To my father Hessu
ABSTRACT

Chromium (Cr) and vanadium (V) are heavy metals that exist naturally in trace amounts in soils. However, their concentrations have increased due to loading from anthropogenic sources, e.g. chemical industry and tannery wastes, leachates from mine tailings, wood preservatives and combustion of fossil fuels. Moreover, both Cr and V are deposited in soils as impurities from fertilizers and soil amendments.

Chromium exists predominantly as Cr$^{\text{III}}$ and Cr$^{\text{VI}}$ species. The trivalent species (Cr$^{\text{III}}$) is an essential nutrient, whereas the hexavalent species (Cr$^{\text{VI}}$) is highly toxic. The stable V species under environmental conditions are V$^{\text{IV}}$ and V$^{\text{V}}$, with V$^{\text{V}}$ considered to be more harmful. The environmental impacts of Cr and V species rely on their availability for biological uptake, i.e. on their chemical bioavailability. Soluble species are easily taken up by biota and transferred to natural waters by leaching. However, research on the reactions and processes dictating the chemical bioavailability of Cr and V in soil is scarce, particularly for V.

In this research, the pH-dependent reaction patterns that dictate the chemical bioavailability of Cr and V species were unraveled. Furthermore, the risks of the utilization of alkaline steel industry slags as liming materials was assessed in terms of their Cr and V content chemically bioaccessible in soil. In particular, the mechanisms controlling the oxidation of slag-derived Cr$^{\text{III}}$ to hazardous Cr$^{\text{VI}}$ by manganese oxide (MnO$_2$) were carefully assessed.

The chemical reactions of V species were studied with two fine sand soils (surface soil and subsoil) mainly differing in their organic matter (OM) content. Soils were incubated with added V$^{\text{IV}}$ and V$^{\text{V}}$ species (0–500 mg V kg$^{-1}$) over a pH range of 4.0–6.9. Retention of both V species to solid organic phase were found to be higher in surface soil rich in OM (3.5%) than in subsoil poor in OM (0.5%). This result was driven by the ability of OM to both reduce V$^{\text{V}}$ to V$^{\text{IV}}$ and bind both V species. At higher pH, the reduction of V$^{\text{V}}$ by OM diminished, whereas the oxidation of V$^{\text{IV}}$ to V$^{\text{V}}$ increased. Due to the predominance of V$^{\text{V}}$ species, the chemical bioavailability of V increased in response to elevated soil pH, irrespective of the initial V speciation.

Similar to V, the chemical reaction patterns of Cr species were also highly pH-dependent. Field soil samples (fine sand, OM 6.2%) were incubated over
a chemically adjusted pH range of 3.9–6.3 with or without synthetic MnO₂. In addition, soil samples were incubated separately with BOFS dosages equivalent to 10 and 100 t ha⁻¹. Net-oxidation of Cr³⁺ to Cr⁶⁺ (i.e. the oxidation of Cr³⁺ minus subsequent reduction of produced Cr⁶⁺) in soil suspended in a 1 mM CrCl₃ solution occurred only in samples incubated with added MnO₂. In these particular samples, less than 5% of added Cr³⁺ was net-oxidized to Cr⁶⁺. The amount of Cr⁶⁺ formed in oxic soil conditions was regulated by the balance between two counteracting reactions: 1) oxidation of Cr³⁺ to Cr⁶⁺ by MnO₂ and 2) the subsequent reduction of Cr⁶⁺ to Cr³⁺ by organic matter. The production of Cr⁶⁺ was lowest under acidic soil conditions of pH ~4. At low pH, net-oxidation of Cr³⁺ diminished due to the enhanced reduction of Cr⁶⁺ back to Cr³⁺. At higher pH, the Cr³⁺ oxidation was limited by greater precipitation (or adsorption) of Cr³⁺, which lowered the overall amount of Cr³⁺ available for oxidation. Moreover, the oxidation reactions were found to be inhibited by formation of Cr(OH)₃ on the surface of MnO₂. Furthermore, the Cr³⁺ and the Cr⁶⁺ species produced during net-oxidation differ in terms of their pH-dependent chemical bioavailability. At elevated pH the chemical availability of added Cr³⁺ decreased, whereas that of newly produced Cr⁶⁺ increased.

Steel industry slags were efficient as liming materials. The release of Cr³⁺ or Cr⁶⁺ species from BOFS to soil was insignificant. Because of the low solubility of Cr³⁺, its oxidation on the oxidative surfaces of MnO₂ can be expected to be negligible. However, the apparent enhanced net-oxidation of Cr³⁺ (observed with excessive amounts of oxidative MnO₂ added to soil suspensions after Cr³⁺) indicated that in highly oxidizing conditions in soils rich in MnO₂ and poor in organic matter, inorganic Cr³⁺ deposits are susceptible to oxidation to Cr⁶⁺. In the terms of ecotoxicity, the risk that slag-derived Cr³⁺ will be oxidized to Cr⁶⁺ by soil MnO₂, is low. In addition, the chemical bioavailability of Cr species in slags is negligible at the pH conditions typical of agricultural soils. Instead, the release of V from BOFS/HVS is potentially problematic to soil organisms and surrounding natural waters.
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Helsinki, May 2017

Inka Reijonen
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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, which are referred to in the text by their roman numerals:


Additional material

This thesis also consists of previously unpublished material on the chemical bioavailability of V in various slags under oxic soil conditions.
CONTRIBUTION OF THE AUTHORS

I Inka Reijonen was the corresponding author and responsible for the experimental design to detail. Method validation was conducted in collaboration with Martina Metzler. Reijonen was in charge of presentation and interpretation of results. Author prepared the manuscript and conducted most of the statistical analyses, excluding normal probability plot of residuals for the relative water solubility of V species by Hannu Rita. Martina Metzler, Noora Manninen, Anu Ahvenainen and Mirva Kauppinen assisted in laboratory work. Co-author Helinä Hartikainen is responsible for the critical evaluation and corrections to manuscript.

II The idea to study Cr species (and Cr in slags) originated from Helinä Hartikainen. Inka Reijonen designed the study and conducted the laboratory work. She was in charge of selecting suitable methods and confirming their reliability. Reijonen also designed additional new methods (modification of the net-oxidation test, modification of EPA7196A method). She was the corresponding author, and in charge of the demonstration and interpretation of results. Helinä Hartikainen acted as the co-author and supported the writing process by with valuable comments and suggestions.

III The basic idea for the paper was developed by Inka Reijonen and Helinä Hartikainen. Inka Reijonen was responsible for the practical and analytical work in this paper. Author was also in charge of the experimental design. In addition, she designed the new experiments used (i.e. enhanced net-oxidation tests for Cr). Author was responsible for the manuscript (as corresponding author) with Helinä Hartikainen as the co-author.

Additional material. Inka Reijonen was solely responsible for the work related to additional material.
ABBREVIATIONS

Al  Aluminum
BOFS Blast Oxygen Furnace Slag
Ca(OH)₂ Calcium hydroxide
Cr Chromium
DOC Dissolved Organic Carbon
FA Fulvic acid
Fe Iron
GBFS Granulated Blast Furnace Slag
HA Humic acid
HCl Hydrochloric acid
H₂SO₄ Sulfuric acid
HVS High Vanadium Slag
ICP-OES Inductively Coupled Plasma- Optical Emission Spectrometry
KOH Potassium hydroxide
KCl Potassium chloride
KH₂PO₄ Potassium phosphate buffer
MnO₂ Manganese dioxide
NaOH Sodium hydroxide
P-buffer Potassium phosphate buffer
Si Silicon
SOM Soil Organic Matter
V Vanadium
WHC Water Holding Capacity
1 INTRODUCTION

1.1 INNATE CHROMIUM AND VANADIUM IN SOIL

Chromium (Cr) is the 24th and vanadium (V) the 21st abundant element in the Earth’s crust (Ščančar & Milačič, 2014; Rehder, 2015). In soil, a typical concentration of Cr is 10–50 mg kg\(^{-1}\) (Shanker et al., 2005) and for V, the range is 20–110 mg kg\(^{-1}\) (Kabata-Pendias, 2004). In soils derived from mafic or ultramafic rocks, the semi-total concentration of Cr can be as high as 1500 mg kg\(^{-1}\) and that of V 460 mg kg\(^{-1}\). On the other hand, soils originating from acidic rock material are very low in both Cr and V (<10 mg kg\(^{-1}\)) (Lindsay, 1979). Owing to their extensive use, these heavy metals are of high economic relevance and, consequently, released into the environment in significant amounts.

