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Long-term fate and transformations of vanadium in a pine forest soil with added converter lime

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ABSTRACT

A field-trial with different application rates of converter lime (0.2, 0.7 and 1.0 kg m^{-2}) was set up in a pine forest stand in southern Sweden in 1984. The lime contained 14.6 g kg^{-1} vanadium. The aim with this study was to evaluate the vanadium concentration and speciation in the soil 26 years after application. Samples of the organic mor layer and the mineral soil were analysed separately. The vanadium concentration decreased with soil depth, from 680 to 8 mg kg^{-1} soil. Analysis by vanadium K-edge XANES spectroscopy showed that vanadium(IV) was the predominant species in the mor layer. Further, iron and/or aluminium (hydr)oxides were important sorbents for vanadium(V) in the mineral soil. The speciation of dissolved vanadium, as determined by HPLC-ICP-MS, was dominated by vanadium(V), which is considered the most toxic vanadium species. However, the vanadium sorption capacity of the soil was sufficient to reduce the total bioavailable vanadium below phytotoxic levels. By combining two different vanadium speciation methods, this study was able to conclude that vanadium speciation in soils is governed by soil properties such as pH. organic matter content and the content of metal (hydr)oxides, but not by the vanadium species added to the soil.

Keywords: Vanadium; Soil; Converter lime; Speciation; XANES spectroscopy; HPLC-ICP-MS

1. Introduction

Vanadium (V) is a redox-sensitive metal that naturally occurs in rather low concentrations in soils (Salminen et al., 2005). By-products, slags, formed during the making of iron and steel can contain elevated vanadium concentrations (Proctor et al., 2002). This may be due to vanadium additions during the process, but vanadium can also be inherently present in the raw material used. These slags are frequently used in other fields of application e.g. for soil improvement and in landfills (Chaurand et al., 2007a; Frank et al., 1996). There are extreme cases with high vanadium releases to the environment. During the 1980's, cattle died from acute vanadium toxicity due to inappropriate use of basic slag that contained 3 % vanadium (Frank et al., 1996). Another example is the accidental release of the bauxite residue "red mud" in Hungary that contained about 1,100 mg kg^{-1} vanadium (Burke et al., 2012).

Common valence states of vanadium in nature are +4 and +5 (Wanty and Goldhaber, 1992). The most soluble species is the pentavalent oxyanion vanadate, $H_2VO_4^-$ or HVO_4^{2-}, which predominates under oxic and high-pH conditions. Its mobility in soil is to a large extent influenced by sorption to metal (hydr)oxides, especially those containing iron (Blackmore et al., 1996; Naeem et al., 2007; Peacock and Sherman, 2004; Wällstedt et al., 2010). In strongly acidic and aerobic environments vanadium(V) may coexist with the oxocation of vanadium(IV), vanadyl (VO^{2+}) (Wanty and Goldhaber, 1992). The mobility of vanadyl is determined by complexation to different ligands such as organic compounds (Lu et al., 1998; Wilson and Weber, 1979). Vanadium is rather immobile in soil (Cappuyns and Swennen, 2014; Martin and Kaplan, 1998), and its mobility and bioavailability is mainly determined by time and soil properties (Baken et al., 2012; Gäbler et al., 2009). Clay minerals together with metal (hydr)oxides and organic matter are important for vanadium retention (Cloy et al., 2011; Gäbler et al., 2009) and with time, the retained vanadium can become practically insoluble by incorporation into the soil matrix (Baken et al., 2012; Martin and Kaplan, 1998). Vanadium toxicity in soils is to a large extent controlled by the sorption properties of the soil (Larsson et al., 2013).

Additionally the vanadium redox chemistry also affects the toxicity (Seargeant and Stinson, 1979). Due to the similarities between vanadate and phosphate, vanadate is the most toxic vanadium species as it can inhibit phosphate-metabolizing enzymes.

There is a lack of knowledge regarding the long-term behavior of vanadium in soils, especially concerning its redox chemistry. Several methods have been developed to determine the solution speciation of vanadium in environmental samples. This is challenging due to the low concentrations and the redox-sensitive nature of vanadium (Pyrzynska and Wierzbicki, 2004). Most of the methods have been developed for water samples and not for soils. Further, changes of pH and redox conditions are often involved in the procedure. In one group of methods, complex-forming agents such as EDTA are added prior to analysis to prevent possible speciation changes (Aureli et al., 2008; Chen et al., 2007). The EDTA complexes $[VO(EDTA)]^{2-}$ and $[VO_2(EDTA)]^{3-}$ are formed for vanadium(IV) and vanadium(V) species, respectively (Komarova et al., 1991). The complexes can further be separated by anion exchange chromatography, which when coupled on-line to ICP-MS enables the measurement of vanadium species at low concentrations (Aureli et al., 2008).

By use of X-ray Absorption Near Edge Structure (XANES) spectroscopy, vanadium speciation can be determined on samples with no or only minor pre-treatment (Burke et al., 2012; Chaurand et al., 2007b). The vanadium K-edge XANES spectra have a pre-edge peak for which the area and intensity increase with increasing oxidation state. Moreover, its position changes with coordination and crystallinity (Chaurand et al., 2007b; Sutton et al., 2005; Wong et al., 1984). The main edge (often referred to as $E_{1/2}$) appears at higher energies with higher oxidation states (Sutton et al., 2005; Wong et al., 1984). Evaluation methods have been developed mainly for geological and metallurgical samples (Chaurand et al., 2007b; Giuli et al., 2004; Sutton et al., 2005). A third-degree polynomial relationship between the pre-edge peak intensity and oxidation state was used to determine the vanadium oxidation state in glasses (Sutton et al., 2005). Others have used a combination of the pre-edge peak intensity or area and centroid position (Burke et al., 2013; Chaurand et al., 2007b; Giuli et al., 2004). Comparing the $E_{1/2}$ for known and unknown samples is perhaps the simplest approach as it is easily compared with other studies (Burke et al., 2012; Mansour et al., 2002). However, the shape of the main edge may also give indications of the vanadium valence state and binding mode (Wong et al., 1984). With linear combination fitting (LCF) the spectra can be compared to a set of standards (Gerke et al., 2010). So far, this method has been more commonly used for e.g. phosphorus (Eveborn et al., 2009; Prietzel et al., 2010).

The objective of this study was to evaluate the fate and speciation of vanadium that was added by converter lime to a forest stand in southern Sweden in the 1980s. The main goal was to improve the knowledge of vanadium mobility in the environment on a long-term basis and to deepen the understanding of vanadium speciation in soils. Two speciation methods were used, XANES spectroscopy and HPLC-ICP-MS with EDTA complexation, to determine vanadium oxidation states in the solid and dissolved phase of the soil.

2. Materials and Methods

2.1. Field trial design

A field trial designed to investigate the effect of converter lime applications to soil was set up in the autumn of 1984 in a 15 year pine forest stand (*Pinus sylvestris*) with an undergrowth of Norway spruce (*Picea abies*). The field layer was dominated by blueberry (*Vaccinium myrtillus*) and ferns (*Pteridophyta*). The soil was formed in granitic glacial till (SGU, 2014) and is podzolised with a clear accumulation of oxalate-extractable Fe and Al in subsoil horizons. However, it is classified as a Dystric Arenosol (IUSS Working Group WRB, 2014) due to the presence of significant amounts of oxalate-extractable Fe and Al also in the A horizon. The site was located in Ringamåla in southern Sweden (N 56°19’48”, E14°48’14”), which has an annual precipitation of 600 mm and a mean annual temperature of 7 ºC (SMHI, 2014a and 2014b). The converter lime originated from the SSAB production site in Oxelösund, Sweden. It contained 14.6 g kg^{-1} vanadium (determined by inductively coupled plasma atomic emission spectroscopy after microwave digestion with perchloric acid; B. Nihlgård, unpublished data). The vanadium speciation of the converter lime at the time of application (1984) is not known. The calcium and iron contents were 310 and 155 g kg^{-1} respectively. The lime was added manually as a powder, however it also contained particles that were up to 3 mm in diameter. Nominal converter lime concentrations of 0, 0.2 and 0.7 kg m^{-2} were applied on top of the mor layer in triplicate plots of 10 × 10 m. A concentration of 1.0 kg lime m^{-2} was applied in one replicate plot. Theoretically, the lime concentrations corresponded to vanadium additions of 2.9, 10.2 and 14.6 g V m^{-2}.

2.2. Soil sampling and sample preparation.

In May 2010, soil samples were taken at the site at three different depths of the soil profile. One sample was collected from the organic horizon (mor) using an auger (⌀ = 56 mm) and between 140 - 460 g of sample was collected in each parcel. The sample weight generally decreased with increasing lime dose. Samples of the mineral soilwere collected from two different depths, at 0-10 and 10-20 cm (auger ⌀ = 32 mm) and weighed between 220 - 270 g and 310 - 400 g respectively. The samples of the mineral soil were divided at ten centimeters where there was a natural difference in color. Ten subsamples were evenly distributed over two diagonals of each plot. These were bulked to one sample for every soil depth. The fresh soils were weighed and sieved the day after sampling. The mor was sieved to < 8 mm and the mineral soil to < 2 mm. The samples were subsequently stored at 8 °C until analysis.

