Vanadium in Soils

Chemistry and Ecotoxicity

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Abstract

Vanadium is a redox-sensitive metal that is released to soils by weathering and anthropogenic emissions. Swedish metallurgical slags are naturally high in vanadium and used as soil amendments and in road materials. However, understanding of vanadium chemistry and bioavailability in soils is limited. The aim of this thesis was to provide knowledge of vanadium in soils in terms of sorption, toxicity and speciation, in order to enable improved environmental risk assessments. Vanadium sorption to ferrihydrite was evaluated in batch experiments. Toxicity assays using microorganisms and plants were conducted to measure vanadium toxicity in different vanadium soil treatments; freshly spiked, aged and blast furnace slag (800 mg V kg^{-1}). Vanadium speciation in a podzolic soil amended with converter lime (14.6 g V kg^{-1}) 26 years previously was assessed by using XANES spectroscopy and HPLC-ICP-MS.

Ferrihydrite adsorbed vanadium strongly, but adsorption was reduced by large additions of phosphate. EXAFS spectroscopy revealed that a vanadate(V) edge-sharing bidentate complex formed on the ferrihydrite surface. In the toxicity assays, increasing vanadium sorption strength in the freshly spiked soils reduced the toxicity. Toxicity was also reduced by soil ageing, possibly because of vanadium incorporation into metal (hydr)oxides. No toxicity was observed when soils were amended with up to 29% blast furnace slag, probably owing to the low solubility of vanadium in slag. The variation in toxicity between soils and vanadium treatments was due to differences in bioavailability of vanadium which was explained by the vanadium concentration in soil solution. The vanadium added with converter lime was in pentavalent form, but the main fraction of the vanadium recovered from the mor layer sorbed to organic matter as vanadium(IV). In the mineral soil layers, the added vanadium sorbed to metal (hydr)oxides as vanadium(V). The most toxic vanadium form, vanadium(V), dominated in the soil solution but the concentrations were below toxic levels.

In conclusion, vanadium toxicity varies between soils and treatments and is most accurately described by the vanadium concentration in the soil solution. Vanadium speciation in soil is mainly controlled by soil properties, and not by the vanadium species added to the soil.

Keywords: vanadium, soil, ferrihydrite, sorption, toxicity, bioavailability, speciation, XANES spectroscopy, HPLC-ICP-MS.

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Till Mamma

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Larsson, M.A., Persson, I., Sjöstedt, C. & Gustafsson, J.P. (2014). Vanadate complexation to ferrihydrite: X-ray absorption spectroscopy and CD-MUSIC modelling. *Manuscript.*

II Larsson, M.A., Baken, S., Gustafsson J.P., Hadialhejazi, G. & Smolders, E. (2013). Vanadium bioavailability and toxicity to soil microorganisms and plants. *Environmental Toxicology and Chemistry* 32 (10), 2266-2273.

III Baken, S., Larsson M.A., Gustafsson, J.P., Cubadda, F. & Smolders E. (2012). Ageing of vanadium in soils and consequences for bioavailability. *European Journal of Soil Science* 63 (6), 839-847.

IV Larsson, M.A., Baken, S., Smolders E., Cubadda F. & Gustafsson, J.P. (2014). Vanadium bioavailability in soils amended with blast furnace slag. *Submitted manuscript*.

V Larsson, M.A., D'Amato, M., Cubadda, F., Raggi, A., Öborn, I., Berggren Kleja, D. & Gustafsson, J.P. (2014). Long-term fate and transformations of vanadium added by converter lime to a forest soil. *Submitted manuscript*.

Papers II and III are reproduced with the permission of the publishers.

The contribution of Maja A. Larsson to the papers included in this thesis was as follows:

I Planned the study together with the fourth author. Performed the laboratory work and XAS analysis with some assistance. EXAFS and wavelet analyses were performed by the second and third author, respectively. Performed the modelling and writing with assistance from the co-authors.

II Planned the study together with the second, third and fifth author. Performed the experimental work together with the second author. Performed data analyses and writing with assistance from the co-authors.

III Planned the study together with the first, third and fifth author. Performed the experimental work together with the first author and assisted in data analyses and writing.

IV Planned the study together with the third and fourth author. Performed experimental work together with the second author. Performed data analyses and writing with assistance from the co-authors.

V Planned the study together with the seventh author. Performed soil sampling, laboratory work and XANES data analysis. Performed writing with assistance from the co-authors.

Abbreviations

EC10	Effective concentration at 10% inhibition
EC50	Effective concentration at 50% inhibition
EXAFS	Extended X-Ray Absorption Fine Structure
Fh	Ferrihydrite
HAO	Aluminium (hydr)oxide
LCF	Linear combination fitting
OM	Organic matter
PNR	Potential Nitrification Rate
V	Vanadium
XANES	X-Ray Absorption Near Edge Structure
XAS	X-Ray Absorption Spectroscopy

1 Introduction

Vanadium, V, is a transition metal and is among the 20 most abundant elements in the Earth's crust, in the same concentration range as lead and copper. Its main application in human society is within the steel industry, in alloys. The anthropogenic input to the environment is dominated by burning of fossil fuels. The steel industry generates by-products that due to their alkalinity and physical properties are suitable as soil amendments, road fill materials and cement. In Sweden, these materials are naturally high in vanadium. Since the human body always contains traces of vanadium, there are ethical and practical issues with investigating the impact of vanadium deficiency in humans. Thus vanadium essentiality to humans has still not been confirmed (Anke *et al.*, 2005). However, excessive vanadium concentrations may be carcinogenic (Beyersmann & Hartwig, 2008). Historically, there are cases of accidental releases of vanadium to the environment. One of the most recent was a spillage of the bauxite residue "red mud" in Ajka, Hungary, in 2010. In addition to alkalinity and sodium concentrations, the red mud also contained 900 mg kg^{-1} vanadium (Ruyters *et al.*, 2011). In the 1980s, basic slag containing 3% vanadium was inappropriately applied as a soil amendment in Lillpite in northern Sweden. The amendment resulted in contamination of hay, which caused the death of 23 cattle due to acute vanadium toxicity (Frank *et al.*, 1996).

Knowledge of vanadium behaviour in soils is poor compared with that of heavy metals such as copper, lead and zinc, and many countries lack threshold values for vanadium in soils and waters. The median value of total vanadium concentration in European topsoils is 60 mg kg^{-1}, but some soils may have up to 500 mg V kg^{-1}. In comparison, most toxicity-based values for unacceptable risks range from 90 to 500 mg V kg^{-1} for those member states of the European Union that have established limit values for vanadium in soils (Carlon, 2007).

2 Aim

The overall aim of this thesis was to obtain knowledge of the behaviour of vanadium in soils in terms of sorption, toxicity and speciation, in order to enable improved environmental risk assessments.

Specific objectives were to:

- Assess the sorption pattern of vanadium to 2-line ferrihydrite in single sorbate systems and in competition with phosphate; examine the vanadium complex formed on the ferrihydrite surface by means of EXAFS spectroscopy; and optimise surface complexation constants using the CD-MUSIC model (Paper I).
- Determine critical vanadium concentrations for microorganisms and higher plants in soils with different vanadium amendments; freshly spiked, aged and blast furnace slag (Papers II, III and IV).
- Identify soil properties that explain vanadium bioavailability in soils (Papers II, III, IV).
- Assess the long-term solubility and speciation of vanadium in a forest soil treated in the past with converter lime rich in vanadium (Paper V).

3 Background

3.1 Vanadium in soils and waters

3.1.1 Sources

The vanadium content in soils and waters is primarily determined by the geological parent material (Hope, 1997). However, anthropogenic emissions, mainly from combustion of fossil fuels (Pacyna & Pacyna, 2001), may enhance soil vanadium concentrations locally. Vanadium inputs to soils related to human activities derive e.g. from phosphate fertilisers (Molina *et al.*, 2009), soil amendments and roadfill materials derived from steel slag (Shen & Forssberg, 2003).

Many of the slags generated in the steel production process have properties suitable for various applications within society, but slag reuse may be restrained by elevated concentrations of trace elements (Motz & Geiseler, 2001). Swedish blast furnace slags are naturally high in vanadium, which can reach concentrations above 500 mg kg^{-1} (Nehrenheim & Gustafsson, 2008). This is 10-fold higher than reported for e.g. blast furnace slags in the USA (Proctor *et al.*, 2000). Data on vanadium leaching from blast furnace slags are scarce (Cornelis *et al.*, 2008). Laboratory-based availability tests indicate that the potential leaching capacity of vanadium from Swedish blast furnace slags is approximately 10% of the total vanadium content (Fällman & Hartlén, 1994). Two important factors that control the leaching from different slags are the pH and redox conditions (De Windt *et al.*, 2011; Fällman & Hartlén, 1994). However, it should be noted that leaching tests performed in the laboratory may not adequately represent the leaching conditions in the field (Chaurand *et al.*, 2007a; Fällman & Hartlén, 1994).

3.1.2 Redox chemistry

Vanadium can exist in a range of oxidation states (from -2 to +5). The prevailing valence states in nature are vanadium(III), vanadium(IV) and vanadium(V) of which the latter two are the most soluble (Wanty & Goldhaber, 1992). Vanadium(III) is stable in extremely reducing environments, such as lake sediments, and is readily oxidised in the unsaturated zone of the soil (Crans *et al.*, 1998). In soils, the oxocation vanadyl(IV), VO^{2+}, occurs at lower pH values and in moderately reducing conditions (Figure 1). Vanadyl(IV) forms strong complexes with organic matter, which may stabilise the ion at higher redox potentials (Wehrli & Stumm, 1989). The oxyanion vanadate(V), $H_2VO_4^-$, is usually the predominant form in soils. It prevails above pH 3.6 and has three protonation states. However, protonation to vanadic acid, H_3VO_4, is insignificant due to the formation of the oxocation vanadyl(V), VO_2^+ (Crans *et al.*, 1998). Vanadate resembles phosphate and is the most soluble and toxic form of vanadium due to its ability to inhibit phosphate-metabolising enzymes (Perlin & Spanswick, 1981; Seargeant & Stinson, 1979). In waters, the relative concentrations of different vanadium(V) species are affected by the total vanadium concentration, the ionic strength and the pH. At concentrations above 100 µM, polymers of vanadium, in particular decavanadates, start to form (Baes & Mesmer, 1976).