1.2 ANTHROPOGENIC SOURCES OF CHROMIUM AND VANADIUM

1.2.1 Use of chromium and vanadium

Chromium and vanadium are used for various purposes e.g. as catalysts, color pigments and as components of steel and other metal alloys. In 2015, the world total production of (marketable) chromite ore, the main source of Cr, was 27 000 000 tons (Ober, 2016). The commercial demand for Cr is partly satisfied by re-cycling. In U.S., 34 % of the consumption originated from secondary sources in 2015 (Ober, 2016).

Most of V is recovered as a by-product of ores that are primarily mined for other elements, such as iron. Vanadium is a constituent in 65–80 different minerals, particularly in titaniferrous magnetite or phosphate minerals (Nriagu, 1998; Lide, 2008). The global mining rate in 2015 was 79 400 tons, with most V minerals originating from China.

In addition to their industrial use, the possibilities to use Cr and V in pharmaceuticals have been investigated. Some compounds of V have shown potential as antidiabetic-agents (Thompson et al., 1999; Thompson et al., 2009). However, the use of V in the treatment of diabetes is not generally applied. Chromium is also demonstrated to enhance the insulin response in type II diabetic patients, but its functionality in actual treatment of diabetes mellitus is not recognized (Anderson, 1998; Landman et al., 2014). Nonetheless, Cr is sold as a common nutrient supplement in the form of, for instance, Cr picolinate (Lukaski, 1999; USHHS 2002).
1.2.2 Release of chromium and vanadium

The Cr and V in soils have increased from their natural levels by loading from anthropogenic sources, e.g. wastes from chemical industry (color pigments, catalysts, and reagents), leachates from mine tailings and municipal wastes and sludges (James, 1996; Zayed & Terry, 2003; ATSDR, 2012; Ding et al., 2016). Chromium is also released from tannery wastes, chromite ore processing residues (COPR) and CCA (Chromium Copper Arsenate) wood preservatives. Vanadium is abundant in almost all coal and crude oils as VO$_{2+}$ porphyrin complexes (Buchler & Smith, 1975; ATSDR, 2012; Rehder, 2015). Thus, during past decades, the elevated combustion of fossil fuels has notably increased especially V emissions. In addition, Cr and V are deposited into soils as impurities from fertilizers and soil amendments. In particular, phosphate fertilizers and steel industry slags (used as liming materials or as ground materials for roads and other constructions) contain Cr and V residues (ATSDR, 2012).

1.2.3 Steel industry slags

Slags are produced in massive quantities as by-products of steel manufacturing. Granulated blast furnace slag (GBFS) is formed in the smelting process of iron ore/pellets with coke and flux (limestone, burned lime or dolomite). Silicate and aluminate impurities in the ore and coke are chemically bound to lime (CaO), and then removed as a molten slag. Granulation of the blast furnace slag is performed by rapid cooling with large volumes of water. Blast oxygen furnace slag (BOFS) is formed in the basic oxygen converter during the conversion of pig iron into crude steel. In this process, molten metal from blast furnace is treated with oxygen to remove impurities via oxidation at 1400–1650 ºC (Yildirim & Prezzi, 2011). Oxidation is followed by slag formation with burned lime.

The principal components of both slags are silicates, aluminates and oxides of calcium (Ca), or to lesser extent of magnesium (Mg) (Waligora et al., 2010). In BOFS, the level of silica (Si) is lower than in GBFS (Song & Jennings, 1999). Conversely, the amount of manganese (Mn) and, particularly, iron (Fe) oxides is greater. In addition, slags contain residues of Cr and V. The proportion of Cr in BOFS varies within the range 0.1–0.5%, whereas the concentration for V typically is 0.01–1.5 % (Tossavainen et al., 2007; Chaurand et al., 2007). In GBFS, Cr and V levels are substantially lower. For instance, in U.S., the mean level of Cr and V in GBFS is reported to be as low as 0.013% and 0.005%, respectively (Proctor et al., 2000).

Manufacturing a ton of pig iron produces 0.2–0.3 tons of blast furnace slag (BFS) that can be further granulated to GBFS (Jewell & Kimball, 2014). In 2015, the global production rate of pig iron was 1.2 billion tons (World Steel Association, 2016). Thus, 240–360 million tons of BFS was simultaneously produced. The output mass of BOFS per ton of crude steel is
0.1–0.15 tons (Jewell & Kimball, 2014). The worldwide production of crude steel in 2015 was 1.6 billion tons, from which 74.4% was produced by the oxygen converter process (also known as Linz-Donawitz- or basic oxygen furnace processes). Consequently, 119–179 million tons of BOFS was formed (World Steel Association, 2016). The amount of slags produced can be expected to increase with the increasing trend of steel manufacturing.

Natural resources are, however, limited. Consequently, recycling or re-use of the substantial slag volumes is essential from both an environmental and economic perspective. In U.S., 15–50% of BOFS is piled and deposited to landfills. The waste rate for BFS is lower (<10%) (Yildirim & Prezzi, 2011). Slags can be used in various applications, e.g. as constituents of cements, road pavements, construction components and insulation material. Some steel industry slags are used as raw materials in the production of phosphorus (P) fertilizers (Hosseini et al. 2016). Steel slags are also utilized to remove P from run-off and waste waters (Johansson, 1999; Bowden et al., 2009; Penn et al., 2012). Also the possibility to re-use these P saturated slags as fertilizers has been investigated (Bird & Drizo 2009). Moreover, slags are efficient as soil liming materials owing to their high CaO content. However, the re-use of steel industry by-products need to meet the criteria of environmentally sustainable use. Therefore, it is necessary to assess the risks related to Cr and V in GBFS and BOFS under conditions typical in soil.

1.3 CHALLENGES IN RISK ASSESSMENT: CHEMICAL BIOAVAILABILITY

Soil contamination by heavy metals, including Cr and V, is a global problem that exerts adverse effects on human health and the functions of ecosystems. Remediation of contaminated sites is expensive and, thus, not always economically plausible. In Europe, 2.5 million hectares of soil is exposed to loading by heavy metals or mineral oil. The expected annual management costs for these sites are estimated to be ~6 billion euros (Panagos et al., 2013). Negative economic impacts also arise from the deprivation of productive land use. For instance, in China, over 20 million hectares of arable area has been lost due to soil contamination by heavy metals (Hu et al., 2014).

In most European countries, the hazard evaluation in the risk assessment of soils and, consequently, the need of remediation is based on determination of the (semi)total amounts of harmful elements (Provoost et al. 2006). This practice is problematic as the total concentrations are poor indicators of the actual ecological risks associated with a given element. The natural levels of metals rely on the mineralogy of the soil parent bedrock material. Consequently, some soils are naturally rich in a given element without being contaminated, while others can be severely affected by the same levels originating from anthropogenic sources.
Even when the natural variations in background levels of metals are thoroughly considered in the risk assessment, the chemical behavior of the contaminants in soil needs further attention. From the perspective of ecological risk assessment, the critical issue is the concentration of the element that is readily soluble or will potentially be released from the solid phase. Thus, the metals in the soil solution and soil particles that are available to receptor organisms can be taken to represent the potentially bioavailable available fraction (Naidu et al. 2008). Toxic heavy metals in this fraction threaten not only terrestrial organisms, but also the organisms in water ecosystems. Soluble and potentially soluble elements are at risk of leaching into recipient watercourses and groundwater. Therefore, even soils that have relatively low total concentrations can be hazardous if the bioavailability of the contaminant is high. On the other hand, soil naturally rich in a given element may not be contaminated.

Availability of contaminants to organisms is an important factor in risk assessment, but the term “bioavailability” is somewhat poorly defined. In general, bioavailability refers to the concentration of an element actually taken up by a biological receptor (Stokes et al., 2005). In the present work, the terms chemical bioavailability and bioaccessibility are used to describe the proportion of an element in the soil that is easily available for biological uptake.

Soils are complex heterogeneous systems where the chemical bioavailability of metals is regulated by various chemical reactions: adsorption-desorption, precipitation-dissolution and organic complexation (reaction with solid organics, differing from those of soluble organics of small molecular weight). These reactions are influenced by soil properties, e.g. pH, redox-status, ionic strength (I) and composition of the soil solution, the amount and quality of soil organic matter (SOM) and (hydr)oxides of iron (Fe), aluminum (Al) and manganese (Mn) (Alloway, 2013; Bolan et al. 2014). Furthermore, the reaction patterns of metals in soil are influenced by biological activities, e.g. plant root exudates and microbial functions. Overall, the chemical processes (abiotic and biological) in soil make up the backbone of the ecological risk assessment.

