution Al (ml)
1,2	0.32	31.68	-	-	-	-	-	-
3,4	0.32	30.88	-	-	-	0.8	-	-
5,6	0.32	30.08	-	-	-	1.6	-	-
7,8	0.32	31.36	0.32	-	-	-	-	-
9,10	0.32	31.04	0.64	-	-	-	-	-
11,12	0.32	30.72	0.96	-	-	-	-	-
13,14	0.32	30.08	1.6	-	-	-	-	-
15,16	0.32	30.88	-	-	-	-	0.8	-
17,18	0.32	30.08	-	-	-	-	1.6	-
19,20	0.32	31.36	-	0.32	-	-	-	-
21,22	0.32	31.04	-	0.64	-	-	-	-
23,24	0.32	30.72	-	0.96	-	-	-	-
25,26	0.32	30.08	-	1.6	-	-	-	-
27,28	0.32	31.68	-	-	-	-	-	-
29,30	0.32	30.88	-	-	-	-	-	0.8
31,32	0.32	30.08	-	-	-	-	-	1.6
33,34	0.32	28.48	-	-	-	1.6	1.6	-
35,36	0.32	31.04	0.32	0.32	-	-	-	-
37,38	0.32	30.72	0.48	0.48	-	-	-	-
39,40	0.32	30.08	0.8	0.8	-	-	-	-

APPENDIX II

pH of filtrates of Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet B soil solutions of series A to series D.

<i>pH of series A</i>							
Sample	pH	Sample	pH	Sample	pH	Sample	pH
A1	5.39	A11	5.61	A21	5.10	A31	4.96
A2	5.37	A12	5.63	A22	5.17	A32	4.97
A3	5.54	A13	5.67	A23	4.98	A33	4.92
A4	5.57	A14	5.59	A24	4.97	A34	4.92
A5	5.62	A15	5.50	A25	4.69	A35	4.97
A6	5.58	A16	5.54	A26	4.72	A36	4.93
A7	5.67	A17	5.43	A27	4.96	A37	4.88
A8	5.67	A18	5.43	A28	4.95	A38	4.89
A9	5.64	A19	5.30	A29	4.96	A39	4.81
A10	5.62	A20	5.34	A30	4.97	A40	4.83

<i>pH of Series B</i>							
B1	4.80	B11	4.92	B21	4.67	B31	5.24
B2	4.77	B12	4.94	B22	4.66	B32	5.32
B3	4.84	B13	4.92	B23	4.58	B33	5.56
B4	4.84	B14	4.96	B24	4.60	B34	5.49
B5	4.87	B15	4.80	B25	4.45	B35	5.43
B6	4.87	B16	4.83	B26	4.46	B36	5.44
B7	4.91	B17	4.80	B27	5.42	B37	5.36
B8	4.91	B18	4.79	B28	5.50	B38	5.40
B9	4.93	B19	4.77	B29	5.30	B39	5.25
B10	4.92	B20	4.75	B30	5.42	B40	5.14

<i>pH of Series C</i>							
C1	4.70	C11	4.67	C21	4.46	C31	4.62
C2	4.77	C12	4.66	C22	4.44	C32	4.60
C3	4.75	C13	4.60	C23	4.35	C33	4.83
C4	4.76	C14	4.60	C24	4.33	C34	4.81
C5	4.74	C15	4.74	C25	4.23	C35	4.80
C6	4.76	C16	4.74	C26	4.20	C36	4.82
C7	4.74	C17	4.70	C27	4.76	C37	4.76
C8	4.75	C18	4.69	C28	4.75	C38	4.78
C9	4.69	C19	4.58	C29	4.69	C39	4.69
C10	4.70	C20	4.58	C30	4.69	C40	4.71

<i>pH of Series D</i>							
D1	5,0	D11	5,30	D21	4,90	D31	4.88
D2	5,0	D12	5,30	D22	4,90	D32	4.89
D3	5,12	D13	5,28	D23	4,81	D33	5.31
D4	5,12	D14	5,30	D24	4,83	D34	5.13
D5	5,16	D15	5,05	D25	4,66	D35	5.12
D6	5,18	D16	5,04	D26	4,64	D36	5.10
D7	5,22	D17	5,02	D27	5,03	D37	5.04
D8	5,24	D18	5,02	D28	5,05	D38	5.03
D9	5,28	D19	4,99	D29	4,98	D39	4.96
D10	5,29	D20	4,99	D30	4,98	D40	4.96

APPENDIX III Ion Chromatography analysis of Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet B soils in series A to series D.