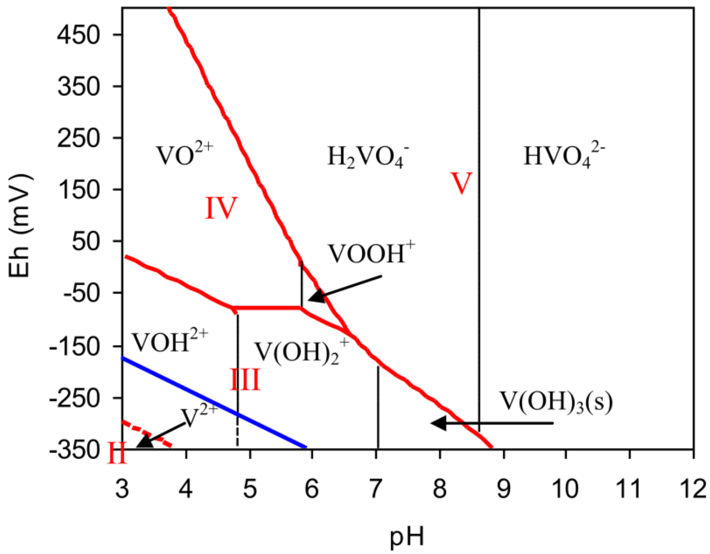

Figure 1. Eh-pH diagram of vanadium species formed in water at a vanadium concentration of 0.01 mM, in a background electrolyte of 0.01 M NaCl at 25ºC. Red lines indicate the transition between oxidation states and the blue line is the stability limit for water. Source: Gustafsson & Johnsson, (2004).

3.1.3 Retention in soils

Vanadium is considered to be well retained in soils (Cappuyns & Swennen, 2014; Martin & Kaplan, 1998; Mikkonen & Tummavuori, 1994b). In one study, less than 3% of the vanadium (0.56 mg m^{-2}) applied to a coastal plain soil migrated below the amended soil depth during a 30-month period (Martin & Kaplan, 1998). In another study, between 70 and 80 % of the added vanadium (510 mg kg^{-1} soil) was found to be retained at pH 4 in three Finnish mineral soils (Mikkonen & Tummavuori, 1994b). Application of different extraction and leaching methods to field-contaminated soils and sediments has demonstrated that a very small fraction (generally <1%) of the vanadium is readily dissolved (Cappuyns & Swennen, 2014; Teng *et al.*, 2011). Extremely low pH values enhance the solubility (Cappuyns & Swennen, 2014; Mikkonen & Tummavuori, 1994b). A sorption study conducted on 30 different mineral soils with a range of vanadate(V) concentrations (from 25 to 125 mg V kg^{-1} soil) found different sorption characteristics depending on the soil type (Gäbler *et al.*, 2009). The content of iron, aluminium and manganese (hydr)oxides was the main property that controlled vanadium sorption, but it was also affected by the clay and organic matter contents (Figure 2). Competition with other anionic species such as phosphate and arsenate may also reduce vanadium sorption in soils (Mikkonen & Tummavuori, 1994a). Over a long-term perspective, the behaviour of vanadium in soils is less well known, but its solubility has been shown to decrease with time (Martin & Kaplan, 1998).

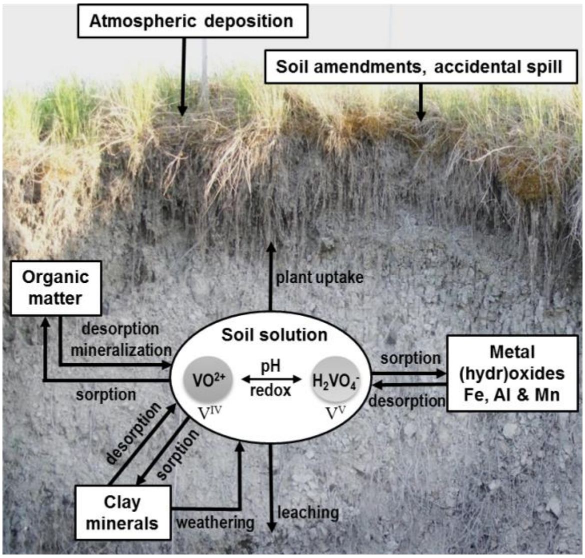

Figure 2. Processes affecting vanadium cycling in soils. Background photo: Ann Kristin Eriksson.

Metal (hydr)oxides

The concentration of vanadium in natural waters is positively correlated to the iron concentration (Wällstedt *et al.*, 2010; Auger *et al.*, 1999). This has been attributed to strong adsorption of vanadate(V) to colloidal iron (hydr)oxides (Wällstedt *et al.*, 2010). In natural soils, the metal (hydr)oxide content is considered one of the most important properties for vanadium sorption (Gäbler *et al.*, 2009). The sorption depends on the type of (hydr)oxide, as well as on solution pH and the ratio between solid and solute. Similar to other oxyanions such as phosphate, molybdate and arsenate (Antelo *et al.*, 2010; Su *et al.*, 2008; Gustafsson, 2003), vanadate(V) is strongly retained at lower pH, when (hydr)oxide surfaces are positively charged (Naeem *et al.*, 2007). Spectroscopic measurements have shown the formation of a vanadate(V) corner-sharing bidentate complex on the surface of goethite (Peacock & Sherman, 2004). Although vanadate is somewhat more strongly adsorbed than phosphate, high concentrations of phosphate in relation to vanadate can reduce vanadate sorption (Blackmore *et al.*, 1996). Sorption of vanadyl(IV) on metal (hydr)oxides may also occur (Wehrli & Stumm, 1989).

Organic matter

Soil organic matter influences the speciation and mobility of vanadium in soils (Gäbler *et al.*, 2009; Lu *et al.*, 1998). Firstly, dissolved organic matter may occupy the binding sites on metal (hydr)oxides and thereby reduce the sorption of oxyanions (Geelhoed *et al.*, 1998), although the significance of this process has been questioned (Guppy *et al.*, 2005). Another aspect is the capacity of organic matter to bind vanadium, in particular as vanadyl(IV) (Poledniok & Buhl, 2003; Lu *et al.*, 1998). The vanadyl ion coordinates to oxygen donor atoms, most likely on carboxylate ligands (Lu *et al.*, 1998). Humic substances may also reduce vanadium(V) to vanadyl(IV).

Tyler (2004), who studied the vertical distribution of trace elements in the soil profile of a Haplic Podzol, found that the surface (mor) layer, high in organic matter, retained relatively large concentrations of vanadium. The possibility to remove vanadium from waste waters by the use of a biosorbent has been tested and the maximum adsorption is reported to occur around pH 4 (Urdaneta *et al.*, 2008). In that study, vanadium sorption was found to be around 50% which was low in comparison with the maximum of 95% removal observed for other cationic metals such as lead(II), nickel(II) and chromium(II).

3.1.4 Toxicity and bioavailability

Soil microorganisms are known to be sensitive to metals (Giller *et al.*, 1998), but knowledge of vanadium toxicity is scarce. Nitrification and nitrogen mineralisation can be inhibited by vanadium addition (Liang & Tabatabai, 1978; Liang & Tabatabai, 1977). However, over a longer period of time (9 years) vanadium addition is reported to have no effects on nitrification (Wilke, 1989). Furthermore, the enzyme phosphatase, which is mainly released by soil microorganisms to mineralise organic phosphorus, has shown reduced activity as a result of vanadium addition to spruce needle mor (Tyler, 1976). In general, metal toxicity to soil microorganisms differs between soils due to variations in bioavailability, but also due to the natural diversity of microbial communities (Giller *et al.*, 1998).

Concerning vanadium toxicity to plants, vanadium is mainly accumulated in the roots (Yang *et al.*, 2011; Gil *et al.*, 1995; Kaplan *et al.*, 1990a). This is probably due to the reduction of vanadate(V) to vanadyl(IV) during root uptake, which decreases further translocation within the plant (Morrell *et al.*, 1986). For solution cultures of plants, the range of observed toxic vanadium levels is relatively wide and varies between plant species. Inhibition of radicle elongation, tested by solution cultures, has been reported for turnip, cabbage and collard greens at solution concentrations between 2.5 and 3.0 mg V L^{-1} (Carlson *et al.*, 1991; Kaplan *et al.*, 1990b). However, no decrease in radicle elongation of wheat was observed at vanadium concentrations up to 40 mg V L^{-1}, at which concentration millet even showed a stimulatory effect (Carlson *et al.*, 1991). In a recent study, five different plant species grown in an artificial soil with different nutrient additions showed a 50% reduction in plant biomass at soil vanadium concentrations ranging from 21 to 180 mg V kg^{-1} soil (Smith *et al.*, 2013).

As for other metals, soil type is important for vanadium bioavailability. For example, no toxic effects were observed in a study on collard greens grown on a loamy sandy soil at vanadium concentrations of 100 mg kg^{-1}, whereas collard green biomass was reduced at 80 mg V kg^{-1} when grown on a sandy soil (Kaplan *et al.*, 1990b). In a pot experiment with soybean seedlings, vanadium concentrations of 30 mg kg^{-1} soil were toxic in a Fluvaquent but concentrations of 75 mg V kg^{-1} soil showed no negative effects on the seedlings in an Oxisol (Wang & Liu, 1999). The differences in toxicity were attributed to the differing vanadium sorption capacity of the soils.

3.2 Determining vanadium speciation in soils

Vanadium speciation in soils is important not only from a purely chemical perspective but also when evaluating toxic risks. Several analytical methods have been developed to determine vanadium speciation in environmental samples (Pyrzynska & Wierzbicki, 2004a). The analytical procedure is complex due to the low vanadium concentrations that commonly occur in natural samples. Moreover, interference by other metals is a common problem. Some methods require changes of *e.g.* pH and redox conditions in the samples that may change the initial vanadium speciation. Consequently, methods that involve minimal pre-treatments are preferable.

3.2.1 Extraction and separation techniques

There are few published methods that cover vanadium speciation in soil samples, but extraction with *e.g.* phosphate to quantify leachable vanadium(V) has been suggested (Mandiwana *et al.*, 2005). Determination of vanadium speciation in natural waters is more common, and those methods may also be applicable to soil water. The use of chelating resins to separate the vanadium species has been proposed (Wang & Sanudo-Wilhelmy, 2008; Pyrzynska & Wierzbicki, 2004b; Soldi *et al.*, 1996). The resins tested in those studies (Chelex 100 and Cellex P) achieved a maximum sorption of vanadium(IV) and vanadium(V) at about pH 4.5. It was therefore necessary to adjust the sample pH before the samples could be run through the column. In principle, the vanadium species could then be eluted separately at different pH, or by addition of ethylenediaminetetraacetic acid (EDTA) or trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA). The complex-forming ligand EDTA shows good vanadium selectivity (Chen & Naidu, 2002). It forms complexes with both the cationic vanadyl(IV) and the anionic vanadate(V) by forming the anionic complex $[VO(EDTA)]^{2-}$ and $[VO_2(EDTA)]^{3-}$, respectively (Komarova *et al.*, 1991). This principle has been used to determine the vanadium speciation in bottled mineral waters (Aureli *et al.*, 2008). In that process, the vanadium-EDTA complexes are separated by high-performance liquid chromatography (HPLC) with an anion-exchange column with different retention times for the two complexes. The low vanadium concentrations can then be measured by inductively coupled plasma mass spectrometry (ICP-MS) (Aureli *et al.*, 2008).