Chromium and vanadium belong to the group of transition metals that typically have more than one oxidation state. This renders their chemical behavior rather complicated. Consequently, the risk assessment of Cr and V is exceptionally challenging. In natural environmental conditions, chromium exists predominantly as Cr\textsuperscript{III} and Cr\textsuperscript{VI}. The prevalent species of vanadium are V\textsuperscript{IV} and V\textsuperscript{V}, although in some primary and mafic minerals V\textsuperscript{III} is also found (Essington, 2015). Nonetheless, in terms of risk assessment the trivalent species of V is not relevant as it is not stable in environmental solutions. The oxidation state of Cr and V dictates the formation of their ionic species. As a result, Cr and V can exist as both cationic and anionic species. These ionic species differ decisively in their geochemical and environmental behavior, as well as in their toxicity. At present, the chemical reaction patterns that
underpin their chemical bioavailability in soils are not fully understood. In particular, research on the chemical processes of V in soil is relatively scarce.

1.4 BIOLOGICAL FUNCTIONS

The impact of Cr on biological systems depends on its speciation. The hexavalent species, CrVI, is a strong oxidizer, teratogen and mutagen, and classified as a human carcinogen by International Agency of Cancer Research (IARC 2012; De Flora, 2000). In contrast, the trivalent form of Cr, CrIII, is considered an essential micronutrient for several animals as well as humans. Several functions are suggested for CrIII in the glucose and fat metabolism (Anderson, 1989). Nonetheless, the specific structures of Cr containing enzymes are not explicitly described (Stearns, 2007). At higher doses, however, CrIII is harmful to living organisms.

The toxicity of CrVI is estimated to be 100-1000 fold higher than that of CrIII (Miller-Ihli, 1992). Oxyanionic CrVI can easily enter eukaryotic cells via sulfate and phosphate transporters. Uptake of CrVI is followed by its reduction to CrIII that induces breakage of DNA-strands (Salnikow & Zhitkovich, 2007; Stearns, 2007). Oxidative damage attributable to the formation of free radicals, particularly hydroxyl radicals (·OH), during the reduction processes contribute to the toxicity of CrVI (De Flora, 2000).

The essentiality of Cr for plants has not been demonstrated. However, at low levels, CrIII stimulates the plant growth, but at higher dosages it is phytotoxic (Zayed & Terry, 2003). Several symptoms of CrIII and CrVI stress in plants have been described: reduction of photosynthesis, enzyme activity and germination, as well as the impaired growth of stems, leaves and roots (Shanker et al., 2005). The transport of both Cr species to upper parts of plants is limited by their accumulation in roots. Nevertheless, CrVI is recognized to be more harmful to plants than CrIII. In soil, the phytotoxicity of added CrVI is recorded at extremely low concentrations (at 0.1 mg kg⁻¹) (Martí et al., 2007). The high toxicity of CrVI is suggested to be associated with its relatively high availability in soil and easy transport into plant cells (Lopez-Luna et al., 2009).

The biological functions of V are less clear than are those of Cr. There is no consensus on the role of V as a micronutrient to humans. However, it appears to be essential to some animals. Deficiency symptoms are described, for example, for goats, chicken and rats (Nriagu, 1998; Anke et al., 2005). A range of biologically active V compounds is thoroughly discussed in a review by Rehder (2015). The properties and activities of V containing proteins are diverse. For instance, V is found in the prosthetic groups of the oxidizing haloperoxidase enzymes in some green algae, seaweeds and lichens (Crans et al., 2004). It also acts as a substitute for molybdenum in the nitrogenase enzyme of the nitrogen fixing Azotobacter-bacteria (Bellenger et al., 2011). Some eukaryotes, e.g. mushrooms of the Amanita genus, ascidians (sea
squirts) and the *Pseudopotamilla accelata* sea worm even accumulate V (Rehder, 2013). However, accumulation of V is not demonstrated to exert any specific benefits (Rehder, 2015).

**In general, it appears that V^{V} is more toxic than V^{IV}**. Acute toxicity values (LD$_{50}$) of V$^{V}$ on several mammals are notably higher than are those of V$^{IV}$ (Thompson *et al.*, 1998). The toxicity of V$^{V}$ is suggested to result from the inhibition of various vital enzymes, e.g. Na$^{+}$-K$^{+}$-ATPase, Ca$^{2+}$-ATPase and various phosphatase enzymes (Leonard & Gerber, 1998). Nonetheless, both V$^{V}$ and V$^{IV}$ species are reported to have toxic mutagenic and teratogenic properties (Rehder, 1991; Rodríguez-Mercado *et al.*, 2011). However, only V$^{V}$ is classified as potential carcinogen to humans (in the form of vanadium pentoxide, V$_{2}$O$_{5}$) (IARC, 2012).

### 1.5 CHEMICAL SPECIATION

#### 1.5.1 Chromium in aqueous solution

**Inorganic** Cr$^{III}$ exists as cationic species. At pH<4, Cr$^{III}$ is prevalent as Cr$^{3+}$. At elevated pHs, it is hydrolyzed to weakly soluble Cr(OH)$_{3(s)}$ that controls the solubility of inorganic Cr$^{III}$ species (Saleh *et al.*, 1989):

\[
\begin{align*}
    \text{Cr}^{3+} + \text{H}_2\text{O} & = \text{Cr(OH)}^{2+} + \text{H}^+ & \text{pK}_{a1} & \approx 3.9 \\
    \text{Cr(OH)}^{2+} + \text{H}_2\text{O} & = \text{Cr(OH)}^{2+} + \text{H}^+ & \text{pK}_{a2} & \approx 6.3 \\
    \text{Cr(OH)}^{2+} + \text{H}_2\text{O} & = \text{Cr(OH)}_{3(s)} + \text{H}^+ & \text{pK}_{a3} & \approx 7.8 \\
    \text{Cr(OH)}_{3} + \text{H}_2\text{O} & = \text{Cr(OH)}_{4}^- + \text{H}^+ & \text{pK}_{a4} & \approx 11.5
\end{align*}
\]

In theory, the presence of anionic Cr(OH)$_{4}^-$ in solutions is possible, but only in extremely alkaline conditions (pKa=11.5). Thus, anionic species of Cr$^{III}$ are not relevant in environmental conditions.

**At higher oxidation state**, Cr$^{VI}$ exists as oxyanionic chromate species, HCrO$_{4}^-$ and CrO$_{4}^{2-}$ (Sperling *et al.*, 1992). Chromic acid (H$_2$CrO$_{4}$) is a strong acid (pK$_{a1}$<1), that readily dissociates to HCrO$_{4}^-$ in solutions:

\[
\begin{align*}
    \text{H}_2\text{CrO}_4 & = \text{HCrO}_4^- + \text{H}^+ & \text{pK}_{a1} & \approx 0.7
\end{align*}
\]

At elevated pH, HCrO$_{4}^-$, a moderately strong acid, is further deprotonated to form CrO$_{4}^{2-}$:

\[
\begin{align*}
    \text{HCrO}_4^- & = \text{CrO}_4^{2-} + \text{H}^+ & \text{pK}_{a2} & \approx 6.5
\end{align*}
\]
1.5.2 Vanadium in aqueous solution

**Inorganic V**

**IV** is always coordinated to oxygen and exists mainly as cationic species. In acidic conditions, **V**

**IV** is predominant as VO**2**+ species (Crans et al., 1998). Above pH 4, VO**2**+ is hydrolyzed to VO(OH)**+** (pKa≈5.4). At pH 5–6, the solubility of inorganic **V**

**IV** is controlled by formation of insoluble VO(OH)2(s) (Crans et al., 2004). Above circumneutral and anaerobic conditions, soluble **V**

**IV** is reported to exist as anionic species: (VO)2(OH)5– dimer or VO(OH)3– monomer (Crans et al., 2004). However, in oxic conditions these species are considered unstable. Overall, the hydrolysis reactions of **V**

**IV** are rather complex, and hydrolysis constants for most of the reactions are not reported. The following simplified hydrolysis reactions are given in the literature (Wehrli & Stumm, 1989):

\[
\begin{align*}
VO^{2+} + H_2O &= VO(OH)^+ + H^+ \quad pK_{a1} = 5.4 \text{ (Rosotti & Rosotti, 1955)} \\
2 \cdot VO^{2+} + 2 \cdot H_2O &= (VOOH)_{2^{+}} + 2 \cdot H^+ \\
VO^{2+} + 2 \cdot H_2O &= VO(OH)_{2(s)} + 2 \cdot H^+ \\
VO(OH)_{2(s)} + H_2O &= VO(OH)_3^- + H^+
\end{align*}
\]

**The predominant species of V**

**V** are oxyanionic. At pH above 3.5, H3VO4 is the main species and under alkaline conditions HVO42– (Heath & Howarth, 1981):

\[
\begin{align*}
H_3VO_4 &= H_2VO_4^- + H^+ \quad pK_{a1} = 3.5 \\
H_2VO_4^- &= HVO_4^{2-} + H^+ \quad pK_{a2} = 7.8 \\
HVO_4^{2-} &= VO_4^{3-} + H^+ \quad pK_{a3} = 12.7
\end{align*}
\]

Under highly acidic conditions (pH below ~3) **V** exists also as cationic VO2+ because the uncharged vanadic acid (H3VO4) is not thermodynamically stable (Crans et al., 2004).

