Preface

This is a master thesis written at the Institute of Plant and Environmental Sciences, at The Norwegian University of Life Sciences (UMB). The thesis is the end result of a master degree in the study program Environment and Nature Resources with Terrestrial Environment as the special field.

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Ås, 14. December 2011.

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Summary

Increasing DOC concentrations have been observed in many areas in the Northern Hemisphere, where a warmer and wetter climate is most likely among the causes. Increasing DOC concentrations in ground- and surface waters are of concern due to deterioration of water quality and water habitats. Aluminium (Al) and iron (Fe) sesquioxides in soils has been regarded as important DOC adsorbents. Such compounds can be precipitated in the soil B-horizon by the podsolization process. Podzols are one of the most common soil types in well drained mineral soils of the Northern Hemisphere. As the most pronounced climate changes are predicted to occur in northern regions, the focus of our study was on a poorly podzolized soil in Neiden, Finnmark County, Norway. The objectives of this study were to determine the DOC adsorption in the B-horizon of this soil, compare it with soils that are more podzolized and determine the soil properties controlling the DOC adsorption. The hypothesis of the present study is that the poorly podzolized soil has a lower DOC adsorption capacity than more podzolized soils due to a low content of Al and Fe sesquioxides. The net DOC adsorption was determined by adding six different DOC concentrations (0-129 mg C L^{-1}) to ten field replicates of the poorly podzolized soil. The same procedure was performed on two soil samples from podzolized soils with contrasting content of sesquioxides, one with a high content of Al and one with a high content of Fe. Three isotherm approaches were tested; two versions of the modified Langmuir isotherm and the Initial Mass isotherm. A Mid-infrared reflectance (MIR) spectroscopy analysis was performed to obtain information about the hydrophobicity of the functional groups in the O- and B-horizon. The MIR analysis suggested an enrichment of hydrophobic organic functional groups in the B-horizon in comparison to the O-horizons. The variation in both soil properties and DOC adsorption between field replicates for the poorly podzolized soil was high. At the highest DOC concentration, the net DOC adsorption for the poorly podzolized soil ranged from 5 to 47%, with an average of 19%. The partition coefficient, which is a measure of the reactive DOC fraction adsorbed by the soil in the linear concentration range (0-67 mg C L^{-1}), ranged from 0.29 to 0.63 with an average of 0.41. The DOC adsorption for this soil was within the range reported by previous studies focusing on podzol soils, and it could therefore not be concluded that this poorly podzolized soil has a lower DOC adsorption capacity than more podzolized soils. A stepwise multiple regression analysis revealed that clay content, in addition to amorphous Al and Fe content (oxalate soluble) were the best predictors of the DOC adsorption capacity of the poorly podzolized soil. The DOC adsorption seemed to be limited by occupied adsorption sites, as a high release of initial adsorbed DOC seemed to result in a lower adsorption capacity.

Sammendrag

Økende DOC konsentrasjoner har blitt observert for mange områder på den nordlige halvkule, hvor klimaendringer hvor varmere og våtere klima er mest sannsynlig en av grunnene. Økende DOC konsentrasjoner i grunn- og overflatevann er av bekymring grunnet forringelse av vannkvalitet og vannhabitater. Aluminium (Al)- og jernseskvioksider (Fe) i jord har blitt ansett som viktige DOC adsorbenter. Disse kan felles ut i jordsmonnets B-sjikt i podsoleringsprosessen. Podsol er en av de vanligste jordtypene i veldrenerte mineraljordsmonn i på den nordlige halvkule. Siden de største klimaendringene er forventet å inntreffe i nordlige områder, var vårt fokus på en svakt podsolert jord lokalisert i Neiden, som ligger i Finnmark i Nord Norge. Målene med studiet var å bestemme DOC adsorpsjonen til et B-sjiktet for denne jorda, sammenlikne denne med mer podsolerte jordsmonn og bestemme hvilke jordegenskaper som bestemmer DOC adsorpsjonen. Hypotesen i dette studiet er at den svakt podsolerte jorda har en lavere DOC adsorpsjons kapasitet enn mer podsolerte jordsmonn grunnet et lavere innhold av jern og aluminium seskvioksider. Netto DOC adsorpsjon ble bestemt ved å tilsette seks ulike DOC konsentrasjoner (0-129 mg C L^{-1}) til jord fra B-sjiktet for ti feltreplikater av den svakt podsolerte jorda. Den samme prosedyren ble utført på to jordprøver fra mer podsolert jord med ulikt innhold av seskvioksider, ett med et høyt innhold av Al og ett med et høyt innhold av Fe. Tre ulike isotermer ble prøvd ut; to utgaver av en modifisert Langmuir isoterm og Initial Mass isoterm. En Mid-infrared reflectance (MIR) spektroskopi analyse var utført for å få informasjon om graden av hydrofobisitet til de funksjonelle gruppene i O- og B- sjiktet. MIR analysen foreslo at det er anrikning av hydrofobe funksjonelle grupper i B-sjiktet, sammenliknet med O-sjiktet. Variasjonen i både jordegenskaper og DOC adsorpsjon mellom feltreplikatene var stor. Ved den høyeste DOC konsentrasjonen, hadde den svakt podsolerte jorda en netto DOC adsorpsjon fra 5 til 47 %, med et gjennomsnitt på 19 %. Fordelingskoeffisienten (m), som er et mål på fraksjonen DOC som er adsorbert i det lineære konsentrasjonsområdet (0-67 mg C L^{-1}), var fra 0,29 til 0,63, med et gjennomsnitt på 0,41. DOC adsorpsjonen var innenfor adsorpsjonsområdet rapportert i tidligere studier for mer podsolerte jordsmonn, og det kunne dermed ikke konkluderes at denne jorda har en lavere DOC adsorpsjon kapasitet enn mer podsolerte B-sjikt. En trinnvis multippel regresjonsanalyse viste at leirinnhold, og i tillegg innhold av amorft Al og Fe (oksalatløselig) var de beste prediktorene for DOC adsorpsjonen til det svakt podsolerte B-sjiktet. Det virket sannsynlig at DOC adsorpsjonen ble begrenset av antall bindingsplasser, ettersom en høy desorpsjon av allerede adsorbert DOC så ut til a føre til en lavere DOC adsorpsjon.

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1. Introduction

Dissolved organic matter (DOM) plays an essential role in many biogeochemical processes in soil and water (Kalbitz et al. 2000; Thurman 1985). It is an important factor in soil forming (McDowell & Wood 1984) and weathering processes (Lindroos et al. 2003). Dissolved compounds are generally defined as compounds that can pass through a 0.45 μm filter. DOM can contain a complex mix of different compounds and molecules, and is therefore difficult to measure. Carbon (C) represents a fraction of the DOM, the term dissolved organic carbon (DOC) is therefore used as a measure for the DOM as it is easier to a define and determine (Thurman 1985). The main sources of DOC are plant litter, humus, root exudates and microbial biomass (Kalbitz et al. 2000). DOC concentrations in the forest floor are commonly ranging from 20 to 90 mg C L^{-1} while soil solution concentrations are normally in the range from 2 to 35 mg C L^{-1} (Michalzik et al. 2001). Both abiotic and biotic processes can buffer inputs of DOC to soil solution, it can be metabolized by microorganisms and it can be retained in the soil mineral horizons (McDowell & Wood 1984; McDowell & Likens 1988).

Increasing DOC concentrations in surface waters have been observed for many areas in North America and Europe (Monteith & Evans 2000; Monteith et al. 2007). Similar trends have also been observed in Norway (Hongve et al. 2004). Increased temperature, precipitation and CO_2 concentration are among the main causes proposed. The link between climate change and increasing DOC concentrations is well studied (e.g. Freeman et al. 2001; Freeman et al. 2004; Hessen et al. 1997). An incubation study by Christ and David (1996) demonstrated that the soil microbial activity increased with increasing temperature and moisture content, which resulted in increased DOC production. Hessen et al. (1997) reported higher DOC concentrations in lakes in eastern Norway in periods with high precipitation. The highest DOC concentrations were observed in autumn when high rainfall and defoliation occurred. Other suggested explanations for the DOC increases are reduced acid deposition and reduced frequency of winter storms (Evans et al. 2006). Despite being a thoroughly studied subject, the mechanisms regulating DOC concentrations in soils are not fully understood (McDowell 2003).

On a world basis, prognoses from IPCC (2007) are predicting temperature increases, change in water availability and more extreme weather. The most significant temperature increases are predicted to occur in the Northern Hemisphere. Higher latitudes are expected to receive increased precipitation while increased frequencies of droughts are expected at low latitudes. A

regional model study for Europe shows consistent results; the greatest future climatic changes are predicted to occur in northern regions (Haugen & Iversen 2008).

DOC transport to water bodies is of concern due to deterioration of the water quality, giving a more complex and expensive water purification process (Delpla et al. 2009). The DOC compounds can influence the mobility of nutrients and toxic compounds which can result in a poor water quality, eutrophication and destruction of water habitats (Kalbitz & Wennrich 1998; Thurman 1985). Increasing DOC levels can also result in a higher bacterial level due to increased energy supply (Anesio et al. 2004). The presence of DOC in water can increase the production of methyl-mercury due to decreased photo oxidation and increased microbial energy supply. Methyl-mercury is a toxic compound which can bio accumulate in water living organisms and can also bio magnify in the food chain (Downs et al. 1998).

Many studies have focused on the capability of soils to retain DOC in the mineral soil horizons (e.g. Jardine et al. 1989; Kothawala et al. 2009). A mineral soil horizon can hold back compounds by different processes, where adsorption has been considered as the most important one (McDowell & Wood 1984; Moore et al. 1992). Biodegradation of soil solution DOC is in general a slower process, and adsorption has been considered as a more important buffering mechanism (McDowell & Wood 1984; Qualls & Haines 1992a). A podzol soil is characterized by a B-horizon, showing an accumulation of active amorphous organic material and aluminium (Al) with or without iron (Fe), beneath a strongly weathered eluvial (E) horizon. The E-horizon has a lower content of organic matter, base cations, Al and Fe ions than the B-horizon (Ponomareva 1969). Podzols are common in Scandinavia, in well drained parent material (Driessen & Dudal 1991). Podzol soils have been studied due to the good capability of the B-horizon to retain compounds such as DOC (Kaiser et al. 1996; Moore et al. 1992; Vance & David 1992). The retention of DOC in the B-horizon is an important part of the podzolization process and can restrict the mobility of the organic molecules. Most studies focusing on the DOC adsorption have focused on well-developed podzols in forested areas (e.g. Kaiser et al. 1996; Kaiser & Guggenberger 2000; Vance & David 1992), while poorly podzolized soils with low content of Al and Fe sesquioxides have received less attention. The poorly podzolized soil which is the focus in the present study is not fulfilling the podzol (Spodosol) classification criteria due to the low content of sesquioxides; however, the characteristic podzol morphology is present (Soil Survey Staff 2010).

Given the projected climate changes in northern areas, the production and water transport of DOC can be expected to increase. In this master thesis, the main objectives are:

(i) To determine the DOC adsorption capacity of a poorly podzolized high latitude soil, and compare this soil with contrasting soils;

(ii) To determine the soil properties controlling the adsorption capacity of this soil, and;

(iii) To discuss the DOC adsorption capacity in relation to expected future DOC concentrations.

The hypothesis of the present study is that the poorly podzolized high latitude soil in this study has a lower DOC adsorption capacity than more podzolized soils due to a low content of Al and Fe sesquioxides.

2. Background

2.1 Future climate predictions

The study area is located in Finnmark County in northern Norway. For this area, the annual temperature is predicted to increase by 1.5 – 3.0°C and the annual precipitation is predicted to increase by 1-15% within a 50 year period due to climate change (Hanssen-Bauer et al. 2009). A scenario from IPCC (2007) shows an expected rise in winter precipitation of 20% in Norway for the period 2090-2099 relative to 1980-1999 (Fig. 1). However, these estimates have high uncertainties, and depend on the choice of scenarios and models.
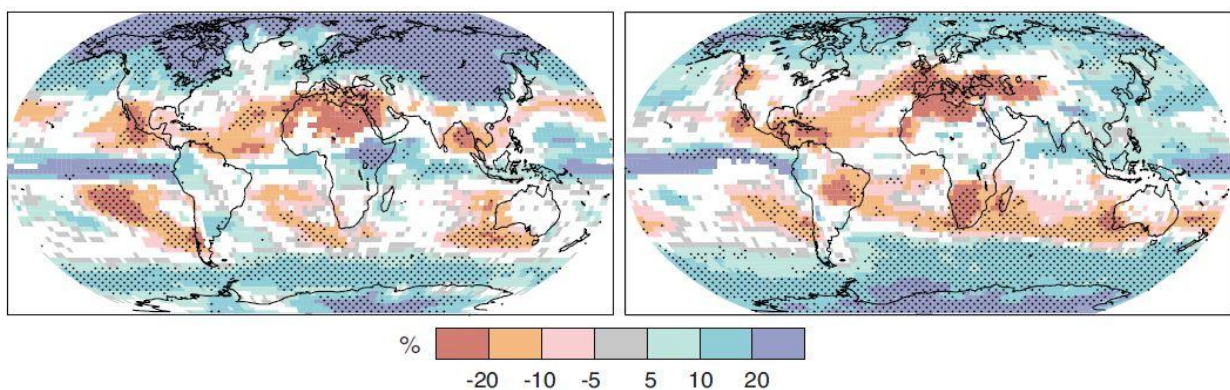
Figure 1. Predicted relative changes in precipitation (%) for the period 2090-2099 relative to 1980-1999. The left illustration shows the expected relative change for December-February, while the right illustration shows relative change for June-August. The model is based on the scenario SRES A1B which is a scenario which assumes use of both fossil fuel and renewable energy. The dark blue colour indicates a precipitation increase of 20%, while areas with red colour an decrease of 20% is expected (IPCC 2007).

2.2. The fate of soil organic carbon in a global climate perspective

The pool of the soil organic carbon (SOC) is about two thirds of the total C in terrestrial ecosystems (Post et al. 1982). Thus, destabilization of these stocks can result in major C losses and alteration of the global C cycle (Kirschbaum 1995; von Lutzow & Kogel-Knabner 2009). SOC can either be lost through gaseous or aqueous form, both of concern from an environmental point of view. Carbon dioxide (CO_2) released from SOC decomposition can result in global warming resulting in a further C release to the atmosphere (Jenkinson et al. 1991). Consequently, the sensitivity of the SOC to climate change is of great importance when studying the terrestrial C balance. The soil C pool is primary determined by C input from net primary production and the soil C pool decomposition rate; both of these factors can be influenced by climate change (von Lutzow & Kogel-Knabner 2009). SOC stabilisation mechanisms are important when considering the DOC losses from soils. The SOC stabilisation mechanisms in soils are namely preservation of recalcitrant C, inaccessibility to the degraders due to occlusion and aggregation, metal chelation and adsorption (von Lutzow et al. 2006). The adsorption of DOC has been regarded as an important mechanism buffering the DOC inputs to water bodies (McDowell & Wood 1984).

2.3 The origins of dissolved organic carbon

As primary plant production is the main source of DOC to soils and surface water, the DOC consists mainly of plant derived compounds. DOC consists of humic substances, including fulvic, humic and hydrophilic acids. Included in the DOC term are also carbohydrates, amino acids, carboxylic acids and hydrocarbons (Thurman 1985). For soils in a catchment dominated by podzols and peat located in southern Norway, Easthouse et al. (1992) reported that the DOC consisted mainly of hydrophobic and hydrophilic acids. Guggenberger et al. (1994) studied the chemical structures of the DOC derived from a coniferous forest floor, and concluded that the DOC was mainly derived from microbial decomposition of plant material. McDowell & Likens (1988) reported that the decomposition of humified organic matter is the main source of DOC in forest soils, and found that a great fraction of the litter leachates can be metabolised by microorganisms. Forest canopy runoff and leaching from fresh litter have also been considered as important DOC sources (Dalva & Moore 1991; Hongve 1999). Litter leachate from certain vegetation types can have a greater DOC concentration than others. Hongve (1999) compared the DOC leachate from areas with different vegetation, and reported that leachate from deciduous litter contained six times more DOC than leachate from coniferous litter. Soil microbial biomass and root exudates can also contribute as important soil DOC inputs, but are

not considered as main sources (Kalbitz et al. 2000). The age and origin of the DOC can be examined using ^{14}C dating. Observations done by Karltun et al. (2005) showed that for a young forest stand with low litter input, most of the DOC originated from older SOC. A decreasing fraction of old C was observed with increasing forest age, which was explained by a greater litter input in the old forests, where litter leaching and litter decomposition were more dominant.

2.4 Controls on dissolved organic carbon in soils

The factors and mechanisms controlling the dynamics of DOC have been well studied (e.g. Bolan et al. 2011; Kalbitz et al. 2000; McDowell & Wood 1984). However, the mechanisms controlling the DOC dynamics are not fully understood (McDowell 2003). Due to a large number of interfering factors, this is a complex field of study. The most important factors determining the DOC concentration and flux are vegetation, land use, pH and climate (Kalbitz et al. 2000). Biodegradation, adsorption, photo degradation and leaching are among the mechanisms controlling the DOC dynamics in soils (Bolan et al. 2011). In this section, factors related to the predicted climate changes are given the main focus.