3.2.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is a technique that utilises X-ray radiation generated by cyclic particle accelerators, synchrotrons (Kelly *et al.*, 2008). In principle, the specific binding energy of core electrons in atoms can be used to determine the oxidation state, coordination and binding geometries of different elements. The core electrons are tightly bound closest to the nucleus in an atom and their binding energy differs between elements and oxidation states. In XAS, samples are exposed to an X-ray energy range that covers the core electron binding energy for the element of interest. The electron absorbs the X-ray photons and is subsequently excited to higher orbitals or out into the continuum. The core hole thus formed is filled by another electron in an outer shell, which emits energy that gives rise to the absorption spectrum.

The XAS technique comprises two different methods; X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. XANES spectroscopy is applied to determine the oxidation state and coordination geometry of single elements. The binding environment of the element under study can be evaluated by EXAFS spectroscopy due to scattering of the photoelectron when it interacts with other atoms that surround the absorber atom. The advantages with this technique include the ability to detect low concentrations of a single element using minimum pre-treatment of the sample. In addition, its applicability to both solid and liquid samples makes the XAS method suitable for soil samples.

In the case of vanadium, the K absorption edge is at 5465 eV and the oxidation state may be determined from the main edge and features of the pre-edge peak (Figure 3). Wong *et al.* (1984) studied the XANES spectra of a large set of different vanadium minerals and laboratory standards with different

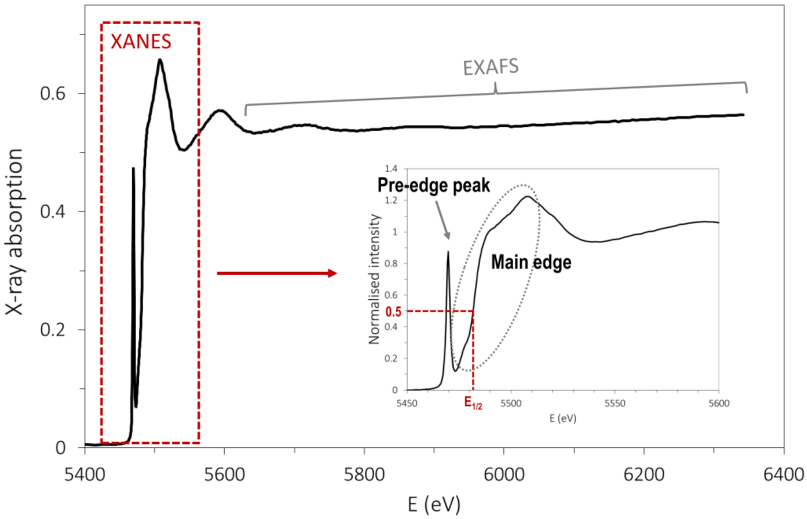

Figure 3. Vanadium K-edge X-ray absorption spectrum including the XANES and EXAFS regions. Inserted: Enlargement of the XANES region, showing its main features.

oxidation states and coordination geometries. The intensity and area of the pre-edge peak, and the position of the main edge, generally increased with increasing oxidation state, but they were also affected by the symmetry of the compound. Hence there may be overlaps in the main edge position and pre-edge peak intensity between oxidation states (Chaurand *et al.*, 2007b). Despite some limitations, these absorption features are still commonly evaluated and compared with vanadium standards when determining the vanadium oxidation state in unknown samples (Burke *et al.*, 2012; Sutton *et al.*, 2005; Mansour *et al.*, 2002; Rossignol & Ouvrard, 2001). There are also methods available that involve analysis of the pre-edge peak position plotted against the pre-edge peak intensity or area, which can provide further insights into vanadium symmetry (Chaurand *et al.*, 2007b; Giuli *et al.*, 2004). So far, vanadium K-edge XANES spectroscopy has commonly been applied to more heterogeneous samples, such as those originating from metallurgical processes, rather than to soils. However, it has been applied to soils for other elements, such as phosphorus (Prietzel *et al.*, 2010; Eveborn *et al.*, 2009). In that case, the shape of the main edge is of interest as it changes depending on the soil constituents with which the phosphorus is associated. This can be evaluated by linear combination fitting (LCF), where the sample spectrum is fitted to a set of standards representing the possible phosphorus forms in the soil. In the case of vanadium, the shape of the main edge also changes with binding mode (Wong *et al.*, 1984). LCF analysis is not commonly applied, but it has been tested for assessing vanadium binding to iron pipe corrosion by-products (Gerke *et al.*, 2010).

4 Materials and Methods

This thesis is based on five studies (Papers I-V) dealing with various aspects of vanadium behaviour in soils. These include the sorption pattern of vanadium to 2-line ferrihydrite (Paper I); vanadium sorption and speciation in soils and toxicity and bioavailability to soil microorganisms and plants in different mineral soils and with different vanadium treatments (Papers II, III, and IV); and the long-term impact of vanadium solubility and speciation in a forest soil (Paper V). The main experimental approach used throughout the work consisted of batch experiments and toxicity assays (Table 1). The batch experiments were applied to different soils and soil constituents to evaluate vanadium sorption, solubility and speciation. Speciation analysis was conducted on both solid samples and solutions by applying XANES spectroscopy and HPLC-ICP-MS, respectively (Table 1). In addition, EXAFS spectroscopy was used to determine the structure of the vanadium surface complex(es) formed on ferrihydrite.

Table 1. *Description of experimental and analytical methods applied in Papers I-V.*

	Paper I	Paper II	Paper III	Paper IV	Paper V
Batch experiments	√	√	√	√	√
Toxicity assays		√	√	√	
EXAFS	√				
XANES	√			√	√
HPLC-ICP-MS			√	√	√

4.1 Vanadium sorption to 2-line ferrihydrite (Paper I)

Ferrihydrite (Fh) is a poorly ordered naturally occurring iron (hydr)oxide with a large surface area that can retain a number of different elements (Cornell & Schwertmann, 2003). The ferrihydrite used in this study was synthesised in the laboratory using an adapted version of the method described by Swedlund and Webster (1999) and Schwertmann and Cornell (2000), resulting in 2-line ferrihydrite. The sorption experiments were conducted by adding dissolved vanadate(V), in a background electrolyte of 0.01 M $NaNO_3$, to Fh in a series of centrifuge tubes. In four single-sorbate series at different Fh:V ratios, vanadium sorption was studied as a function of pH by addition of HNO_3 or NaOH. In one ternary system, sorption competition was evaluated by adding dissolved phosphate together with vanadate(V) at different pH values. In addition, three series involved pH-dependent phosphate sorption in single sorbate systems and at different Fh:P ratios. The samples were equilibrated during 48 h in an end-over-end shaker and then centrifuged to separate the dissolved phase from the sorbent. The pH value was measured in the supernatant, which was then filtered (0.2 µm Acrodisc PF filter) and analysed for vanadium and other relevant elements (*e.g.* Fe, Al & P). The amount of sorbed vanadium was estimated by subtracting the measured vanadium concentration in solution from the total added vanadium.

Vanadium speciation and coordination to ferrihydrite were evaluated by XANES and EXAFS spectroscopy, respectively (see below). The results were used to define surface complexation reactions and constants in the CD-MUSIC model (Hiemstra & van Riemsdijk, 1996) within the Visual MINTEQ equilibrium software (Gustafsson, 2013). In the model, the surface area of the ferrihydrite was set at 650 m^2 g^{-1} and the site density at 7.8 sites nm^{-2} (Tiberg *et al.*, 2013). The inner and outer layer capacitances were set at 1.15 and 0.9 F m^{-2}, respectively. The model was calibrated using data from the single sorbate systems of vanadate(V) and phosphate. The optimised constants were then used to predict vanadate(V) and phosphate sorption in the binary systems. The final model was also applied to previously published data on vanadate sorption (Blackmore *et al.*, 1996).

4.2 Vanadium toxicity and bioavailability (Paper II-IV)

Vanadium toxicity and bioavailability were evaluated in detail for six different European mineral soils (Table 2). The soils were taken from the 20 cm surface horizon (A-horizon) and were selected to cover ranges of soil textures, pH values and metal (hydr)oxide contents. Three different vanadium amendments were analysed; soils freshly spiked with vanadate(V) (Paper II), soils that had

Table 2. *Name, origin and soil properties of different soils used for the toxicity assays.*

	Land use	pH	Org. C	$CaCO_3$	Mineral fraction[b] Sand	Silt	Clay	eCEC	V[c]	P-AL[d]	Oxalate extractable Al	Fe	Mn	Included in paper
		0.01 M $CaCl_2$	%	%		%		$cmol_c\ kg^{-1}$	$mg\ kg^{-1}$	$mg\ kg^{-1}$		$g\ kg^{-1}$		
Guadalajara (ES)[a]	Olive orchard	7.8	0.5	23	23	57	24	14.1	17	58	0.4	0.2	<0.1	II
Zwijnaarde (BE)	Arable land	5.2	1.6	n.d.	85	10	6	3.0	15	225	1.2	0.9	<0.1	II
Ter Munck (BE)	Arable land	6.6	0.9	n.d.	19	64	17	7.3	38	141	0.6	2.2	0.4	II
Pustnäs (S)	Grassland	5.9	1.1	n.d.	86	3	11	4.3	27	93	0.8	1.4	0.1	II, III and IV
Säby (S)	Arable land	5.5	2.5	n.d.	34	37	29	10.2	58	41	1.3	4.4	<0.1	II, III and IV
Hygum (DK)	Grassland	5.2	2.1	n.d.	56	31	13	7.6	31	n.d.	1.8	3.4	0.7	III

n.d.= not determined

[a]ES=Spain, BE= Belgium, S= Sweden and DK=Denmark

[b]Reported as percentage of the mineral fraction

[c]Vanadium soil concentration determined by *aqua regia* digestion

[d]Soil phosphorus soil content determined by ammonium lactate extraction

been spiked with vanadate(V) 5-10 months earlier (aged) (Paper III) and soils amended with blast furnace (BF) slag containing relatively large amounts of vanadium (Paper IV). Freshly spiked soils were subjected to five different toxicity assays (Table 3); two microbial tests (respiration and nitrification), and three plant tests (barley root elongation, barley shoot growth and tomato shoot growth). The three plant assays were also performed on the aged soils and the barley shoot growth assay was conducted on the BF slag-treated soils.