2.3. Soil analysis

Soil texture analyses were performed on the two mineral layers of the three reference samples by use of the pipette method (ISO, 1998). In both layers the mineral fraction consisted of 50 % sand, 45 % silt and 5 % clay. For an air-dried subsample of soil the total vanadium concentration was determined after aqua regia digestion in a microwave oven, and subsequently measured by ICP-AES (Table 1). The pH in water was determined using a 1:4 soil:solution ratio. The organic carbon content was determined using a LECO CNS-2000 analyzer. Oxalate-extractable iron and aluminum were determined by extracting 1.00 g dry soil with 100 ml of 0.2 M oxalate solution (pH 3.0) for four hours (van Reeuwijk, 1995). Vanadium was extracted from all soil samples by adding 20 mL of 0.01 M $CaCl_2$ to 10 g of fresh soil; this fraction of vanadium is referred to as “dissolved” as we have observed that it agrees well with the vanadium concentration in the pore water obtained after centrifugation (Larsson et al. 2015, in preparation). The samples were equilibrated on an end-over-end shaker for six days and subsequently centrifuged and filtered at 0.2 μm. All samples were stored in 8 °C until analysis.

2.4. XANES spectroscopy

X-ray near edge structure (XANES) spectroscopic measurements were performed at the wiggler beam line 4-3 at Stanford Synchotron Radiation Lightsource (SSRL), Stanford, USA. The station operated at 3.0 GeV with a current of ~100 mA and with a Si(111) double crystal monochromator. The spectra were collected in fluorescence mode (using a 13-element Ge array fluorescence detector) at the vanadium K-edge of 5465 eV (Thompson et al. 2009). The energy was calibrated with a metallic vanadium foil and the samples were measured over an energy range from 5235 to at least 5645 eV. The experimental resolution of the samples was ±0.5 eV.

The XANES spectra were collected on fresh soil samples from the Ringamåla field trial without pre-treatment. The samples were stored for a month in a cold room at +5°C before being measured. Care was taken during transport by placing the samples in a cooler bag with ice packs to reduce the risk of compositional change. One sample from each soil depth and lime dose was measured with a minimum of three scans. Further, spectra were collected for five vanadium laboratory standards with a valence ranging from +3 to +5. These included three oxides (V_2O_3(s), V_2O_4(s) and V_2O_5(s) from Sigma-Aldrich) and two aqueous samples with dissolved vanadyl (VO^{2+}(aq)) and vanadate ($H_2VO_4^-$(aq)). The aqueous standard samples were prepared from the dissolution of $VOSO_{4(s)}$ (Alfa Aesar) and NaVO3(s) (Sigma-Aldrich), respectively, in deionized water to obtain vanadium concentrations of 15 mM. Standards of vanadium sorbed to ferrihydrite (V+Fh), vanadium sorbed to aluminum hydroxide (V+HAO) and vanadium sorbed to organic matter (V+OM) were also prepared as explained in detail in Appendix A. A minimum of two XANES scans were collected for all standards except for the $H_2VO_4^-$(aq) standard for which one scan was collected.

The data treatment of the XANES spectra was performed using the Athena software (Ravel and Newville, 2005), version 0.8.056. The scans were energy-calibrated to a common energy scale using a vanadium foil, then aligned, merged and normalized before evaluation of the spectra. Hence E_0 was set to 5465 eV, i.e. at the first derivative maximum of the K edge of vanadium metal. Normalization was performed as described by Wong et al. (1984) In brief, the spectra were baseline-corrected by subtracting a linear regression through the pre-edge region and background-corrected using a quadratic function through the post-edge region The energy ranges that were used to fit the pre-edge and post-edge regions varied between samples due to variations in data quality and spectral configurations between samples. For example, the vanadium spectra for the soil samples were disturbed by the barium L_2 edge at 5624 eV(Thompson et al. 2009).Therefore, the post-edge region could not be fitted any further than 140 eV above E_0.

The pre-edge peak characteristics were determined by applying peak fit analysis in Athena. A baseline was fitted with a combination of an arctangent and an error function. The peak was fitted with up to three Gaussian functions. The best fit was selected based on the reported R-factor ($\Sigma(\text{data-fit})^2/\Sigma(\text{data})^2$), which varied between spectra depending on the data quality (from 0.023 to 0.00017). The pre-edge peak intensity and area were subsequently determined from the net peak (summed Gaussian functions), whereas the pre-edge peak position was determined from the centroid position. The $E_{1/2}$ (the energy position of the main edge where the normalized intensity equals 0.5) was determined from the normalized spectra.

The linear combination fit (LCF) function of Athena was used to evaluate the vanadium speciation of the soil samples treated with 1.0 kg converter lime m^{-2}. Standards of V+OM (pH 3.5), V+Fh (pH 4.5) and V+HAO (pH 6.7) were included in the LCF together with a spectrum of native mineral-bound vanadium (mineral V), for which the reference sample of the 10-20 cm mineral soil layer was used. The fits were based on a maximum of three standards, and the summed contributions of the standards had to range between 90 and 110 % for the fit to be accepted. The fitting range was from -5 to 60 eV relative to E_0. This range includes the pre-edge and the main edge. The fits were ordered according to the reported R-factor in Athena. For each sample the best fit is shown in the paper, whereas three additional fits are presented in Supplementary content, Appendix B.

2.5. HPLC-ICP-MS analysis

The speciation of dissolved vanadium, extracted by 0.01 M $CaCl_2$, was determined by the analytical approach of Aureli et al. (2008), modified to handle the sample matrices. The method development focused on the optimal Na_2EDTA concentration to achieve complete species complexation and on sample preparation issues affecting method accuracy. After centrifugation at 10000 rpm for 30 minutes at 4 °C, a double filtration (0.45 μm + 0.22 μm) was required due to the occurrence of fine particles. Na_2EDTA (50 mM) was immediately added to the extracts and the solution stirred for a minimum of 15 min. The extracts were analyzed within two weeks. Preliminary studies using species-specific spikes on a simulated-matrix sample (data not included) showed that a 50 mM Na_2EDTA concentration could quantitatively complex both V(IV) and V(V) at the highest observed concentrations. The species composition was kept intact for all samples only when Na_2EDTA was added immediately after filtration (t=0).

An Elan DRC II ICP-MS (Perkin Elmer-Sciex, Norwalk, CT, USA) equipped with a Meinhard quartz concentric nebulizer and a quartz cyclonic spray chamber was used to determine the total vanadium and vanadium speciation. For total vanadium, ammonia was selected as the reaction gas in the DRC and the gas conditions were optimized (flow rate 0.25 mL min^{-1}, RPq 0.25, and RPa 0). The limit of detection (LOD) was 0.048 µg L^{-1}.

Chromatographic separations were performed isocratically by means of a metal-free HPLC apparatus consisting of Perkin Elmer Series 200 LC binary pumps equipped with a Perkin Elmer Series 200 autosampler. A Dionex IonPac AG-5 4x50 mm column (Dionex Corporation, Sunnyvale, CA, USA) was connected by means of PEEK capillary tubing to the sample introduction system of the ICP-MS instrument. Chromatographic data were collected, stored and processed using the Perkin Elmer software Chromera®.

In diluted samples, quantification of vanadium species was carried out by external calibration. In undiluted samples, however, the method of standard additions was used. The LODs for each vanadium species were calculated as three times the standard deviation of the background signal of ten method blanks, and the resulting LODs were 0.18 µg L^{-1} for vanadium(IV) and 0.07 µg L^{-1} for vanadium(V). Spike recoveries in extract samples were on average 113 and 99% (n=3) for vanadium(IV) and vanadium(V), respectively.

Post-column recovery was evaluated by comparing the sum of the vanadium species determined by HPLC-ICP-MS with total vanadium determined by ICP-MS and was found to be 89% on average.

3. Results

3.1. *Total vanadium concentrations*

The total vanadium concentrations in the reference plots, based on aqua regia digestion, were 8 mg V kg^{-1} dw in the mor layer and 17-19 mg V kg^{-1} dw in the mineral soil (Table 1). Dissolved vanadium (extracted with 0.01 M $CaCl_2$) of the same samples were on average 3.7 µg V L^{-1} (10 µg V kg^{-1} soil)in the mor layer and 0.6 µg V L^{-1} (1 µg V kg^{-1} soil) in the 0-10 cm layer of the mineral soil. Only one reference sample in the 10-20 cm mineral soil had detectable concentrations of dissolved vanadium, being 0.1 µg V L^{-1} (0.1 µg V kg^{-1} soil).

The converter lime additions generally increased the pH, oxalate extractable iron and vanadium concentrations, but the data were variable (Table 1, Figure 1). A significant difference in vanadium concentration in the mor layer was recorded for the dose of 0.7 kg m^{-2} for total as well as dissolved vanadium. There was an increase in vanadium content with increasing lime dose in the 0-10 cm mineral soil (Figure 1), whereas the 10-20 cm mineral layer had no clear differences in vanadium concentration as a function of lime dose. Added vanadium (corrected for the native vanadium in the reference samples) was consistently highest in the mor layer in all lime-treated soils and decreased with depth. On average, 64 % of the recovered vanadium was in the mor layer, 21 % in the 0-10 cm and 15 % in the 10-20 cm mineral soil. Considering the whole sample depth, the recovery of the added vanadium was on average only 36 % (range 27-44 %) for the different lime additions. This would correspond to an annual loss of 2.5 % between 1984 and 2010, which is unreasonable (c.f. Discussion).

