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## Vanadium sorption by mineral soils: Development of a predictive model

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### HIGHLIGHTS

- A Freundlich model with a pH term described vanadium sorption to 26 mineral soils.
- XANES spectroscopy for 3 soils confirmed the predominance of adsorbed vanadate(V).
- Vanadate(V) sorption was weakly pH-dependent, with 0.36 H<sup>+</sup> co-adsorbed per V.
- Vanadate(V) sorption was related to oxalate-extractable Fe and Al.

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### ABSTRACT

The toxicity of vanadium in soils depends on its sorption to soil components. Here we studied the vanadate(V) sorption properties of 26 mineral soils. The data were used to optimise parameters for a Freundlich equation with a pH term. Vanadium K-edge XANES spectroscopy for three selected soils confirmed that the added vanadate(V) had accumulated mostly as adsorbed vanadate(V) on Fe and Al hydrous oxides, with only minor contributions from organically complexed vanadium(IV). Data on pH-dependent V solubility for seven soils showed that on average 0.36 H<sup>+</sup> accompanied each V during adsorption and desorption. The resulting model provided reasonable fits to the V sorption data, with  $r^2 > 0.99$  for 20 of 26 soils. The observed  $K_{ds}$  value, i.e. the ratio of total to dissolved V, was strongly dependent on V addition and soil; it varied between 3 and 4 orders of magnitude. The model was used to calculate the Freundlich sorption strength (FSS), i.e. the amount of V sorbed at  $[V] = 2.5 \text{ mg L}^{-1}$ , in the concentration range of observed plant toxicities. A close relationship between FSS and oxalate-extractable Fe and Al was found ( $r^2 = 0.85$ ) when one acidic soil was removed from the regression. The FSS varied between 27 and 8718 mg V kg<sup>-1</sup>, showing that the current environmental guidelines can be both under- and overprotective for vanadium.

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### 1. Introduction

Vanadium is a metal used in steel production, and therefore by-products (slags etc.) from the steel industry can be elevated in vanadium. In European soils, the median pseudo-total vanadium concentration (i.e. vanadium extracted by aqua regia) is 60.4 mg kg<sup>-1</sup>, with a range from 1.28 to 537 mg kg<sup>-1</sup>, according to the FOREGS database (Salminen et al., 2005). In many soils, only a very small part of the total V is easily leached (Cappuyns and

Slabbinck, 2012; Cappuyns and Swennen, 2014).

Relatively little is known about the speciation of V in soils. The geochemically active soil vanadium is generally expected to be present either as vanadium(IV) or as vanadium(V). The former occurs mainly as the oxocation VO<sup>2+</sup> (vanadyl), whereas vanadium(V) exists as the oxyanions H<sub>2</sub>VO<sub>4</sub><sup>-</sup> or as HVO<sub>4</sub><sup>2-</sup> (collectively referred to as vanadate) depending on the pH value. Vanadate(V) is considered the most toxic vanadium species (Martin and Kaplan, 1998; Larsson et al., 2013). In three Swedish soils it was found that the soil appears to be dominated by vanadium(IV) bound in primary minerals (Larsson et al., 2015a, 2015b); this V has probably a low bioavailability. However, when vanadium is added to soils (either as vanadium(IV) or vanadium(V) salts), it tends to accumulate as vanadate(V) sorbed to iron and aluminium hydrous oxides, except

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in acid organic soils, in which vanadyl(IV) complexed to organic matter will predominate (Larsson et al., 2015a, 2015b).

The sorption of vanadate(V) to iron(III) hydrous oxides is strong and involves the formation of inner-sphere bidentate complexes (Peacock and Sherman, 2004). As expected for anion adsorption, vanadate(V) is adsorbed most strongly at low pH, although some adsorption occurs at pH values as high as 10–11, against electrostatic repulsion (Blackmore et al., 1996). The values of the surface complexation constants, as well as results from competition experiments, show that vanadate(V) is bound even more strongly than phosphate and arsenate on Fe hydrous oxides (Rietra, 2001; Brinza et al., 2008; Wällstedt et al., 2010). The role of Al hydrous oxides for vanadate(V) sorption is less well known, although results from vanadium K-edge XANES experiments show that they contribute significantly to adsorption (Burke et al., 2013; Larsson et al., 2015a).

Vanadium is toxic to plants at high doses. For the most sensitive plants, toxic effects start to appear at solution concentrations of  $1 \text{ mg L}^{-1}$  (Kaplan et al., 1990; Larsson et al., 2013). The amount of V that can be added to a soil without giving toxic effects is, however, strongly dependent on the extent of vanadium sorption (Baken et al., 2012; Larsson et al., 2013). For these reasons it is of interest to develop models that can predict vanadium sorption to soils.

There are different approaches to the development of models for simulation of metal binding in soils. One is to use process-oriented surface complexation models (Gustafsson, 2006; Dijkstra et al., 2009; Weng et al., 2011). However, although these models provide insights to the mechanisms involved, they are difficult to set up for soils due to the large number of parameters that need to be estimated. Another approach is to use empirical isotherm equations. Although they are not process-oriented they can still be useful for predicting anion sorption as they require less input. For vanadium, the use of empirical partition relations (Groenberg et al., 2012) and of an extended Freundlich equation (Gäbler et al., 2009) were tested, with promising results. The Freundlich model can also be extended with a term accounting for the influence of pH, which is often the most important parameter that governs metal sorption in soils (Sauvé et al., 2000). We recently showed a new way to include such a pH term for describing  $\text{SO}_4$  adsorption to soils (Gustafsson et al., 2015). An important prerequisite for the use of a Freundlich model is that only one type of adsorption process is important. In the case of vanadium, the model is not likely to perform well if both vanadium(IV) complexation to organic matter and vanadate(V) sorption to Fe and Al hydrous oxides are significant. Therefore it may be hypothesized that the Freundlich models may work in mineral soils in which vanadate(V) sorption may be the predominant process.