4.2.1 Soil treatments

The freshly spiked and aged soils were amended with different initial concentrations of dissolved vanadate(V) (0, 3.2, 10, 32, 100, 320, 1000 and 3200 mg V kg^{-1} soil). The freshly spiked soils were amended one week before the assays were carried out. The aged soils were kept outdoors in plastic pots with free drainage before starting the toxicity assays. Two soils, Pustnäs and Säby, were aged for approximately 10 months at an experimental facility in Sweden (Figure 4) and one soil, Ter Munck, was aged for five months at a facility in Belgium. The Pustnäs and Säby soils were also amended with two different BF slags (M-kalk and Merit 5000). These are two commercially available products, produced in the SSAB Oxelösund steelworks. M-kalk is an air-cooled blast furnace slag that is used as a soil amendment. Merit 5000 is a ground granulated blast furnace slag that is used in concrete. Both slags had a total vanadium concentration of approx. 800 mg kg^{-1} and were added at concentrations of 0.1, 1, 10 and 29 weight-% BF slag kg^{-1} dry soil. These corresponded to vanadium additions of 8-230 mg V kg^{-1} soil. The aged and BF slag-amended soils were again air-dried after the ageing period, sieved and then stored until the assays were conducted. Before starting the toxicity assays, all soils were wetted to half field capacity and then incubated for 1 week at 20 ºC in the dark.

Table 3. *Summary of toxicity assays performed for the different vanadium soil treatments.*

Soil treatment	Microbial assays		Plant assays		
	Respiration	Nitrification	Root elongation	Shoot growth	
			Barley	Barley	Tomato
Freshly spiked	√	√	√	√	√
Aged			√	√	√
BF slag				√	√

Figure 4. Ageing of the Pustnäs and Säby soils, after vanadate(V) addition, during the Swedish winter (above) and summer (right).

4.2.2 Toxicity assays

Microorganism

The two assays of soil microbial response, using respiration and nitrification as indicators, were performed following the standard procedure according to OECD 217 (OECD, 2000) and ISO 14238 (ISO, 1997), respectively. The respiration assay was conducted by adding 5 g of soil to plastic vials (three replicates per treatment), which were spiked with ^{14}C labelled glucose. The vials were then placed in bottles containing 5 mL 1 M NaOH to trap respired CO_2. After 24 h, the NaOH was sampled, a scintillation cocktail was added, and the $^{14}CO_2$ concentration was measured by beta scintillation counting (Tri Carb 2800 Tr; Perkin Elmer). The respiration rate was calculated based on the amount of labelled glucose respired per g of soil and day.

The potential nitrification rate (PNR) was evaluated after adding 100 mg kg^{-1} NH_4-N to 100 g of wetted soil, with three replicates per vanadium treatment. The soils were then stored in the dark at 20 ºC and three subsamples were taken from each soil after 0, 7 and 28 days. The subsamples were extracted with 1M KCl and the NO_3^- concentration in the extracts was measured calorimetrically (SA40; Skalar). The PNR was estimated by the increase in NO_3^- during the first seven days and expressed as µg NO_3-N g^{-1} soil day^{-1}. Due to the low nitrification activity in the Zwijnaarde soil, the calculated PNR was based on the NO_3^- concentration after 28 days.

Plants

The two different plant toxicity assays performed were a root elongation assay according to ISO 11269-1 (ISO, 1993) and a plant shoot assay according to ISO 11269-2 (ISO, 2005). All plants were grown in plastic pots containing

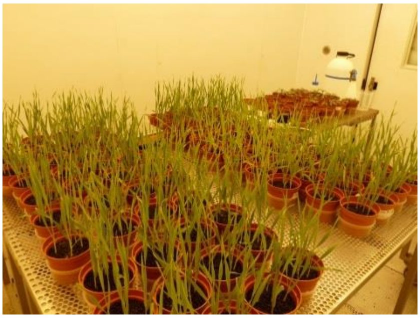

Figure 5. Barley plants growing in the growth chamber during the plant shoot assay.

approximately 500 g of soil and with a 1 cm layer of inert plastic beads placed on the soil surface to reduce water losses. During the growing period, the pots were placed in a growth chamber that was set to a 16 h light (20 ºC) and 8 h dark (16 ºC) cycle (Figure 5). Water losses from the soils were monitored and replaced on a daily basis.

The root elongation test was conducted with barley by planting 10 germinated seeds just below the soil surface in each pot (three replicates per treatment). The pots were then placed in the growth chamber for five days, after which the seedlings were carefully removed from the soils. The longest root of each seedling was measured and a mean value was calculated for each pot.

Two different plant shoot assays were performed; tomato and barley shoot growth, with four replicates per treatment. The soils were fertilised with 50 mg P kg^{-1} and 100 mg N kg^{-1} one week before commencing the assays to avoid nutrient deficiency. Twenty tomato seeds or 10 germinated barley seeds were placed just below the soil surface and the pots placed in the growth chamber. When 70% of the seedlings had emerged above the surface (8-11 days for tomato and 3 days for barley), they were reduced to five shoots per pot and left to grow for 12-14 days. After the growing period, the aerial parts of the plants were cut and weighed, air-dried at 70 ºC and then weighed again.

4.2.3 Soil and plant vanadium

The pseudo-total vanadium concentration in the soils (soil vanadium) was determined by *aqua regia* digestion, which was performed in duplicate for the freshly spiked and aged soils and in one replicate per treatment for the BF slag-treated soils. The dissolved vanadium concentration in the soils was established by soil solution extractions according to Merckx *et al.* (2001). The extractions were performed in duplicate on the freshly spiked and aged soils, which were wetted to just below field capacity and incubated at 20 ºC for three days. Soil solution was then collected from approximately 50 g of soil that had been centrifuged at 3000 *g* for 15 minutes. The amount of dissolved vanadium in the

BF slag-treated soils was determined by 0.01 M $CaCl_2$ extraction at a 20 g soil:20 ml $CaCl_2$ ratio with an equilibrium time of 24 h. The two extraction methods were compared for some samples of the freshly spiked soils and the vanadium concentrations were found to be within the same range.

The vanadium concentration in the plant (plant vanadium) was determined for the barley plants from the shoot assay by digesting 200 mg of plant material with 3-4 mL of 67% nitric acid at 180 ºC. All vanadium concentrations determined for soils and plants were measured by ICP-OES.

4.2.4 Statistical evaluation

The EC10 and EC50 values represent the concentration of added vanadium in the soil at which a 10 and 50% reduction in the response occurs, respectively. These values were determined for all toxicity assays performed on the freshly spiked and aged soils by a log-logistic dose response model (Equations 1-2):

$$Y = \frac{c}{1 + \frac{1}{9} exp(b \times ln \frac{X}{EC10})} \qquad Equation\ 1$$

$$Y = \frac{c}{1 + exp(b \times ln \frac{X}{EC50})} \qquad Equation\ 2$$

where *Y* represents the response (*i.e.* barley shoot biomass), *c* is the response parameter in the control, *b* is the slope parameter and X is the added vanadium concentration (total vanadium concentration minus the background vanadium in the soils from *aqua regia* digestions).

Significant differences in threshold values between soils and assays were pair-wise tested by single-sided *t* tests with 95% confidence limits.

4.2.5 Soil sorption properties

Vanadium sorption isotherms were determined for five of the mineral soils (Paper II). The isotherms were determined by performing batch experiments in which a range of dissolved vanadate(V) concentrations (0-15 mg V kg^{-1}) was added to the soils and equilibrated for six days. The vanadium sorption isotherms were then determined according to the Freundlich equation (Equation 3):

$$n_{init} + n_{sorb} = K_F \times c^m \qquad Equation\ 3$$

where the total concentration of sorbed vanadium is the initially sorbed vanadium (n_{init}) plus the vanadium sorbed from additions (n_{sorb}) and *c* is the measured dissolved vanadium concentration in solution. K_F (the Freundlich coefficient) and *m* (non-ideality parameter) are adjustable parameters. The n_{init} was fitted by trial and error, using the linear regression tool on log-transformed values in Microsoft Excel. The best fit was selected based on the highest obtained R^2 value and the optimised *m* and K_F could be obtained from the linear equation derived. Furthermore, the Freundlich sorption strength (FSS) was determined from the sorption isotherms for each soil and represented the amount of sorbed vanadium when the solution contained 2.6 mg V L^{-1}.

In one experiment in paper III, the vanadium reaction kinetics were studied. In addition to the three aged soils, a fourth soil (Hygum, Table 2) was included. The four soils were treated with two different concentrations of vanadium (32 and 100 mg V kg^{-1}) and incubated at 20 ºC. Between 3 and 100 days after soil spiking, sub-samples were taken and extracted with 0.01 M $CaCl_2$ to evaluate the change in soluble vanadium over time. Oxalate extractions was also performed on the amended and non-amended Pustnäs, Säby and Ter Munck soils to quantify the amount of vanadium retained by metal (hydr)oxides.

The Pustnäs, Säby and Ter Munck soils were also subjected to speciation analysis by XANES spectroscopy and/or HPLC-ICP-MS, as described in the "Analytical methods" section.

4.3 Long-term field study (Paper V)

The long-term field study was carried out in a pine forest stand at Ringamåla in southern Sweden that had been amended with converter lime in 1984, 26 years prior to sampling (Figure 6). The converter lime contained 14.6 g V kg^{-1} and had been added manually to the soil surface at concentrations of 0, 0.2, 0.7 and 1.0 kg V m^{-2} in 10 m × 10 m plots, corresponding to vanadium additions of 2.9, 10.2 and 14.6 g m^{-2}. Each lime addition was made in triplicate plots except for the highest addition, for which only one replicate was available. Separate

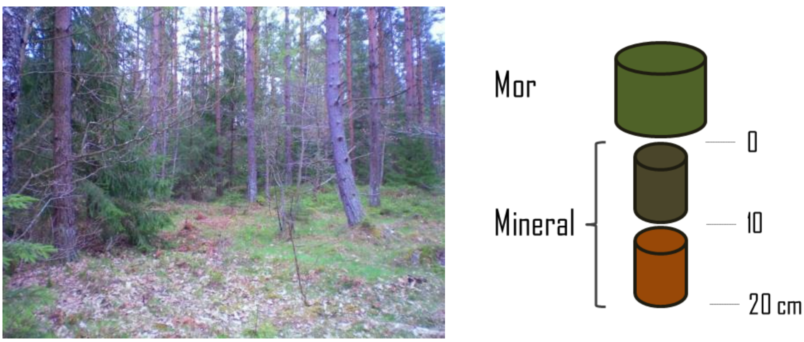

Figure 6. (Left) The Ringamåla field site and (right) schematic diagram of the soil layers sampled.

samples were taken from the mor layer (⌀ = 56 mm) and from the 0-10 and 10-20 cm layers (⌀ = 32 mm) of the mineral soil (Figure 6). A total of 10 soil cores were taken along two diagonals over each plot and bulked to one sample.