1.5.3 The pH-Eh dependency of speciation

**The chemical speciation of Cr and V is dependent on the solution pH and redox-conditions.** Their predominant aqueous species are described in Figure 1. Soil Eh can vary from a well-oxidized 800 mV to extremely reducing ~500 mV, with anoxic conditions prevailing at Eh below 0 mV (Evangelou, 1998). In general, at high pH and under oxidizing conditions, the oxyanionic species of Cr**VI** and **V** are predominant. In contrast, acidic and reducing conditions enhance the formation of cationic species of Cr**III** and **IV**.
Figure 1. Eh-pH diagram of aqueous a) Cr species (10^-6 M) (modified from Kotaś & Stasicka, 2000) and b) V species (10^-4 M) (modified from Langmuir et al., 2003). Dashed line illustrates the range of soil redox and pH conditions.

Speciation also depends on the Cr and V concentration. This should be acknowledged particularly for V(V), as the self-condensation reactions of vanadate become relevant at mM concentrations. For instance, below pH 6 and above 0.2 mM concentration, decavanadate (H$_2$V$_{10}$O$_{28}^{5-}$) is suggested to be the predominant V(V) species (Tracey et al., 2007). Concerning Cr(VI), polymeric species (mainly dimeric Cr$_2$O$_7^{2-}$) exist only at rather high concentrations (>10^-2 M) (Kotaś & Stasicka, 2000). In dilute solutions, Cr(VI) and V(V) are prevalent as monomeric species. In contaminated soils, however, the formation of polymeric V(V) species may be significant. In addition, V(V) forms polymeric species with other oxyanions, e.g. phosphates and arsenates (Gresser & Tracey, 1990; Mikkonen & Tummavuori, 1994). These multielemental species are potentially relevant in soils high in soluble V.

In soils, the speciation chemistry of Cr and V as a function of pH-E$_h$ conditions is not as straightforward as in solutions of pure elements. The chemical composition of soil solution is far more diverse and complicated than that of solutions of pure elements that do not contain soluble and particulate organic matter, oxidizing material, etc. The activity of Cr and V species in soil solution is controlled by adsorption-desorption, complex and chelate formation as well as precipitation-dissolution reactions. Some programs, such as Visual Minteq, have been developed to model speciation chemistry in soils. However, practical experiments are needed as the multiple chemical reaction patterns in soils are influenced by not only abiotic, but also biological factors (e.g. biological uptake, root exudates, microbial activity). In addition, the exceptionally complicated speciation chemistry of V renders its modelling very challenging. In fact, the speciation chemistry of V is not yet fully understood. For instance, the identification of the EPR (Electron Paramagnetic Resonance, also known as Electron Spin Resonance, ESP) silent species, has been difficult. The silent species have a net-zero electron spin under the electromagnetic radiation and, thus, they
are difficult to detect by the EPR-method. Thus, some chemical equilibria are typically absent from the reaction data of modelling softwares.

1.6 CHEMICAL BIOAVAILABILITY AND THE POTENTIAL REACTIONS PATTERNS OF CHROMIUM AND VANADIUM SPECIES IN SOIL

Research on the chemical bioavailability of Cr and V in soils is relatively scarce, particularly for V. However, the prerequisite to assess the potential bioavailability and, thus, ecological risks of Cr and V, is to understand the chemical reaction patterns of their various species in soil where numerous reactions and processes occur concomitantly. Adsorption and precipitation of Cr and V species reduce their concentration in soil solution, which in turn can be expected to lower their bioavailability. On the other hand, desorption of Cr and V from soil particles back to solution (or dissolution of precipitates) makes these heavy metals available for biological uptake.

Sorption mechanisms especially depend on the speciation of Cr and V. Consequently, the chemical bioavailability of Cr and V is anticipated to be influenced by redox-reactions that govern their ionic speciation. In addition, to chemical accessibility, the toxicity of Cr and V is also impacted by chemical speciation. Therefore, it is essential to understand the mechanisms that control the formation of hazardous CrVI and VV species in soil. Equally, it is of importance to identify reactions that can lower the toxicity of CrVI and VV species, for instance by their reduction into less toxic and less mobile CrIII and VIV species. The chemical reactions to be discussed below form the theoretical background of the working hypotheses (given in detail in Chapter 2) of this study.

1.6.1 Irreversible adsorption and precipitation of CrIII and VIV

In general, the mobility of CrIII and VIV species in the biosphere is considered low due to their precipitation as reluctantly soluble hydroxides (Bartlett & Kimble, 1976; Tracey et al., 2007). Cations of Cr3+ and VO2+ are hard Lewis acids (high positive charge and d1 electron configuration), wherefore they form strong inner-sphere complexes with the oxygen donating sites of minerals. Consequently, in addition to self-precipitation, the mobility of CrIII and VIV is diminished by their irreversible and specific adsorption onto Fe-, Al-(hydr)oxide surfaces and clay minerals (Wehrli & Stumm, 1989; Wehrli et al., 1990; Bradl, 2004). The chemical bond formed in the inner-sphere surface complex is covalent. Therefore this adsorption is not electrostatic, and the retention occurs also on positively charged surfaces. Certainly, the attraction/repulsion between adsorbing surface and the CrIII and VIV species is influenced by electrostatic forces. Moreover, this retention is irreversible wherefore CrIII and VIV sorbed as hydroxide cations are poorly bioaccessible.
1.6.2 Adsorption and desorption of oxyanionic Cr$^{VI}$ and V$^{V}$

Chromate (HCrO$_4^-$ and CrO$_4^{2-}$) and vanadate (H$_2$VO$_4^-$) species are oxyanionic analogs of phosphates. Therefore, similar to phosphates their chemical availability and, consequently, biological uptake is lowered by their adsorption onto (hydr)oxides surfaces. This type of specific sorption of anions is based on ligand exchange between the surface –OH and –OH$_2$ groups (e.g. Goldberg & Sposito, 1984; Grossl et al. 1997). In the inner-sphere surface complex formed, the oxyanionic ligand is bound onto the adsorbent by means of co-ordination bond (either mono- or bidentate). For Cr$^{VI}$, sorption onto Fe- and Al- (hydr)oxides is well demonstrated (Zachara et al., 1987; Zachara et al., 1989, Choppala et al., 2016). For V, only experiments with Fe-(hydr)oxides are reported (Peacock & Sherman, 2004). However, on the basis of the oxyanionic speciation, it can be anticipated that V$^{V}$ is also retained by Al-(hydr)oxides. The specific sorption of oxyanionic species of Cr$^{VI}$ and V$^{V}$ by ligand exchange is reversible. In other words, replacement of Cr$^{VI}$ and V$^{V}$ from sorption sites by competing anions (such as –OH, arsenate, phosphate, selenite, and fluoride) releases HCrO$_4^-$ or CrO$_4^{2-}$ and H$_2$VO$_4^-$ back to soil solution.

1.6.3 Binding to soil organic matter

In soils, soil organic matter (SOM) consists of easily degradable organic constituents and humic substances, i.e. humin, humic acids (HAs) and fulvic acids (FAs). The cationic Cr$^{III}$ (mainly as Cr$^{3+}$ and Cr(OH)$^{2+}$) is retained by organic matter, including humic compounds, by complex formation and chelation (Kozuh et al., 2000; Kyziol et al., 2006). Similarly, V$^{IV}$ (as VO$^{2+}$) is reported to be bound onto humic substances (Templeton & Chasteen, 1980). Retention of Cr$^{III}$ and V$^{IV}$ to SOM is strong owing to the formation of covalent bonds with the oxygen donating sites of organic compounds. Consequently, various organic species of Cr$^{III}$ and V$^{IV}$ are highly stable.

The sorption of Cr$^{III}$ and V$^{IV}$ to insoluble SOM can be expected to reduce their levels in the soil solution. On the other hand, binding to soluble SOM can enhance the chemical accessibility of Cr$^{III}$ and V$^{IV}$. The ability of SOM to retain Cr$^{VI}$ and V$^{V}$ species remains unclear. In theory, the sorption of oxyanionic Cr and V species is notably weaker than that of cationic Cr$^{III}$ and V$^{IV}$ species (which act as hard Lewis acids).