3.2. *Vanadium speciation*

For the laboratory standards, the pre-edge peak area and intensity of the vanadium K-edge XANES spectra increased with increasing oxidation state (Fig. 2. and Table 2). Additionally, the $E_{1/2}$ (the position where the normalized intensity of the main edge equals 0.5) increased, as expected. The standard oxidation states were plotted against the corresponding pre-edge peak intensities (Fig. 3). A second-order polynomial function ($R^2 = 0.95$) was fitted:

$$y = 0.087x^2 - 0.371x + 0.408 \quad (1)$$

where x is the calculated oxidation state and y is the normalized pre-edge peak intensity. One point was included at the oxidation state +2 with an intensity of zero as in Sutton et al. (2005), who referred to the data obtained by Wong et al. (1984) for vanadium(II) oxide, which did not show any pre-edge absorption feature. Equation 1 was used to calculate the average vanadium valence states.

The speciation of the sorbed vanadium standards did not depend on the vanadium species added during the preparation (Table A.1, Fig. A.1 and Fig. A.2, Supplementary content). Regardless of whether vanadyl(IV) or vanadate(V) was added, the V+OM standard was always dominated by vanadyl(IV), whereas the V+Fh and V+HAO standards were dominated by vanadate(V).

The vanadium K-edge XANES spectra of the Ringamåla reference samples were noisy due to the low vanadium concentrations (Fig. 2). The average vanadium oxidation state was +3.7 in the mor layer, and +4.0 and +3.8 in the mineral soil layers (Table 2). In the HPLC-ICP-MS analysis of dissolved vanadium, the two vanadium species as well as the $^{35}Cl^{16}O^+$ interference were chromatographically resolved within six minutes (Fig. 4). The dissolved vanadium had an average oxidation state of +4.2 and +4.0 in the reference samples of the mor layer and mineral soil, respectively (Fig. 5).

The average vanadium valence estimated from the pre-edge peak intensity of the XANES spectra ranged from +4.1 to +4.2 in the lime-treated mor layers (Table 2). Linear combination fitting (LCF) of the sample treated with 1.0 kg lime m^{-2} indicated that the main fraction of the vanadium was sorbed to organic matter, whereas a fourth of the vanadium was sorbed to ferrihydrite (Table 3, Fig. 6). As concerns the dissolved vanadium, the speciation was variable within replicates. However, the fraction of vanadium(V) generally increased with increasing lime dose. The concentrations of dissolved vanadium(IV) were considerably higher in the lime-treated mor layer samples as compared to the reference samples.

The average vanadium oxidation state in the lime-treated mineral soil (0-10 cm) ranged from +4.4 to +4.6 (Table 2). According to the LCF, about 40 % of the vanadium was sorbed to organic matter and another 40 % to ferrihydrite and the remaining 20 % was represented by native mineral-bound vanadium (Table 3, Fig. 6). Further, the lime-treated mineral soil from the 10-20 cm layer had an average valence ranging from +4.1 to +4.4 (Table 2) and the LCF suggested that the main fraction (49 % as compared to the calculated fraction of 68 %) was native mineral-bound vanadium, whereas a third was sorbed to organic matter and the rest was sorbed to aluminum (hydr)oxide (Table 3, Fig. 6). The dissolved vanadium speciation as determined by HPLC-ICP-MS was similar in the two mineral soil layers. Therefore the fraction of vanadium(IV) and vanadium(V) was calculated as an average for each dose, including both mineral layers (Fig. 5). The mineral soil references consisted only of vanadium(IV), and the speciation in the samples subjected to converter lime additions were similar across doses with an average oxidation state of approximately +4.8.

4. Discussion

4.1. *Vanadium distribution and speciation in soil*

The vanadium concentrations in the Ringamåla reference samples corresponded well to those reported for forest soils in southern Sweden (20 mg V kg^{-1}) (Salminen et al., 2005). The gradient of increasing vanadium concentrations with depth was probably due to the predominance of vanadium of minerogenic origin. However, the vanadium concentration in the mor layer was partly influenced by atmospheric deposition and by biocirculation. The inherent vanadium was dominated by vanadium(IV), in both the solid and dissolved phase. Vanadium(IV) has been reported to be located in the octahedral layers of clay minerals (Gehring et al., 1993; Mosser et al., 1996; Schosseler and Gehring, 1996). Further, vanadyl(IV) is complexed strongly by organic matter (Lu et al., 1998). The presence of dissolved organic matter may therefore greatly affect the vanadium speciation in solution.

The vanadium concentrations in the soils treated with converter lime were highest in the mor layer and decreased with depth, implying that a large fraction was retained by organic matter. To date, few studies have highlighted the interactions between vanadium and organic matter in soil. In one column experiment, strong binding of vanadium in organic soil layers was observed when artificial rainwater was applied to a mor layer. Extrapolation of the results indicated that only 10 % of the vanadium would be leached during 17 years at a soil pH of 4.2 (Tyler, 1978). This supports the hypothesis that the dissolved vanadium from the applied lime in the Ringamåla soil had been retained mainly by organic matter. However, assuming that the nominal application rates are correct, the Ringamåla soil had been subjected to a loss of more than 50 % of the added vanadium, being roughly 2.5 % on an annual basis. If there had been a considerable leaching of vanadium from the mor layer, higher concentrations would have been expected in the 0-20 cm mineral soil which was high in oxalate-extractable iron and aluminum. The importance of metal (hydr)oxides, especially those containing iron, for vanadium retention has been consistently highlighted (Blackmore et al., 1996; Gäbler et al., 2009; Naeem et al., 2007; Peacock and Sherman, 2004). Consequently, a major loss of vanadium from this layer is not probable. In a field experiment such as the one in Ringamåla, there may be some uptake of vanadium by trees and field layer vegetation, which can explain some of the vanadium losses from the soil. Furthermore, liming experiments in the field commonly have large spatial variations concerning the areal mass of the applied lime (Lundström et al., 2003). The converter lime was added manually which may have caused uneven spreading both within and between the parcels.

The main fraction of the applied vanadium had been stabilized as vanadium(IV) sorbed to the organic matter of the mor layer. This was indicated by the pre-edge peak intensity together with the LCF of the vanadium K-edge XANES spectra. Although the $E_{1/2}$ was slightly higher in the mor layer samples compared to the VO^{2+}(aq) standard, it was still in accordance with other values reported for VO^{2+} compounds (Burke et al., 2012; Wong et al., 1984). Organic matter is important for vanadium retention in soils (Cloy et al., 2011; Gäbler et al., 2009; Poledniok and Buhl, 2003) and it has been established that vanadate(V) is reduced to vanadium(IV) by different organic compounds (Lu et al., 1998; Wilson and Weber, 1979). The rate of reduction increases with decreasing pH. In contrast to the vanadium speciation determined by XANES spectroscopy in the solid phase of the mor layer, the average oxidation state determined by HPLC-ICP-MS of dissolved vanadium generally increased with lime dose. This is likely related to the increase in pH, which favors the occurrence of vanadate(V) (Baes and Mesmer, 1976). Thus vanadyl(IV) predominated in the solid phase and vanadate(V) in the solution phase.

In the 0-10 cm mineral soil, 40 % of the vanadium was vanadyl(IV) complexed to organic matter. Here however, the LCF showed the additional importance of vanadate(V) sorbed to iron and/or aluminum (hydr)oxides. Finally in the 10-20 cm horizon, most of the vanadium originating from the lime seemed to be sorbed to organic matter, which may originate from complexes that had migrated from the surface horizon. However, the spectra from the 10-20 cm layer was rather noisy and the R-factors were all rather similar, hence it is uncertain how important the aluminium (hydr)oxides were for vanadium sorption in this layer. The importance of vanadate(V) sorption in soils has been shown before (Burke et al., 2013; Peacock and Sherman, 2004). The involvement of iron (hydr)oxides in vanadium sorption in soils is well known but so far less evidence is available concerning the importance of aluminum (hydr)oxides or similar compounds (e.g. allophane, imogolite). In one study, the sorption of vanadium to activated alumina was similar to the sorption of arsenate(V) and selenite(IV) (Su et al., 2008). Clearly, further research is needed to properly evaluate the involvement of aluminium (hydr)oxides, allophane and imogolite for vanadium sorption in soils.

The fact that the vanadium speciation of the V+OM, V+Fh and V+HAO standards was not affected by the vanadium species added (Table A.1, Fig. A.1 and Fig. A.2, Supplementary content) suggests that the vanadium redox reactions are quick and consequently that the vanadium speciation of the applied converter lime is not likely to have been important for the observed speciation in the soil.

4.2. Vanadium speciation analysis – implications for assessment of bioavailability

The combination of XANES spectroscopy and HPLC-ICP-MS provided us with a promising tool not only to study vanadium redox chemistry in soils, but also to explore the link between chemical speciation and bioavailability. XANES spectroscopy has many advantages for determining vanadium oxidation states. However, there is no standard evaluation procedure, and assessments of the pre-edge peak intensities and $E_{1/2}$ are uncertain (Burke et al., 2012; Chaurand et al., 2007b; Sutton et al., 2005). The use of LCF analysis, which considers both the pre-edge and the main edge features, enabled us to obtain more detailed information on the overall spectra in addition to the average oxidation state (Wong et al., 1984). For example, the $E_{1/2}$ values were similar for the different lime-treated soil samples. However, when applying LCF, different sources of e.g. vanadium(IV) from native mineral-bound vanadium(IV) and from vanadyl(IV) complexed to organic matter could be identified. In general, the LCF fits of the mineral soil layers were realistic considering that the fraction of native mineral-bound vanadium corresponded well to the fraction of native vanadium determined by aqua regia. Also, the R-factors were low and in the same range as presented for previous LCF analysis performed on vanadium samples (Gerke et al., 2010).