The vanadium concentrations in the soil samples were analysed by *aqua regia* digestion and XANES spectroscopy was applied to the fresh soil samples to determine the vanadium oxidation state in the bulk solid phase. In addition, the fresh soil samples were extracted with 0.01 M $CaCl_2$ (10 g soil:20 ml solution ratio) to determine the vanadium concentration in the dissolved phase of the soil and the vanadium oxidation state by means of HPLC-ICP-MS (see detailed description under "Analytical methods").

4.4 Analytical methods

4.4.1 X-Ray Absorption Spectroscopy

The XAS measurements were performed using the wiggler beam line 4-3, Stanford Synchrotron Radiation Lightsource (SSRL, Stanford, USA). Some of the measurements for collection of the EXAFS spectra were conducted at the wiggler beamline I811 at MAX-Lab, Lund, Sweden. Both stations were operated with a Si[111] double crystal monochromator and measurements were performed in fluorescence mode. The spectra were collected over an energy ranging from 5235 eV to at least 5645 eV for XANES spectroscopy samples, covering the vanadium K-edge of 5465 eV (Thompson *et al.*, 2009). For EXAFS spectroscopy measurements, the energy range was extended up to 6345 eV. The energy was calibrated with a vanadium foil that was measured simultaneously with, or between, sample measurements.

XANES data analysis

Vanadium K-edge XANES spectra were collected for vanadium sorbed to ferrihydrite (Paper I), two blast furnace slags (M-kalk and Merit 5000) (Paper IV) and soil samples collected at the Ringamåla site (Paper V). All spectra were imported into the Athena software version 08.056 (Ravel & Newville, 2005), where replicate scans were energy-calibrated and subsequently merged. To enable comparisons between samples, the merged spectra were normalised as described in Wong *et al.* (1984). In principle, two parallel lines were fitted to the pre-edge and post-edge regions of the spectra and the distance between the lines at E_0 was set to 1.

The pre-edge peak was estimated by means of peak fit analysis in the Athena programme, in which a baseline together with a combination of Gauss functions were fitted to the peak. The best fit was selected based on the lowest R-factor (Equation 4) reported by the programme.

$$R - factor = \frac{\Sigma(data - fit)^2}{\Sigma(data^2)} \qquad Equation\ 4$$

The area and maximum intensity were then determined from the net peak and the pre-edge peak position was established from the centroid position. The $E_{1/2}$ value, which describes the energy at which the normalised intensity equals 0.5, was determined from the normalised spectra.

Vanadium K-edge XANES spectra were also collected for five laboratory vanadium standards with oxidation states ranging from +3 to +5 (Table 4). The pre-edge peak features and the position of $E_{1/2}$ were evaluated and used as references to determine the vanadium oxidation states in the other samples. Different approaches for determining the vanadium oxidation state in unknown samples have been suggested. A method that employs the positive correlation between the pre-edge peak intensity and the oxidation state, as applied by Sutton *et al.* (2005), was used in Paper V. The standard pre-edge peak intensity (y) was plotted against the known oxidation state (x), to which a second order polynomial function was fitted (Equation 5):

$$y = 0.087x^2 - 0.371x + 0.408 \qquad Equation\ 5$$

Furthermore, vanadium spectra from sorption experiments conducted on ferrihydrite (Fh), aluminium (hydr)oxide (HAO) and organic matter (OM) were included as standards in Paper V. Together with a sample of native mineral-bound vanadium (inherent V), these standards were used in the LCF analysis in the Athena programme. The LCF was applied to identify soil constituents important for vanadium sorption in the Ringamåla soils. The

Table 4. Vanadium XANES standards included in Paper I, IV and V.

Standard	Pre-edge peak			Main edge	Oxidation
	Area	Intensity	Centroid position (eV)	$E_{1/2}$ (eV)	state
$V_2O_{3(s)}$	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 (pH4.5)	1.9	0.78	5469.9	5481.9	+5[a]
V+HAO (pH 6.7)	1.3	0.52	5469.8	5481.0	+5[a]
V+OM (pH 3.5)	1.0	0.36	5469.9	5479.7	+4[a]

[a]Oxidation state determined based on literature and comparisons with standards.

fits were set to include a maximum of three standards and were ordered according to the reported R-factor (Equation 4).

EXAFS spectroscopy

Vanadium K-edge EXAFS spectroscopy was performed on the ferrihydrite samples to identify the vanadium complex(es) formed on the ferrihydrite surface (Paper I). The method can be used to determine the distance between the central atom (in this case vanadium) and other atoms in the first and second coordination shells. Vanadium EXAFS spectra were collected for ferrihydrite samples ranging from pH 3.6 to 9.4 and for two standards of solid and dissolved vanadate (Na_3VO_4 and $H_2VO_4^-$, respectively). A total of 3-6 scans were collected for each sample, averaged and energy-calibrated by means of the EXAFSPAK programme package (George & Pickering, 1993). The programme was further used to draw and subtract the background (spline) function and for modelling the spectra.

4.4.2 HPLC-ICP-MS with EDTA complexation

HPLC-ICP-MS measurements were performed on dissolved vanadium samples. The method has been described by Aureli *et al.* (2008) and is designed to prevent changes in vanadium speciation by adding EDTA prior to analysis. The V-EDTA complexes are then run through a HPLC coupled to an ICP-MS.

The method was applied to the Ringamåla soil samples, for which 10 g of fresh soil were extracted using 20 mL 0.01 M $CaCl_2$ (Paper V). The aged soil samples included in Paper III were extracted using 0.01 M $CaCl_2$ (20 g:20 mL ratio) and water leachate of BF slag, together with sorption experiments performed on the Pustnäs and Säby soils, were analysed following the procedure described (Paper IV). A 50 mM aliquot of Na_2EDTA was added to the filtered samples immediately after extraction and stirred for 15 min. The samples were then stored at 8 °C until analysis which was performed within three weeks.

5 Results and Discussion

5.1 Vanadium adsorption to ferrihydrite (Paper I)

Iron (hydr)oxides are considered important for the retention of vanadium in soils and in the case of 2-line ferrihydrite, vanadium was strongly adsorbed (Figure 7). The adsorption increased with decreasing pH similarly to the oxyanions of *e.g.* molybdenum and phosphorus (Antelo *et al.*, 2010; Gustafsson, 2003), indicating adsorption of vanadate(V). The enhanced adsorption at lower pH is due to the increase in positively charged surface sites, which attract the negatively charged ion. Moreover, the adsorption edge moved towards higher pH values with decreasing Fe:V ratio and hence the adsorption strength increased with pH when the fraction of ferrihydrite increased in relation to the vanadium. Adding phosphate to the system reduced vanadium adsorption (Figure 7) but considering the large amount of phosphate in comparison with vanadate (200 and 50 µM respectively), vanadate was a strong competitor for the sorption sites.

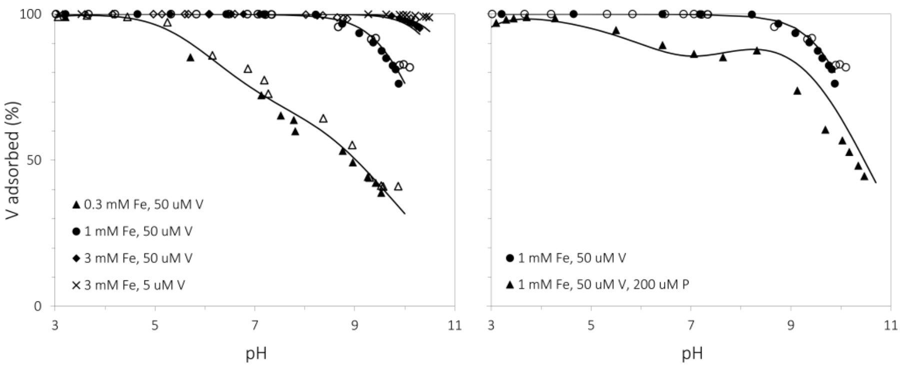

Figure 7. Vanadium sorption to 2-line ferrihydrite (left) at different Fe and V concentrations and (right) in competition with phosphate. Points are experimental observations and lines are modelled fits.

The vanadium K-edge XANES spectra of the ferrihydrite samples confirmed the adsorption of vanadate(V) (Figure 8). The pre-edge peak features together with the $E_{1/2}$ corresponded well to the $H_2VO_4^-{}_{(aq)}$ standard. In addition, interpretations of the EXAFS region showed that the vanadate adsorbed as an edge-sharing bidentate complex over the pH range studied (3.6-9.4) (Figure 8). This was a different complex than that determined for vanadate(V) adsorbed to goethite, which has been identified as a corner-sharing bidentate complex (Peacock & Sherman, 2004). Differences in complex formation between ferrihydrite and goethite have also been observed for copper(II) (Peacock & Sherman, 2005; Scheinost *et al.*, 2001) and for arsenite (Ona-Nguema *et al.*, 2005).

Adsorption was modelled with the CD-MUSIC model where three surface complexes, representing different protonation states of the bound vanadate, were used. The model was based on bidentate complexes as determined by EXAFS spectroscopy. The sorption pattern could be explained fairly well when applying the model to the system including vanadate and phosphate (Figure 7). The model also fitted to a dataset on vanadium sorption to ferrihydrite reported by Blackmore *et al.* (1996).

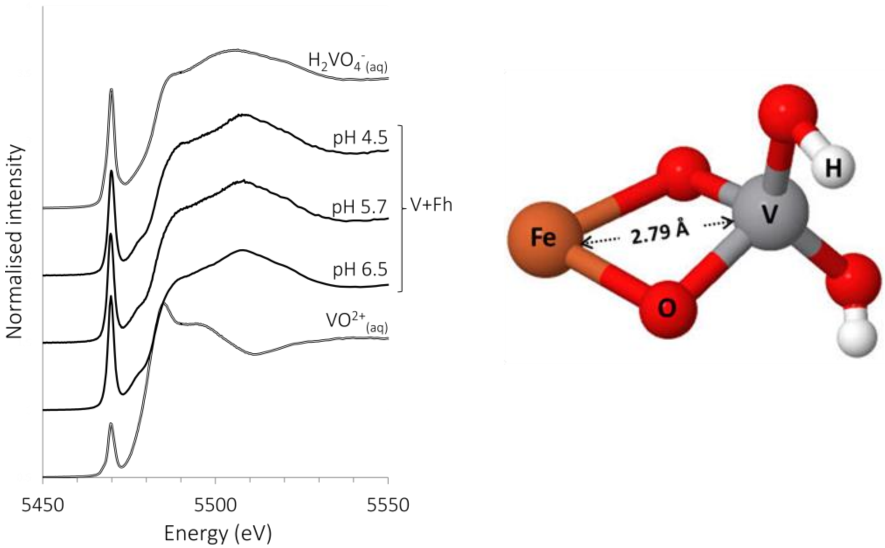

Figure 8. K-edge XANES spectra of vanadium adsorbed to 2-line ferrihydrite (V+Fh) together with two vanadium standards (left) and the edge-sharing bidentate complex formed on the ferrihydrite surface (right).