1.6.4 Oxidation of Cr$^{III}$ to Cr$^{VI}$ by MnO$_2$

Molecular oxygen as well as amorphous or well-crystallized manganese (Mn$^{IV}$/Mn$^{III}$) (hydr)oxides (referred to as MnO$_2$) are known to oxide Cr$^{III}$ to hazardous Cr$^{VI}$. Oxidation by O$_2$ takes place only under highly alkaline conditions at pHs above 9 (Zachara et al., 1989). Therefore, in soils, the oxidation of Cr$^{III}$ to Cr$^{VI}$ is considered attributable to poorly crystalline MnO$_2$.
Their ability to oxidize Cr\textsuperscript{III} is favored by their generally low PZC (Point Zero Charge) and large surface area. However, also well-structured pyrolusite (\(\beta\text{-MnO}_2\)) with high PZC is found to be a strong oxidizer of Cr\textsuperscript{III} (Eary & Rai, 1987). The oxidation reaction occurs on the surfaces of solid Mn\textsuperscript{IV}O\textsubscript{2} (or Mn\textsuperscript{III} oxides) after the formation of an inner-sphere complex with Cr\textsuperscript{III} (Fendorf, 1995). Consequently, only soluble Cr\textsuperscript{III} species are considered susceptible to oxidation. The overall oxidation reaction at pH 5 is (Fendorf, 1995):

\[
1.5\text{ MnO}_2 + \text{Cr(OH)}^{2+} = \text{HCrO}_4^- + 1.5\text{ Mn}^{2+}
\]

The oxidation reaction of Cr\textsuperscript{III} to Cr\textsuperscript{VI} by MnO\textsubscript{2} is regulated by pH. Its impact on Cr\textsuperscript{III} oxidation has been extensively studied with various MnO\textsubscript{2} minerals but without soil (Eary & Rai, 1987; Fendorf & Zasoski, 1992). Actually, there are no studies available on the role of pH in the oxidation mechanism of Cr in soil. Soil redox-conditions differ decisively from those in the experiments with pure minerals. In soil, the redox reactions of Cr are influenced by numerous physico-chemical and biological factors. For instance, microbial activity influences the formation of MnO\textsubscript{2}, the Cr\textsuperscript{III} oxidizer. Most of the highly reactive MnO\textsubscript{2} in soils is considered to be biogenic in origin, attributable to the ability of various bacteria and fungi to oxidize Mn\textsuperscript{2+} to MnO\textsubscript{2} (Tebo \textit{et al.}, 2004). The microbially catalyzed oxidation of Mn\textsuperscript{2+} can occur rapidly, and in conditions differing markedly from those in abiotic oxidation by O\textsubscript{2}.

### 1.6.5 Oxidation of V\textsuperscript{IV} to V\textsuperscript{V} by oxygen

The main oxidizer of V\textsuperscript{IV} is molecular oxygen. Thus, in oxic conditions the availability of O\textsubscript{2} does not limit the oxidation of V\textsuperscript{IV} to V\textsuperscript{V}. This reaction is enhanced by increased pH and by adsorption of the hydrolyzed species of vanadyl, VO\textsuperscript{2+}, onto hydroxide surfaces (Wehrli & Stumm, 1989). However, the oxidation processes of V have not been studied in soil.

### 1.6.6 Reduction reactions of chromium and vanadium

In oxic soils, Cr\textsuperscript{VI} is reduced by SOM to Cr\textsuperscript{III} (Fendorf, 1995). The reduction of V\textsuperscript{V} to V\textsuperscript{IV} can be expected to occur similarly by organic soil constituents. Easily degradable organic matter is a better reductant than stable humic substances. However, reduction of Cr\textsuperscript{VI} to Cr\textsuperscript{III} and that of V\textsuperscript{V} to V\textsuperscript{IV} by humic and fulvic acids are also reported (Wilson & Weber, 1979; Nakayasu \textit{et al.}, 1999). Furthermore, the reduction reaction is followed by the binding of the reduced species to humic substances. In anoxic conditions, ferrous iron (Fe\textsuperscript{II}) and sulfides act, in turn, as the main reductants (Wanyt & Goldhaber, 1992; Patterson \textit{et al.}, 1997; Fendorf \textit{et al.}, 2000).
Reduction of Cr and V occurs via abiotic and biological pathways. Microbiological reduction of V\textsuperscript{V} to V\textsuperscript{IV} is ascribed to several organisms, e.g. Microccous bacteria genus and Pichia guillermondii yeast isolated from silty clay loam soil (Bautista & Alexander, 1972). In addition, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Shewanella oneidensis mediate the reduction of V\textsuperscript{V} (Carpentier et al., 2003; Bredberg et al., 2004). It is even suggested that microbes play a major in the formation of V precipitates via reduction of V\textsuperscript{V} to V\textsuperscript{IV} (Lovley, 1993). Concerning Cr, there are several studies on the aerobic and anaerobic bacterial reduction of Cr\textsuperscript{VI} to Cr\textsuperscript{III} (e.g. Wang & Shen, 1995; Quilntana et al., 2001; Pal & Paul, 2004).

Furthermore, plants also participate in the biological reduction reactions. For instance, plant root exudates of broad leaf cattail (Typha latifolia) and shallow sedge (Carex lurida) are shown to reduce Cr\textsuperscript{VI} to Cr\textsuperscript{III} (Zazo et al., 2008). Overall, reduction of Cr and V is enhanced with decreasing pH. The impact of acidity is illustrated, for instance, in the simplified redox reaction of Cr\textsuperscript{VI} with SOM (Losi et al., 1994):

\[ 4 \text{HCrO}_4^- + 3 \text{CH}_2\text{O} + 5 \text{H}^+ = 4 \text{Cr(OH)}_3(s) + 3 \text{HCO}_3^- \]

The reduction of Cr\textsuperscript{VI} by non-humified organic material is reported to occur even under circumneutral conditions (Bolan et al., 2003; Park et al., 2008).
The aim of this work was to unravel the pH-dependent reaction patterns of Cr and V that form the basis of a scientifically sound risk assessment in soil (Paper I and II). This insight on the chemical behavior of Cr and V can be adapted for various purposes, e.g. when the need of soil remediation and suitable remedial strategies will be assessed. Moreover, knowledge of the reactions of Cr and V in soil can be used in the risk assessment of the use of industrial by-products, such as steel industry slags, in new applications.

Working hypotheses. The redox-reactions were considered to play a major role dictating the chemical bioavailability and, thus, the environmental consequences of Cr and V added to soil (Scheme 1 and Scheme 2). Owing to their dissimilar sorption mechanisms, in oxic soils, the adsorption tendency of Cr\textsuperscript{III} and V\textsuperscript{IV} species was expected to be significantly stronger than that of Cr\textsuperscript{VI} and V\textsuperscript{V} species. Therefore, the oxidation of Cr\textsuperscript{III} by MnO\textsubscript{2} and V\textsuperscript{IV} by molecular O\textsubscript{2} was hypothesized to enhance the chemical bioavailability of these heavy metals. On the other hand, a counteracting reaction, the reduction of Cr\textsuperscript{VI} and V\textsuperscript{V} by SOM, was expected to lower the chemical bioavailability of these heavy metals. Elevated soil pH was assumed to enhance the formation of Cr\textsuperscript{VI} and V\textsuperscript{V} via oxidation, as well as the bioaccessibility of these species. Instead, under acidic soil conditions the prevalence and chemical availability of Cr\textsuperscript{III} and V\textsuperscript{IV} species was expected to increase.

As a practical implementation, the risks of the steel industry slags used as liming materials were assessed in terms of the chemical bioavailability of Cr and V released from them to soil (Paper III and Additional material). In slags, Cr exists mainly as Cr\textsuperscript{III}, wherefore its risk of being oxidized (in potential leachates from steel slags) to hazardous Cr\textsuperscript{VI} by MnO\textsubscript{2} was assessed (Paper III). Moreover, the pH-dependent reaction mechanisms of Cr\textsuperscript{VI} formation by MnO\textsubscript{2} were investigated (Paper II).

The contribution of soil microbes to the redox-reactions of Cr and V is recognized. However, this thesis focuses on the overall reactions of Cr and V species in soil and, therefore, the abiotic and biological processes are not distinguished.
Scheme 1. Working hypotheses of the simplified pH-dependent reaction pathways of Cr species in soil subjected to oxidation by MnO\(_2\) and to reduction by SOM and their potential environmental consequences.