2.4.1 Temperature

The release of DOC varies among different climatic regions, as it is generally observed higher DOC concentrations in surface waters in temperate areas than in the tropics (Meybeck 1982). The low DOC concentrations in warm climates are mostly due to low SOC pools and high C turnover rate (Kirschbaum 1995). The size of the SOC pool can be directly related to the DOC flux, a soil with a large SOC pool tends to have a greater DOC flux (Aitkenhead et al. 1999). A temperature rise in areas with large soil C pools might enhance the decomposition and the release of DOC, which have created concerns (Freeman et al. 2001). Incubation studies have demonstrated that increased temperature is enhancing the soil microbial activity and therefore the DOC production (Andersson et al. 2000; Christ & David 1996). In a field study, Michalzik & Matzner (1999) found a positive correlation between the temperature and the DOC concentration in the soil solution. However, the temperature did not correlate to the DOC flux and suggested that abiotic processes buffered the DOC release. A rise in DOC concentrations in surface waters has been observed in England and Northern Europe, where a temperature increase has been hypothesised as the cause (Freeman et al. 2001; Monteith & Evans 2000). The importance of the temperature on the DOC increase was questioned by Tranvik & Jansson (2002) who claimed that a temperature rise alone could not be the main cause, and other causes were suggested. Further, a

temperature increase can result in drought, which can give reduced DOC water transport. Schindler et al. (1997) measured declining DOC concentrations in lakes in Ontario, Canada, which was most likely due to reduced stream flow caused by drought. Corresponding results were found by Sowerby et al. (2010) who found an overall 9% decline in DOC flux after an 8 year drought experiment in the field. However, the soil DOC concentrations increased by 56%. In areas where vegetation growth is limited by temperature, a temperature rise can affect the primary production, giving increased litter fall and thus increased DOC production (Hopkins & Hüner 2009). In summary, temperature seems to have an effect on DOC concentration in soil solution, but the effects on DOC flux seem to be less evident.

2.4.2 Precipitation and water fluxes

Precipitation, water flux and large precipitation events can have an impact on both the DOC production and the DOC flux. Laboratory studies show that increasing soil moisture content can enhance the production of DOC (Christ & David 1996). Seasonal variations in DOC concentrations have been reported for several studies (Dalva & Moore 1991; McDowell & Likens 1988), the elevated DOC fluxes are most commonly found in spring and autumn due to high water fluxes (Hessen et al. 1997). It has been postulated that warm and moist summers have the potential to release the highest amounts of DOC (Christ & David 1996). Hongve et al. (2004) observed a relationship between increasing precipitation and DOC fluxes to Norwegian lakes, where periods of high precipitation had the highest DOC fluxes. By increasing precipitation during the growth season in a field manipulation study, Haaland et al. (2008) did not observe any significant change in the average DOC runoff. Hence, the DOC fluxes followed the increases in water runoff, suggesting that the soil buffered the DOC fluxes. Large precipitation events can result in increased DOC fluxes. When such events occur, macro pore flow can be favoured due to the high water flux. Water percolating through macro pores can have a lower retention time in the soil which gives less contact with the mineral phase, and therefore less DOC retention can occur (Jardine et al. 1990). On the other hand, the increased water flux can also result in a lower contact time in the organic horizons, resulting in a reduced DOC flux due to reduced dissolution and dilution. This was seen by McDowell & Wood (1984) who measured lower DOC concentrations in the organic horizons when high precipitation events occurred. Large precipitation events can result in a dilution effect, resulting in a lower DOC concentration (Easthouse et al. 1992). In summary, previous studies show that the soil moisture and water flux influences the soil DOC in different ways; increased soil moisture has been observed to increase

the DOC production. Field studies conclude that periods with high precipitation can release high amounts of DOC, but it depends on the water retention time in the soil and also of the size of the water catchment (Löfgren et al. 2003).

2.4.3 Other factors in an environmental point of view

The soil pH can have an important effect on the DOC in soil solution. Acid compounds can prevent the dissolution of organic compounds due to H^+ replacement at the organic molecules (Krug & Frink 1983). During the last decades, reduced sulphate (SO_4^{2-}) and sea salt deposition have been observed (Skjelkvale et al. 2005), which have both been related to the rise in DOC concentrations in Europe (Evans et al. 2006; Monteith et al. 2007; Skjelkvåle et al. 2007). Sea salt deposition may give an immediate acid release to soil solution due to ion exchange, and can therefore inhibit dissolution of the organic compounds (Wiklander 1975). Another focus has been on the effect on wet-dry and freeze-thaw cycles. Freeze-thaw cycles have been shown to increase the DOC flux from the O-horizon due to disruption of the organic material (Wang & Bettany 1993). A study by Lundquist et al. (1999) focusing on wet-dry cycles demonstrated that the soil DOC concentrations increase after rewetting a dry agricultural soil, mainly caused by increased DOC availability due to low microbial activity and cell death during drought in addition to alteration of the soil structure. Elevated CO_2 concentrations have also been proposed as a cause of the increased DOC concentrations. With increasing CO_2 exposure over a three year period, Freeman et al. (2004) reported a significant increase in DOC release for three peat soils with different nutrient availability. This study proposed that the CO_2 increase is enhancing the plant primary production which can cause increased DOC release due to increased litter fall and DOC exudation.

2.5 Adsorption of dissolved organic carbon

Different soil types have shown varying capabilities to retain DOC in the soil profile. As adsorption is considered as an important C stabilization mechanism, the adsorption of DOC is important when determining the fate of the DOC in the environment (von Lutzow et al. 2006). McDowell & Wood (1984) found low DOC concentrations in stream water compared to the soil concentration, and suggested that the adsorption by the mineral soil was responsible for the DOC removal. Much focus has been on the adsorption of DOC to podzol B-horizons, but e.g. volcanic soils can also adsorb significant amounts of DOC (Kothawala et al. 2009). In podzols, the DOC concentration in soil solution is decreasing with depth in the soil profile, mainly due to

adsorption processes (e.g. McDowell & Wood 1984; Michalzik & Matzner 1999). Al and Fe sesquioxides have been considered as important adsorbents due to large surface areas. DOC adsorption can also occur at the clay mineral edges, but has not been considered as important as the adsorption by Al and Fe sesquioxides (Kaiser & Zech 2000; Oades 1989). In general, the clay content, organic C, pH, and content of Al and Fe sesquioxides have been regarded as the most important factors controlling the soil DOC adsorption (e.g. Jardine et al. 1989; Kaiser et al. 1996; Kaiser & Zech 2000; Moore et al. 1992).

2.5.1 The podzolization process

Three main processes characterize the podzolization process, namely mobilisation, translocation and immobilisation. Organic acids leaching through the soil profile are increasing the weathering rate and enhance the eluviation of the E-horizon (Drever & Stillings 1997). In soil solution, organic acids can form complexes with Al^{3+} and Fe^{3+} ions and thus a mobilization can occur. The fulvic acids are the most effective complexing agents due to carboxylic and phenolic groups which are chelating the metal ions. These complexes can be translocated when they are transported downwards in the soil profile. Further, the organic complexes can be immobilized, forming the B-horizon (Driessen & Dudal 1991). Two main theories have been suggested to explain the formation of the B-horizon, precipitation and adsorption due to saturation of the soil solution or due to microbial degradation of the complex. In areas where precipitation exceeds evapotranspiration and there is a descending water flow, the podzolization process is favoured (Mokma & Buurman 1982). The downward water flow is enhanced in coarse material. Podzolization is less common in fine material as silt and clay deposits due to minimal vertical water movement. A principal factor impacting the podzolization process is the vegetation, as plant material are the main source of organic acids (Tamm 1950). For a more detailed description of the podzolization process, it is referred to Lundstrom et al. (2000).

2.5.2 Aluminium and iron sesquioxides

Al and Fe sesquioxides is a collective term for Al and Fe oxides, oxyhydroxides and hydroxides. These colloids are important in soils due to high adsorption capacities and high specific surface area (McLaren & Cameron 1996). Sesquioxides are occurring as inorganic crystalline and amorphous compounds. The most common crystalline forms in soil are gibbsite ($Al(OH)_3$), heamatite (Fe_2O_3) and goethite (FeOOH). Gibbsite is the most common Al sesquioxide found in soils, which is usually formed by silica removal from kaolinite. The most common Fe oxide in

soils is goethite, which is primary formed by weathering of iron rich minerals. The non-crystalline silicates imogolite (Al), allophane (Al) and ferrihydrite (Fe) have high specific surface area and adsorption capacities (Allen & Hajek 1989). Imogolite and allophane are often associated with volcanic soils, however they are found in podzol B horizons as well (Gustafsson et al. 1995; McLaren & Cameron 1996). Ferrihydrite forms in bog iron deposits and podzol B-horizons (Allen & Hajek 1989). Many studies have emphasized on the importance of the sesquioxides on the soil adsorption capacity (e.g. Kaiser & Zech 1998; Kothawala et al. 2009; Moore et al. 1992). Kaiser & Zech (1998) prepared Al and Fe oxide-hydroxide coatings which were precipitated onto the soil. They found the greatest DOC adsorption when the soil was coated with inorganic amorphous Al, followed by ferrihydrite and goethite. Corresponding results were found by Kothawala et al. (2009), where the inorganic amorphous Al had the most dominating control on the maximum DOC adsorption. Lilienfein et al. (2004) found that the DOC adsorption increases with increasing age of the soil, the highly weathered soils with large amounts of sesquioxides had large DOC adsorption capacities. In summary, studies seem consistent that the content of sesquioxides in soils is one of the most important factors when studying the DOC adsorption capacity of a soil.

2.5.3 Adsorption mechanisms

The mechanisms of DOC adsorption are not fully understood and different mechanisms have been proposed (e.g. Jardine et al. 1989; Oades 1989; Tipping 1981). The main DOC adsorption mechanisms suggested are:

I. Ligand exchange where OH^- groups are exchanged with the organic compounds

II. Adsorption due to entropy changes

III. Co-precipitation of the organic-metal complex

IIII. Anion exchange, the organic molecule are interacting with surfaces electrostatically

The DOC adsorption is dependent on the amount of available adsorption sites in the soil. Ions that are already bound to the mineral surface must be displaced by the organic molecules, which are requiring energy dependent on the size and the valence of the ion that is replaced (Oades 1989). Kaiser et al. (1996) suggested ion exchange processes as the most important mechanism. Tipping (1981) studied adsorption on Fe oxides and demonstrated that the ion exchange decreased with increasing pH. The decreased ion exchange was mainly caused by decreasing number of adsorption sites (Fe-OH and $FeOH_2^+$); the adsorption sites were deprotonated as the

pH increased. Therefore, in soils with high pH, the adsorption affinity is lowered due to a greater occurrence of Fe-O$^-$ sites. DOC adsorption has also been explained by changes in entropy (Jardine et al. 1989). Jardine et al. (1989) reported that the primary adsorption mechanism was entropy driven while the ligand exchange mechanism releasing OH$^-$ accounted for only 25% of the adsorption. By comparing the DOC adsorption affinity for a podzol B-horizon with the adsorption affinity for different anions, Nodvin et al. (1986) concluded that the soil had a medium affinity for DOC. They found an adsorption affinity for the different compounds in the following order: PO_4^{3-} > F$^-$ > DOC > SO_4^{2-} > Cl$^-$ > NO_3^-. These findings were supported by Kaiser & Zech (1998) who found an increasing SO_4^{2-} concentration in the soil equilibrium solution with increasing DOC addition.

2.5.4 Hydrophobicity

Many adsorption studies have reported that the adsorption of hydrophobic DOC fractions is preferred compared to hydrophilic compounds. The hydrophobic DOC can easily exchange hydrophilic DOC adsorbed on the mineral soils; resulting in a change in the composition of the soil solution DOC (e.g. Jardine et al. 1989; Kaiser et al. 1996; Kaiser & Zech 1998). Jardine et al. (1989) fractionated the DOC adsorbed to the soil into hydrophilic and hydrophobic fractions using resins. Of the total adsorbed DOC, more than 80% was hydrophobic and less than 20% was hydrophilic. The hydrophobic DOC fractions were adsorbed by physical adsorption due to entropy changes, as these fractions can achieve higher entropy by leaving the water phase.

2.5.5 Adsorption isotherms

An adsorption isotherm is an equation that is used to describe the adsorption of a compound from the soil solution. The Initial Mass (IM) isotherm (Eq. 1) has been commonly used in DOC adsorption experiments (e.g. Kaiser et al. 1996; Moore et al. 1992; Vance & David 1992). This approach is commonly used at a low concentration range where saturation is not reached (Nodvin et al. 1986). This isotherm has the benefit that it is accounting for the release of initial adsorbed DOC.

$$RE = m \cdot Xi - b \qquad\qquad (1)$$

Where *RE* is the net DOC adsorption or desorption (mg C kg^{-1}) and *b* is the amount desorbed to a solution containing no DOC (mg C kg^{-1}), in other words the release of initial adsorbed DOC,

which is always less than or equal to 0. X_i is the initial DOC mass of the solution added to the soil system (mg C kg^{-1}). A partition coefficient m (unit less) can be obtained as the slope of the adsorption isotherm when the adsorption is plotted as a function of the initial DOC mass (mg C kg^{-1}). The partition coefficient is a measure of the fraction of reactive DOC adsorbed by the soil, and it is always between 0 and 1. If the partition coefficient is 1, all reactive DOC is adsorbed. The reactive soil pool (RSP) is defined as the amount reactive DOC present in the soil (Nodvin et al. 1986), and is determined by Eq. 2:

$$RSP = \frac{b}{(1 - m)} \tag{2}$$

The IM-isotherm is lacking the possibility to calculate an adsorption maximum (Q_{max}), where the Langmuir equation has been helpful (vanLoon & Duffy 2005). The release of initial adsorbed DOC are limiting the use of the regular Langmuir equation in DOC adsorption experiments, but a modified equation was suggested by Lilienfein et al. (2004), which accounts for the release of initial adsorbed DOC (Eq. 3).

$$RE = \frac{(k \cdot Q_{max} \cdot X_f)}{(1 + k \cdot X_f)} - b \tag{3}$$

In the modified Langmuir equation, the term b is subtracted, which is derived from the IM-isotherm. The parameter k represents the bonding energy (kg solution kg^{-1} soil), while the parameter Xf is the final concentration (mg C L^{-1}) after soil solution equilibrium is reached. The parameter b can be obtained by a second modified Langmuir approach where initial concentration (X_i; mg C L^{-1}) is used instead of final concentration (Eq. 4).

$$RE = \frac{(k \cdot Q_{max} \cdot X_i)}{(1 + k \cdot X_i)} - b \tag{4}$$

The modified Langmuir isotherm has the disadvantage that is not possible to transform the equation to linear form and use the linear fit to calculate a Q_{max}, as it is commonly done in adsorption experiments (vanLoon & Duffy 2005). Therefore, the Q_{max} has been obtained using non-linear regression methods (Lilienfein et al. 2004; Vandenbruwane et al. 2007).

3. Materials and methods

3.1 Study area

The study location is Bøttemyra, a bog in Neiden, approximately 30 km southwest of Kirkenes, Norway. Neiden is a small community situated in Sør-Varanger Municipality in Finnmark County (Fig. 2). There is no settlement near the bog. The main road to Finland is crossing the bog, there is also a gravelled road following the moraine west of the bog, which is leading to a nearby reindeer pen.
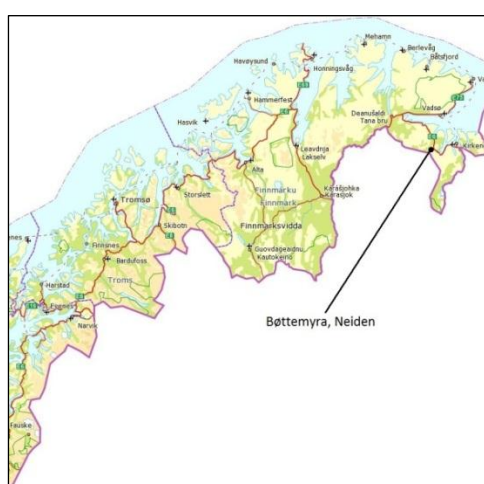
Figure 2. The location of the study area in Finnmark, Norway (Norwegian Geological Survey 2011b).

The climate of the area is continental with an average annual temperature of -0.6°C and an average annual precipitation of 435 mm (1961-1990; Table 1). The warmest month is July with an average temperature of 12.1°C, while the January is coldest with an average temperature of -11.8°C. Most of the precipitation is deposited during the summer, only 20% of the precipitation falls during winter (Norwegian Meterological Institute 2011). The study area is located in vegetation-geographic region northern boreal to weak continental zone, Nb-C1 (Moen 1983).

Table 1. Climate data - monthly normal values for the area, 1961-1960. P=Precipitation, T=Temperature (Norwegian Meterological Institute 2011)

Weather Station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
Veines in Neiden P (mm)	31	22	21	21	24	43	60	59	45	39	40	30	435
Kirkenes Airport P (mm)	32	23	21	20	23	41	60	62	47	35	33	33	430
Kirkenes Airport T (°C)	-11.8	-11.3	-7.4	-2.4	3.0	8.5	12.1	10.5	6.2	0.4	-5.5	-9.7	-0.6

The bog is characterised by having palsas, peat mounds formed by permafrost. The occurrence of palsas have shown a declining trend the last part of the 19th century, most likely due to global warming (Hofgaard 2003; Hofgaard 2009). Changes in the vegetation at the study area can be related to the topography. There is a moisture gradient from east to west, moist peatland can be found in depression zones in contrast to more dry conditions at the upland moraine ridges (Fig. 3). This study is focusing on soils from the moraine ridge, not on the bog. At the moraine, the dominating vegetation is Mountain birch (*Betula pubescens*), *Empetrum nigrum*, *Vaccinium vitis-idea* and *Vaccinium myrtillus* while *Vaccinium uliginosum* and *Betula nana* occurs in some areas. The occurence of lichen and *Erica*-species, such as *Loiseleuria procunbens* and *Arctostaphylos alpines* increases with elevation. More details about the vegetation in given in Appendix 1.
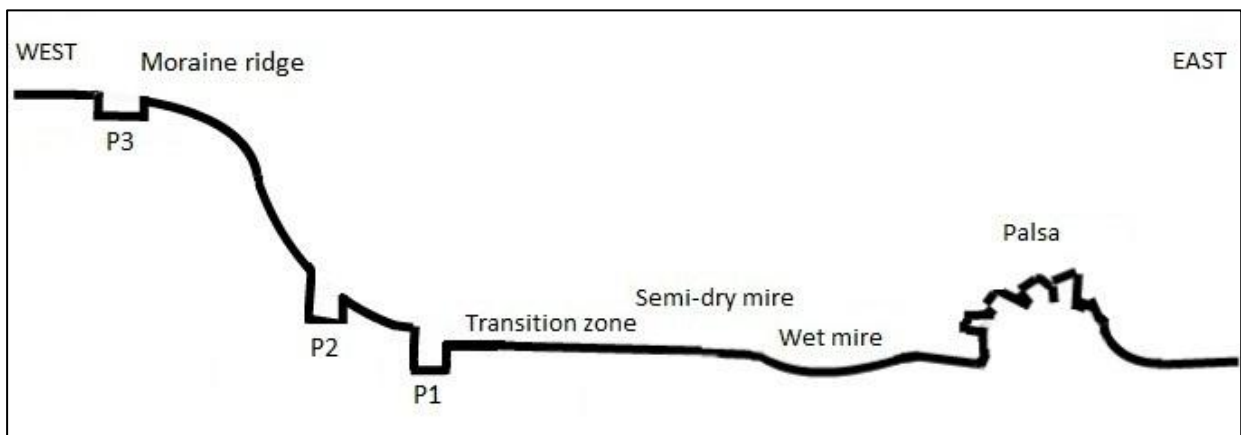
Figure 3. The location of the soil profiles and the sections at Bøttemyra.