The HPLC-ICP-MS method for vanadium speciation in solution was previously applied to natural mineral water (Aureli et al., 2008). It was further developed in the present study, taking into account the challenges posed by the complex sample matrixes investigated. For higher plants, the vanadium concentration in the soil solution is a good estimate of the bioavailable vanadium concentration in the soil (Larsson et al., 2013). In addition, the occurring vanadium oxidation state in the soil solution is important from a toxicological perspective as vanadium(V) is the most toxic redox state (Seargeant and Stinson, 1979). The dissolved vanadium added by converter lime to the Ringamåla soil was dominated by vanadium(V). However, the vanadium sorption capacity of the soil was sufficient to reduce the total concentration of bioavailable vanadium to low levels.

In conclusion, a large fraction of the vanadium that was added by converter lime to a podzolised forest soil was sorbed to the organic matter in the mor layer. Two vanadium speciation methods, XANES spectroscopy and HPLC-ICP-MS, could be adapted for vanadium in soil samples. By combining the two methods, it could be revealed that the distribution of vanadium species between different phases of the soil was determined by the soil pH and the content of organic matter and metal (hydr)oxides, but not by the vanadium species added to the soil.

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Figure captions

Fig. 1. Vanadium distribution in the Ringamåla soil profile for reference plots and converter lime-treated plots (0.2, 0.7 and 1.0 kg m^{-2}). Left: aqua regia extracted vanadium; right: 0.01 M $CaCl_2$-extracted vanadium. Error bars are standard error of the mean ($n = 3$) and letters denote significant differences between doses within each depth (ANOVA followed by unpaired t-test with Bonferroni correction, $\alpha = 0.05$).

Fig. 2. Normalized vanadium K-edge spectra for selected laboratory standars (dashed lines) and the Ringamåla soil samples (solid lines). Reference soils (grey lines) and soils treated with 1.0 kg converter lime m^{-2} (black lines) are shown.

Fig. 3. Normalized vanadium K-edge XANES pre-edge peak intensity plotted against oxidation state (equation 1). area second order polynomial trend line was fitted ($R^2 = 0.95$) to the laboratory standards of this study. For comparsion, measured intensities from other studies are also included in the plot.

Fig. 4. HPLC-ICP-MS chromatogram of a 0.01 M $CaCl_2$ extract of a Ringamåla mor sample treated with 0.2 kg converter lime m^{-2}. The $^{35}Cl^{16}O^+$ interference is resolved chromatographically.

Fig. 5. Vanadium speciation distribution (shown with standard errors) as determined by HPLC-ICP-MS on $CaCl_2$ extracts of Ringamåla soil samples subjected to different converter lime additions. The speciation in the mineral soil is represented by samples from two different depths (0-10 and 10-20 cm).

Fig. 6. Linear combination fitting of the normalized vanadium K-edge XANES spectra of different Ringamåla soil samples treated with 1.0 kg converter lime m^{-2}. The spectra were fitted with standards of native mineral-bound vanadium (mineral V), vanadium sorbed to organic matter (V+OM), vanadium sorbed to 2-line ferrihydrite (V+Fh) and vanadium sorbed to aluminium hydroxide (V+HAO).

Tables

Table 1. Soil properties of reference and converter lime-treated samples at three different depths[a]

Sample	Dose ($kg\ m^{-2}$)	pH 0.01 M $CaCl_2$	Org. C (%)	Al_{OX} ($g\ kg^{-1}$ dw)	Fe_{OX} ($g\ kg^{-1}$ dw)	Tot V (mg V kg^{-1} dw)
Mor	0	3.2 ± 0.1^{a}	34± 4	1.29 ± 0.04	1.52 ± 0.13^{a}	8 ± 0.5^{a}
	0.2	3.8 ± 0.3^{ab}	29± 3	1.15 ± 0.21	3.67 ± 0.56^{ab}	100 ± 48^{ab}
	0.7	4.0 ± 0.1^{b}	29± 2	1.53 ± 0.12	5.43 ± 0.47^{b}	211 ± 38^{b}
	1.0	4.6 ± n.a.	26 ± n.a.	1.66 ± n.a.	4.14 ± n.a.	680 ± n.a.
Mineral 0-10 cm	0	3.6 ± 0.02^{a}	5.1 ± 0.1^{a}	2.40 ± 0.07	4.80 ±0.15	19 ± 2.3
	0.2	4.1 ± 0.2^{ab}	5.6 ± 0.1^{ab}	2.11 ± 0.22	4.57 ±0.29	47 ± 6.7
	0.7	4.5 ± 0.2^{b}	5.7 ± 0.2^{b}	2.54 ± 0.41	4.88 ±0.43	90 ± 23
	1.0	4.5 ± n.a.	5.0 ± n.a.	2.46 ± n.a.	4.39 ± n.a.	89 ± n.a.
Mineral 10-20 cm	0	4.2 ± 0.02	2.8 ± 0.1	5.08 ± 0.89	5.57 ± 0.16	17 ± 1.1
	0.2	4.3 ± 0.1	3.3 ± 0.2	4.21 ± 0.58	6.52 ±0.16	31 ± 6.7
	0.7	4.6 ± 0.2	3.5 ± 0.2	5.13 ± 0.77	5.83 ±0.70	44 ± 4.6
	1.0	4.6 ± n.a.	2.5 ± n.a.	4.37 ± n.a.	5.38 ± n.a.	25 ± n.a.

[a] Data are presented with standard error of the mean ($n = 3$) and letters indicate significant differences within each depth (ANOVA followed by unpaired *t*-test with Bonferroni correction, α=0.05).

Abbreviations: Al_{OX} = oxalate-extractable aluminum, Fe_{OX} = oxalate-extractable iron

Table 2. Vanadium K-edge XANES properties of standards and Ringamåla soil samples[a]

Sample	Pre-edge peak			Main edge	Average valence
	Area	Intensity	Centroid position (eV)	$E_{1/2}$ (eV)	
Standards[b]					
$V_2O_{3(s)}$	0.39	0.12	5470.2	5476.9	+3
$V_2O_{4(s)}$	1.0	0.23	5469.6	5478.4	+4
$VO^{2+}_{(aq)}$	1.0	0.36	5469.9	5478.8	+4
$V_2O_{5(s)}$	1.9	0.66	5469.4	5480.6	+5
$H_2VO_4^{-}{}_{(aq)}$	2.2	0.81	5469.8	5481.0	+5
V+Fh (pH 4.5)	1.9	0.78	5469.9	5481.9	+5
V+HAO (pH 6.7)	1.3	0.52	5469.8	5481.0	+5
V+OM (pH 3.5)	1.0	0.36	5469.9	5479.7	+4
Ringamåla, Mor					
Reference	0.80	0.23	5469.2	5478.9	+3.7
0.2 $kg\ m^{-2}$	0.96	0.35	5470.0	5479.9	+4.1
0.7 $kg\ m^{-2}$	1.0	0.35	5470.0	5479.7	+4.2
1.0 $kg\ m^{-2}$	1.1	0.37	5469.9	5479.8	+4.2
Ringamåla, Mineral 0-10 cm					
Reference	0.81	0.30	5470.0	5479.7	+4.0
0.2 $kg\ m^{-2}$	1.3	0.45	5469.9	5480.1	+4.4
0.7 $kg\ m^{-2}$	1.3	0.53	5469.9	5480.0	+4.6
1.0 $kg\ m^{-2}$	1.4	0.54	5470.0	5479.9	+4.6
Ringamåla, Mineral 10-20 cm					
Reference	0.75	0.26	5470.1	5479.7	+3.8
0.2 $kg\ m^{-2}$	1.2	0.40	5470.1	5479.9	+4.2
0.7 $kg\ m^{-2}$	1.1	0.38	5469.9	5479.3	+4.2
1.0 $kg\ m^{-2}$	0.95	0.35	5470.0	5479.5	+4.1

[a] $E_{1/2}$ is the position of the main edge where the normalized intensity measured 0.5. The average valence for the Ringamåla soil samples was determined by a second polynomial function.

[b] V+Fh = vanadate(V) sorbed to ferrihydrite; V+HAO = vanadate(V) sorbed to aluminium hydroxide, V+OM = vanadyl(IV) sorbed to organic matter (mor), see details in Appendix A.

Table 3. The four best linear combination fits of the Ringamåla soil samples that were treated with 1.0 kg converter lime m^{-2}. Four different standards were used in the fitting procedure: native mineral-bound vanadium (Mineral V), vanadium sorbed to organic matter (V+OM), vanadium sorbed to ferrihydrite (V+Fh) and vanadium sorbed to aluminium hydroxide (V+HAO).