Scheme 2. Working hypotheses of the simplified pH-dependent reaction pathways of various V species entering soil, their oxidation and reduction, sorption and precipitation reactions and potential environmental consequences.

The detailed objectives of the systematic laboratory studies were to:

- Unravel the impact of pH on the potential chemical bioavailability of Cr\(^{III}\) and that of Cr\(^{VI}\) produced via oxidation by MnO\(_2\) in field soil (Paper II).

- Study the pH-dependent mechanisms of Cr\(^{III}\) oxidation in field soil to Cr\(^{VI}\) by MnO\(_2\) by using net-oxidation test and its modifications. Oxidation risk was also assessed with soils incubated with BOFS (Paper II and III).
• Discover the pH-dependent reaction patterns dictating the chemical bioavailability of $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$ in two contrasting soils differing in their SOM content. To distinguish the potentially bioavailable species from the reluctantly soluble fraction, a sequential extraction procedure was developed. In addition, the role of SOM in the chemical bioavailability of V species was assessed. Solid organic matter was expected to bind, but also to reduce $\text{V}^{\text{V}}$ into less toxic $\text{V}^{\text{IV}}$ (Paper I).

• Assess the potential risks of V in BOFS and GBFS used as liming materials. For this purpose, the pH-dependent chemical behavior of $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$ species in soil was investigated (Paper I). In addition, the release and distribution of V from three different slags were studied in two soils differing in their SOM content (Additional material).
3 MATERIALS AND METHODS

3.1 TEST SOILS

Three different soils used in the experiments were labeled as surface soil, subsoil and field soil. From those, surface soil and subsoil were collected from the same site (60°22’7”N, "E 25°04’2”E), whereas field soil was collected from another location (60°13’3”N 25°02’1”E) in southern Finland. Surface soil and field soil were selected to represent soils that are used for crop production, and could be potentially limed with steel industry slags. Subsoil excavated below the surface soil was included to unravel the role of organic matter in chemical behavior of V in soil. Soil samples were sieved (Ø 4 mm) and temporarily stored at 5°C and water holding capacity (WHC). Surface soil and subsoil were used in the experiments regarding chemical reaction patterns of V (Paper I and Additional Material) and field soil in those of Cr (Paper II and III). The methods used to characterize the soil properties are given in Table 1.

3.1.1 Surface soil and subsoil (Paper I and Additional material)

Sampling of surface soil and subsoil was conducted from a bare arable land before growing season, wherefore soil organic matter (SOM) mainly consisted of humic and decomposed material. Both soils were classified fine sand according to the U.S.D.A (U.S. Department of Agriculture) system. The clay content was low, being 2 % in the surface soil and 1% in the subsoil. Surface soil (0–30 cm, pH 5.5) was high in SOM (3.5%), whereas subsoil (40–70 cm, pH 5.8) rather low (0.5%). Solubility of organic matter was determined as DOC (Dissolved Organic Carbon). In surface soil and subsoil it amounted to 1.3 mg kg⁻¹ and 0.9 mg kg⁻¹, respectively. Soil samples were similar in terms of Al-(hydr)oxide content (~1200 mg kg⁻¹). Instead, the amount of Fe-(hydr)oxides was higher in the surface soil (1700 mg kg⁻¹) than in the subsoil (800 mg kg⁻¹). The semi-total V (determined by aqua regia microwave digestion) was relatively low in both soils (~13 mg kg⁻¹).

3.1.2 Field soil (Paper II and III)

Field soil was collected from the plough layer (0–30 cm) of agricultural soil. According to USDA classification system, it was determined as fine sand by texture. The clay fraction of the mineral texture amounted only to 3%, whereas the content of SOM was high (6.1%). The semi-total concentrations of Cr and Mn were 15 mg kg⁻¹ and 93 mg kg⁻¹, respectively. Concentration of poorly crystallized Al amounted to 1990 mg kg⁻¹, and that of Fe to 2700 mg...
The amorphous Mn amounted to 32 mg kg\(^{-1}\), whereas the concentration of Cr (hydr)oxides was rather low (5 mg kg\(^{-1}\)). Soil pH in calcium chloride suspension (1:2.5) was 5.6. Further information on field soil properties is reported in Paper II.

### Table 1. Analysis methods used in characterization of soil properties. Abbreviation A stands for Additional Material published only in this thesis.

<table>
<thead>
<tr>
<th>Soil properties:</th>
<th>Paper:</th>
<th>Analysis method:</th>
<th>Analyzer:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Carbon (OC)</td>
<td>I, II, III, A</td>
<td>Dry combustion of 500 mg air-dry powdered soil</td>
<td>Vario Max C/N</td>
</tr>
<tr>
<td>Soil Organic Matter (SOM)</td>
<td>I, II, III, A</td>
<td>Conversion from OC by coefficient 1.9 (appropriate for non-calcareous soils)</td>
<td></td>
</tr>
<tr>
<td>Soil texture</td>
<td>I, II, III, A</td>
<td>Pipette method for air dry and dispersed soil samples (Elonen, 1971)</td>
<td></td>
</tr>
<tr>
<td>Iron (Fe), aluminum (Al), manganese (Mn) and Cr (hydr)oxides</td>
<td>I (Fe, Al), II, III (Fe, Al, Mn, Cr) A (Fe, Al)</td>
<td>Dark extraction by ammonium oxalate (((\text{NH}_4)\text{C}_2\text{O}_4, 1:20) soil to solution, pH 3.3) (Tamm, 1922; Niskanen, 1989)</td>
<td>ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) (\lambda_{\text{Fe}}=238.2/259.9) nm, (\lambda_{\text{Mn}}=309.3/396.29) nm (\lambda_{\text{Cr}}=2267.7/283.5) nm and (\lambda_{\text{Al}}=309.3/396.2) nm</td>
</tr>
<tr>
<td>Water Holding Capacity (WHC)</td>
<td>I, II, III, A</td>
<td>Soil samples were saturated with Milli-Q water for 24 hours. Total water absorbed by soil was estimated by subtracting dry weight from the saturated soil mass.</td>
<td></td>
</tr>
<tr>
<td>Dissolved Organic Carbon (DOC)</td>
<td>I, III</td>
<td>Milli-Q water extraction of soil samples in moisture content of 50/60% of WHC (1:50 soil to solution, moist soil was weighed on its dry weight basis, 1 h, 250rpm/min + 17 h settling +15 min, 250rpm/min) followed by centrifugation and syringe filtration (0.45 µm, Millipore)</td>
<td>Shimadzu TOC-V cph/TNM-1</td>
</tr>
<tr>
<td>Semi-total V, Mn, Cr</td>
<td>I, II, III</td>
<td>U.S. EPA3051A microwave acid digestion</td>
<td>ICP-OES (\lambda_{\text{Mn}}=309.3/396.29) nm (\lambda_{\text{Cr}}=2267.7/283.5) nm and (\lambda_{\text{V}}=290.8/292.4) nm</td>
</tr>
<tr>
<td>pH</td>
<td>I, II, III, A</td>
<td>1:2.5 (0.01 M CaCl(_2) soil to solution)</td>
<td>Mettler DL25, ST 20 GWB sample changer</td>
</tr>
</tbody>
</table>

### 3.2 STEEL INDUSTRY SLAGS

Three types of steel industry slags were used as liming materials in this research: blast oxygen furnace slag (BOFS), granulated blast furnace slag (GBFS) and High Vanadium Slag (HVS). The chemical bioavailability of the V-content in all slags was investigated in experiments with soils (Additional material). The chemical reactions of slag-derived Cr in soil, however, were
studied only with BOFS (Paper III). The BOFS material used in the Cr and V research originated from different batches. Therefore, the composition and chemical properties of the BOFS batches are presented separately. Properties of slags were analyzed in the laboratory of SSAB Raahe.

3.2.1 Slags: BOFS, GBFS, and HVS (used in Additional material)

The main components of blast oxygen furnace slag (BOFS), granulated blast furnace slag (GBFS) and High Vanadium Slag (HVS) were analyzed by XRF (X-ray Fluorescence) spectroscopy (Table 2). Distributions of calcium (Ca), silicon (Si), aluminum (Al), magnesium (Mg), sodium (Na) and potassium (K) are given as oxides. The proportion of oxygen (O) in minerals other than those of Ca, Si, Al, Mg, Na and K is expressed separately. BOFS and HVS were somewhat similar in their chemical composition, except for the concentration of SiO$_2$, V and Fe. BOFS and HVS are both formed in blast oxygen furnace but from HVS the magnetic Fe is removed. The proportion of V in HVS was 2.6%, whereas in BOFS it was below 1.5%, and in GBFS as low as <0.06%. On the other hand, the proportions of Mg (determined as MgO) and Al (Al$_2$O$_3$) in GBFS were higher than those are in blast oxygen furnace slags (i.e. BOFS and HVS).