The geology in the study area is mainly banded gneiss composed of amphibolite, hornblende-gneiss and glimmer gneiss, while migmatites may occur in some areas (Norwegian Geological Survey 2011a). The deglaciation of Norway during the last ice age started in the northern areas, the Varanger Peninsula in Finnmark was deglaciated approximately 13 500 B. P. (Olsen et al. 1996). Under the bog at the study site we found fine silt material, which suggests that the area has marine or glacial lake deposits. It is presumed that the moraine deposits located west of the bog consist of the same minerals as the local bedrock.

3.2 Field work

In this study, the main focus was on the upland soils on the moraine ridge west of the bog, not on the bog itself. Soil sampling was carried out in September 2008 and 2010. The soil samples were collected from three podzolized soils. Three soil profiles (P1, P2 and P3) were dug, described and sampled in September 2008. The soils were classified according to Soil Survey Staff (2010). In September 2010, ten additional sampling points east of the transition zone were chosen for a more detailed study of the poorly podzolized soil, equivalent to soil profile P1 (Fig. 4). The sample points for the poorly podzolized soil were distributed with ten metres distance at a line following the vegetation type (Fig. 5).

Figure 4. Soil profile P1, the poorly podzolized soil
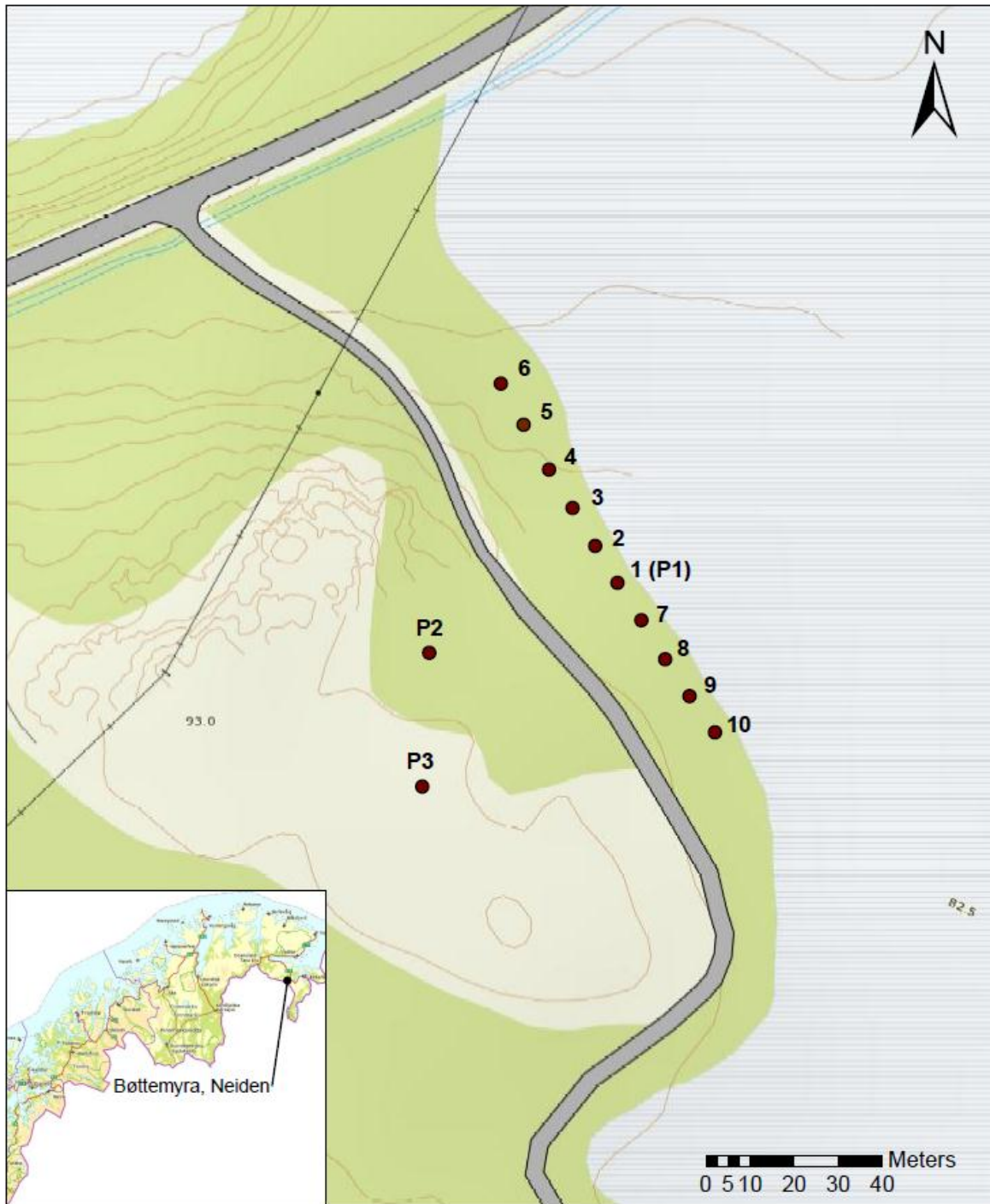
Figure 5. Map showing the location of the sample points. Soil samples 1-10 represent the poorly podzolized soil, while P2 and P3 are the soil profiles of the contrasting soils. All soil samples were collected from the moraine ridge west of the bog. The map was constructed in ArcGIS 9.3.1 with background derived from NGU's map database (Norwegian Geological Survey 2011b).

Soil samples were collected from the O- and B-horizon using a cylindrical hand auger. Living plant tissue, intact plant residues and roots were removed from the O-horizon and the upper 2-5 cm was collected. Where it was possible, the entire core of the B-horizon was sampled.

Approximately 0.5 L of soil from each of the two soil horizons was sampled at each sample point. The occurrence of rocks limited the number of auger cores at some sample points, but 5-10 cores were mixed to achieve a representative soil sample for each of the two soil horizons (Fig. 6). The soil from soil profiles P1, P2 and P3 was collected directly from the soil profile wall. The B-horizons from P2 and P3 were selected for further study, along with the 10 field replicates of the P1 soil. The P2 and P3 soils were chosen due to a high content of Al and Fe sesquioxides. Field moist samples were stored at 4°C to limit microbial activity.

Figure 6. An example of a soil core sampled from the poorly podzolized soil (P1).

3.3 Pre-treatment of soil samples

Moist mineral and organic soil samples were sieved through a 2 mm and 4 mm sieve, respectively (Fig. 7). Mineral soil samples were dried at 35°C for 24 hours, while a fraction of the organic samples were dried at the same temperature for three days, as they were not dry after 24 hours. Soil samples for total-N, total-C and MIR-analysis were in addition crushed using a mortar. The remaining O-horizon samples were stored in moist condition at 4°C.

Figure 7. Field moist organic samples were sieved at 4 mm.

3.4 General properties of the soil

3.4.1 Organic and dry matter content

Organic matter content was measured by loss on ignition. Soil (1-2 g) was weighed in a porcelain crucible, dried at 105°C and the dry matter content was calculated by measuring the weight loss. Further, the soil was ignited at 550°C and the organic matter content was determined by measuring weight loss of the sample after complete ignition. The soil samples were cooled in a desiccator before measuring the weight loss.

3.4.2 Total carbon

Total C content was determined by dry combustion (Nelson & Sommers 1996). Approximately 200 mg of the crushed sample material was covered in tinfoil before the analysis. The samples were combusted and the C was oxidized to CO_2 which was measured by infrared light (Leco CHN-1000). It was corrected for dry matter content.

3.4.3 Total nitrogen

Total nitrogen content was determined by the Dumas method according to Bremer and Mulvaney (1996). Nitrogen oxide compounds (NO_x) were reduced to nitrogen gas (N_2) using copper. Concentration of nitrogen gas was measured by a thermic conductivity cell (Leco CHN-1000).

3.4.4 pH

The pH measurements were performed according to Thomas (1996). The pH was measured potentiometrically in water with a soil solution ratio of 1:2.5. The solution was shaken and left to sediment overnight. Further, the soil solution was again shaken, and pH was measured in the

upper suspension. The pH-meter (Ross electrode, Orion 720) was calibrated using two buffers (pH 4 and 7).

3.4.5 Grain size distribution
A grain size distribution analysis was conducted on the 10 field replicate P1 samples. The fractions of sand were estimated by sieving, while the silt and clay fractions were estimated by the hydrometer method. For more details regarding the grain size distribution analysis, it is referred to Elonen (1971).

3.4.6 Extractable iron and aluminium
Three extractions were used to determine the fractions of Al and Fe sesquioxides in the B-horizon samples. Dithionite-citrate (Al_d and Fe_d), acid ammonium oxalate (Al_o, Fe_o & Si_o) and sodium pyrophosphate (Al_p and Fe_p) extractions were performed in triplicates on all 12 B-horizon samples (10xP1, P2 and P3). Extractions followed the procedure described by Van Reeuwijk (1995). Total amount of the respective elements in the extracts were determined by ICP spectroscopy (ICP-OES, Perkin Elmer Optima 5300DV). The different sesquioxide fractions were estimated according to McKeague (1967) and McKeague & Day (1966). The oxalate extraction dissolves the inorganic amorphous and organically complexed fractions. As the sodium pyrophosphate extraction extracts the organically complexed fractions, the difference between these two extractions was used to estimate the Al and Fe associated with inorganic amorphous forms in the soil ($Fe_{IA}=Fe_o-Fe_p$ and $Al_{IA}=Al_o-Al_p$). It should be noted that the pyrophosphate extraction can dissolve some of the inorganic amorphous and crystalline forms (McKeague 1967). To estimate the crystalline Fe fraction, the difference between dithionite and oxalate fractions was calculated ($Fe_{cry}=Fe_d-Fe_o$).

3.5 Dissolved organic carbon extraction
The dissolved organic carbon extraction followed the procedure of Kothawala et al. (2009) with some modifications. Organic matter (~1300 g), bulked from the 10 field replicates of the P1 O-horizon, and 6 litres of distilled water were added to a 10 litre bottle. The mixture was shaken for 30 min and the bottle was left to settle overnight. To extract the organic C solution, the bottle was shaken and left upright to settle for 30 minutes before the supernatant was extracted by suction. This procedure was repeated for six days until nine litres of extract was obtained. The extract was centrifuged (10 000 rpm) for 20 minutes before it was filtered through a 1.2 µm glass

fibre filter (Whatman GF/C) followed by filtration through a 0.45 µm glass fibre filter (Fig 8; Whatman GF/F). A DOC concentration of 73 mg C L^{-1} was obtained in the final solution. Five litres of the final solution was concentrated by evaporating the sample using a rotary evaporator (Rotavapor RE 120) with a water temperature of 35°C. A final concentration of 129 mg C L^{-1} was obtained in the concentrated extract. A null solution containing 0 mg C L^{-1} was made with a conductivity of 118 µS cm^{-1}, corresponding to conductivity of the final extract. The null solution contained 10 mg NaCl L^{-1}, 20 mg CaCl$_2$·H$_2$O L^{-1} and 24 mg K$_2$SO$_4$ L^{-1}. The DOC extract was stored at 4 °C and used in the following adsorption experiments within 1-2 weeks.

Figure 8. The dissolved organic carbon extract was filtered at 0.45 µm.

3.6 Adsorption experiment

The DOC adsorption experiment was modified after Kothawala et al. (2009). This experiment was conducted on triplicates of all 12 B-horizon samples. Six initial DOC solutions with concentrations of ~ 0, 23, 48, 67, 101 and 129 mg C L^{-1} were prepared by diluting the two stock DOC solutions (73 and 129 mg C L^{-1}) using the null-solution. The initial DOC solution (30 mL) and 3 g of soil from the B-horizon were added to a 100 mL glass bottle. The bottles were placed on a shaker for 24 hours (100 cycles/min), at 4°C and placed to sediment for 30 minutes. The final solution was filtrated through a 0.45 µm glass fibre filter (Whatman GF/F) and analysed for non-purgeable organic C (Shimadzu TOC-V CPN), which corresponded to DOC in solution. Four standards were used (0, 20, 50, 100 mg C L^{-1}) to construct a standard curve. It was corrected for sample evaporation. Determination of DOC in solution followed the Norwegian standard method (NSF 1997). The pH was measured in soil solution after sorption equilibrium

(Ross electrode, Orion 720). The amount DOC adsorbed/desorbed was estimated by taking the difference between the concentration before and after sorption equilibrium. The procedure was repeated for each of the six DOC solutions.

3.7 Adsorption isotherms

Due to the presence of initial adsorbed DOC, it was not possible to use the regular Langmuir equation and transform it to linear form as it is commonly done for other compounds in adsorption experiments (Lilienfein et al. 2004; vanLoon & Duffy 2005). In this study, three different isotherm approaches were tested; the Initial Mass (IM) isotherm approach and a modified Langmuir isotherm with final concentration and initial concentration approach. Adsorption isotherms for the modified Langmuir approaches were plotted using the best fit, and the IM isotherms were obtained using a linear fit, using Microsoft Excel 2010. For the IM isotherm, the partition coefficient (m), the release of initial adsorbed DOC (b_{IM}), and the reactive soil pool (RSP) were calculated according to Eq. 2 and 3 (Section 2.5.5). The partition coefficient (m) was calculated as the slope of the linear fit of the Initial Mass isotherm approach, while b_{IM} was calculated as the y-intercept. In addition, the release of initial adsorbed DOC (b_L) was calculated for the modified Langmuir approach with initial concentration approach, as the y-intercept. The parameters b_{IM} and b_L are the same parameter obtained from the two different approaches, but both were obtained as a comparison. Kothawala et al. (2008) reported that the b-parameter obtained from the modified Langmuir isotherm with initial concentration approach (b_L) is a better estimate than the b calculated by the IM approach (b_{IM}). Therefore, the parameter b_L was included further in the data evaluation. The Langmuir parameters Q_{max} and k were not possible to estimate due to limitation in number of data points and high standard deviations when using the G-Newton non-linear regression method (JMP 9.0.0) suggested by Kothawala et al. (2008). However, the adsorption at the highest initial concentration (RE_{130}; 129 mg C L^{-1}), was used to rank the soil samples after DOC adsorption capacity (RE_{130}). The net DOC adsorption (%) relative to the different initial concentrations was calculated to estimate the net DOC removal from the soil solution.

3.8 Mid-infrared reflectance spectroscopy (MIR)

Spectral characterisation of finely ground O- and B- horizon samples was performed by diamond attenuated total reflectance (DATR) spectroscopy using a Nicolet iS10 FT-IR Spectrometer (Thermo Fisher Scientific Inc., Madison, WI, USA). Approximately 2-3 spatulas of soil were

placed on the sample holder of the instrument. To achieve the same sample density between replicate samples, the soil was flattened to a height of approximately 2-3 mm using the spatula before it was compressed further using the instrument pressure device. Background was analysed at the beginning of the analysis and after every tenth sample. All samples were analysed in 5 replicates over the spectral range 500 - 4000 cm^{-1}, with spectral resolution of 4 cm^{-1} and 32 scans per replicate. Spectral data were processed and analysed using R software (version 2.13.1). Spectra were normalised to the waveband at 3350 cm^{-1} (OH-group in H_2O) after baseline correction, with an additional local baseline correction after spectra normalisation (Fig. 9). The saturated, aliphatic (SAT) region 3000-2800 cm^{-1} was chosen for further characterisation and calculation of hydrophobicity index (HI). For the B-horizon samples, spectra in the SAT region were smoothed using a Savitzky-Golay filter prior to curve fitting. Gaussian curves were fitted to peaks within this waveband region in order to calculate the total absorbance caused by the respective functional groups, i.e. methyl (-CH$_3$), methylene (-CH$_2$) and methine (-CH) functional groups. The hydrophobicity index was calculated according to Eq. 5:

$$HI = SAT/SOC \qquad (5)$$

The hydrophobicity index (HI) gives an indication of the contribution of aliphatic C−H, present in methyl, methylene and methine functional groups, to total SOC. Alkyl functional groups are present in e.g. carbohydrates, proteins and lipids, but an enrichment is generally found in e.g. sandy soils with a low content of labile compounds such as carbohydrates and proteins (Capriel et al. 1995).
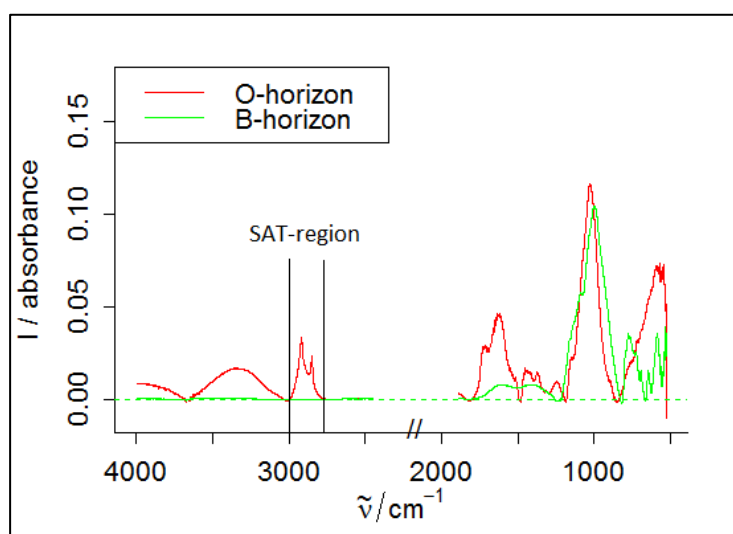
Figure 9. Example of baseline corrected MIR spectra from O- and B-horizon, soil profile P1. The absorption in the area 2450-1900 cm^{-1} is excluded (diamond interference and CO_2 absorption). The SAT-region was used to calculate the HI-index.