	Standard				
	Mineral V (%)	V+OM (%)	V+Fh (%)	V+HAO (%)	R-factor*
Mor					
Fit 1	7	70	23	-	0.0003
Fit 2	-	77	23	-	0.0003
Fit 3	3	57	-	39	0.001
Fit 4	-	60	-	40	0.001
Mineral, 0-10 cm					
Fit 1	21	40	39	-	0.0003
Fit 2	-	45	30	25	0.0004
Fit 3	-	59	41	-	0.0005
Fit 4	35	-	21	43	0.0006
Mineral, 10-20 cm					
Fit 1	49	32	-	19	0.0008
Fit 2	52	39	9	-	0.0008
Fit 3	60	40	-	-	0.001
Fit 4	74	-	-	26	0.001

*$\Sigma(\text{data-fit})^2/\Sigma(\text{data}^2)$

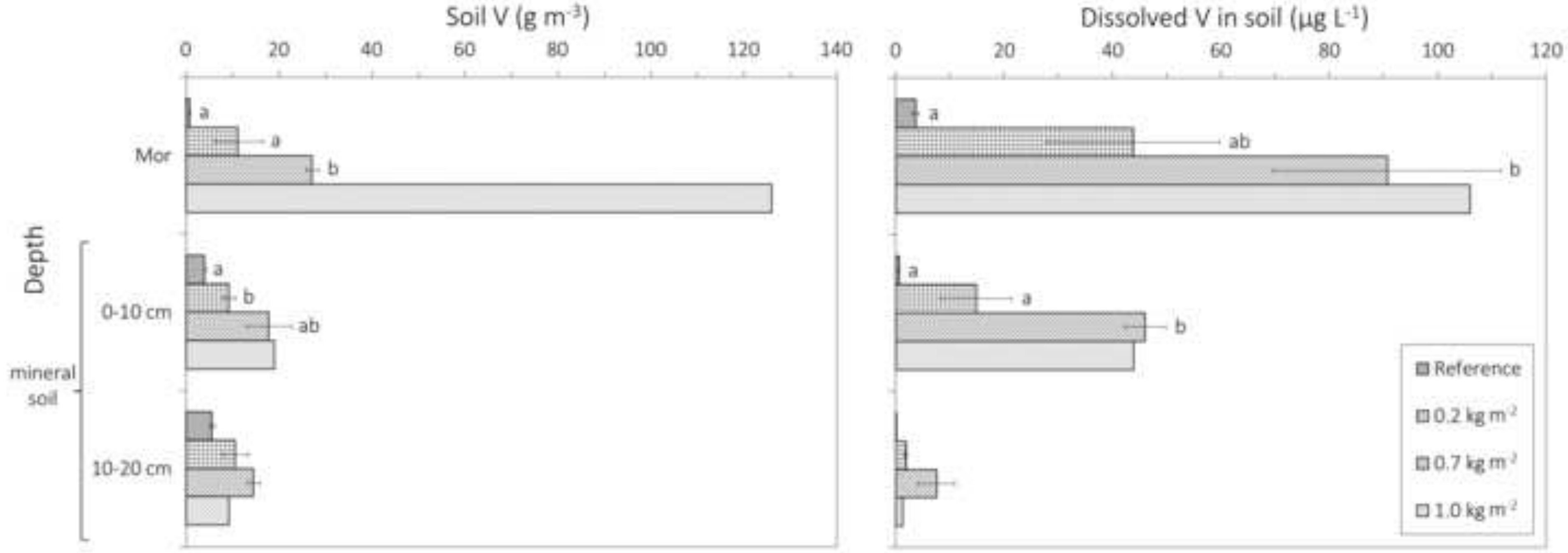

Soil V (g m^{-3})
0
20
40
60
80
100
120
140
Dissolved V in soil (µg L^{-1})
0
20
40
60
80
100
120
Depth
Mor
0-10 cm
10-20 cm
mineral soil
a
a
b
a
b
ab
a
ab
b
a
a
b
Reference
0.2 kg m^{-2}
0.7 kg m^{-2}
1.0 kg m^{-2}

Fig. 1

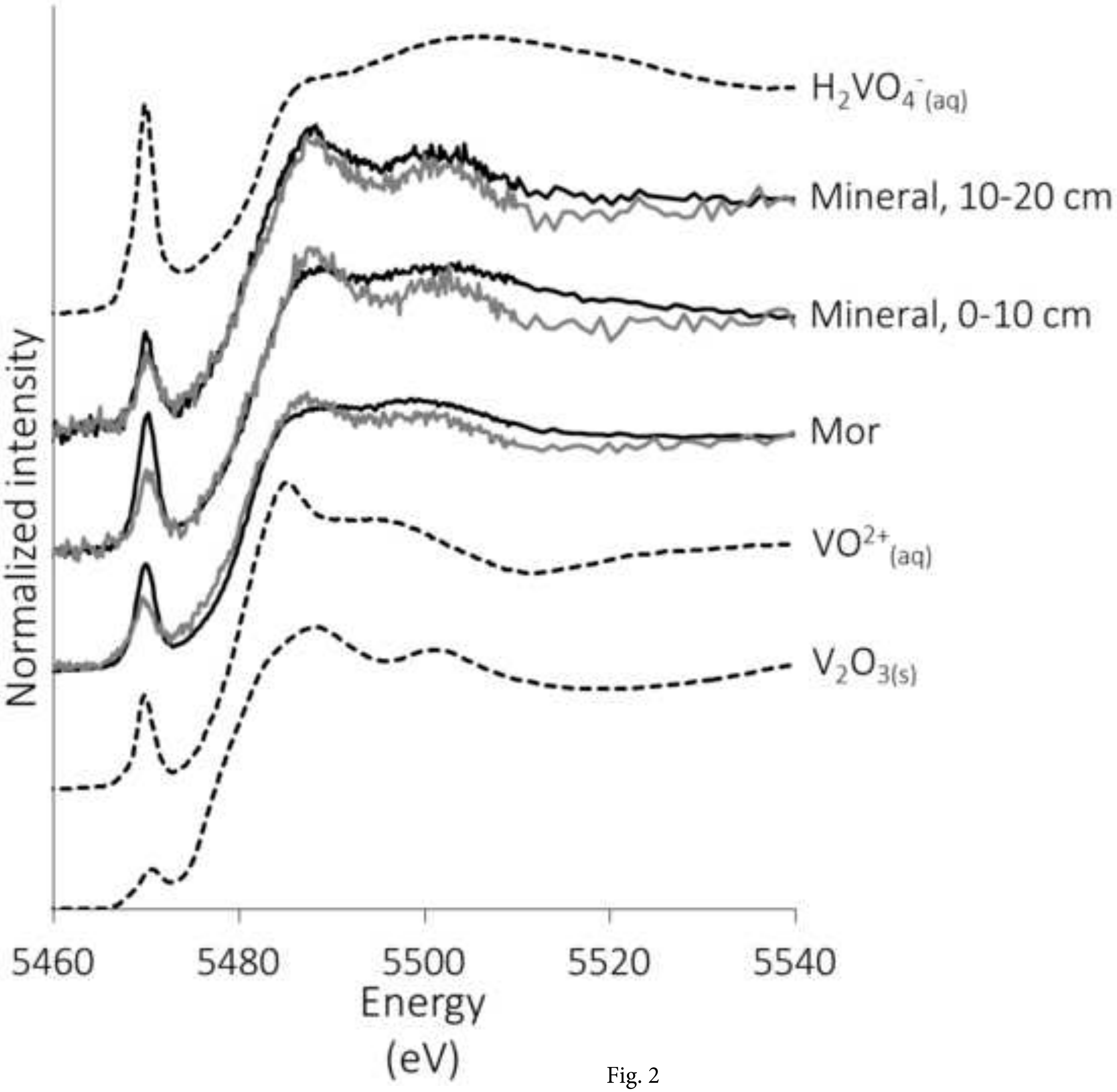

Normalized intensity
$H_2VO_4^-{}_{(aq)}$
Mineral, 10-20 cm
Mineral, 0-10 cm
Mor
$VO^{2+}{}_{(aq)}$
$V_2O_{3(s)}$
5460
5480
5500
5520
5540
Energy
(eV)