5.2 Vanadium toxicity and bioavailability (Papers II-IV)

5.2.1 Threshold values

The toxicity assays showed a clear negative response to increasing vanadium concentration in the soils. Hence no hormesis effects were observed for any of the toxicity assays performed.

Microorganisms

The EC50 values obtained in the substrate-induced respiration assay ranged from 200 to 580 mg added V kg^{-1} and the EC10 values from 8.4 to 58 mg added V kg^{-1} soil (Table 5). Many of the threshold values were uncertain, however, with large standard error. In the potential nitrification rate assay, EC50 values ranged from 28 to 690 mg added V kg^{-1} soil, which is a 24-fold difference between soils. Most of the EC10 values were within the range of the vanadium background concentrations. The potential nitrification assay is known to be a sensitive endpoint (Broos *et al.*, 2005). The response in the untreated control soils varied by a factor of up to 20 between soils. This demonstrated that the conditions in the soil itself had a strong influence on the microbial populations. Inhibition of nitrification and nitrogen mineralisation, in the short term, has previously been observed at a dose of 250 mg V kg^{-1} soil (Liang & Tabatabai, 1978; Liang & Tabatabai, 1977) but as indicated here the inhibiting vanadium concentration may span a much wider range in different soils.

Table 5. Vanadium toxicity threshold values (EC10 and EC50) for microorganisms in five different soils. Values are based on the added vanadium concentration ± standard error of the mean.

	Substrate-induced respiration			Potential nitrification rate		
Soil[a]	Control[b] (µg glucose g^{-1} d^{-1})	EC10 (mg V kg^{-1})	EC50 (mg V kg^{-1})	Control[b] (µg NO_3-N g^{-1} d^{-1})	EC10 (mg V kg^{-1})	EC50 (mg V kg^{-1})
G	46 ± 5	58 ± 26	580 ± 97	11.5 ± 0.7	19 ± 4	130 ± 11
P	321 ± 13	10 ± 4	200 ± 28	2.3 ± 0.2	14 ± 3	100 ± 8
S	502 ± 70	24 ± 11	320 ± 57	4.7 ± 0.1	190 ± 30	690 ± 46
T	190 ± 13	8.4[c]	320 ± 133	10.2 ± 0.2	35 ± 8	330 ± 30
Z	25 ± 2	26[e] ± 15	220[e] ± 50	2.1[d] ± 0.1	2.2[d] ± 0.7	28[d] ± 4

[a]See Table 1 for abbreviations.
[b]Microbial response in uncontaminated control soil with standard deviation (*n*=3).
[c]Standard error > threshold value.
[d]Value based on 28 observation days, see text.
[e]Threshold value based on nominal vanadium concentration.

Plants

The plant assays performed on the freshly spiked soils produced EC50 values that varied between 18 and 510 mg added V kg^{-1} soil (Figure 9). Tomato shoot growth was the most sensitive to increasing vanadium addition, while barley root elongation was the least sensitive. The latter finding was unexpected considering that vanadium is accumulated in plant roots (Yang *et al.*, 2011; Gil *et al.*, 1995; Kaplan *et al.*, 1990a). The reason may be the relatively short period of time (5 days) over which the assay was conducted. Comparing with other plant species grown in a standard soil with different V_2O_5 additions (Smith *et al.*, 2013) the EC50 values determined here were within the same range. However, as for the microbial assays, it was found that the variation increased when different soils were tested. In contrast to the microbial assays, the threshold values in the plant assays correlated to the soil type. The lowest threshold values were obtained in the sandy Zwijnaarde soil for all three plant assays and the highest values in the more clayey Säby soil.

In comparison with the freshly spiked soils, ageing of the soils increased the threshold values for plants by a factor of between 1.3 and 2.9. This resulted in EC50 values ranging from 46 to 780 mg added V kg^{-1} soil (Figure 9). The ageing process is known to reduce the bioavailability of other elements (Smolders *et al.*, 2009). In the case of vanadium, prior to this thesis work, ageing has only been briefly mentioned (Martin & Kaplan, 1998).

Soils amended with BF slag did not exert any negative impact on barley shoot growth up to the highest addition of 29 weight-% BF slag. However, the added vanadium concentrations in the BF slag-amended soils were within the range of threshold values determined for the freshly spiked soils. Hence, the bioavailability was much lower when the vanadium was added by BF slag.

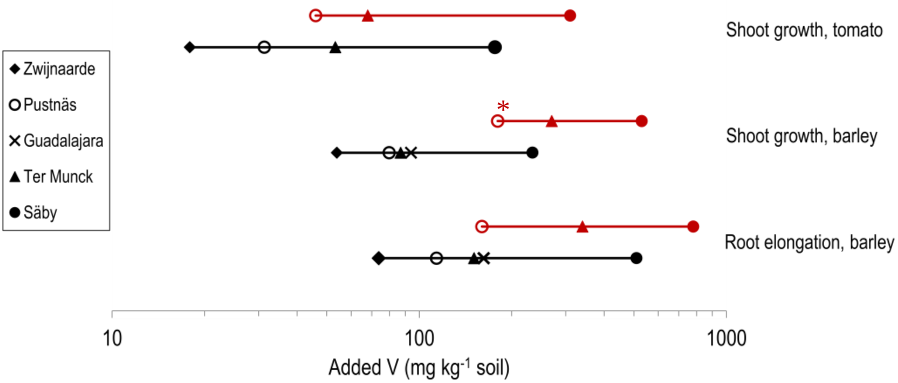

Figure 9. Range of vanadium EC50 values obtained for plant assays conducted on freshly spiked (black) and aged soils (red). Markers represent the EC50 value determined in the respective soil. The soil marked with * had an EC50 value larger than the stated value.

5.2.2 Bioavailability

The dissolved vanadium speciation was estimated by HPLC-ICP-MS on $CaCl_2$-extracts of the aged Pustnäs, Säby and Ter Munck soils (Paper III), and on the solutions obtained from sorption experiments performed with the Pustnäs and Säby soils (Paper IV). The results were consistent with the hypothesis that the prevailing oxidation state is vanadium(V). In most soils vanadium(V) comprised more than 90% of total dissolved vanadium concentration (Table 6). Considering the conditions in the soils used in the toxicity experiments, such as pH and organic matter content, the measured bioavailable vanadium was expected to mainly consist of vanadium(V) in all soils.

It was evident from the large range of toxic threshold values that different soils and different vanadium treatments affected the concentration of bioavailable vanadium. The FSS value, which was determined for the soils used in the freshly spiked treatment, was positively correlated to the measured EC50 values (Figure 10). In a correlation analysis performed on the EC50 values and different soil properties, none of the soil properties included could statistically be identified as significantly affecting the threshold values. However, there was a correlation between EC50 values and oxalate-extractable iron for four of the soils, excluding the Guadalajara soil. Metal (hydr)oxides are important for vanadium sorption in soil, but they are not the only controlling factor (Gäbler *et al.*, 2009).

Ageing of the soils decreased the vanadium bioavailability. This was shown not only by the EC50 values obtained, but also by the kinetic experiments in which the concentration of soluble vanadium decreased by approximately a half between 14 and 100 days after vanadium spiking. The importance of metal

Table 6. *Vanadium speciation in the dissolved phase of the soil, determined by HPLC-ICP-MS on $CaCl_2$-extracts of aged soils and on the solution of soils subjected to sorption experiments.*

Soil	V addition		Dissolved V	V(IV)	V(V)
		(mg kg^{-1})	(mg L^{-1})	(%)	
Aged soils (Paper III)					
Pustnäs	$H_2VO_4^-{}_{(aq)}$	150	3.03	4	96
Säby	$H_2VO_4^-{}_{(aq)}$	290	0.65	9	91
Ter Munck	$H_2VO_4^-{}_{(aq)}$	270	3.16	4	96
Sorption experiments (Paper IV)					
Pustnäs	$VO^{2+}{}_{(aq)}$	115	2.00	3	97
Pustnäs	$H_2VO_4^-{}_{(aq)}$	115	4.67	4	96
Säby	$VO^{2+}{}_{(aq)}$	115	0.23	32	68
Säby	$H_2VO_4^-{}_{(aq)}$	115	0.42	25	75

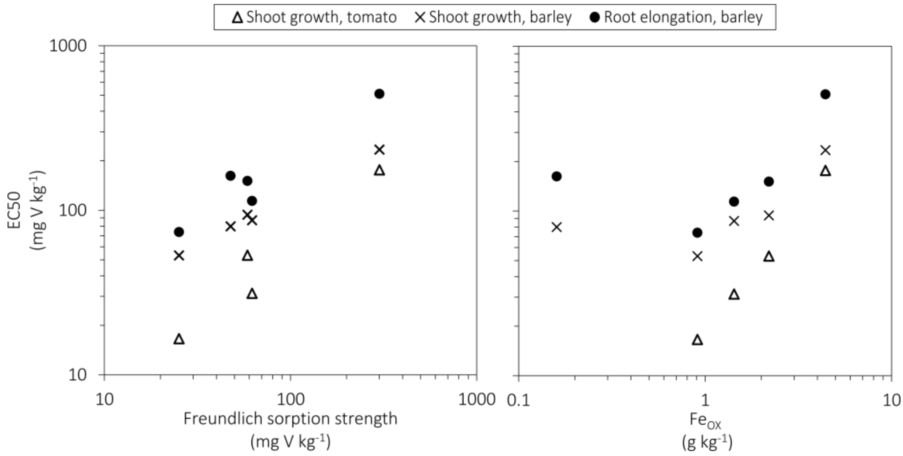

Figure 10. (Left) Vanadium sorption strength and (right) oxalate-extractable iron in relation to estimated EC50 values in the plant growth assays.

(hydr)oxides for vanadium sorption was confirmed by oxalate extractions of the aged soils, according to which extractable vanadium increased with ageing time. This is probably because vanadium was incorporated into the metal (hydr)oxides during ageing, as suggested by Martin and Kaplan (1998).