Table 2. Distribution of the main components (%) in blast furnace slag (BOFS), granulated blast furnace slag (GBFS) and high vanadium slag (HVS) by XRF (X-Ray Fluorescence) spectroscopy. Additional material.

<table>
<thead>
<tr>
<th>Main components:</th>
<th>Blast oxygen furnace slag (BOFS)</th>
<th>Granulated blast furnace slag (GBFS)</th>
<th>High vanadium slag (HVS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>45.5%</td>
<td>36.7%</td>
<td>44.9%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>14.3%</td>
<td>36.0%</td>
<td>22.7%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.95%</td>
<td>9.45%</td>
<td>2.6%</td>
</tr>
<tr>
<td>MgO</td>
<td>1.71%</td>
<td>12.3%</td>
<td>1.6%</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.12%</td>
<td>0.53%</td>
<td>0.24%</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.08%</td>
<td>0.46%</td>
<td>0.20%</td>
</tr>
<tr>
<td>O in other minerals</td>
<td>15.3 %</td>
<td>0.40%</td>
<td>9.0 %</td>
</tr>
<tr>
<td>Fe</td>
<td>15.60%</td>
<td>0.68%</td>
<td>12.00%</td>
</tr>
<tr>
<td>Mn</td>
<td>2.55%</td>
<td>0.44%</td>
<td>2.60%</td>
</tr>
<tr>
<td>Ti</td>
<td>0.74%</td>
<td>1.42%</td>
<td>0.78%</td>
</tr>
<tr>
<td>V</td>
<td>1.40%</td>
<td>0.055%</td>
<td>2.60%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.24%</td>
<td>0.004%</td>
<td>0.20%</td>
</tr>
<tr>
<td>P</td>
<td>0.30%</td>
<td>0.00%</td>
<td>0.43%</td>
</tr>
<tr>
<td>S</td>
<td>0.10%</td>
<td>1.42%</td>
<td>0.09%</td>
</tr>
<tr>
<td>Other elements</td>
<td>0.13%</td>
<td>0.12%</td>
<td>0.08%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
The concentration of water soluble V in BOFS and HVS was analyzed according to SFS-EN 12457-3. In BOFS it was 0.16 mg kg$^{-1}$ and in HVS as high as 52 mg V kg$^{-1}$. As for GBFS, the solubility of V was not determined.

The particle size was similar (Ø<3 mm) in BOFS and GBFS. However, texture of HVS was notably finer (Ø<1 mm). BOFS and HVS were highly alkaline due to their high CaO content. In water solution (1:2), the pH of BOFS was 11.4 and that of HVS was 11.8. For GBFS, the pH was not determined.

### 3.2.2 BOFS (Paper III)

The elemental composition of BOFS used in the Cr studies is presented in Table 3. BOFS consisted mainly of CaO (47.2%), wherefore material was highly alkaline (pH 11.3). The amount of SiO$_2$ (12.3%) and Fe (16.7%) were rather high as well. In addition, the Mn content (2.5%) in BOFS was notable. The total Cr content was 0.21%. The concentrations of soluble Cr (without speciation) and Cr$^{VI}$ in BOFS were analyzed according to SFS-EN 12457-3. The water-soluble Cr (without speciation) in BOFS amounted to 0.2 mg kg$^{-1}$ and Cr$^{VI}$ to 0.1 mg kg$^{-1}$.

<table>
<thead>
<tr>
<th>Component</th>
<th>Proportion in BOFS:</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>47.2%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>12.3%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.6%</td>
</tr>
<tr>
<td>MgO</td>
<td>1.7%</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.06%</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.03%</td>
</tr>
<tr>
<td>O in other minerals</td>
<td>4.9%</td>
</tr>
<tr>
<td>Fe</td>
<td>16.7%</td>
</tr>
<tr>
<td>Mn</td>
<td>2.50%</td>
</tr>
<tr>
<td>Ti</td>
<td>0.78%</td>
</tr>
<tr>
<td>V</td>
<td>1.50%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.21%</td>
</tr>
<tr>
<td>Other elements</td>
<td>0.09%</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
</tr>
</tbody>
</table>

### 3.3 EXPERIMENTAL DESIGN: VANADIUM

Two incubation experiments with *surface* and *subsoil* samples (Scheme 1) were undertaken to study:
a) Impact of pH and SOM on the chemical bioavailability of V species (Paper I)

b) Potential release of V from steel industry slags and its subsequent chemical accessibility in soil (Additional material)

Both incubation experiments were carried out with the test soils differing in their OM content to identify reaction patterns that dictate the ecological risks of V in slags used as liming materials. The soils were divided into subsamples that were separately incubated as three replicates with chemical salts of VIV or VV or with slags. Calcium hydroxide (Ca(OH)₂) served as a control liming material. After incubation, the subsamples were subjected to various chemical analyses to unravel the potential mobility of V and the retention of V species into fractions differing in their chemical bioavailability. The overall design of the experiments is described in Scheme 3.

**Scheme 3.** The overall design of experiments with two test soils on pH-dependent reactions patterns of V affecting its chemical bioavailability relevant in the risk assessment of BOFS used as liming material.
3.3.1 Incubation experiments with surface soil and subsoil

a) Incubation with different V chemicals (Paper I). The impact of pH and SOM (Soil Organic Matter) on the chemical bioavailability of V species was investigated in surface soil and subsoil under oxic conditions. The soil subsamples were separately treated with increasing concentration (0–500 mg kg\(^{-1}\)) of \(V^V\) (added as NaVO\(_3\)) or with \(V^IV\) (added as VOSO\(_4\)). To unravel the impact of pH on reactions of V species, the addition of V salts was followed by adjustment of soil pH. To reach the target pHs (ranging from 4.0 to 6.9) soil samples were treated with potassium hydroxide solution (KOH) or dilute hydrochloric acid (HCl). The soil samples added with V-salts were incubated for 2–3 months at three pH levels (at 22ºC and moisture level 60% WHC) (Table 4). Details of the incubation experiment and conditions are reported in Paper I.

Table 4. Setup of the experiment with surface and subsoil samples treated with \(V^V\) (added as NaVO\(_3\)) or \(V^IV\) (added as VOSO\(_4\)) and incubated at three pH levels. Soil pH and \(E_h\) are the mean values, \(N=3\) (standard deviations in Paper I).

<table>
<thead>
<tr>
<th>Group</th>
<th>Surface soil (0–30 cm)</th>
<th>Subsoil (40–70 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-spiking</td>
<td>(V^V)</td>
<td>(V^IV)</td>
</tr>
<tr>
<td>(mg kg(^{-1}))</td>
<td>pH</td>
<td>(E_h) (mV)</td>
</tr>
<tr>
<td>I</td>
<td>0</td>
<td>4.9</td>
</tr>
<tr>
<td>50</td>
<td>4.9</td>
<td>457</td>
</tr>
<tr>
<td>100</td>
<td>4.9</td>
<td>467</td>
</tr>
<tr>
<td>500</td>
<td>4.9</td>
<td>477</td>
</tr>
<tr>
<td>II</td>
<td>0</td>
<td>5.5</td>
</tr>
<tr>
<td>50</td>
<td>5.5</td>
<td>556</td>
</tr>
<tr>
<td>100</td>
<td>5.4</td>
<td>541</td>
</tr>
<tr>
<td>500</td>
<td>5.4</td>
<td>512</td>
</tr>
<tr>
<td>III</td>
<td>0</td>
<td>6.4</td>
</tr>
<tr>
<td>50</td>
<td>6.5</td>
<td>520</td>
</tr>
<tr>
<td>100</td>
<td>5.9</td>
<td>508</td>
</tr>
<tr>
<td>500</td>
<td>5.9</td>
<td>487</td>
</tr>
</tbody>
</table>

b) Incubation with V-containing slags (Additional material). The mobility and chemical accessibility of V in various slags (BOFS, GBFS, and HVS) were investigated with the same surface and subsoil. They were incubated without or with slags at two addition levels (Table 5). The slag dosages (5 and 50 g per kg soil), were equivalent to additions of 10 and 100 t ha\(^{-1}\). Application mass for the slags was calculated on the basis that dry weight of soil samples was ~ 2·10\(^6\) kg ha\(^{-1}\) (20 cm layer). In liming, the recommended amount of BOFS is 7–10 t ha\(^{-1}\), followed by additions of 4–6 t ha\(^{-1}\) from every three to five years. On this basis, 10 t ha\(^{-1}\) was selected to
represent the “normal” slag dosage, whereas the higher dosage was tenfold to that.