<i>Ion Chromatography Analysis results for Series A</i>							
Sample	SO ₄ (mg/l)	Sample	SO ₄ (mg/l)	Sample	SO ₄ (mg/l)	Sample	SO ₄ (mg/l)
A1	0,4824	A11	27,523	A21	12,8805	A31	4,8192
A2	0,5119	A12	28,124	A22	12,6341	A32	5,1699
A3	2,1819	A13	47,326	A23	19,4974	A33	8,9878
A4	1,9593	A14	47,151	A24	19,7911	A34	9,1106
A5	4,1173	A15	1,8441	A25	33,6371	A35	18,8844
A6	4,0318	A16	1,9131	A26	33,2406	A36	19,1119
A7	8,3005	A17	3,0533	A27	0,8400	A37	28,2092
A8	8,1304	A18	2,8766	A28	0,8601	A38	28,7212
A9	17,3200	A19	6,1914	A29	2,5523	A39	48,0948
A10	17,4019	A20	6,3531	A30	2,5989	A40	48,3500

<i>Ion Chromatography Analysis results for Series B</i>							
B1	1,7949	B11	25,639	B21	12,4622	B31	2,2224
B2	1,7094	B12	24,926	B22	12,6516	B32	2,3123
B3	2,9815	B13	42,848	B23	18,5641	B33	7,0091
B4	3,1459	B14	43,569	B24	18,3497	B34	7,1072
B5	4,6900	B15	2,7028	B25	32,2453	B35	14,9442
B6	4,8127	B16	2,7677	B26	33,0855	B36	14,8316
B7	8,5925	B17	3,9983	B27	0,4999	B37	23,6275
B8	8,4165	B18	3,9202	B28	0,6288	B38	23,3206
B9	16,3643	B19	6,7762	B29	1,2075	B39	39,7426
B10	16,4147	B20	6,7242	B30	1,3250	B40	39,7890

<i>Ion Chromatography Analysis results for Series C</i>							
C1	0,4	C11	27,9	C21	15,8	C31	3,5
C2	0,3	C12	28,1	C22	16,0	C32	3,5
C3	2,0	C13	47,4	C23	24,5	C33	7,4139
C4	2,0	C14	47,8	C24	25,0	C34	7,3918
C5	4,0	C15	2,0	C25	42,4	C35	14,9385
C6	4,0	C16	2,0	C26	43,0	C36	14,4841
C7	8,4	C17	3,8	C27	0,4	C37	22,4471
C8	8,7	C18	3,8	C28	0,4	C38	22,9183
C9	17,3	C19	7,8	C29	1,8	C39	38,5700
C10	18,1	C20	7,8	C30	1,8	C40	38,9223

<i>Ion Chromatography Analysis results for Series D</i>							
D1	1,2922	D11	25,9129	D21	11,6995	D31	2,3722
D2	1,2479	D12	25,9296	D22	11,3612	D32	2,4351
D3	2,7775	D13	43,8206	D23	17,5536	D33	7,3478
D4	2,7357	D14	44,2471	D24	17,2820	D34	7,2789
D5	4,4895	D15	2,2590	D25	30,1737	D35	15,2239
D6	4,5257	D16	2,1976	D26	30,2145	D36	14,5075
D7	8,4509	D17	3,3721	D27	1,2537	D37	22,5430
D8	8,5112	D18	3,4284	D28	1,2911	D38	21,8371
D9	16,6165	D19	5,9318	D29	1,9956	D39	37,2191
D10	16,5428	D20	5,8599	D30	1,8897	D40	37,8992

APPENDIX IV *Moisture content of Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet soils.*

No	Soil Sample	Moisture %age
1	Tärnsjö B	5.54 %
2	Risfallet B	21.46 %
3	Risbergshöjden B	17.38 %
4	Österström B	18.78 %
5	Kloten Bs1	32.69 %

APPENDIX V *Data used to calibrate extended Freundlich model for Tärnsjö B, Risbergshöjden B, Österström B, Kloten Bs1 and Risfallet B soils for Calculation of Cadded ($\mu\text{mol/l}$), Caq (mmol/l), and Csorbed (mmol/kg).*