3.9 Statistical analysis

The statistical analyses were performed using the statistical software Minitab 16.1.1 (Minitab Inc., USA). A linear correlation analysis was performed using non-parametric Spearman rank correlation. All soil and adsorption properties were included in the correlation analysis (n=12), except for correlations with clay and sand % which did only include P1 replicates (n=10) as grain size distribution analysis was not performed on P2 and P3. Stepwise multiple regression analysis with forward selection (alpha-to-enter 0.25) was performed, with the partition coefficient (m) for P1 field replicates as the response (n=10). A set of potential predictor variables were selected based on prior correlation analysis and knowledge about soil properties that are generally found to best explain the adsorption of DOC in mineral soils, which included pH, clay content, soil C content, crystalline Fe (Fe_{cry}), inorganic Al and Fe (Al_{IA} and Fe_{IA}), oxalate extractable Al and Fe (Al_o and Fe_o), and pyrophosphate extractable Al and Fe (Al_p and Fe_p). Residual plots indicated that the assumptions of normality were fulfilled.

4. Results

Soil samples 1-10 are considered as field replicates of the poorly podzolized soil (P1; Fig. 5) and values presented for P1 in the tables are calculated as an overall mean ± SD based on the triplicate analyses for each of the 10 field replicate samples. The respective means and standard deviations of the soil properties and adsorption characteristics for the individual soil samples obtained from the triplicate analyses are given in Appendix 2 and 3. As there are no field replicates for P2 and P3, values presented for P2 and P3 are calculated as the means ± SD based on the lab triplicate analysis.

4.1 Soil characteristics

P1 showed in general a low content of both Al and Fe sesquioxides (Table 2); however, the variation between field replicates was high. The contrasting soil P2 had a high Fe content, while the Al content was not higher than for P1. In comparison, P3 had a larger Al content and a much lower Fe content. P3 was rich in amorphous Al, approximately five times higher than the P1 average. P2 showed a higher content of amorphous and crystalline Fe than the two other soils. P1 had in general low clay content; most field replicates had a clay fraction lower than 10%, and as for other properties, the variability was high. The soil C content was $1.7 \pm 0.8\%$ for P1, 1.3% for P3, and 2.3% for P2. There was not seen any great differences in pH between the three soils. The calculated hydrophobicity index (HI) for the B-horizons ranged between 9.5 and 12 and from 2.3 to 3.8 for the O-horizon samples. The soil properties for P1 field replicates are attached in Appendix 2. Soil profile descriptions for soil profile P1, P2 and P3 are attached in appendix 1.

Table 2. B- and O-horizon properties for the soils P1, P2 and P3, located in Neiden, Finnmark. P1 is the poorly podzolized soil, the average of ten field replicates. P2 and P3 were included as soils with contrasting Al and Fe content. Standard deviation for P1 indicates the variation between the ten field replicates and their lab triplicates, while the standard deviation P2 and P1 indicates variation between the lab triplicates.

Soil property	B horizons			O-horizons		
	P1*	P2	P3	P1*	P2	P3
Soil pH (in H_2O)	5.00 ± 0.20	4.79	5.04	4.00 ± 0.06	3.89	4.08
Sand (%)	68 ± 11	n. d.	n. d.			
Clay (%)	7 ± 3	n. d.	n. d.			
Soil C (%)	1.7 ± 0.8	2.3	1.3	50.6 ± 1.9	48.9	33.1
Soil N (%)	0.05 ± 0.03	0.08	0.05	1.10 ± 0.25	1.20	1.00
C/N	38 ± 7	31	27	46 ± 10	41	33
Organic matter (%)	4.6 ± 1.8	n. d.	n. d.	88.0 ± 7.0	n. d.	n. d.
Dry matter (%)	99.3 ± 0.4	n. d.	n. d.	94.5 ± 1.0	n. d.	n. d.
HI	12.9 ± 7.0	12.1	9.5	2.4 ± 0.2	2.3	3.7
Fe_d (mg Fe kg^{-1})[a]	14017 ± 5839	24212 ± 999	6903 ± 66			
Fe_o (mg Fe kg^{-1})[b]	5973 ± 2363	11217 ± 159	5277 ± 60			
Fe_p (mg Fe kg^{-1})[c]	2599 ± 1145	2519 ± 159	189 ± 9			
Al_d (mg Al kg^{-1})[a]	4187 ± 1798	6511 ± 320	2552 ± 50			
Al_o (mg Al kg^{-1})[b]	4779 ± 2161	6197 ± 173	21897 ± 365			
Al_p (mg Al kg^{-1})[c]	2983±1319	4639 ± 331	2959 ± 69			
Si_o (mg Si kg^{-1})[a]	648 ± 539	390 ± 0	8550 ± 159			
Fe_{cry} (mg Fe kg^{-1})[d]	8044 ± 5218	12995 ± 1152	1626 ± 122			
Fe_{IA} (mg Fe kg^{-1})[e]	3374 ± 1533	8699 ± 159	5089 ± 58			
Al_{IA} (mg Al kg^{-1})[f]	1797 ± 1186	1559 ± 291	18939 ± 340			

* Average of 10 field replicates, the poorly podzolized soil
a Dithionite soluble
b Oxalate soluble, a measure of the amorphous forms
c Pyrophosphate soluble, a measure of the forms associated with organic complexes
d Crystalline iron, Fe_d-Fe_o
e Inorganic amorphous iron, Fe_o-Fe_p
f Inorganic amorphous aluminium, Al_o-Al_p
n.d not determined

4.2 Adsorption isotherms

The data fitted to the modified Langmuir isotherm with final concentration approach showed a good fit to the data (Fig. 10). However, a point of saturation was not reached for any of the soils, and the equation parameters could not be obtained using this approach. The only parameter obtained from this approach was the null-point (np), the concentration where no net desorption or adsorption occurred. A negative adsorption (RE) indicates a net DOC desorption from the soil while a positive RE shows a net DOC adsorption to the soil. The null point is the point where there are no net adsorption or desorption; the x-axis intercept. The poorly podzolized soil (P1)

adsorbed DOC in the concentration range between P2 and P3; P3 adsorbed more DOC and P2 adsorbed less DOC than P1 until the highest initial concentration where there was an overlap with P1. The individual plots for all 12 soil samples are attached in Appendix 5.

Figure 10. Modified Langmuir isotherm approach for the B-horizons with adsorbed/desorbed DOC (RE) as a function of final concentration (X_f). P1 is the poorly podzolized soil, average of ten field replicates. P2 and P3 were included as soils with contrasting Al and Fe content. Error bars for P1 indicate the variation between the ten field replicates and their lab triplicates, while error bars for P2 and P3 indicate the standard deviation between the lab triplicates. The initial DOC concentration range was 0-129 mg C L^{-1}.

When using the modified Langmuir isotherm approach with initial concentration at the x-axis (Fig. 11), the best fit was used to obtain the release of initial adsorbed DOC (b_L) and the net DOC adsorption at the highest initial concentration (RE_{130}), according to Kothawala et al. (2008). The individual plots for all soil samples are attached in Appendix 6.
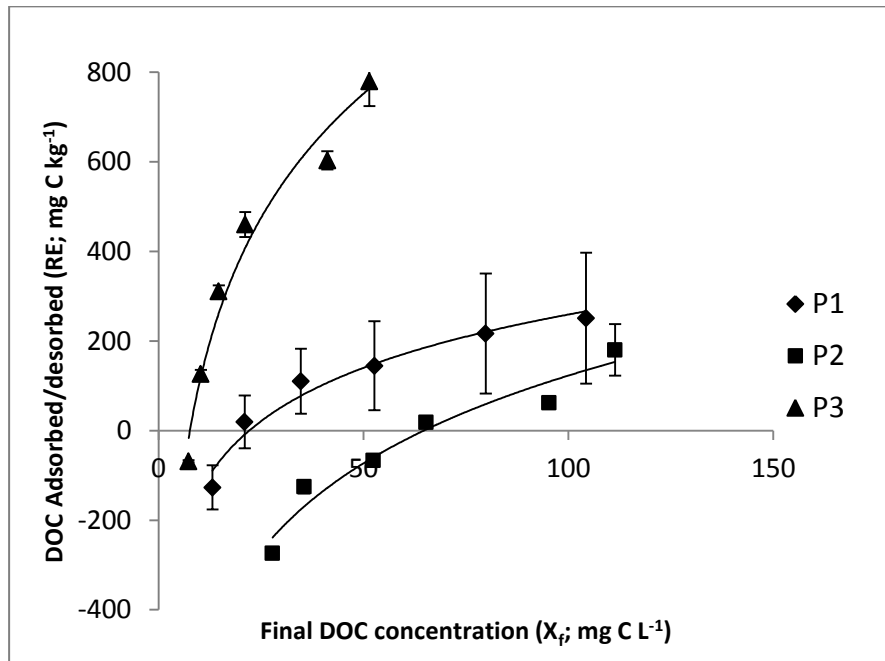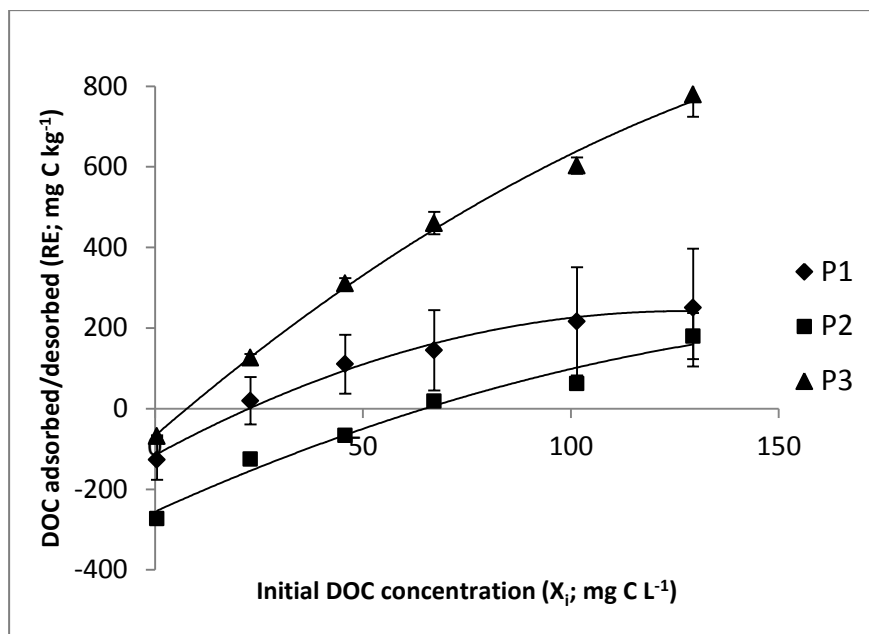
Figure 11. Modified Langmuir isotherm approach for the B-horizons with adsorbed/desorbed DOC (RE) as a function of initial concentration (X_i). P1 is the poorly podzolized soil, average of ten field replicates. P2 and P3 were included as soils with contrasting Al and Fe content. The initial DOC concentration range was 0-129 mg C L^{-1}. Error bars for P1 indicate the variation between the ten field replicates and their lab triplicates, while error bars for P2 and P3 indicate the standard deviation between the lab triplicates.

At the addition of 23 mg C L^{-1}, P1 adsorbed only 9% of the added DOC (Table 3), and most of the field replicates showed a net desorption at this initial DOC concentration. It should be noted that it was a large variation in DOC adsorption capacities between the field replicates. With increasing initial DOC concentration, the net adsorption for P1 increased to 24% at the initial concentration of 46 mg C L^{-1}, but declined to 19% at the highest initial concentration. P2 adsorbed only 3-14% of the total added DOC, while P3 adsorbed 55-68%.

Table 3. Net DOC adsorption (%) relative to the six initial DOC concentrations (mg C kg^{-1}). At the initial concentration where the adsorption is not given, a net desorption occurs.

Initial concentration (mg C L^{-1})	Net DOC adsorption (%)		
	P1*	P2	P3
0	-	-	-
23	9 ± 26	-	55 ± 2
46	24 ± 16	-	68 ± 1
67	22 ± 15	3 ± 4	69 ± 1
101	21 ± 13	6 ± 2	59 ± 1
129	19 ± 11	14 ± 4	60 ± 4

* Average of 10 field replicates, poorly podzolized soil

The Initial Mass isotherm could be applied in the concentration range 0-67 mg C L^{-1} (Fig. 12). The linear fits were almost as good as the nonlinear fits. By using this approach, all adsorption

parameters from Eq. 1 and Eq. 2 could be obtained (Table 4). A linear fit was, however, not achievable when the whole concentration range was included. The release of initial adsorbed DOC (b_{IM}) is the linear y-axis intercept, and the slope of the curve is the partition coefficient (m; Nodvin et al. 1986). P3 adsorbed the highest amount at the low concentration range, which corresponded with the results obtained from the Langmuir isotherm. P2 adsorbed the least DOC at this concentration range. The individual IM isotherm plots for each soil sample are attached in Appendix 7.
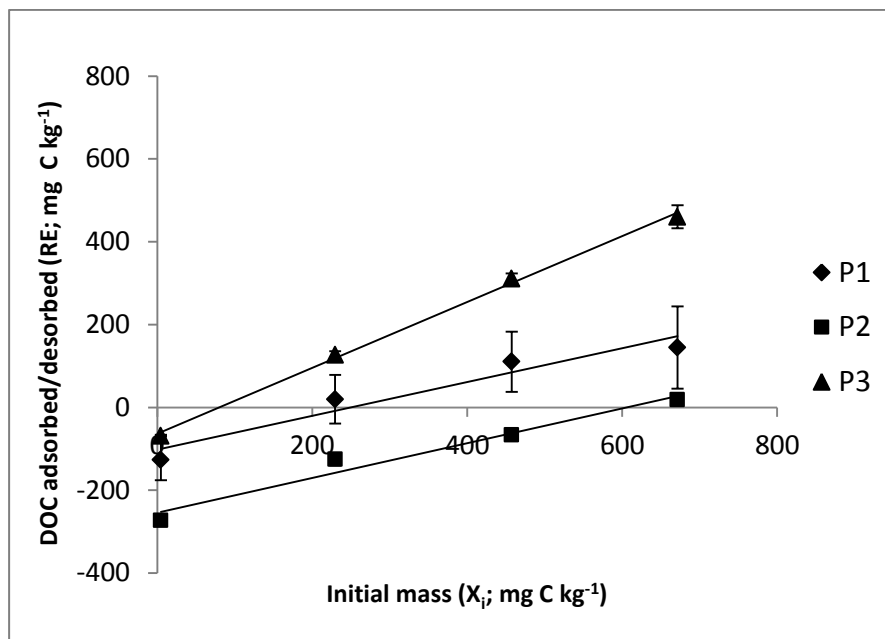
Figure 12. Initial mass isotherms, adsorbed/desorbed (RE) versus the initial DOC mass added to soil solution. P1 is the poorly podzolized soil, average of ten field replicates. P2 and P3 were included as soils with contrasting Al and Fe content. The DOC concentration range was 0-67 mg C L^{-1}. Error bars for P1 indicate the variation between the ten field replicates and their lab triplicates, while error bars for P2 and P3 indicate the standard deviation between the lab triplicates.

Adsorption parameters obtained from the different isotherm approaches are listed in Table 4. The net DOC adsorption at the highest initial concentration (RE_{130}) for P1 ranged from 61 to 604 mg C kg^{-1}, with an average of 251 mg C kg^{-1}. All P1 field replicates had a RE_{130} lower than 350 mg C kg^{-1}, except one field replicate sample which adsorbed 604 mg C kg^{-1}. In comparison, P3 had a large RE_{130} which was about three times larger than the average for P1 (780 mg C kg^{-1}). P2 showed in contrast a lower net DOC adsorption, with a RE_{130} of 180 mg C kg^{-1}. Release of initial adsorbed DOC (b_L) for P1 ranged from 51 to 185 mg C kg^{-1}, with an average of 114 mg C kg^{-1}. The release of initial adsorbed DOC for P2 was 255 mg C kg^{-1}, while it was low for P3, the DOC release was only 67 mg C kg^{-1}. The release of initial adsorbed DOC (b_{IM} & b_L) is given in

absolute values as the net adsorption is negative at 0 mg C L⁻¹. The reactive soil pool (RSP) was higher for both P2 and P3 than for P1, being 438, 310 and 171 mg C kg⁻¹, respectively. P1 and P2 had almost similar partition coefficients (m; 0.41 and 0.42 respectively), while it was about twice as high for P3 (0.79).

