



## 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<sup>-2</sup>) was set up in a pine forest stand in southern Sweden in 1984. The lime contained 14.6 g kg<sup>-1</sup> 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 analyzed separately. The vanadium concentration decreased with soil depth, from 680 to 8 mg kg<sup>-1</sup> soil. Analysis by vanadium K-edge XANES spectroscopy showed that vanadium(IV) was the predominant species in the mor layer. Further, iron and/or aluminum (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.

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### 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 1980s, 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 1100 mg kg<sup>-1</sup> 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<sub>2</sub>VO<sub>4</sub><sup>-</sup> or HVO<sub>4</sub><sup>2-</sup>, 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<sup>2+</sup>) (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

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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  $[\text{VO}(\text{EDTA})]^{2-}$  and  $[\text{VO}_2(\text{EDTA})]^{3-}$  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 iron and aluminum 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 iron and aluminum 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 °C (SMHI, 2014a and 2014b). The converter lime originated from the SSAB production site in Oxelösund, Sweden. It contained 14.6 g kg<sup>-1</sup> 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<sup>-1</sup> 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<sup>-2</sup> were applied on top of the mor layer in triplicate plots of 10 × 10 m. A concentration of 1.0 kg lime m<sup>-2</sup> 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<sup>-2</sup>.

### 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 ( $\varnothing = 56$  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 soil were collected from two different depths, at 0–10 and 10–20 cm (auger  $\varnothing = 32$  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<sub>2</sub> 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). The samples were equilibrated on an end-over-end shaker for six days and subsequently centrifuged and filtered at 0.2  $\mu\text{m}$ . 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 Synchrotron 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  $\pm 0.5$  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

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