Fig. 2

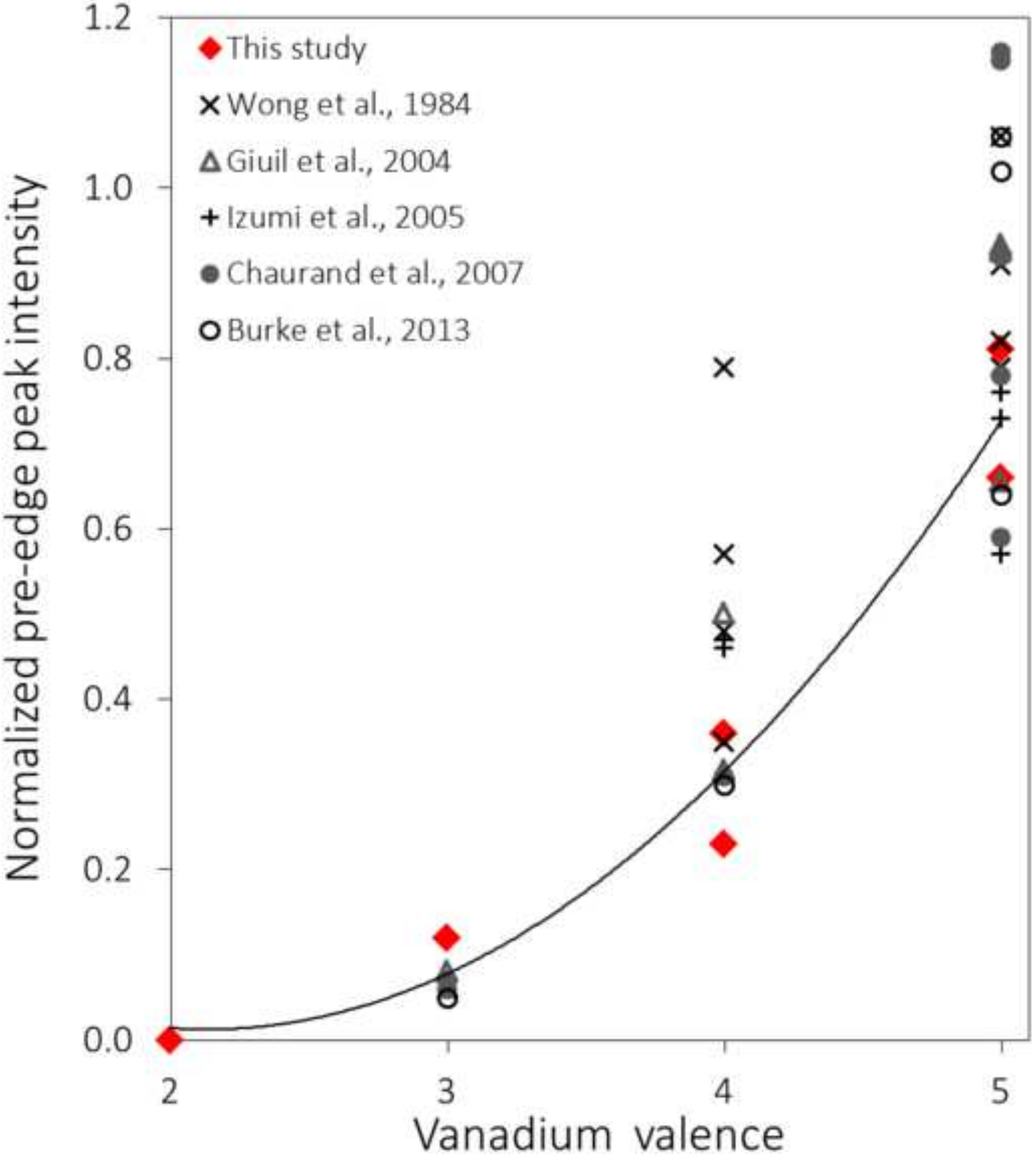

Normalized pre-edge peak intensity
Vanadium valence
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2
3
4
5
This study
Wong et al., 1984
Giuil et al., 2004
Izumi et al., 2005
Chaurand et al., 2007
Burke et al., 2013

Fig. 3

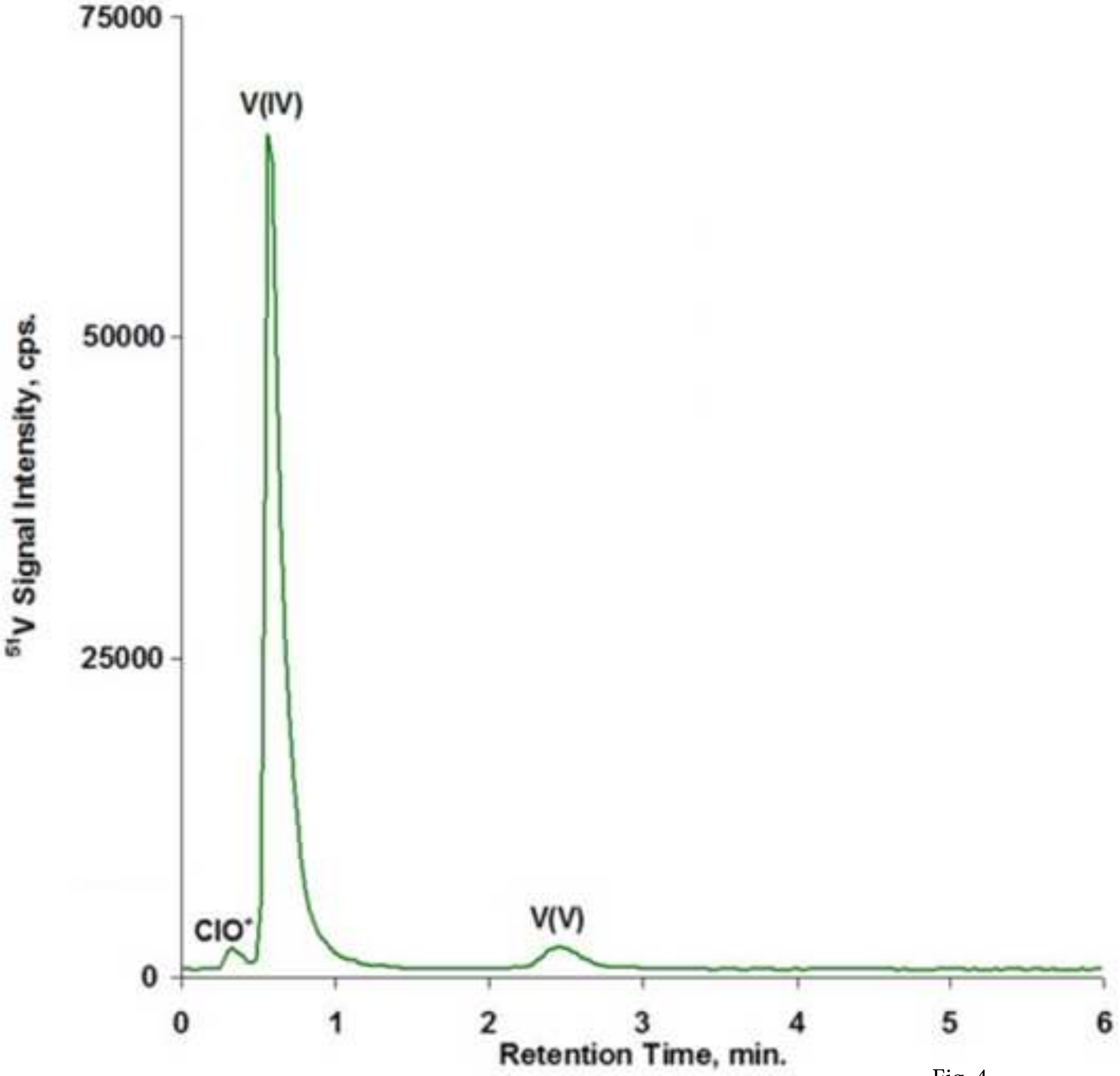
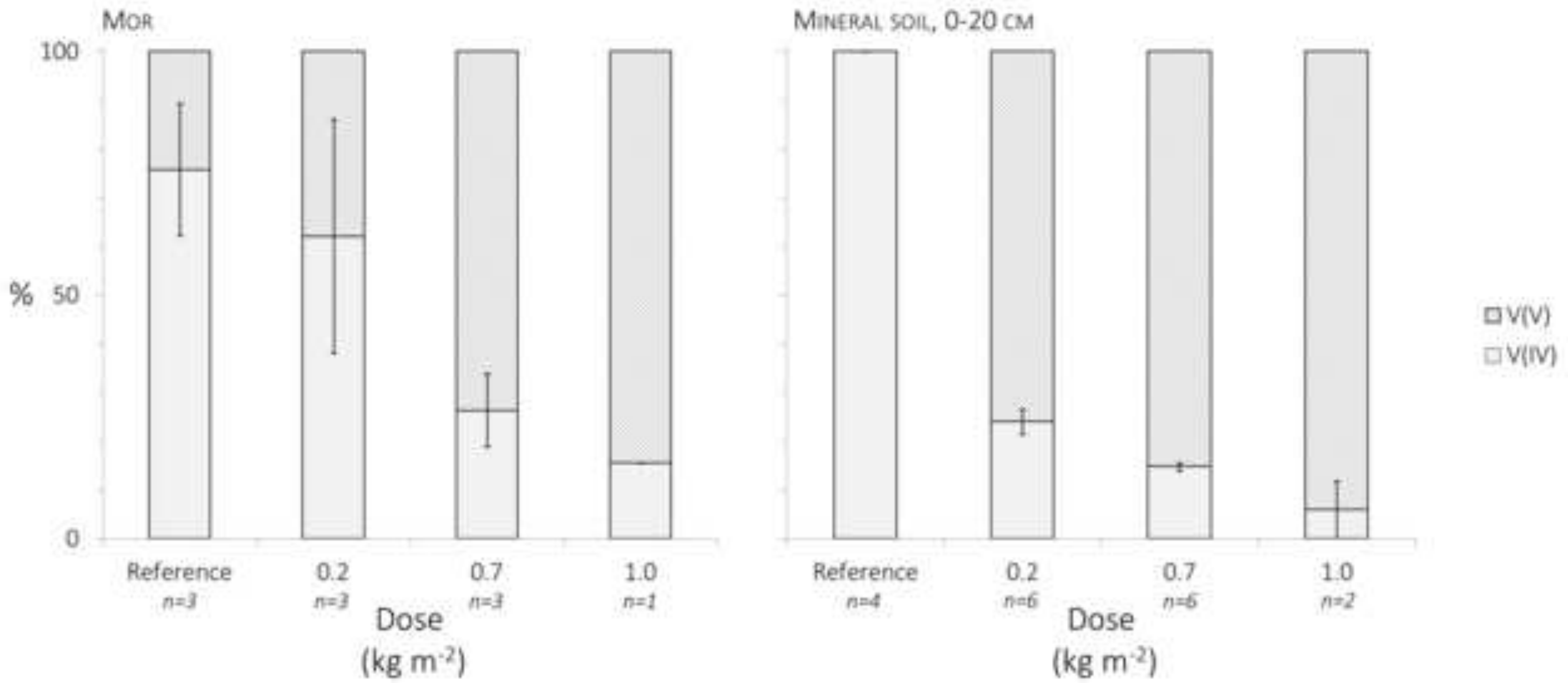

75000
50000
25000
0
^{51}V Signal Intensity, cps.
V(IV)
ClO^+
V(V)
0
1
2
3
4
5
6
Retention Time, min.