Table 4. Adsorption parameters obtained from the three isotherm approaches

Adsorption parameter	P1*	P2	P3
RE_{130} (mg C kg⁻¹)[a]	251 ± 146	180±56	780 ± 57
np (mg C L⁻¹)[b]	263 ± 153	620	70
b_L (mg C kg⁻¹)[c]	114 ± 53	255	67
b_{IM} (mg C kg⁻¹)[d]	101 ± 50	254	64
m (unitless)[e]	0.41 ± 0.11	0.42	0.79
RSP (mg C kg⁻¹)[f]	171 ± 57	438	310

* Average of 10 field replicates, poorly podzolized soil.
a the adsorption at the highest initial concentration (~130 mg C L⁻¹)
b null-point, the concentration where no net adsorption or desorption occurs
c net DOC desorbed at 0 mg C L⁻¹, obtained from the modified Langmuir approach
d net DOC desorbed when 0 mg C L⁻¹ were added, obtained from the IM approach
e the partition coefficient, obtained from the IM isotherm approach
f the reactive soil pool, obtained from the IM isotherm approach

4.3 Controls on the dissolved organic matter adsorption

It was a significant relationship between the clay content and both the partition coefficient (m; Table 5; p=0.005) and the DOC adsorption at the highest initial concentration (RE_{130}, p=0.02). Thus, the DOC adsorption increased with increasing clay size fraction. The correlation between clay and amorphous Fe (Fe_o) suggested that the amorphous Fe content was increasing with increasing clay content (p=0.05). A similar relationship was not seen between clay and amorphous Al content (Al_o). The net DOC adsorption at the highest DOC concentration was strongly correlated to the partition coefficient; a large partition coefficient reflected a high DOC adsorption. The amorphous Al content showed a significant correlation with the partition coefficient (m), which indicated a larger DOC adsorption with increasing amorphous Al content (p=0.03). The highest inorganic amorphous Al content was seen for P3, which had the highest partition coefficient. The same relationship was seen for the inorganic amorphous Al content (Al_{IA}, p=0.04). The release of initial adsorbed DOC (b_L) had a significant relationship to soil C content (p=0.02). Amorphous Fe content (Fe_o) showed a positive significant relationship to the release of initial adsorbed DOC (b_L, p=0.002) and soil C (p=0.002), indicating an increasing release of initial adsorbed DOC with increasing amorphous Fe content. P2 had the highest

amorphous Fe content and therefore a high release of initial adsorbed DOC. P1 field replicates showed a similar relationship. It was also a significant correlation between the release of initial adsorbed DOC and the null point (np); a high DOC release resulted in a high null-point (p=0.001). The null-point was negatively correlated to the DOC adsorption at the highest initial concentration (RE_{130}), indicating that an increasing null-point decreased the DOC adsorption. There was not a significant relationship between the DOC adsorption and the amorphous Fe. No significant correlations were seen for crystalline Fe (Fe_{cry}).

Table 5. Coefficients of correlation (R) between key soil properties and adsorption parameters.

	pH	Soil C (%)	Clay (%)	Fe_{crv}	Fe_{IA}	Al_{IA}	Fe_o	Al_o	RE_{130}	np	b_L	m
pH	-											
Soil C (%)	0.05	-										
Clay (%)	-0.12	0.25	-									
Fe_{cry}	-0.22	0.08	0.39	-								
Fe_{IA}	-0.62*	0.59*	0.60	0.22	-							
Al_{IA}	0.29	0.32	0.25	0.06	0.26	-						
Fe_o	-0.40	0.80***	0.64*	0.16	0.86***	0.00	-					
Al_o	0.18	0.59*	0.33	0.01	0.53	0.87***	0.36	-				
RE_{130}	0.32	0.01	0.69*	0.05	0.11	0.52	0.04	0.42	-			
np	-0.50	0.34	-0.13	0.31	0.34	-0.43	0.44	-0.27	-0.78**	-		
b_L	-0.56	0.67*	0.22	0.30	0.71**	-0.15	0.79**	0.17	-0.49	0.84***	-	
m	0.09	0.22	0.80**	0.24	0.45	0.61*	0.32	0.63*	0.91***	-0.56	-0.16	-

* Significance at the 0.05 level
** Significance at the 0.01 level
*** Significance at the 0.001 level

A stepwise multiple regression analysis (Table 6) revealed that the clay size fraction and the content of amorphous Al and Fe (Al_o and Fe_o) were the best predictors for the partition coefficient (m), the regression was significant (p=0.015). Among predictor variables, clay content was the best predictor for the partition coefficient, as also supported by the results from the correlations between soil properties and adsorption parameters.

Table 6. Stepwise multiple regression analysis with forward selection identifying the key relationships between the partition coefficient (m) and soil properties.

Equation	R^2	R^2 (adj)	R^2 (pred)	RMSE	P (regression)
m = 0.236+ 0.031 clay (%) - 0.000023 Fe_o (mg kg^{-1}) + 0.00002 Al_o (mg kg^{-1})	0.80	0.71	0.39	0.0595	0.015

The pH in the final solution was measured for each of the six initial DOC concentrations. At the addition of 0 mg C L^{-1}, the pH ranged from 4.44 to 5.28. With increasing DOC addition, a pH rise was observed, which was observed for all 12 soil samples (Fig. 13). At the fifth initial concentration ($\sim$ 101 mg C L^{-1}), some of the soil samples showed a slight decrease in pH, while all samples had a pH rise from the fifth to the sixth addition.
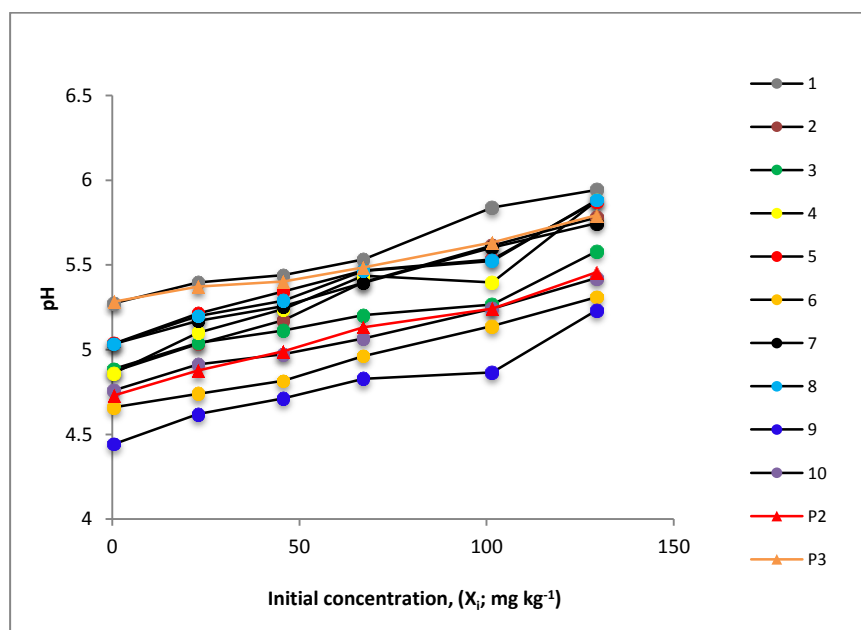

Figure 13. Final pH values in the final concentration, with increasing initial DOC concentration. Soil sample 1-10 are P1 field replicates, indicated by the black lines. P2 are the soil sample with high iron sesquioxide content, while P3 are the soil sample with high aluminium sesquioxide content.

5. Discussion

5.1 Adsorption capacity

The net DOC adsorption for the poorly podzolized soil (P1) at the highest initial concentration was 251 mg C kg^{-1}, which corresponded to 19% of the added DOC (Tables 3 & 4). However, it was a high variability between P1 field replicates, the net DOC adsorption at the highest initial concentration ranged from 5 to 47% (Appendix 4). In comparison, P2 and P3 which were included as contrasts adsorbed 14 and 60% of the highest concentration, respectively (Table 3). None of the soils reached a point of saturation, suggesting that the maximum DOC adsorption was not reached (Fig. 10). The net DOC adsorption for P1 was within the range reported by previous studies focusing on podzol soils, which suggests that this soil cannot be regarded as a soil with a lower DOC adsorption capacity than more developed podzols. The net DOC adsorption relative to the initial concentration has been used as a measure of the DOC adsorption capacity (Guggenberger & Kaiser 2003; Zysset & Berggren 2001). Zysset & Berggren (2001) measured an average net DOC adsorption of 25% for a podzol located in southern Sweden, which was developed on little weatherable material. For a more developed podzol located in Quebeck, Canada, Kothawala et al. (2008) reported a DOC adsorption 290 mg C kg^{-1} at an initial concentration of 100 mg C L^{-1}, which corresponded to an average net DOC adsorption of 29% of the initial DOC concentration.

Only a limited number of studies report the net DOC adsorption at a given DOC concentration. Most studies which focusing on DOC adsorption have used the Initial Mass (IM) approach and report the partition coefficient (m), which is a measure of the fraction of reactive DOC adsorbed by the soil (Nodvin et al. 1986). For P1, the partition coefficient ranged from 0.29 to 0.63, with an average of 0.41. In comparison, the partition coefficients for P2 and P3 were 0.42 and 0.79, respectively (Table 4). A good correlation between the partition coefficient (m) and the adsorption at the highest initial concentration (RE$_{130}$) suggested that a large partition coefficient reflects a high DOC adsorption capacity (Table 5). The correlation between the net DOC adsorption and partition coefficient seem to be in accordance with previous studies that report the net DOC adsorption; the partition coefficient is higher for soils with higher DOC adsorption capacity (Kothawala et al. 2008; Zysset & Berggren 2001). For three podzols with different sesquioxide content situated in southern Quebeck, Canada, Moore et al. (1992) found partition coefficients ranging from 0.21 to 0.75 for the B-horizon. Vance & David (1992) studied the DOC adsorption for three podzol soils located in Bear Brook Watershed in Maine, and reported

partition coefficients ranging from 0.81 to 0.91 for the B-horizons. Many properties have been shown to control the adsorption capacity of a soil, including clay content, sesquioxide content, C content and pH (Jardine et al. 1989; Moore et al. 1992). Consequently, a direct comparison of the DOC adsorption between soils in different studies is difficult.

The DOC adsorption by the soils in this study could not be adequately described by the regular Langmuir isotherm approach due to the release of initial adsorbed DOC (b_L & b_{IM}). Therefore, it was attempted to obtain the adsorption parameters using a modified Langmuir isotherm accounting for the release of initial DOC (Fig. 10 & 11). Due to few observations for each isotherm plot (Appendix 5), it was not possible to obtain a DOC adsorption maximum (Q_{max}). However, the isotherm plots were useful as a visual comparison of the DOC adsorption between the soils. The DOC adsorption was well described by the IM approach, but only in a lower concentration range (Fig. 12; 0 - 67 mg C L^{-1}). Many studies have found that the IM approach is useful when studying the DOC adsorption to soils (Kaiser et al. 1996; Moore et al. 1992; Zysset & Berggren 2001). However, it is not possible to use it in a broad concentration range due to non-linearity, which can limit the use of this isotherm (Nodvin et al. 1986). It has only been found a few numbers of studies which have used the modified Langmuir isotherm approach (Kothawala et al. 2008; Kothawala et al. 2009; Lilienfein et al. 2004).

The DOC adsorption capacity obtained in this laboratory adsorption experiment can only be seen as a relative indication of the soil DOC adsorption capacity. Dahlgren and Marrett (1991) reported that the DOC adsorption was rapid and the soil-solution equilibrium occurred within few hours even at low temperatures, which supports that soil-solution equilibrium was achieved in our DOC adsorption experiment (24 h duration, 4 °C). In batch adsorption experiments, the soil is shaken and suspended in solution for many hours. This does not mimic the soil in field conditions where the soil water can move through pores of different size and thus, the water retention time can differ between soils. Much of the soil mineral surface could have limited contact with the soil solution due to soil aggregates and preferential water flow (Jardine et al. 1990). By comparing the IM-isotherm approach for a batch experiment and adsorption by undisturbed soil cores, Qualls & Haines (1992b) found that isotherms obtained from the two experiments were comparable. The isotherm based on the undisturbed soil core experiment showed a slightly larger partition coefficient than for the one obtained from the batch experiment. A DOC adsorption column experiment using undisturbed soil cores could have increased the relevance of our results to field conditions.

5.2 Controls on the adsorption capacity

5.2.1 Soil properties

The variation in the partition coefficient between the P1 field replicates was mainly explained by the clay content and the amorphous Al and Fe content (Al_o & Fe_o), the clay content was the property that explained most of the variation (Table 6). In the present study, the clay content was not a measure of the clay mineral fraction, only a measure of the percentage of minerals in the clay size fraction which includes all mineral soil constituents <0.002 mm. As the mineralogy of the soils was not determined, it is not known if this fraction consisted mainly of clay minerals or sesquioxides. Earlier studies show different results regarding the importance of clay as a DOC adsorbent. Nelson et. al (1993) found that soils with a high clay content and a high specific surface area had a higher adsorption capacity than sandy soils, the DOC adsorption capacity ranged from a net DOC desorption (-5%) for the sandy soils, while the soil with a high clay content had a net DOC adsorption of 53%. They found a high coefficient of correlation between the DOC adsorption and the clay content (R=0.75), which corresponded well to our results. Kaiser & Zech (2000) reported a net reduction in the DOC adsorption by 41 to 85% when the sesquioxide coatings on clay surfaces were removed by oxalate extraction and ascorbic acid, indicating that the sesquioxides were responsible for much of the DOC adsorption to the clay size fraction. However, some of the soils adsorbed a substantial fraction even if the sesquioxide coating was removed, which shows that the clay minerals can be important adsorbents. Kothawala et al. (2009) did not find any correlation between the soil maximum adsorption capacity (Q_{max}) and the clay content.

The correlations suggested that the amorphous Al fractions were responsible for more of the DOC adsorption than the amorphous Fe fraction, as the Fe fractions were not significant correlated to the DOC adsorption (Table 5). P2 had a high content of amorphous Fe, but adsorbed only 14% of the highest initial concentration (Table 4). In contrast, P3 had a high content of amorphous Al, and adsorbed 60 % of the highest initial concentration. Previous studies have reported that the content of Fe and Al sesquioxides are important properties controlling the DOC adsorption, where amorphous fractions have been regarded as effective sorbents (Kaiser et al. 1996; Kaiser & Zech 1998; Kothawala et al. 2009; Lilienfein et al. 2004; Moore et al. 1992). Moore et al. (1992) compared the DOC adsorption capacity for soils with different sesquioxide content, including three podzols. The podzol with the highest Al and Fe sesquioxide content had a partition coefficient of 0.72. The two podzols with lower sesquioxide content had partition coefficients of 0.28 and 0.50; it was lowest for the soil with the lowest

sesquioxide content. They did not find any correlation between the clay content and the partition coefficient. By covering the soil material with different sesquioxides, Kaiser & Zech (1998) found a distinct increase in the DOC adsorption. The greatest effect on the DOC adsorption was seen when amorphous Al was added. These findings are in agreement with our results; the correlations showed that the amorphous Al fractions are significant correlated to the partition coefficient (m; Table 5).

In the present study, no direct measurements were performed to obtain information about the dominating adsorption mechanisms. However, a pH increase with increasing DOC addition was observed in the final solution for all soil samples (Fig. 13), which suggests that ligand exchange occurred as a DOC adsorption mechanism. When ligand exchange occurs, the DOC exchanges OH^- on the mineral surfaces which can result in a pH rise (Weigand & Totsche 1998). This is in agreement with results reported by Zysset & Berggren (2001) who suggested ligand exchange as a possible mechanism. Jardine et al. (1989) compared the DOC adsorption for the same soil with different pH and found that the maximum adsorption occurred at pH 4.5. At higher pH (>7), the DOC will be negatively charged as most of the soil minerals, thus the DOC adsorption will be less effective due to repulsion. No correlations were found between pH and the different adsorption parameters, suggesting that pH was not a dominant factor controlling DOC adsorption in the soils in this study.

5.2.2 Release of initial adsorbed dissolved organic carbon

The release of initial adsorbed DOC (b_L) was dependent on the soil organic C (%) content, suggesting that soils with high C content had a large DOC desorption potential (Table 5). This corresponds to results reported by earlier studies (e.g. Kaiser et al. 1996; Kothawala et al. 2009). The release of initial adsorbed DOC is not a measure of the total initial adsorbed DOC as some DOC may be strongly adsorbed (Jardine et al. 1989). The initial desorbed DOC was well correlated with the null-point (np), the DOC concentration where no net adsorption or desorption occurs. Thus, increasing release of initial adsorbed DOC resulted in a larger null-point. The null-point showed a significant negative correlation with the DOC adsorbed at the highest initial concentration (RE_{130}), the DOC adsorption decreased with increasing null-point. Consequently, it seems that soils with high release of initial adsorbed DOC have a lower DOC adsorption capacity. A high DOC adsorption was expected for the P1 field replicate with the highest content of clay and amorphous Al and Fe (Field replicate 10, Appendix 2). However, this soil sample

adsorbed only 22% of the added DOC at the highest initial concentration, which was close to the average DOC adsorption for P1. This soil sample had the largest release of initial adsorbed DOC and also the largest reactive soil pool (RSP) of all the ten P1 field replicates, which could suggest that adsorption sites were occupied (Jardine et al. 1989). According to Nodvin et al. (1986), a high RSP indicates that a high amount of the initial adsorbed DOC is readily exchangeable. Corresponding results were seen for P2, this soil was expected to adsorb a large amount of DOC due to the high content of Fe sesquioxides. However, P2 did only adsorb 14% of the highest initial DOC concentration (Table 3). These findings is supported by results reported by Guggenberger & Kaiser (2003) who observed a high DOC adsorption in horizons with low initial C content. Mineral subsoils are generally low in organic C and can therefore have a higher number of available adsorption sites (Kaiser & Zech 2000). Zysset & Berggren (2001) focused on the DOC adsorption in different horizons of a podzol developed on parent material with a low content of readily weatherable minerals. Despite a lower content of Al and Fe sesquioxides than for our soils, they reported partition coefficients ranging from 0.52 to 0.79. The soil in their study had a much lower release of initial adsorbed DOC than P1, which could have caused the large partition coefficient despite the low content of Al and Fe sesquioxides. The importance of the initial adsorbed DOC could have been studied by grouping the field replicates by content of initial adsorbed DOC.

The positive correlation between the release of initial adsorbed DOC (b_L) and the amorphous Fe content (Fe_o) suggested that increasing content of amorphous Fe can result in a higher potential desorbed DOC (Table 5). The reason of the relationship between b_L and Fe_A is unclear; it seemed that the DOC was more weakly adsorbed to the amorphous Fe (Fe_o) than to the amorphous Al fractions (Al_o). As the Al concentration in soil solution in general is higher than the Fe (Riise et al. 2000), the dissolution of DOC associated with Fe could have been caused by a shift in the soil-solution equilibrium; more Fe was dissolved due to a lower Fe concentration in the stock DOC solution. No publications reporting similar results have been found.