The objective of this paper is to investigate the use of the pH-dependent Freundlich model of Gustafsson et al. (2015) for describing vanadate(V) sorption to 26 mineral soils (all having less than 12% organic C), and to discuss the possible use of the model for risk assessments. To investigate the hypothesis that adsorbed vanadate(V) was the predominant reaction product, vanadium K-edge XANES spectroscopy was performed for three of the soils, which were different concerning pH, content of Fe and Al hydrous oxides, and texture.

## 2. Materials and methods

### 2.1. Soils

A total of 26 samples from different mineral soils in Sweden, Belgium and Spain were used for the batch experiment. These soils represent a wide variation in soil properties and land management. Most of the soils were non-calcareous, with the exceptions of Fors

and Guadalajara. Selected soil properties are shown in Table A1 (Associated content). Most of the soil samples were from A horizons (topsoils). Some of the samples were from spodic B horizons of Spodosols (Kloten, Risbergshöjden, Risfallet and Tärnsjö). A C horizon from the Kloten Spodosol was also included. To study the effect of phosphate, A horizon samples from the Kungsängen fertility experiment were used; these samples are described in more detail by Eriksson et al. (2015, 2016). Briefly, the A3 treatment of the Kungsängen soil received no P fertilizer since 1963, whereas the D3 treatment received replacement of P with the previous year's harvest plus an additional  $20 \text{ P kg ha}^{-1}$  and  $50 \text{ kg K ha}^{-1}$ . The concentration of acid ammonium lactate-extractable P (P-AL) was  $1.0 \text{ mmol P kg}^{-1}$  in the A3 and  $2.9 \text{ mmol P kg}^{-1}$  in the D3 treatment, respectively (Eriksson et al., 2016). After collection, the samples were air-dried and sieved (2 mm) prior to the batch experiments.

### 2.2. Batch experiments

In the batch experiments, 2 g air-dried soil was mixed with 30 mL solution in a polypropylene centrifuge tube with a screw cap. The solution added to the soil always contained 0.01 M  $\text{NaNO}_3$ . For all soils, different concentrations of vanadate(V) (added as dissolved  $\text{NaVO}_3$ ) were added to study vanadate(V) sorption as a function of the equilibrium vanadium concentration in solution. The additions corresponded to 0, 0.15, 0.3, 0.6, 1.05, 1.5, 2.25, 3 and  $4.5 \text{ mmol V kg}^{-1}$  dry soil. For seven soils (Guadalajara, Kungsängen A3, Kungsängen D3, Pustnäs, Säby, Ter Munck, Zwijnaarde), pH-dependent V sorption was studied. In these experiments, varying concentrations of acid (as  $\text{HNO}_3$ ) or base (as  $\text{NaOH}$ ) was added to different centrifuge tubes to produce a range of pH values. These soil suspensions also contained  $50 \text{ }\mu\text{M}$  added vanadate(V) (equivalent to  $0.75 \text{ mmol V kg}^{-1}$  or  $38 \text{ mg V kg}^{-1}$ ) as well as 0.01 M  $\text{NaNO}_3$ . Further, the influence of competing  $\text{PO}_4\text{-P}$  (as  $\text{NaH}_2\text{PO}_4$ ) was studied in a separate series that, in addition to the concentrations of V and  $\text{NaNO}_3$  given above, also contained  $150 \text{ }\mu\text{M}$  added  $\text{PO}_4\text{-P}$  (equivalent to  $2.25 \text{ mmol P kg}^{-1}$ ).

After 6 days of gentle shaking at room temperature, the suspension was centrifuged. The pH of the supernatant was measured with a Radiometer combination glass electrode. The remaining supernatant solution was filtered through a  $0.2 \text{ }\mu\text{m}$  single-use filter (Acrodisc PF) and acidified to 1%  $\text{HNO}_3$  (suprapur) prior to the analysis of  $\text{PO}_4\text{-P}$  (colorimetrically using a Tecator Aquatec 5400 spectrophotometer with flow injection analysis), and of V, Al, Ca, Fe and Mg (ICP-SFMS at a quality-accredited laboratory; only the V results are shown).

### 2.3. XANES spectroscopy

By means of vanadium K-edge XANES spectroscopy, the speciation of vanadium was investigated for three selected soils from the batch experiments: Pustnäs A, Säby A, and Risbergshöjden Bs2 (c.f. Table 1). Unamended soil samples as well as samples treated with  $2.25 \text{ mmol kg}^{-1}$  vanadate(V) (i.e.  $115 \text{ mg V kg}^{-1}$ ) were used. The former samples were used in their air-dried state, whereas the latter were recovered from centrifuged soil suspensions after the batch experiments described in Section 2.1. The samples were left to air-dry to reduce the water content, but they were not allowed to dry out completely.

Vanadium K-edge XANES data were collected at beamline 4–3 at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA. The spectra for Pustnäs A and Säby A have been reported elsewhere (Larsson et al., 2015b), but here we give further details on linear combination fitting results. Procedures for collecting spectra of standards (V oxides, vanadate(V) adsorbed to ferrihydrite, vanadyl(IV) complexed to organic matter, etc) are

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