Fig. 4



MOR
MINERAL SOIL, 0-20 CM
100
%
50
0
Reference
n=3
0.2
n=3
0.7
n=3
1.0
n=1
Dose
(kg m-2)
Reference
n=4
0.2
n=6
0.7
n=6
1.0
n=2
Dose
(kg m-2)
V(V)
V(IV)

Fig. 5

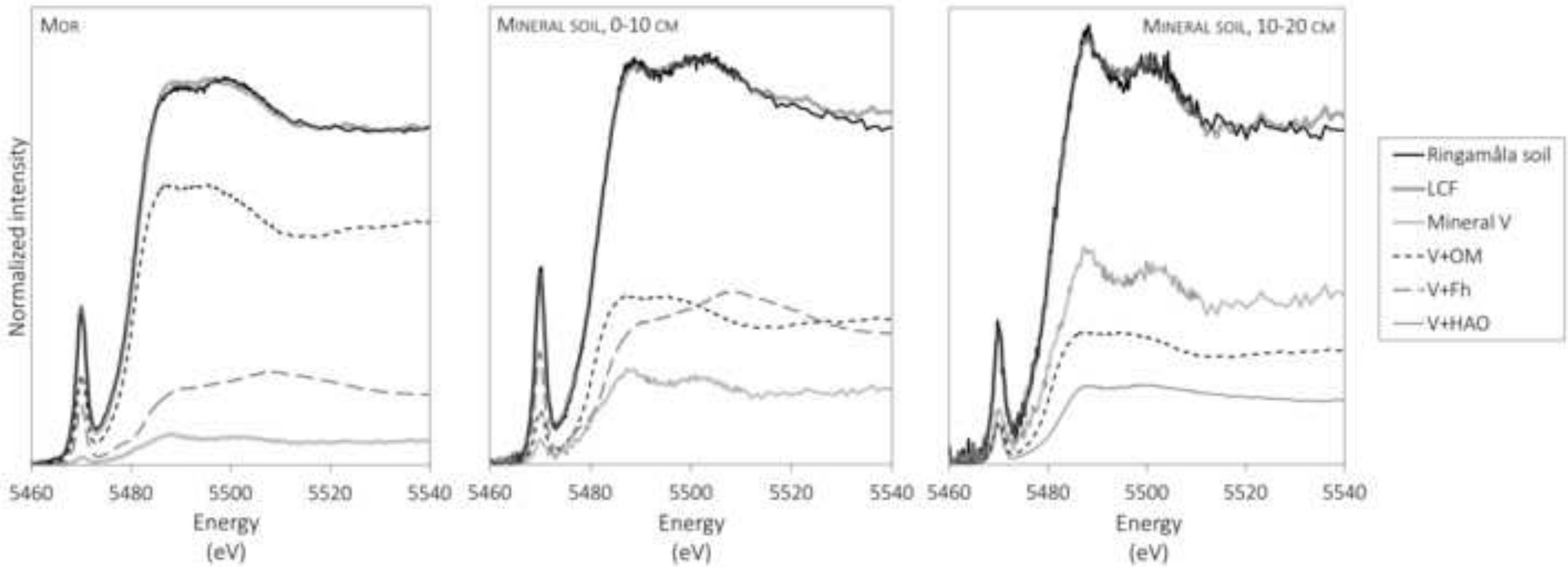

Mor
Mineral soil, 0-10 cm
Mineral soil, 10-20 cm
Normalized intensity
5460
5480
5500
5520
5540
Energy
(eV)
Ringamåla soil
LCF
Mineral V
V+OM
V+Fh
V+HAO

Fig. 6

Supplementary content

Long-term fate and transformations of vanadium in a pine forest soil with added converter lime

Maja A. Larsson, Marilena D´Amato, Francesco Cubadda, Andrea Raggi, Ingrid Öborn, Dan Berggren Kleja, Jon Petter Gustafsson

Contents

Appendix A

Appendix B

Appendix A

Preparation of sorbed vanadium standards

Standard samples of vanadium sorbed to 2-line ferrihydrite (V+Fh), aluminum hydroxide (V+HAO) and organic matter (V+OM) were prepared by batch experiments. The Fh was synthesized as described in detail by Gustafsson (2003). The HAO was prepared in a similar manner by preparing 36 mM $Al(NO_3)_3 \cdot 9H_2O$. The pH was then increased to 7.0 using dropwise additions of 1 M NaOH and the resulting suspension was left to settle for 16 h. The solution was then back-titrated to 5.0 and the suspension was homogenized by vigorous stirring for at least 30 min. The OM was taken from a mor layer in a forest soil with low concentrations of oxalate-extractable iron and aluminum, 0.7 and 0.8 g kg^{-1} dry weight respectively (Risbergshöjden Oe, for more details see Gustafsson and van Schaik, 2003). 50 µM of vanadium (as either dissolved VO^{2+} or $H_2VO_4^-$) was added to separate batches of 3 mM of Fh and HAO and to 30 g L^{-1} of fresh OM. A set of samples with different pH values, adjusted with 0.01 M HNO_3 or 0.01 M NaOH, was prepared for each sorbent. Additions of $NaNO_3$ were made to all samples to a background of 0.01 M. The suspensions containing Fh and HAO were equilibrated for 48 hours and the suspension with OM for six days. After equilibration, the pH was measured and the samples were subsequently centrifuged at 3000 rpm for 15 min after which time the supernatant and sorbent were separated. Vanadium K-edge XANES spectroscopy was performed on the precipitated gel, which was kept in a moist state in sealed polyethylene centrifuge tubes at +5°C for max. one week until analysis at beam line 4-3 at the Stanford Synchrotron Radiation Lightsource, US. 50 mM Na_2EDTA was added to the solution phase and then analyzed for vanadium species using HPLC-ICP-MS. The two phases were analyzed on separate samples as the measurements were performed at two different occasions.

The XANES analysis was performed on six samples of Fh, three samples of HAO and six samples of OM to which either dissolved VO^{2+} or $H_2VO_4^-$ had been added at different pH values (Table A.1, Fig. A.1). There were small differences between different pH values and the additions of either VO^{2+} or $H_2VO_4^-$ did not show any clear differences in the speciation of the sorbed vanadium.

The speciation of dissolved vanadium by HPLC-ICP-MS was determined for all three sorbents. However, the vanadium concentration was below the detection limit for the V+Fh samples (Table A.2). Four samples of V+OM and four samples of V+HAO were measured. The speciation was similar between samples but a larger pH range would have been desirable to evaluate possible changes in speciation with pH.

The standard samples of vanadium sorbed to organic matter (V+OM) contained vanadium(IV), regardless of pH or the vanadium species added. The samples had an average valence of +4.1 for both sorbed (Table A.1) and dissolved vanadium (Table A.2). Further, the pre-edge peak features of the XANES spectra of the V+OM standard agreed with those of the tetravalent VO^{2+}(aq) for which the $E_{1/2}$ also was within the same range, 5479.7 eV compared to 5478.8 eV (Fig. A.2). The $E_{1/2}$ was somewhat higher than for the VO^{2+}(aq) but still in accordance with values reported in other studies for vanadyl compounds (Burke et al., 2012; Wong et al., 1984).

The standards of vanadium sorbed to 2-line ferrihydrite (V+Fh) were similar and independent of pH or vanadium species added, and they contained pentavalent vanadium (Table A.1). The standard spectra had features that corresponded well to that of the vanadate ($H_2VO_4^-$(aq)) standard (Fig. A.2). Further, sorption of vanadate(V) to ferrihydrite was confirmed by EXAFS analysis (Larsson et al. in prep.) and it has also been reported for goethite (Peacock and Sherman, 2004).

The vanadium in equilibrium with aluminum hydroxide (V+HAO) was vanadate(V). The average vanadium oxidation state was +4.5, based on the pre-edge peak intensity (Table A.1), whereas $E_{1/2}$ was 5481.0 eV and within the same range as the vanadate(V) standard (Table A.1, Fig. A.2). Judging from the value of +4.5 obtained from the pre-edge peak intensity, the predominance of sorbed vanadate(V) was not clear, but it has previously been reported that the oxidation state of vanadium sorbed to aluminum hydroxide is better indicated by the $E_{1/2}$ (Burke et al., 2013).

Table A.1. Properties of the vanadium K-edge XANES spectra for vanadium sorbed to 2-line ferrihydrite, aluminum hydroxide and organic matter at additions of 50 µM dissolved vanadium of valence +4 or +5 at different pH values.

Added V valence	pH	Pre-edge peak			Main edge	Average valence*
		Area	Intensity	Centroid position (eV)	$E_{1/2}$ (eV)	
2-line ferrihydrite						
+4	4.5	1.90	0.74	5469.9	5482.3	5.0
+4	5.7	1.94	0.76	5469.6	5481.9	5.1
+5	5.7	1.92	0.70	5469.9	5481.9	5.2
+5	6.2	1.88	0.71	5469.7	5481.7	5.0
+5	6.5	1.97	0.81	5469.7	5481.9	5.2
+4	9.4	1.89	0.75	5469.9	5482.1	5.0
Aluminum hydroxide						
+4	4.6	1.22	0.50	5469.9	5481.1	4.5
+4	6.7	1.27	0.52	5469.8	5481.0	4.5
+5	9.4	1.36	0.59	5469.8	5481.4	4.7
Mor layer						
+4	2.4	0.81	0.31	5469.9	5479.8	4.0
+5	2.4	0.89	0.32	5469.7	5479.2	4.0
+4	3.5	0.98	0.36	5469.9	5479.7	4.1
+5	3.4	0.94	0.34	5469.9	5479.6	4.1
+4	5.0	0.95	0.33	5469.8	5479.8	4.0
+5	5.1	1.03	0.37	5469.8	5479.5	4.2

*Average valence determined by a second polynomial function ($y = 0.087x^2 - 0.371x + 0.408$) fitted to the pre-edge peak intensities of the vanadium standards

Table A.2. Speciation of dissolved vanadium as determined by HPLC-ICP-MS with EDTA complexation in solutions from batch experiments with aluminum hydroxide and organic matter.