5.2.3 Variability between field replicates

For P1, the net DOC adsorption ranged from 5 to 47%, indicating a great variation between field replicates. The ten P1 field replicates were chosen to represent a poorly podzolized soil with a low Al and Fe content, equivalent to soil profile P1. As the sample points were distributed with 10 metres distance at a line following the vegetation and topography, similar soil properties were

expected. However, the variation in soil properties and DOC adsorption capacities for among field replicates was high (Appendix 2 & 4). A soil classification was only performed on soil profile P1, which could not be classified as a podzol (Spodosol) due to low sesquioxide content (Soil Survey Staff 2010). Due to the great variation between P1 field replicates, some of the replicates may have differed from the classification based on soil profile P1 (Appendix 1). The variation between the field replicates illustrates that is difficult to determine the DOC adsorption capacity for a soil based on sample points, even within a confined area.

5.4 Hydrophobicity index

In the present study, the DOC was not fractionated into hydrophobic and hydrophilic fractions. However, a hydrophobicity index (HI) was obtained for both the O- and B-horizon soil samples from the mid-infrared reflectance spectroscopy (MIR) analysis. The HI indicated that there was an enrichment of hydrophobic organic functional groups in the B-horizon in comparison to the O-horizons; all the B-horizon soil samples had a larger HI than the O-horizon samples. This index can be used as a comparison of the relative contribution of hydrophobic C between samples, not as a quantitative measure (Capriel et al. 1995). The enrichment of hydrophobic forms in the mineral horizon is in agreement with earlier findings (e.g. Jardine et al. 1989; Kaiser et al. 1996; Kaiser & Zech 1998). Kaiser et al. (1996) demonstrated that most of the DOC released from the initial adsorbed DOC was mainly hydrophilic, the hydrophobic fractions exchanged the hydrophilic fractions. Jardine et al. (1989) concluded that the hydrophobic DOC fractions were adsorbed by physical adsorption, where 80% of the adsorbed DOC was hydrophobic. No published literature using the MIR approach to measure the hydrophobic C enrichment in mineral soils has been found. Because this method cannot be used as a quantitative measure, the results from the MIR analysis could have been easier to interpret if an additional fractionation of the initial adsorbed DOC and the DOC stock solution into hydrophobic and hydrophilic fractions had been performed, e.g. according to Kaiser et al. (1996).

5.5 Adsorption capacity in relation to future climate changes

Due to the expected increases in DOC production and water transport in northern regions, it was of interest to include a DOC concentration range which was above the concentrations for the study site. The DOC concentration in soil solution at the study site was not measured; however, when reviewing earlier findings, the DOC concentration range used in the DOC adsorption experiments seem to exceed the DOC concentrations expected in the soil solution at the study

site. When extracting DOC from the O-horizon, a DOC concentration of 73 mg C L^{-1} was achieved, the solution had to be concentrated to obtain a solution with a DOC concentration of 129 mg C L^{-1}. Wu et al. (2010) monitored the soil and throughfall DOC concentrations in the period 1996-2006 for 16 locations in Norway. For the upper 5 cm of the soil, the average DOC concentrations in soil solution ranged from 5.0 to 49 mg C L^{-1}, while the concentration decreased with depth. For the same soil horizon at the monitoring station at Svanhovd in Eastern Finnmark, located 40 km south-east of the study area in the present study, the average DOC concentration for was 30 mg C L^{-1}. These findings suggests that substantial increases in the DOC concentrations are needed to exceed a DOC concentration of 129 mg C L^{-1}, which was the highest initial concentration used in the present DOC adsorption experiment.

The low DOC adsorption (19%) at the highest initial concentration for the P1 B-horizon suggested that much of the DOC input to the B-horizons could be leached to the underlying soil. Even at addition of low DOC concentrations, a large fraction of the DOC remained in soil solution (Table 3). The soil adsorbed the largest fraction (24%) at when a DOC concentration of 46 mg C L^{-1}, while the fraction decreased with increasing addition after this concentration. These results showed that the DOC removal from soil solution were different at different concentrations.

The DOC adsorption capacity of the soil will be dependent on the adsorption by the whole soil profile, not on the adsorption capacity of the B-horizon alone. The thickness of the soil horizons and the DOC adsorption capacity of the individual horizons will therefore be important when the adsorption capacity of a soil is evaluated (Guggenberger & Kaiser 2003). As subsoil horizons can adsorb considerable amounts of DOC, these horizons should be evaluated when considering the DOC adsorption capacity of a soil (Kaiser & Zech 2000). Rock, gravel and sand were the main constituents of the poorly podzolized soil's subsoil (Appendix 1), which suggests that the subsoil has a low DOC adsorption capacity and that the B-horizon is the horizon which can adsorb the most significant amounts of DOC.

6. Conclusion

The focus of this study was the DOC adsorption by a poorly podzolized soil situated in Neiden, Finnmark, in northern Norway. The results showed that the poorly podzolized soil had a DOC adsorption capacity in the range reported by earlier studies focusing on more podzolized soils. It could therefore not be concluded that this soil has a lower DOC adsorption capacity than more developed soils. It was a great variability in both the DOC adsorption and the soil properties for the ten field replicates of the poorly podzolized soil, even within a confined area. A stepwise multiple regression analysis revealed that the clay content, in addition to amorphous Al and Fe content, were the best predictors of the DOC adsorption capacity of this soil. In addition, the DOC adsorption seemed to be limited by occupation of adsorption sites, as soils with a high release of initial adsorbed DOC seemed to have a lower DOC adsorption capacity. Few studies have focused on the DOC adsorption by poorly podzolized soils, and few comparisons of DOC adsorption by different soil types have been performed. Adsorption is an important mechanism of DOC removal to ground- and surface water and can act as a buffering process. As the poorly podzolized soil showed a great variability in DOC adsorption, the soil's ability of buffering DOC inputs will also vary. Given increases in production and water transport of DOC in northern regions, the DOC adsorption by mineral soils could be an important buffering mechanism. Increases in DOC can result in deterioration of water quality and destruction of water habitats. Therefore, more studies should be conducted to increase the knowledge regarding DOC adsorption by poorly podzolized soils.

7. List of references

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8. Appendixes

8.1 List of appendixes

Appendix 1. Soil profile descriptions

Soil profile descriptions with pictures of the profile wall for soil profile P1, P2 and P3. P1 are the poorly podzolized soil, P2 are the soil with high iron sesquioxide content while P3 has a high content of aluminium sesquioxides. The soils were classified after Soil Survey Staff (2010).

Soil profile P1

Location	Transition area between the bog and upland Neiden, Sørvaranger, Finnmark 10 m from the gravelled road Coordinates: N69° 41' 06'' E29° 11' 37'' M.a.s.l: 88 m	
Vegetation	Mountain birch (*Betula pubescens*) 2-3 meter high dominated the vegetation. The ground vegetation was dominated by *Empetrum nigrum*, *Vaccinium vitis-idea*, *Vaccinium Myrtillus* and some *Vaccinium uliginosum* and *Betula nana* some *Cladonia*.	
Topography	East(NorthEast) facing gently sloping (5-10%) lower part of a ridge	
Drainage	Well drained	
Parent material	Beach deposits (well sorted fine sand) over till deposits	
Classificaton	Spodic Dystrocryepts	
Comments	Particle size analysis has not been performed these classes are field guesstimates. All colours are given as moist Munsell Soil Colours (Munsell 2000)	

Of	**0-6**	Dark reddish brown (5YR3/2), many roots, partly fermented organic matter, abrupt smooth boundary
E	**6-9**	Pinkish gray (5YR6/2), 1oamy fine sand; no rock fragments; structureless to weak fine angular block; very friable; abrupt wavy boundary
Bs	**9-25**	Brown (7.5YR4/4; 10YR5/3), with patches of strong brown (7,5YR5/6,); loamy fine sand; no rock fragments; structureless to very weak fine angular block; loose; gradual wavy boundary
BC	**25-43**	Olive brown (2.5Y4/3; 2.5Y4/4); loamy sand; no rock fragments; struchtureless; loose; clear smooth boundary
2BC	**43-80**	Dark yellowish brown (10YR4/4) Loamy medium sand; common rock fragments mainly gravel; structureless; loose; clear smooth boundary
2C	**80-90+**	Olive gray (5Y4/2) Loamy medium sand; common rock fragments mainly gravel; structureless; loose

Soil profile P2

Location	Morain ridge Neiden, Sørvaranger, Finnmark 10 m towards west from the dirt road Coordinates: N69° 41' 06'' E29° 11' 33'' M.a.s.l: 94 m
Vegetation	Mountain birch (*Betula pubescens*) and *Ledum palustre*. The ground vegetation was dominated by *Empetrum nigrum*, *Cladonia sps*, *Vaccinium vitis-idea*, *Vaccinium myrtillus* and some *Vaccinium uliginosum*, *Betula nana*, *Loiseleuria procunbens* and *Arctostaphylos alpinus*.
Topography	East(North-east) facing sloping (15%) middle part of a moraine ridge
Drainage	Well drained
Parent material	Till deposits
Classificaton	Typic Duricryods
Comments	Particle size analysis has not been performed these classes are field guesstimates. Cementation and coarse material restricted digging to deeper depths. All colours are given as moist Munsell Soil Colours.

Of	**0-5**	Dark reddish brown (5YR2.5/2) high root density; fermented organic matter in between living roots; abrupt smooth boundary
E	**5-8**	Pinkish gray (7.5YR6/2); medium sand; no rock fragments; structureless to weak fine angular block; very friable; abrupt smooth boundary
Bhs	**8-15**	Brown (7.5YR4/4), medium sand; few rock fragments; weak, fine to medium subangular blocks; clear smooth boundary
Bhsm	**15-35**	Very dusky red (2.5YR2.5/2) with large patches of dark reddish brown (2.5YR3/3), medium sand; common rock fragments; continuously moderately cemented by sesquioxides; very few fine roots; gradual wavy boundary
BC	**35-57+**	Brown (7.5YR4/4) medium sand; many rock fragments; stuctureless

Soil profile P3

Location	Plateau summit Neiden, Sørvaranger, Finnmark 10 m from the dirt road Coordinates: N69° 41' 05'' E29° 11' 32'' M.a.s.l: 98 m	

Vegetation   Few low mountain birch (*Betula pubescens).* The ground vegetation was dominated by *Cladonia* otherwise occurring vegetation was *Empetrum nigrum*, *Vaccinium vitis-idea*, *Vaccinium myrtillus* and some *Vaccinium uliginosum*, *Betula nana*, *Loiseleuria procunbens* and *Arctostaphylos alpinus*.

Topography   East (North East) facing gently sloping (5-10%) lower part of a ridge

Drainage   Well drained

Parent material   Shallow till deposits over bedrock, pinkish coloured gneis

Classificaton   Lithic Dystrocryept

Comments   This is a disturbed soil either from trampling or frostchurning, therefore there is a large variability in the shallow soil, 1, 2, 4 refer to different faces of the profile walls, these are sampled and analysed individually. All colours are given as moist Munsell Soil Colours. Particle size analysis has not been performed, therefore, these classes are field guesstimates.

1	Of	0-3.5	Dark reddish brown (5YR3/2) common thin roots abrupt smooth boundary.
1	B1	3.5-14	Strong brown (7.5YR4/6); loamy sand; structureless; clear smooth boundary.
1	B2	14-24	Brown (7.5YR4/4; 10YR5/3) with patches with strong brown (7.5YR5/6), loamy sand; structureless.
4	Oh	0-3	Very dark brown (7.5R2.5/2); humified organic material with the dark colour characteristic of lichen derived material; few fine roots; abrupt smooth boundary
4	E	3-4.5	Brown (10YR4/3); loamy sand; structureless; abrupt smooth boundary.
4	Bs	4.5-16	Brown (7.5YR4/4) with streaks of strong brown (7,5YR4/6) loamy sand; structureless.
2	A	0-7	Dark brown (10YR3/3); many fine roots; loamy sand; structureless; clear smooth boundary
2	B	7-15	Yellowish brown (10YR5/8) loamy sand; structureless.

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Appendix 2. B-horizon soil properties for the field replicates (1-10) of the poorly podzolized soil (P1)

Soil property	1	2	3	4	5	6	7	8	9	10
Soil pH (in H_2O)	5.47	4.99	5.13	5.10	5.30	4.80	5.25	5.19	4.60	4.87
Sand (%)	77.6	85.1	69.3	76.2	62.8	68.1	61.9	55.8	72.7	48.5
Clay (%)	2.4	1.3	5.8	6.3	8.0	11.0	8.9	10.4	5.1	9.7
Soil C (%)	1.5	1.1	3.4	1.1	1.5	2.1	1.7	1.3	1.0	2.6
Soil N (%)	0.05	0.02	0.11	0.03	0.04	0.07	0.05	0.04	0.02	0.08
C/N	33	53	33	41	36	32	38	33	47	35
Organic matter	3.6	2.8	7.9	3.2	4.1	5.5	4.9	4.3	2.7	7.2
Dry matter content	99.4	99.5	98.6	99.6	99.4	99.2	99.3	99.4	99.9	98.9
Fe_d (mg Fe kg^{-1})[a]	8164±107	9468±276	13460±179	6991±199	11911±149	14535±380	13325±270	21813±265	14845±351	25661±1022
Fe_o (mg Fe kg^{-1})[b]	3697±69	3417±60	9097±296	4677±262	5797±151	9457±284	5277±60	4037±139	5137±139	9137±35
Fe_p (mg Fe kg^{-1})[c]	2079±92	1379±60	4499±262	2399±60	3079±151	4499±317	2459±60	1319±159	1659±92	2619±35
Al_d (mg Al kg^{-1})[a]	3608±88	2511±36	6797±36	3120±134	4055±34	3015±46	4769±78	4894±17	1764±65	7335±302
Al_o (mg Al kg^{-1})[b]	4577±92	3357±159	7657±351	3777±216	4217±69	3357±104	5437±92	5457±216	1277±35	8677±173
Al_p (mg Al kg^{-1})[c]	2899±69	2019±92	5759±262	2639±60	3099±92	2559±183	3399±69	2379±69	839±60	4239±35
Si_o (mg Si kg^{-1})[b]	810±0	570±0	770±69	390±104	370±35	0	63±0	1130±92	0	1810±69
Fe_{cry} (mg Fe kg^{-1})[d]	4467±174	6052±331	4363±358	2314±250	6115±149	5078±151	8048±239	17776±380	9708±380	16524±1056
Fe_{IA} (mg Al kg^{-1})[e]	1619±60	2039±60	4599±227	2279±317	2719±35	4959±517	2819±120	2719±173	3479±180	6519±69
Al_{IA} (mg Al kg^{-1})[f]	1679±159	1339±69	1899±330	1139±275	1119±35	799±271	2039±60	3079±271	439±35	4439±159
RE_{130} (mg C kg^{-1})	102	210	167	229	326	223	299	604	61	285
np (mg C^{-1})	379	148	351	92	140	395	172	75	510	367
b_L (mg C kg^{-1})	113	65	169	51	92	186	82	56	143	185
m (unitless)	0.24	0.31	0.41	0.42	0.46	0.42	0.42	0.63	0.29	0.47
b_{IM} (mg C kg^{-1})	101	54	150	46	73	172	78	44	130	170
RSP (mg C kg^{-1})	133	79	253	79	135	133	299	119	182	321
HI (unitless)[g]	9.8	10.6	4.9	10.4	12.9	10.6	12.9	15.7	31.2	9.5

a Dithionite soluble, b Oxalate soluble, c Pyrophosphate soluble, d $Fe_{cry}=Fe_d-Fe_o$, e $Fe_{IA}=Fe_o-Fe_p$, f $Al_{IA}=Al_o-Al_p$, g hydrophobicity index obtained from the mid infrared (MIR) spectroscopy analysis.