The plant vanadium content increased linearly with increasing *aqua regia*-extractable vanadium concentration in the soil when plotted separately by soil and vanadium treatment (Figure 11). Thus the vanadium concentration in the plant could be used as an estimate of bioavailable vanadium content in the soil. Even though vanadium is mainly accumulated in the roots, this relationship has also been observed in a pot experiment performed with alfalfa (Yang *et al.*, 2011). The largest increase in vanadium uptake (slope) was observed for the freshly spiked soils and the lowest for the aged and BF slag-treated soils (Figure 11). As discussed above, a fraction of the vanadium in the aged soils was incorporated into metal (hydr)oxides, but for the BF slags the slow dissolution of vanadium from the slag matrix was an additional process that controlled the bioavailability.

When all soils and vanadium treatments were plotted together, the correlation between vanadium bioavailability (*i.e.* plant vanadium) and the *aqua regia*-extractable vanadium concentration in the soil was weak, having large variation (Figure 12). This variation was however reduced significantly by comparing the plant vanadium against the dissolved vanadium concentration in the soil. In that case, the variation in plant vanadium was much smaller, regardless of vanadium treatment and soils. In other words, the dissolved vanadium concentration in the soil was a much better estimate of bioavailable vanadium in different soils and vanadium treatments.

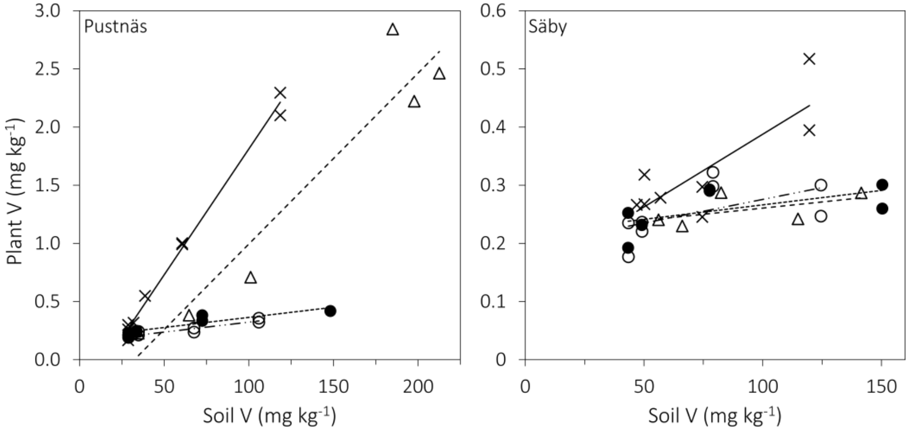

Figure 11. Vanadium concentration in barley shoots in relation to *aqua regia* extractable vanadium concentration in two soils, Pustnäs (left) and Säby (right). The soils were freshly spiked (×) or aged (Δ) with vanadate(V) salt and amended with two blast furnace slags: M-kalk (○) and Merit 5000 (●).

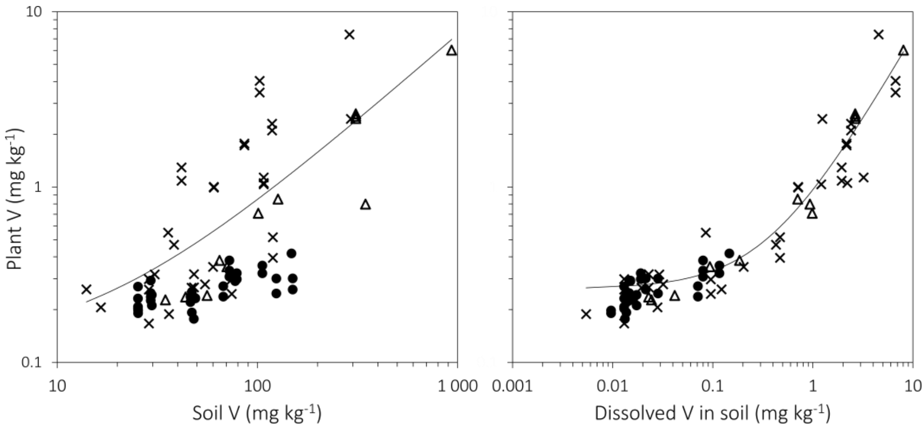

Figure 12. Vanadium concentration in barley shoots (plant V) (left) as a function of the *aqua regia*-extractable vanadium concentration in soil and (right) as a function of dissolved vanadium concentration in soil. Data for freshly spiked (×), aged (Δ) and BF slag-amended (●) soils. A linear regression line fitted the whole dataset (n=81), with R^2=0.50 (left) and R^2=0.80 (right).

5.3 Vanadium speciation - long-term field study (Paper V)

The vanadium concentrations in the forest soil that had received converter lime additions in the 1980s were highest in the mor layer (Figure 13). The fraction of recovered vanadium was estimated by comparing the *aqua regia*-digestible vanadium for the whole sampling depth against the added vanadium dose. The recovery was rather low for all converter lime-amended plots, ranging from 25 to 57%. Uncertainties in the distribution of the lime, the amount of vanadium recovered with *aqua regia* and vanadium uptake by vegetation made it difficult to evaluate the vanadium losses. Considering the strong sorption that has been established for iron (hydr)oxides (Gäbler *et al.*, 2009; Naeem *et al.*, 2007; Peacock & Sherman, 2004; Blackmore *et al.*, 1996), higher vanadium concentrations would have been expected in the mineral soil layers with their relatively high amount of oxalate-extractable iron and aluminium. The accumulation in the mor layer suggested either an important role of vanadium-organic complexes, or the presence of large amounts of unweathered converter lime. Furthermore, uneven distribution during spreading of the lime may have caused spatial variations.

Vanadium K-edge XANES spectroscopy was combined with HPLC-ICP-MS analysis to determine the vanadium speciation in the fresh soil samples. The distribution of different vanadium oxidation states in environmental samples has been the subject of several studies (Pyrzynska & Wierzbicki, 2004a), but very few have focused on soils and to the best of my knowledge, this is the first study to apply these two vanadium speciation methods to soil samples. Vanadium speciation was evaluated in both the sorbed and the dissolved phases of the different soil horizons to get a better understanding of soil properties affecting vanadium speciation in soils.

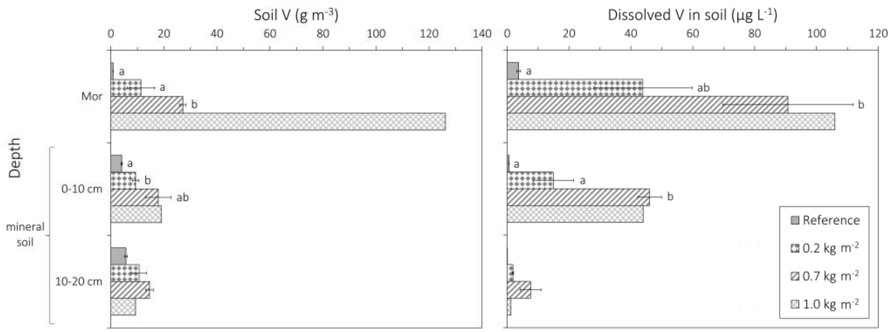

Figure 13. Vanadium distribution in the Ringamåla soil profile. (Left) *aqua regia*-extractable vanadium and (right) 0.01 M $CaCl_2$-extractable vanadium.

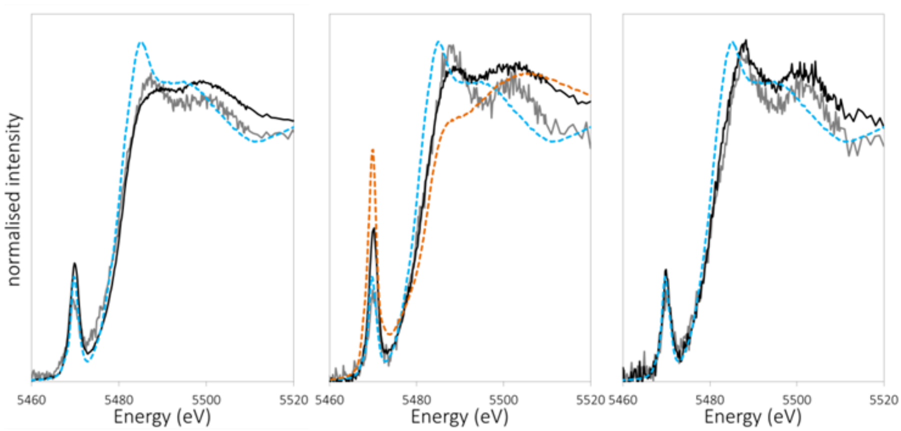

Figure 14. Vanadium K-edge XANES spectra of Ringamåla reference samples (grey lines) and samples treated with 1.0 kg converter lime m^{-2} (black lines). Blue and orange lines are the standard samples of $VO^{2+}_{(aq)}$ and $H_2VO_4^-{}_{(aq)}$, respectively.

In the mor samples, the vanadium K-edge XANES spectra showed a predominance of vanadium(IV) (Figure 14), despite the fact that the vanadium in the converter lime was in the form of vanadium(V). According to the LCF analysis, the added vanadium was mainly sorbed to the organic matter in the mor (Table 7). For the dissolved vanadium, determined by HPLC-ICP-MS, the fraction of vanadium(V) generally increased in the mor layer with increasing converter lime dose (Figure 15). Vanadium(V) is known to be reduced to vanadium(IV) by humic substances, but as the pH increases the reduction rate decreases (Lu *et al.*, 1998). The increasing lime dose increased the soil pH. This may be the reason for the increasing amount of vanadium(V) in the dissolved phase of the mor layer in the Ringamåla soil.

Table 7. *Results of linear combination fit performed on different layers of the Ringamåla forest soil, which had been treated with 1.0 kg converter lime* m^{-2} *26 years prior to analysis.*

	Standard (% of V sorbed)				R-factor
Sample	Inherent V	V+OM	V+Fh	V+HAO	
Mor	7	70	23	-	0.00031
Mineral soil, 0-10 cm	21	40	39	-	0.00029
Mineral soil, 10-20 cm	74	-	-	26	0.00122

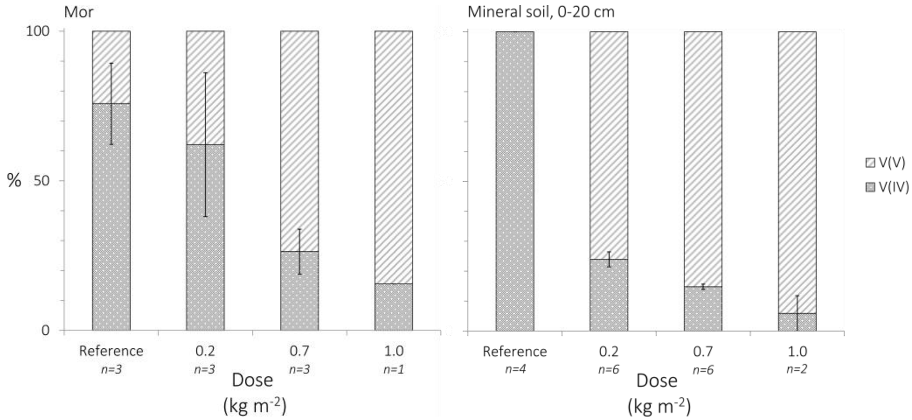

Figure 15. Vanadium speciation in the dissolved phase of the Ringamåla soil layers. Dissolved vanadium was extracted with 0. 01 M $CaCl_2$.