<i>Tärnsjö B</i>							
Sample No	Cadded ($\mu\text{mol/l}$)	Caq $\mu\text{mol/l}$	Caq mmol/l	Cad-Caq	Cinit+(Cad-Caq)	Csorbed $\mu\text{mol/kg}$	Csorbed mmol/kg
A1,A2	0	5.175535076	0.005176	5.17553508	40.77365	693.0312451	0.693031
A3,A4	26.65836	21.55523968	0.021555	5.1031222	51.05231	867.7379507	0.867738
A5,A6	53.31672	42.41623391	0.042416	10.9004899	56.84968	966.2760161	0.966276
A7,A8	106.6334	85.52431702	0.085524	21.1091305	67.05832	1139.792647	1.139793
A9,A10	213.2669	180.7299666	0.18073	32.5369284	78.48612	1334.031336	1.334031
A11,A12	319.9003	289.6518724	0.289652	30.2484701	76.19766	1295.134329	1.295134
A13,A14	533.1672	491.76892	0.491769	41.3983176	87.34751	1484.648686	1.484649
A15,A16	26.65836	19.55632883	0.019556	7.10203305	53.05122	901.7135098	0.901714
A17,A18	53.31672	30.86556984	0.030866	22.4511539	68.40034	1162.603067	1.162603
A19,A20	106.6334	65.29511284	0.065295	41.3383347	87.28752	1483.629154	1.483629
A21,A22	213.2669	132.8052718	0.132805	80.4616232	126.4108	2148.609089	2.148609
A23,A24	319.9003	204.4998763	0.2045	115.400466	161.3497	2742.465855	2.742466
A25,A26	533.1672	348.1036983	0.348104	185.063539	231.0127	3926.5316	3.926532
B27,B28	0	5.87508606	0.005875	5.87508606	40.0741	681.140952	0.681141
B29,B30	25.66179	13.18233073	0.013182	12.4794569	58.42865	993.1137751	0.993114
B31,B32	51.32358	23.60326902	0.023603	27.7203062	73.66949	1252.163036	1.252163
B33,B34	106.6334	73.47651358	0.073477	33.1569339	79.10612	1344.569593	1.34457
B35,B36	213.2669	154.985652	0.154986	58.2812431	104.2304	1771.608374	1.771608
B37,B38	319.9003	244.3686931	0.244369	75.5316494	121.4808	2064.814148	2.064814
B39,B40	533.1672	413.9684774	0.413968	119.19876	165.1479	2807.025593	2.807026

<i>Risbergshöjden B</i>							
Sample	Cad $\mu\text{mol/l}$	Caq $\mu\text{mol/l}$	Caq mmol/l	Cad-Caq	Cinit+(Cad-Caq)	Csorbed $\mu\text{mol/kg}$	Csorbed mmol/kg
B1,B2	0	18,24	0,018	-18,24	214,22	4193,69	4,194
B3,B4	26,46	31,89	0,032	-5,431	227,03	4444,44	4,444
B5,B6	52,93	49,46	0,049	3,46	235,93	4618,56	4,619
B7,B8	105,85	88,53	0,09	17,32	249,78	4889,75	4,89
B9,B10	211,7	170,62	0,171	41,1	273,55	5355,0	5,35
B11,B12	317,55	263,2	0,26	54,35	286,8	5614,7	5,62
B13,B14	529,25	449,82	0,45	79,44	311,91	6105,85	6,11
B15,B16	26,46	28,47	0,028	-2,012	230,45	4511,37	4,51

B17,B18	52,93	41,22	0,04	11,71	244,17	4779,97	4,78
B19,B20	105,86	70,27	0,071	35,58	268,04	5247,27	5,25
B21,B22	211,70	130,72	0,130	80,98	313,44	6136,06	6,14
B23,B24	317,55	192,14	0,192	125,4	357,88	7005,83	7,01
B25,B26	529,25	340,1	0,340	189,2	421,66	8254,54	8,25
C27,C28	0	4,4	0,005	-4,4	228,07	4464,71	4,46
C29,C30	25,47	18,7	0,019	6,79	239,25	4683,71	4,68
C31,C32	50,95	36,8	0,037	14,2	246,66	4828,57	4,82
C33,C34	105,85	77,06	0,077	28,8	261,25	5114,27	5,11
C35,C36	211,7	153,15	0,15	58,55	291,01	5697,0	5,697
C37,C38	317,55	236,13	0,24	81,4204	313,9	6144,66	6,145
C39,C40	529,25	403,35	0,4034	125,9	358,36	7015,34	7,0153

Österström B.