Appendix 3.O-horizon soil properties for the poorly podzolized soil (P1)

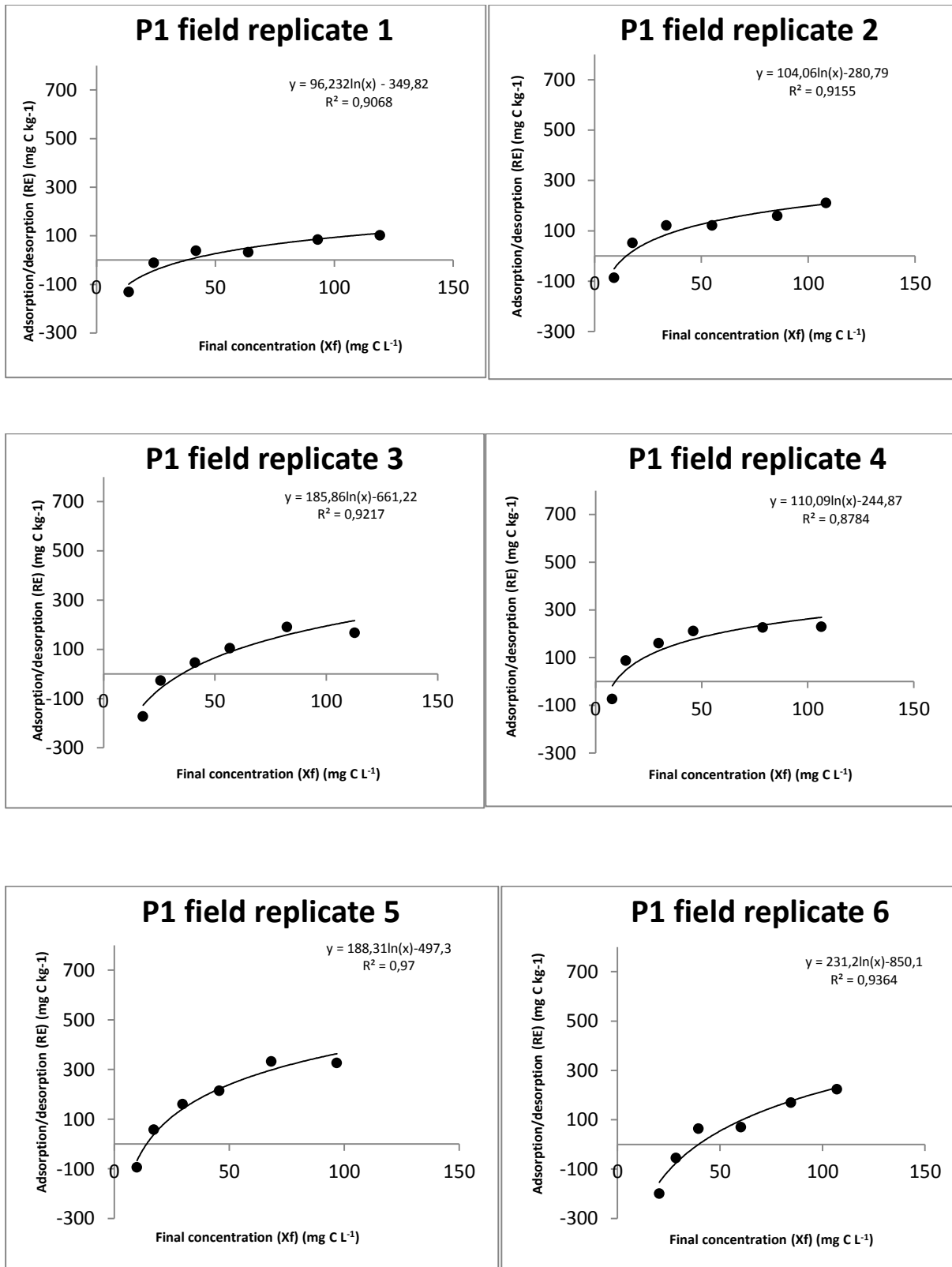| Soil property	O-horizon samples									
	1	2	3	4	5	6	7	8	9	10
Soil pH (H2O)	4.05	4.09	3.95	4.04	3.97	3.89	3.95	4.02	3.96	4.08
Soil C (%)	51.1	48.5	47.7	50.2	50.4	53.3	52.4	52.2	51.8	48.9
Soil N (%)	0.94	0.86	0.69	1.01	1.36	1.20	1.33	1.24	1.45	0.96
C/N	54	56	69	50	37	44	40	42	36	51
Organic matter %)	93.27	87.85	94.45	90.93	74.16	91.79	92.80	78.40	91.73	84.89
Dry matter content (%)	94.37	94.87	94.62	93.23	94.28	94.51	94.08	95.50	94.24	95.18
HI (unitless)	2.3	2.6	2.7	2.1	2.7	2.3	2.1	2.6	2.2	2.5

Appendix 4. Net DOC adsorption/desorption

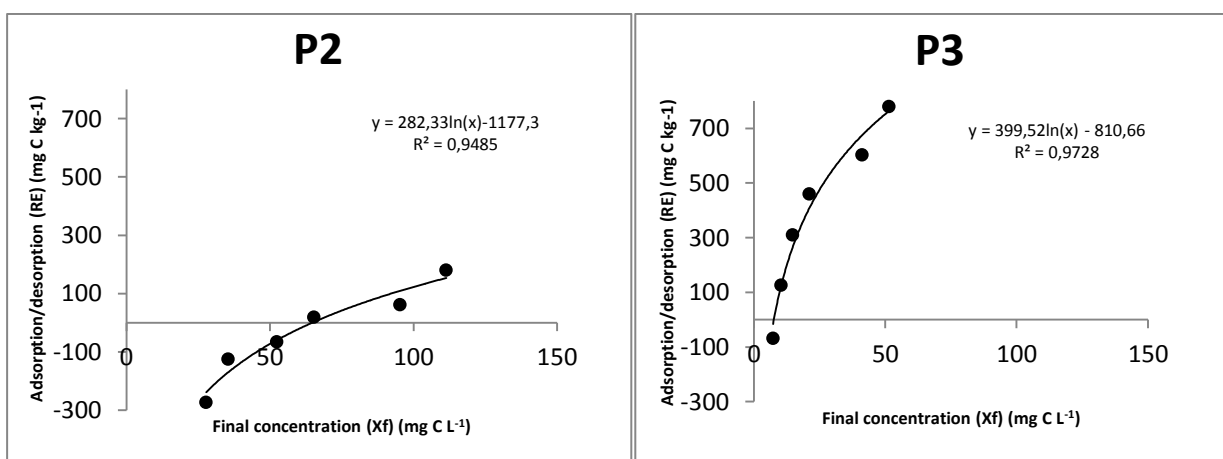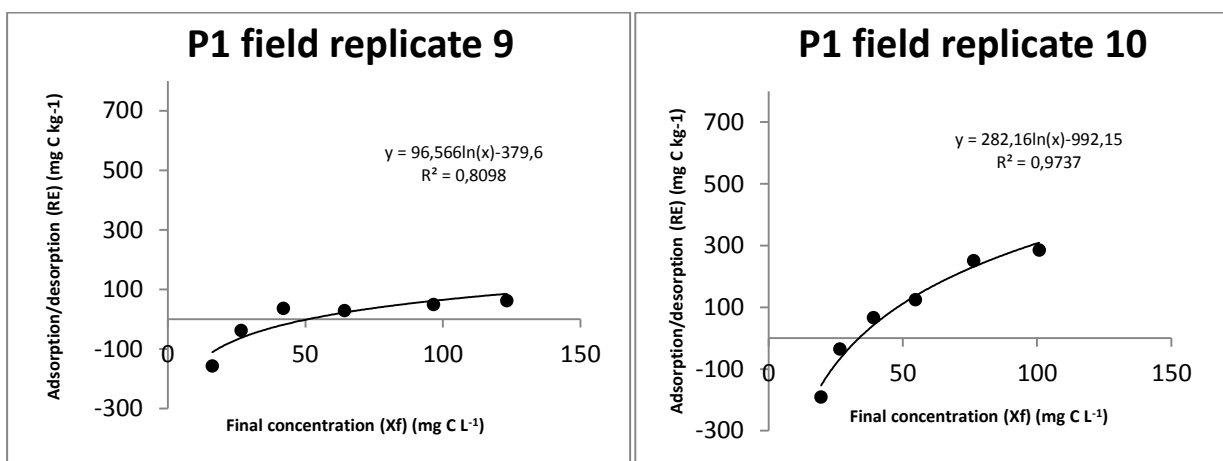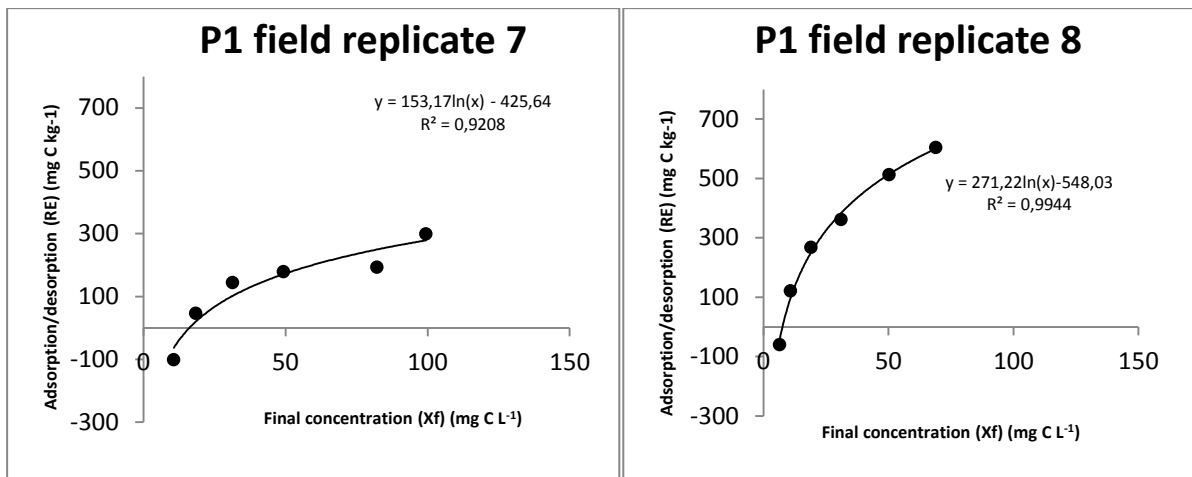Adsorption (mg C kg^{-1}), final concentration (mg C L^{-1}) and net DOC adsorption (%) for the B-horizon soil samples. A negative adsorption indicates a net DOC desorption. Soil samples 1-10 are P1 field replicates, while P2 and P3 are the soil samples with contrasting sesquioxide content.

Soil sample		Initial DOC concentration (mg C L^{-1})						Net DOC (%) adsorbed at 129 mg C L^{-1}
		0	23	46	67	101	129	
1	Final conc(mg C L^{-1})	14±0.8	24±1.0	42±1.5	64±2.4	93±2.8	119±3.4	
	Adsorption(mg C kg^{-1})	-131±8	-12±10	39±15	32±24	84±28	102±34	8
2	Final conc(mg C L^{-1})	9±0.1	18±0.0	34±0.8	55±4.0	86±0.8	109±1.5	
	Adsorption(mg C kg^{-1})	-87±1	53±0.3	121±8	121±40	159±8	210±15	16
3	Final conc(mg C L^{-1})	18±1.4	26±1.6	41±0.3	57±0.5	82±2.7	113±0.5	
	Adsorption(mg C kg^{-1})	-173±14	-27±16	46±3	105±5	191±27	167±5	13
4	Final conc(mg C L^{-1})	8±1.1	14±0.4	30±0.4	46±0.4	79±1.5	107±0.8	
	Adsorption(mg C kg^{-1})	-74±11	87±4	160±4	211±4	226±15	229±8	17
5	Final conc(mg C L^{-1})	10±0.1	17±0.1	30±2.8	46±2.6	68±0.6	97±2.2	
	Adsorption(mg C kg^{-1})	-94±1	58±1	160±28	215±26	332±6	326±22	25
6	Final conc(mg C L^{-1})	20±1.6	28±1.2	39±0.8	60±2.4	85±0.2	107±4.9	
	Adsorption(mg C kg^{-1})	-199±16	-55±12	64±8	70±24	170±2	223±49	17
7	Final conc(mg C L^{-1})	11±0.4	18±0.2	31±1.1	49±4.7	82±15	100±1.4	
	Adsorption(mg C kg^{-1})	-102±4	46±24	144±11	179±47	193±150	299±14	23
8	Final conc(mg C L^{-1})	7±0.1	11±0.5	19±0.5	31±1.5	50±6.0	69±1.1	
	Adsorption(mg C kg^{-1})	-60±1	121±5	267±5	361±15	513±60	604±11	47
9	Final conc(mg C L^{-1})	16±0.5	27±0.3	42±2.6	64±0.7	97±1.6	123±3.9	
	Adsorption(mg C kg^{-1})	-158±5	-38±3	36±26	29±7	48±16	61±39	5
10	Final conc(mg C L^{-1})	20±1.1	27±0.1	39±1.8	55±0.3	76±2.1	101±0.5	
	Adsorption(mg C kg^{-1})	-191±11	-36±1	67±18	124±3	251±21	285±5.4	22
P2	Final conc(mg C L^{-1})	28±0.2	36±0.9	52±1.3	65±2.8	95±2.1	111±5.6	
	Adsorption(mg C kg^{-1})	-273±2	-125±9	-66±13	18±28	62±21	180±56	14
P3	Final conc(mg C L^{-1})	7±0.4	10±1.5	15±0.8	21±0.7	41±1.0	51±5.7	
	Adsorption(mg C kg^{-1})	-68±4	127±15	311±7.5	460±7	603±10	780±57	60

Appendix 5. Modified Langmuir isotherm plots with final concentration approach
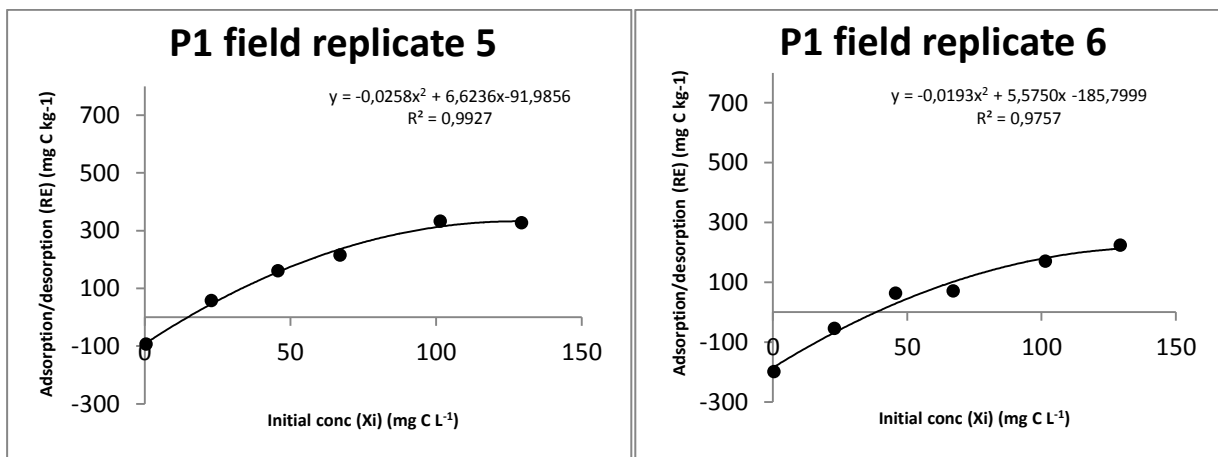
Field replicates 1-10 shows the adsorption for the replicates of the poorly podzolized soil (P1). P2 is the soil with higher iron content, while P3 is the soil with higher aluminium content. The initial DOC concentration range is 0-129 mg C L^{-1}.

P1 field replicate 1

$y = 96,232\ln(x) - 349,82$
$R^2 = 0,9068$

Adsorption/desorption (RE) (mg C kg^{-1})

Final concentration (Xf) (mg C L^{-1})

P1 field replicate 2

$y = 104,06\ln(x) - 280,79$
$R^2 = 0,9155$

Adsorption/desorption (RE) (mg C kg^{-1})

Final concentration (Xf) (mg C L^{-1})

P1 field replicate 3

$y = 185,86\ln(x) - 661,22$
$R^2 = 0,9217$

Adsorption/desorption (RE) (mg C kg^{-1})

Final concentration (Xf) (mg C L^{-1})

P1 field replicate 4

$y = 110,09\ln(x) - 244,87$
$R^2 = 0,8784$

Adsorption/desorption (RE) (mg C kg^{-1})

Final concentration (Xf) (mg C L^{-1})

P1 field replicate 5

$y = 188,31\ln(x) - 497,3$
$R^2 = 0,97$

Adsorption/desorption (RE) (mg C kg^{-1})

Final concentration (Xf) (mg C L^{-1})

P1 field replicate 6

$y = 231,2\ln(x) - 850,1$
$R^2 = 0,9364$

Adsorption/desorption (RE) (mg C kg^{-1})

Final concentration (Xf) (mg C L^{-1})

P1 field replicate 7

y = 153,17ln(x) - 425,64
R² = 0,9208

P1 field replicate 8

y = 271,22ln(x)-548,03
R² = 0,9944

P1 field replicate 9

y = 96,566ln(x)-379,6
R² = 0,8098

P1 field replicate 10

y = 282,16ln(x)-992,15
R² = 0,9737

P2

y = 282,33ln(x)-1177,3
R² = 0,9485

P3

y = 399,52ln(x) - 810,66
R² = 0,9728

Axis labels (all plots):
Adsorption/desorption (RE) (mg C kg-1)
Final concentration (Xf) (mg C L⁻¹)