Added V valence	pH	Total V (ng g^{-1})	V(IV) (%)	V(V) (%)
Aluminum hydroxide				
+4	6.0	11	21	79
+4	6.1	676	17	83
+5	6.0	11	8	92
+5	6.0	6	8	92
Organic matter				
+4	3.4	21	91	9
+5	3.4	30	90	10
+4	4.7	89	87	13
+5	4.6	114	89	11

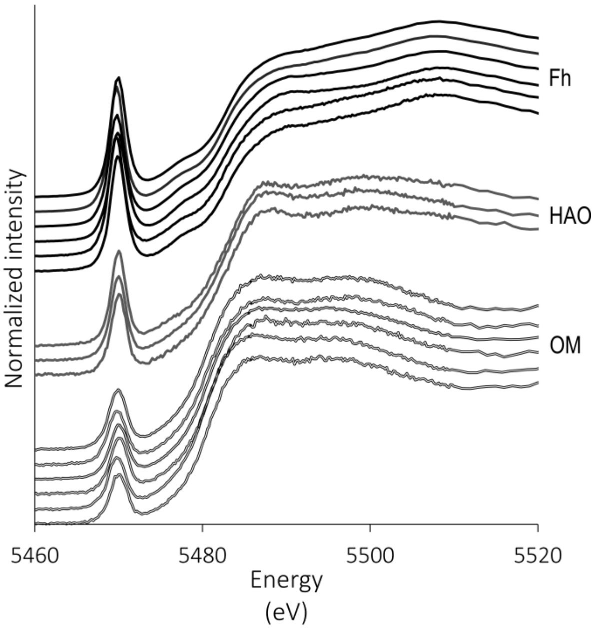


Fig. A.1. Stacked vanadium K-edge XANES spectra of vanadium sorbed to 2-line ferrihydrite (Fh), aluminum hydroxide (HAO) and organic matter (OM). The samples of each sorbent were arranged from higher to lower pH and the pH range of the samples were, 4.5-9.4 for Fh, 4.6-9.4 for HAO and 2.4-5.1 for OM.

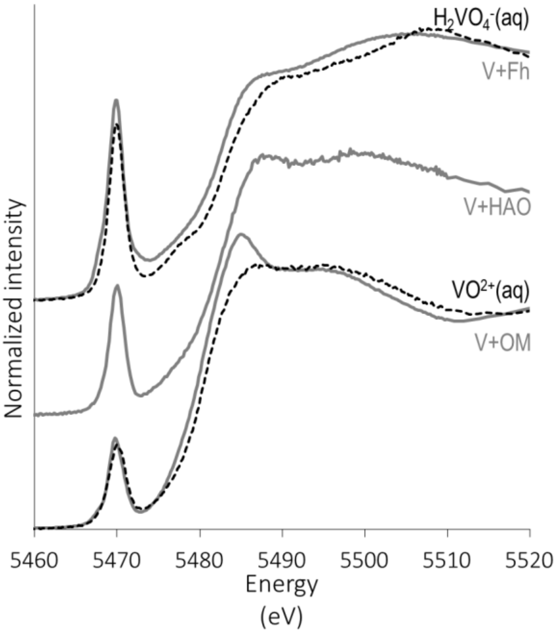


Fig. A.2. Comparison of normalized vanadium K-edge XANES spectra of dissolved vanadium standards, VO^{2+}(aq) and $H_2VO_4^-$(aq) (dashed black lines), and vanadium sorbed to ferrihydrite (V+Fh), aluminum hydroxide (V+HAO) and organic matter (V+OM) (full grey lines).

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Appendix B

Linear combination fitting

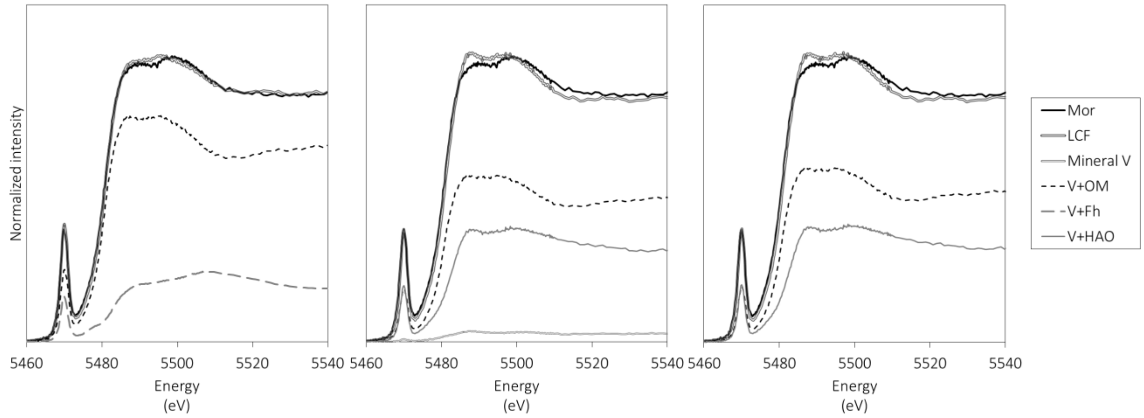

Fig. B.1. Linear combination fitting of the second (left), the third (center) and the fourth (right) best fit according to obtained R-factor of Ringamåla mor sample, treated with 1.0 kg converter lime m^{-2}.

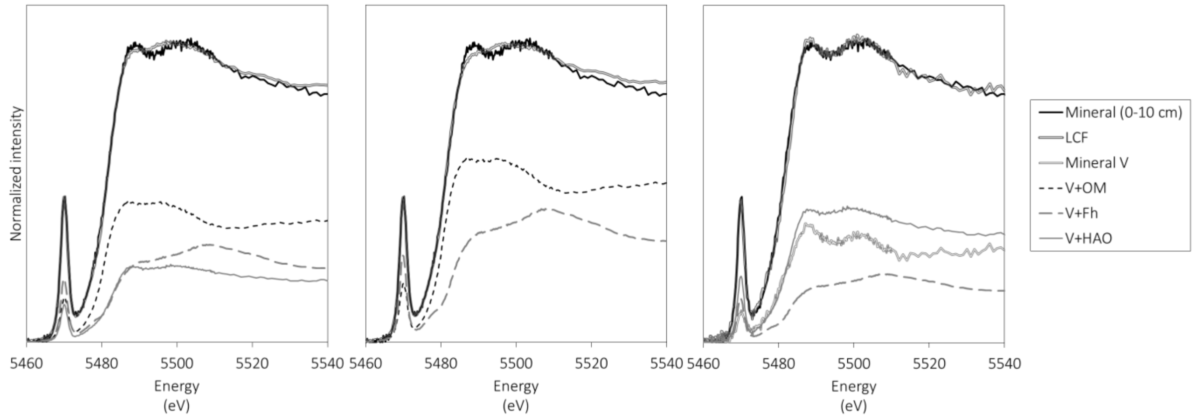

Fig. B.2. Linear combination fitting of the second (left), the third (center) and the fourth (right) best fit according to obtained R-factor of Ringamåla 0-10 cm mineral sample, treated with 1.0 kg converter lime m^{-2}.

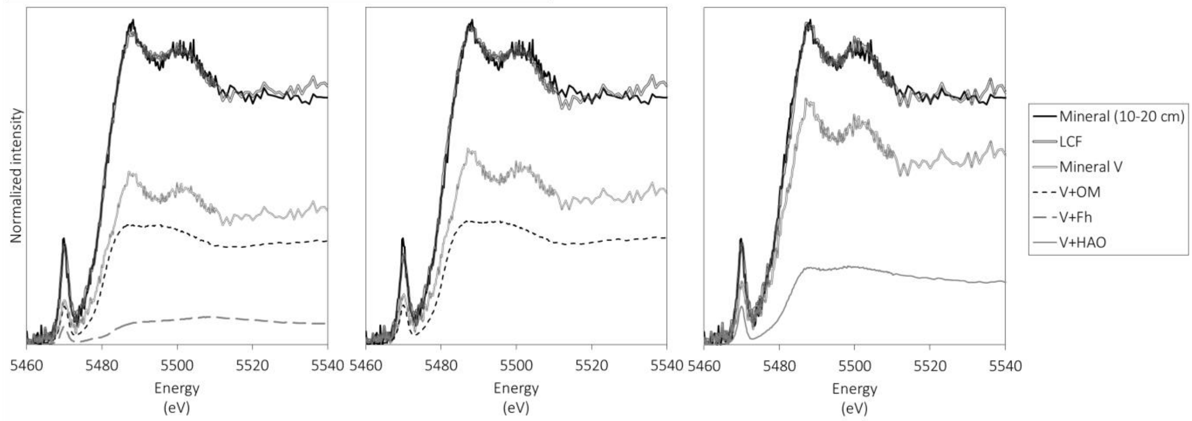

Fig. B.3. Linear combination fitting of the second (left), the third (center) and the fourth (right) best fit according to obtained R-factor of Ringamåla 10-20 cm mineral sample, treated with 1.0 kg converter lime m^{-2}.