Sample No	Cadd umol/l	Caq umol/l	Caq mmol/l	Cad-Caq	Cinit+(Cad-Caq)	Csorbed µmol/kg	Csorbed mmol/kg
C1,C2	0	3,643	0,00	-3,643	26,823	534,594288	0,534594288
C3,C4	26,44	20,802	0,02	5,638	36,103	719,5679415	0,719567942
C5,C6	52,88	41,843	0,04	11,037	41,502	827,1687951	0,827168795
C7,C8	105,8	89,177	0,09	16,583	47,048	937,7122406	0,937712241
C9,C10	211,5	184,37	0,18	27,146	57,612	1148,244394	1,148244394
C11,C12	318,0	291,38	0,29	26,640	57,105	1138,148319	1,138148319
C13,C14	528,8	495,45	0,49	33,356	63,821	1272,005677	1,272005677
C15,C16	26,44	20,83	0,02	5,614	36,079	719,0859706	0,719085971
C17,C18	52,88	39,3	0,04	13,579	44,044	877,8255999	0,8778256
C19,C20	105,8	81,02	0,08	24,736	55,201	1100,196242	1,100196242
C21,C22	211,5	165,4	0,16	46,160	76,625	1527,196579	1,527196579
C23,C24	317,3	257,7	0,25	59,627	90,092	1795,605277	1,795605277
C25,C26	528,8	444,5	0,44	84,299	114,764	2287,348673	2,287348673

Kloten Bs 1.

Sample No	C add umol/l	C aq umol/l	C aq mmol/l	Cadded-Caq	Cinit+(Cad ded-Caq)	Csorbed µmol/kg	Csorbed mmol/kg
D1,D2	0	13,22	0,013	-13,22	158,6	3847,9	3,848
D3,D4	26,21	28,7	0,0287	-2,483	169,37	4108,4	4,11
D5,D6	52,429	46,92	0,047	5,504	177,36	4302,09	4,30
D7,D8	104,86	88,29	0,088	16,57	188,42	4570,5	4,570
D9,D10	209,713	172,59	0,173	37,118	208,97	5068,9	5,069
D11,D12	314,6	269,84	0,267	44,727	216,58	5253,5	5,25
D13,D14	524,3	458,39	0,458	65,89	237,74	5766,7	5,767
D15,D16	26,21	23,197	0,02319	3,0171	174,87	4241,8	4,2418
D17,D18	52,43	35,397	0,036	17,031	188,89	4581,7	4,5817
D19,D20	104,86	61,38	0,061	43,48	215,34	5223,25	5,22
D21,S22	209,71	120,03	0,1200	89,68	261,54	6343,91	6,344
D23,D24	314,570	181,322	0,1813	133,25	305,11	7400,7	7,401
D25,D26	524,3	314,33	0,31	209,96	381,82	9261,42	9,261
D27,D28	0	13,25	0,02	-13,246	158,61	3847,28	3,847

D29,D30	25,23	20,22	0,020	5,0112	176,87	4290,14	4,29
D31,D32	50,469	25,02	0,026	25,45	197,3	4785,80	4,786
D33,D34	104,86	76,13	0,076	28,725	200,58	4865,31	4,865
D35,D36	209,72	154,75	0,155	54,96	226,82	5501,7	5,50169
D37,D38	314,571	231,0	0,23	83,57	255,42	6195,7	6,196
D39,D40	524,28	390,99	0,39	133,29	305,14	7401,7	7,40166

<i>Risfallet B</i>							
Sample	Cadded	C aq umol/l	C aq mmol/l	C added - C aq	Cinit+(Cadded-Caq)	Csorbed μ mol/kg	Csorbed mmol/kg
A27,A28	0	8,95	0,009	-8,9540	53,6751	1108,12	1,108
A29,A30	26,4	26,81	0,027	-0,4165	62,2125	1284,38	1,284
A31,A32	52,8	51,99	0,052	0,7981	63,4272	1309,45	1,309
A33,A34	105,6	94,204	0,094	11,3800	74,0090	1527,92	1,527
A35,A36	211,2	197,77	0,198	13,3941	76,0232	1569,49	1,569
A37,A38	316,8	296,32	0,296	20,4247	83,0538	1714,65	1,714
A39,A40	527,92	502,00	0,502	25,9167	88,5457	1828,03	1,828