Appendix 6. Modified Langmuir isotherm plots with initial concentration approach
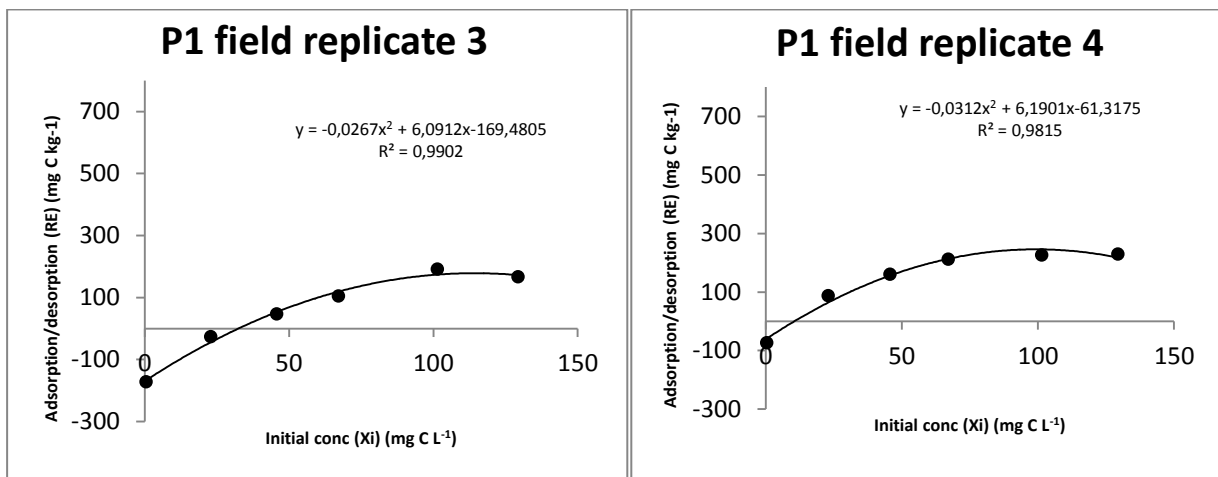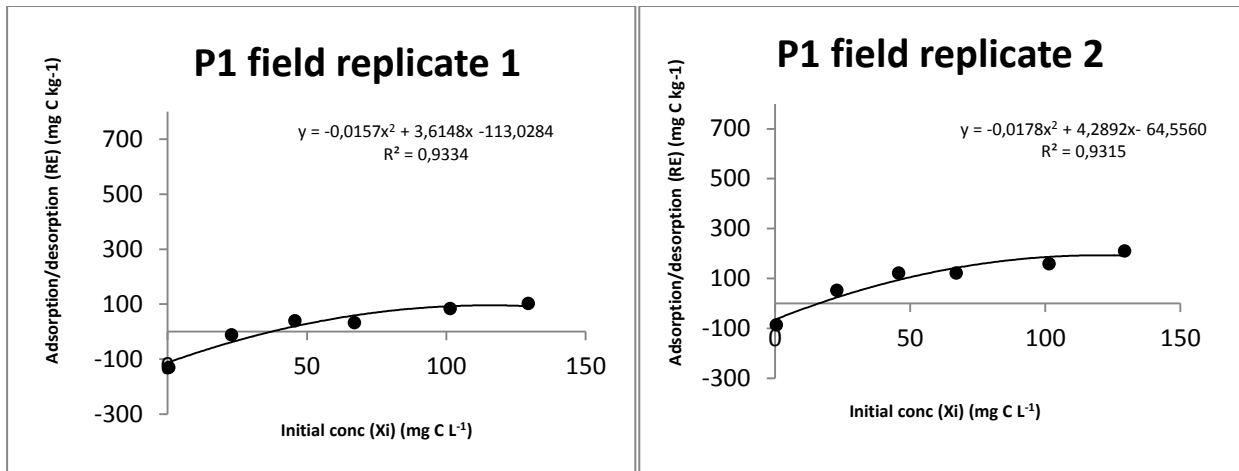
Field replicates 1-10 shows the adsorption for the replicates of the poorly podzolized soil (P1). P2 is the soil with higher iron content, while P3 is the soil with higher aluminium content. The initial DOC concentration range is 0-129 mg C L^{-1}.
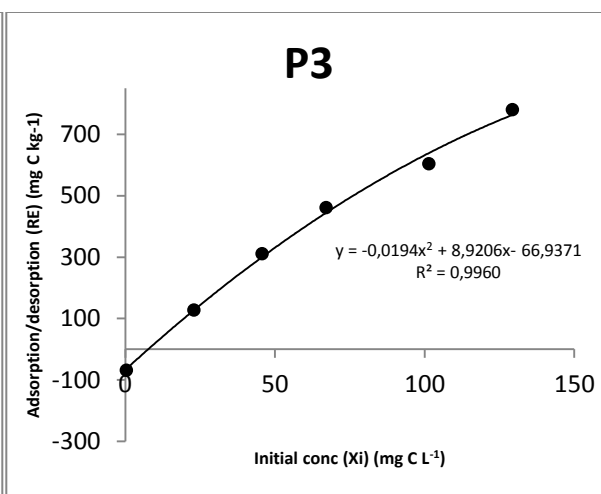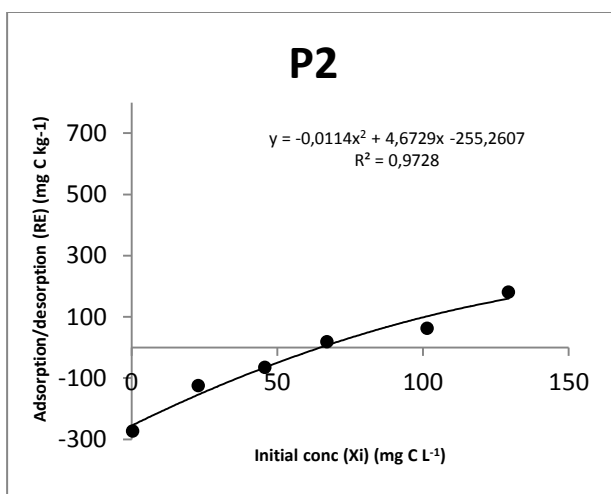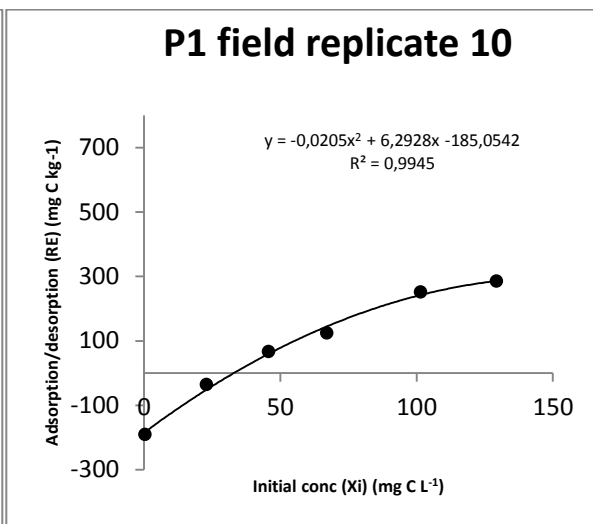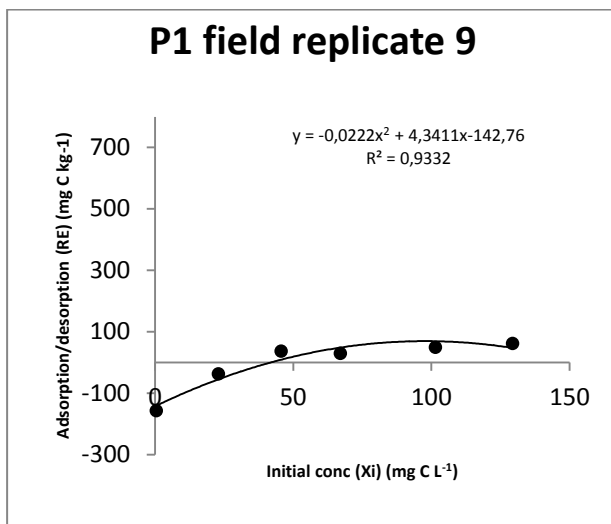

P1 field replicate 1
$y = -0{,}0157x^2 + 3{,}6148x - 113{,}0284$
$R^2 = 0{,}9334$

P1 field replicate 2
$y = -0{,}0178x^2 + 4{,}2892x - 64{,}5560$
$R^2 = 0{,}9315$

P1 field replicate 3
$y = -0{,}0267x^2 + 6{,}0912x - 169{,}4805$
$R^2 = 0{,}9902$

P1 field replicate 4
$y = -0{,}0312x^2 + 6{,}1901x - 61{,}3175$
$R^2 = 0{,}9815$

P1 field replicate 5
$y = -0{,}0258x^2 + 6{,}6236x - 91{,}9856$
$R^2 = 0{,}9927$

P1 field replicate 6
$y = -0{,}0193x^2 + 5{,}5750x - 185{,}7999$
$R^2 = 0{,}9757$

P1 field replicate 7

$y = -0,0188x^2 + 5,1528x - 81,6170$
$R^2 = 0,9418$

Adsorption/desorption (RE) (mg C kg-1)

Initial conc (Xi) (mg C L^{-1})

P1 field replicate 8

$y = -0,0212x^2 + 7,8078x - 56,0338$
$R^2 = 0,9986$

Adsorption/desorption (RE) (mg C kg-1)

Initial conc (Xi) (mg C L^{-1})

P1 field replicate 9

$y = -0,0222x^2 + 4,3411x - 142,76$
$R^2 = 0,9332$

Adsorption/desorption (RE) (mg C kg-1)

Initial conc (Xi) (mg C L^{-1})

P1 field replicate 10

$y = -0,0205x^2 + 6,2928x - 185,0542$
$R^2 = 0,9945$

Adsorption/desorption (RE) (mg C kg-1)

Initial conc (Xi) (mg C L^{-1})

P2

$y = -0,0114x^2 + 4,6729x - 255,2607$
$R^2 = 0,9728$

Adsorption/desorption (RE) (mg C kg-1)

Initial conc (Xi) (mg C L^{-1})

P3

$y = -0,0194x^2 + 8,9206x - 66,9371$
$R^2 = 0,9960$

Adsorption/desorption (RE) (mg C kg-1)

Initial conc (Xi) (mg C L^{-1})

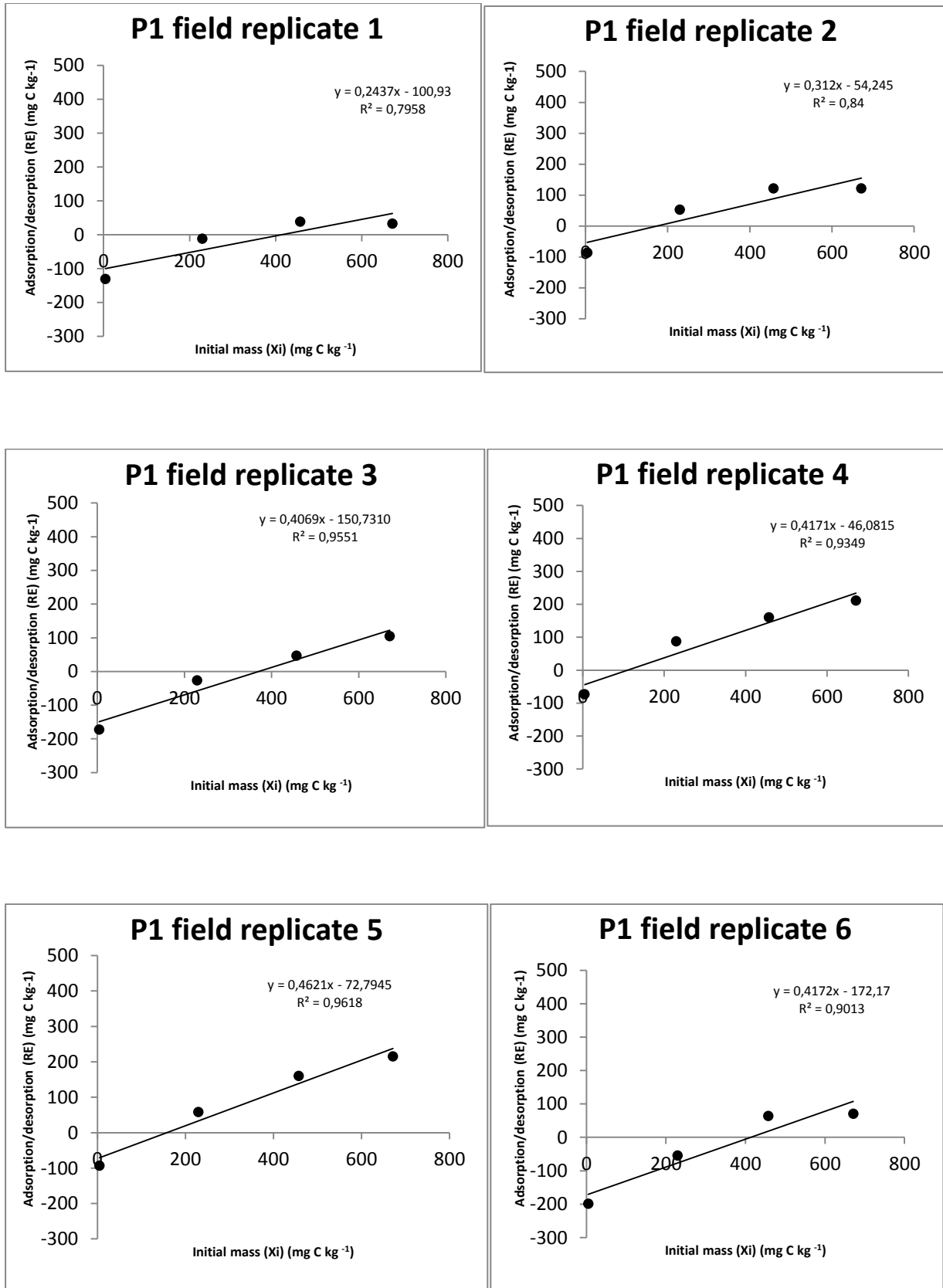# Appendix 7. Initial mass isotherm plots

Field replicates 1-10 shows the adsorption for the replicates of the poorly podzolized soil (P1). P2 is the soil with higher iron content, while P3 is the soil with higher aluminium content. The initial DOC concentration range is 0-67 mg C L^{-1}.
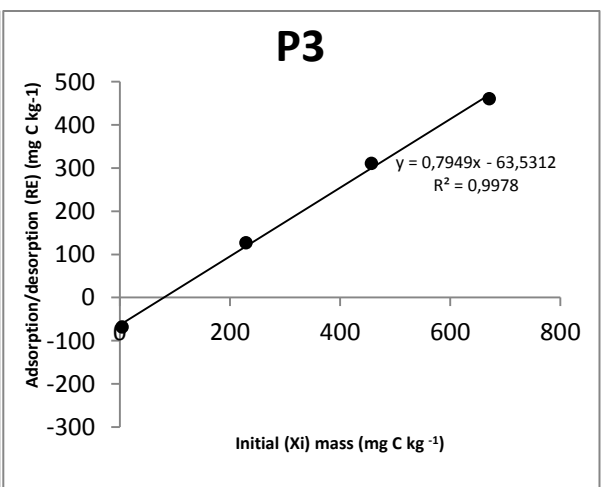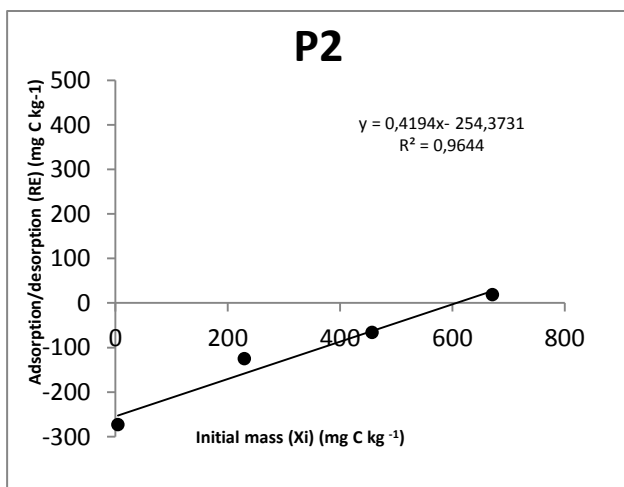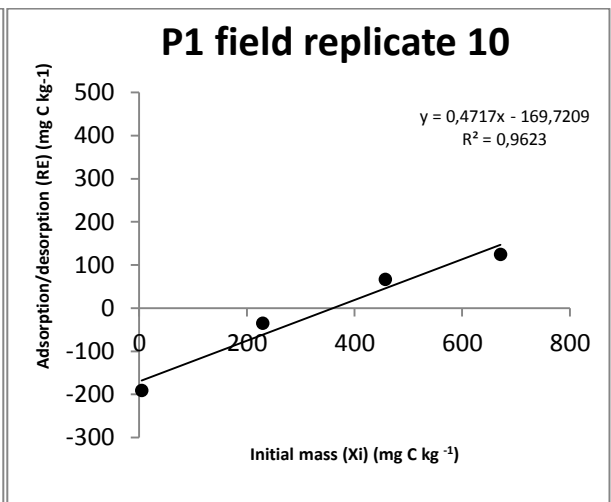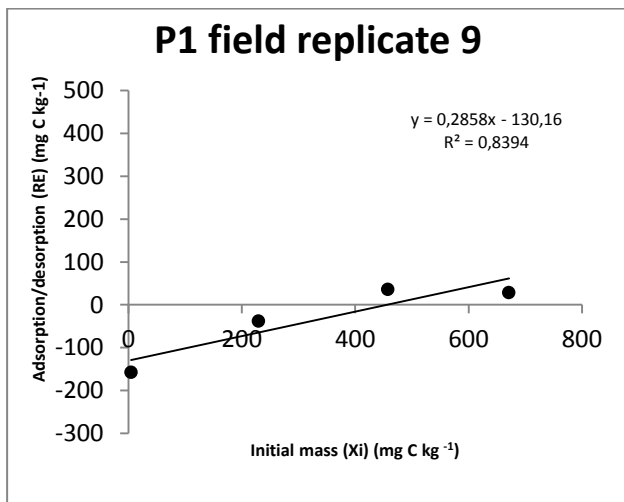

P1 field replicate 1
y = 0,2437x - 100,93
R² = 0,7958

P1 field replicate 2
y = 0,312x - 54,245
R² = 0,84

P1 field replicate 3
y = 0,4069x - 150,7310
R² = 0,9551

P1 field replicate 4
y = 0,4171x - 46,0815
R² = 0,9349

P1 field replicate 5
y = 0,4621x - 72,7945
R² = 0,9618

P1 field replicate 6
y = 0,4172x - 172,17
R² = 0,9013

P1 field replicate 7

$y = 0{,}4234x - 77{,}5592$
$R^2 = 0{,}9388$

P1 field replicate 8

$y = 0{,}6340x - 43{,}6522$
$R^2 = 0{,}9840$

P1 field replicate 9

$y = 0{,}2858x - 130{,}16$
$R^2 = 0{,}8394$

P1 field replicate 10

$y = 0{,}4717x - 169{,}7209$
$R^2 = 0{,}9623$

P2

$y = 0{,}4194x - 254{,}3731$
$R^2 = 0{,}9644$

P3

$y = 0{,}7949x - 63{,}5312$
$R^2 = 0{,}9978$

All plots have axes:
Adsorption/desorption (RE) (mg C kg-1) on the y-axis and Initial mass (Xi) (mg C kg $^{-1}$) on the x-axis.

Appendix 8. Gaussian curve fits

Gaussian curve fit with adsorption at the y-axis and the wavelength at the x-axis, obtained from the mid infrared (MIR) spectroscopy analysis. These curve fits were used to obtain the hydrophobicity index (HI) for O- and B-horizon samples. Sample X1-X10 are field replicate 1-10 of the poorly podzolized soil, while sample X11 and X12 are sample P2 and P3 respectively. The individual curves (coloured) are adsorption by the different functional groups.

B – horizon / X1   B – horizon / X3   B – horizon / X5

B – horizon / X2   B – horizon / X4   B – horizon / X6

B – horizon / X7   B – horizon / X9   B – horizon / X11

B – horizon / X8   B – horizon / X10   B – horizon / X12