In the samples of the 0-10 cm mineral soil amended with converter lime, the pre-edge peak and $E_{1/2}$ of the XANES spectra showed a mixture of vanadium(IV) and vanadium(V) (Figure 14). For respective samples in the 10-20 cm layer, the pre-edge peak intensity and the $E_{1/2}$ were more similar to the standard of vanadium(IV). As indicated by the LCF results, the reason for this difference was the relative concentration of inherent vanadium in the two layers (Table 7). The inherent vanadium in the mineral soil was represented by vanadium(IV), which is reported to be located in the octahedral layers of clay minerals (Mosser *et al.*, 1996; Schosseler & Gehring, 1996; Gehring *et al.*, 1993). The non-inherent vanadium in the mineral soil contained a larger fraction of vanadium(V) in comparison to the mor layer. This was due to sorption to iron and aluminium (hydr)oxides, which involves vanadium(V) surface complexes (Burke *et al.*, 2013; Peacock & Sherman, 2004).

For the dissolved vanadium in the mineral soil, samples amended with converter lime consisted mainly of vanadium(V) (Figure 15). This was probably related to the soil pH and the relatively low concentration of dissolved organic matter. The reference samples contained only vanadium(IV). Since the dissolved vanadium concentration in the mineral soil was very low in the reference samples, it is possible that its speciation was controlled by vanadyl(IV) complexed to dissolved organic matter. However, the vanadium speciation in the different soil layers appeared to be controlled by the soil properties, and not by the oxidation state of vanadium added to the soil.

6 Concluding discussion

The aim of this thesis was to improve existing knowledge regarding vanadium sorption, toxicity and speciation in soils, with the ultimate aim of improving environmental risk assessments.

Vanadium adsorbed strongly to ferrihydrite forming a vanadate(V) edge-sharing bidentate complex. This complex could be used to describe the vanadium adsorption pattern in competition with phosphate by the CD-MUSIC model. The importance of iron (hydr)oxides for vanadium retention in soil was confirmed by adsorption experiments and the long-term field study. Hence, since ferrihydrite is an important sorbent in many Swedish soils, this model could be utilised in a more generalised model explaining vanadium sorption in soils. However, it was also shown that iron (hydr)oxides may not be the only determining factor for the sorption. Other soil constituents, such as organic matter and aluminum (hydr)oxides, may play a significant role in some soils and more detailed information regarding their role for vanadium sorption is needed. This would gain a more profound understanding of vanadium sorption as well as vanadium bioavailability in different soils.

The soil properties did not only affect vanadium sorption but also vanadium speciation in the soil. By combining two vanadium speciation methods, it was shown that vanadium speciation in soils was mainly determined by the conditions in the soil, and not by the vanadium species added to the soil. The two speciation methods used proved promising in terms of estimating the vanadium speciation with almost no pretreatment. Vanadium K-edge XANES spectroscopy had a distinct advantage with the strong correlation between pre-edge peak intensity and the position of the main edge with the oxidation state. However, evaluation of vanadium K-edge XANES spectra for soil samples needs to be improved. A larger library of vanadium standards would help determine the variation in pre-edge peak and main edge with oxidation state. It could also provide a possibility to extend the linear combination fitting approach.

The relationship demonstrated in this thesis between bioavailability and the vanadium concentration in the soil solution represents a great step forward in assessing the toxicity risks arising from vanadium in soils. Toxicity risk assessment could be even more accurate if more were known about factors in the soil solution that affect vanadium uptake. One aspect is the effect of concentration of other oxyanions in terms of competition for uptake by organisms as well as competition for sorption sites. Phosphate and dissolved organic acids are probably the most important compounds to consider since they occur in much higher concentrations in the soil compared to vanadium. Increased knowledge about the competition with other constituents could also be beneficial in terms of formulating remediation measures.

7 Vanadium and risk assessments

In principle, all blast furnace slags generated in Sweden today are re-used in *e.g.* road materials. One of the main concerns about their use in the environment is the elevated concentrations of vanadium they contain. The Swedish generic guideline values for vanadium in soil are 100 and 200 mg V kg^{-1} soil for sensitive and less sensitive land use, respectively, and are based on the pseudo-total vanadium concentration in the soil. In the first phase of an environmental risk assessment, the measured vanadium concentration in the soil is normally compared with generic guideline values. However, as shown in this thesis, vanadium bioavailability varies considerably between different soils and vanadium treatments. Hence the generic guideline values may be misleading by either over- or under-estimating the ecotoxicological risk in a specific soil.

One way to improve site specific risk assessments would be to relate the ecotoxicological risk to the soil solution concentration, which would narrow the range of uncertainty considerably. Soil solution chemistry not only gives a better estimate of vanadium bioavailability, but is also directly linked to the risk of vanadium leaching to groundwater and surface waters. From a practical perspective, a simple leaching test based on $CaCl_2$ extraction would probably be the most appropriate in this respect.

The risk of vanadium contamination of soils through addition of metallurgical slags seems very limited based on the experiments performed in this thesis. However, different slags differ in vanadium concentrations and solubility. Depending on the slag and the soil, the application may pose a risk of vanadium contamination. One aspect that needs to be considered is the leaching of vanadium from the material under field conditions, which should be based on *in situ* measurements over longer time periods. Another aspect is to consider the soil properties in areas where the material is applied, in order to assess the risk of vanadium contamination of waters and organisms.

8 Sammanfattning (Swedish summary)

Vanadin är en metall som förekommer naturligt i många jordar. Dock förekommer även utsläpp av vanadin från mänskliga aktiviteter som exempelvis förbränning av fossila bränslen. I norra Sverige finns det något högre halter av vanadin i berggrunden vilket leder till naturligt högre koncentrationer i de slaggprodukter som bildas under framställningen av råjärn. Dessa slaggprodukter, främst masugnsslagg, används vidare i cement och vägmaterial eller som jordförbättringsmedel. Trots tidigare erfarenhetar av risker med förhöjda vanadinhalter i jorden är kunskapen om vanadins beteende i mark och dess potentiella toxicitet mycket begränsad. Syftet med den här avhandlingen var att öka den kunskapen för att förbättra framtida riskbedömningar. I projektet studerades vanadins adsorption till ferrihydrit, toxicitet och biotillgänglighet i jord samt speciering i mark.

Ferrihydrit är en amorf järnoxid som är vanligt förekommande i svenska jordar. Den har en stor specifik yta vilket möjliggör en effektiv adsorption av olika lösta ämnen i marken. Skakförsök visade att vanadin adsorberades starkt till ferrihydrit. Andelen adsorberat vanadin minskade dock vid förekomst av högre halter fosfat. Med röntgenspektroskopiska metoder kunde det fastställas att vanadinet adsorberade som femvärt vanadat i ett mononukleärt bidentatkomplex. Denna kunskap utnyttjades i samband med utvecklingen av en modell som beskrev vanadinets bindning till ferrihydrit i konkurrens med fosfat.

Vanadins toxicitet och biotillgänglighet i mark utvärderades genom att utföra toxicitetsförsök med mikroorganismer och växter i vanadinbehandlade jordar. Toxiciteten fastställdes genom EC50-värden som jämfördes mellan olika jordar och vanadinbehandlingar. Försöken med mikroorganismer visade, i enlighet med tidigare studier, att dessa typer av försök hade stora variationer i toxicitet både inom och mellan olika jordar. För växterna fanns det ett tydligt samband mellan toxicitet och jordens förmåga att binda vanadin. Med en ökad bindningskapacitet i jorden ökade EC50-värdena vilka varierade upp till tio gånger beroende på jordart. Toxiciteten påverkades även när vanadinbehandlade jordar ”åldrades” i upp till 10 månader innan toxicitetstesterna utfördes. Under åldringsprocessen minskade det växttillgängliga vanadinet genom fixering till metalloxider. I en tredje vanadinbehandling tillsattes masugnsslagg till jordarna. Slaggen innehöll 800 mg V kg^{-1} men trots de relativt höga vanadinhalterna i jordarna kunde ingen vanadintoxicitet fastställas. Detta berodde på att vanadinet i slaggen endast i mycket liten grad var tillgängligt för växterna. Det stora spann av biologiska effektkoncentrationer som fastställdes för olika jordar och vanadinbehandlingar visade att gränsvärden baserade på den totala koncentrationen vanadin i jorden skulle bli osäkra. Detta eftersom jordegenskaperna starkt påverkar biotillgängligheten av vanadin. Dock fanns det ett tydligt samband mellan vanadinets koncentration i marklösning och dess växttillgänglighet, vilket tyder på att den lösta koncentrationen vanadin vore en betydligt bättre utgångspunkt för riskbedömningar.

Ytterligare en aspekt av vanadins kemi i mark är dess speciering. De två vanligaste redoxformerna i jorden är katjonen vanadyl(IV) och anjonen vanadat(V) där vanadat(V) är den mest toxiska. I ett långliggande skogsförsök i Ringamåla, södra Sverige, tillsattes K-kalk 1984. Kalken innehöll nästan 1,5 % vanadin och med hjälp av röntgenspekroskopiska och våtkemiska metoder utvärderades vanadinets speciering i jorden 26 år efter vanadintillsats. Den största delen av det tillsatta vanadinet band till det organiska materialet i måren. Det femvärda vanadin som tillsats med kalken hade samtidigt reducerats till fyrvärt vanadin. I mineraljorden ökade andelen femvärt vanadin till följd av binding till järn- och/eller aluminiumoxider.

Sammanfattningsvis har studien bidragit till en ökad förståelse av vanadins kemi i mark genom att belysa att den biotillgängliga delen vanadin främst styrs av mängden löst vanadin i marklösningen. Dessutom styrs specieringen i marken främst av jordens egenskaper och inte av formen vanadin som tillsatts till jorden.

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