Surface and subsoil subsamples were also incubated with three different levels of Ca(OH)$_2$ to obtain the same pHs as in the samples incubated with slags (Table 5). In subsoil subsamples, the low, medium and high Ca(OH)$_2$ dosages corresponded to the lime added to field soil in amounts of 1, 6 and 10 t ha$^{-1}$ (soil dry weight), respectively. In surface soil, the equivalent dosages were 2, 6 and 12 t ha$^{-1}$. The Ca(OH)$_2$-treated subsamples served as reference material to distinguish between the chemical responses of V owing to increased alkalinity from those attributable to the chemical characteristics of slags. All soil samples were incubated as three replicates in plastic containers for three months at 22ºC and moisture level of 60% of WHC.

Table 5. pH of the surface and subsoil samples incubated without or with slags added at levels equivalent to 10 or 100 t ha$^{-1}$ or with Ca(OH)$_2$ added to obtain the same pHs as in the slag-treated samples (pH = the mean value ± and standard deviation, N=3). Additional material.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Surface soil (fine sand, 3.5% SOM)</th>
<th>Subsoil (fine sand, 0.5% SOM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>pH</td>
</tr>
<tr>
<td>No slag 0 t ha$^{-1}$</td>
<td>5.7 ±0.1</td>
<td>5.9±0.0</td>
</tr>
<tr>
<td>BOFS 10 t ha$^{-1}$</td>
<td>7.1 ±0.2</td>
<td>7.9 ±0.1</td>
</tr>
<tr>
<td>BOFS 100 t ha$^{-1}$</td>
<td>9.4 ±0.1</td>
<td>11.1 ±0.1</td>
</tr>
<tr>
<td>GBFS 10 t ha$^{-1}$</td>
<td>6.0 ±0.1</td>
<td>6.8 ±0.2</td>
</tr>
<tr>
<td>GBFS 100 t ha$^{-1}$</td>
<td>6.9 ±0.1</td>
<td>7.5 ±0.2</td>
</tr>
<tr>
<td>HVS 10 t ha$^{-1}$</td>
<td>7.1 ±0.1</td>
<td>7.9 ±0.1</td>
</tr>
<tr>
<td>HVS 100 t ha$^{-1}$</td>
<td>9.3 ±0.2</td>
<td>9.3 ± 0.0</td>
</tr>
<tr>
<td>Low Ca(OH)$_2$</td>
<td>6.9 ±0.1</td>
<td>7.3 ±0.2</td>
</tr>
<tr>
<td>Medium Ca(OH)$_2$</td>
<td>7.5 ±0.1</td>
<td>9.0 ±0.5</td>
</tr>
<tr>
<td>High Ca(OH)$_2$</td>
<td>8.1 ±0.1</td>
<td>10.8 ±0.4</td>
</tr>
</tbody>
</table>

### 3.3.2 Chemical accessibility and mobility of V species

A specific sequential extraction procedure was designed to unravel the chemical accessibility of V species in the soil samples incubated with V$^{IV}$ and V$^{V}$ salts (Paper I) as well as in those incubated with slags or Ca(OH)$_2$ (Additional material). The extraction protocol adopted was modified from the methods used in fractionation of selenium (Se) (Zhang & Moore, 1996) and phosphorus (P) (Chang & Jackson, 1957) in soil. Vanadium in soil incubated at the moisture level of 60% of WHC was extracted (1:10 soil to solution) in the order of decreasing chemical bioavailability:

1) Readily soluble or electrostatically bound V was removed by 0.25 M potassium chloride (KCl)
2) V adsorbed by the ligand exchange (mainly V$^{V}$) was replaced by 0.1 M phosphate buffer (KH$_2$/K$_2$HPO$_4$, later discussed as P-buffer),
3) V bound to organic matter was dissolved by 0.1 M sodium hydroxide (NaOH) and

4) Strongly bound V was extracted by 0.25 M sulfuric acid (H$_2$SO$_4$)

The moist soil samples incubated at WHC 60% were also extracted by Milli-Q water (1:50) to assess the potential mobility of V species. Both the extraction ratios and the results are expressed on the dry weight (DW) basis (determined after drying 5.0 g of soil at 105°C for ~22 hours). Semi-total V was determined from air-dry soil powder (500 mg) by *aqua regia* microwave digestion. The chemical analyses for V are described thoroughly in paper I.
3.4 EXPERIMENTAL DESIGN: CHROMIUM

Scheme 4 depicts two incubation experiments and the subsequent chemical analyses designed to:

a) Unravel the pH-dependent oxidation mechanisms and chemical bioavailability of Cr in field soil subsamples incubated with or without synthetic MnO$_2$ at pHs adjusted chemically to the range of 3.9–6.3 (Paper II)

b) Investigate the release of Cr species from BOFS and the risk of slag-derived Cr$^{III}$ being oxidized to Cr$^{VI}$ by MnO$_2$ in the experimental field soil. In this test, the soil subsamples were incubated without or with BOFS added as different dosages and also separately with KOH to unravel the impact of elevated pH per se (Paper III)

**Scheme 4.** The overall design of experiments on pH-dependent reactions pattern of Cr and on those dictating the chemical bioavailability of Cr relevant in the risk assessment of BOFS used as liming material.
3.4.1 Incubation experiments with field soil

a) Incubation of field soil with or without added MnO$_2$ at pH 3.9–6.3 (Paper II). The pH-dependent oxidation mechanisms of Cr$^{III}$ to Cr$^{VI}$ by MnO$_2$ and the chemical bioavailability of Cr species were investigated in field soil samples after incubation with or without added MnO$_2$ for 47 days at 22ºC and 50% of the WHC (Table 6). A set of field soil (3.2% SOM, fine sand) samples was divided into subsamples that were chemically treated to obtain a pH range of 3.9–6.3. Half of them were further amended with excessive amounts of MnO$_2$ to assure oxidation of Cr$^{III}$ to Cr$^{VI}$ in measurable amounts. The rest of the soil samples served as controls where the oxidation reactions were attributable to the innate Mn(hydr)oxides.

Finally, all soil samples (incubated with and without added MnO$_2$) were subjected to an oxidation test in a 1 mM chromium chloride (CrCl$_3$) suspension (soil to solution ratio 1:10) (Chapter 3.4.3). The chemical availability of added Cr$^{III}$ in the tests and the Cr$^{VI}$ species produced was further studied by a fractionation analysis (Chapter 3.4.4).

Table 6. Chemical properties of the pH-adjusted soil samples incubated at 22 ºC for 47 days with or without MnO$_2$ (moisture content equivalent to 50% of WHC). Values indicate means (N=3). Paper II.

<table>
<thead>
<tr>
<th>Group</th>
<th>Soil pH</th>
<th>pH adjustment</th>
<th>Eh (0.01 M CaCl$_2$)</th>
<th>Semi-tot. Mn EPA3051A, ICP-OES λ= 257.6/259.3 nm</th>
<th>Amorph. Mn (hydr)oxides ammonoxalate ICP-OES λ= 257.6/259.3 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>pH 4.4</td>
<td>HCl</td>
<td>575</td>
<td>8637</td>
<td>5938</td>
</tr>
<tr>
<td>II</td>
<td>pH 5.5</td>
<td>no adj.</td>
<td>567</td>
<td>8403</td>
<td>6536</td>
</tr>
<tr>
<td>III</td>
<td>pH 6.2</td>
<td>KOH</td>
<td>474</td>
<td>8525</td>
<td>6562</td>
</tr>
<tr>
<td>Soils incubated with MnO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>pH 3.9</td>
<td>HCl</td>
<td>587</td>
<td>91</td>
<td>25</td>
</tr>
<tr>
<td>II</td>
<td>pH 5.6</td>
<td>no adj.</td>
<td>547</td>
<td>93</td>
<td>32</td>
</tr>
<tr>
<td>III</td>
<td>pH 6.3</td>
<td>KOH</td>
<td>493</td>
<td>83</td>
<td>31</td>
</tr>
<tr>
<td>Soils incubated without MnO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b) Incubation with Cr-containing BOFS (Paper III). Potential release of Cr$^{III}$ and Cr$^{VI}$ from BOFS to soil and the risk of the potentially solubilized Cr$^{III}$ to be oxidized to Cr$^{VI}$ by MnO$_2$ were investigated with the same field soil used in the experiment as above. Soil subsamples were incubated without or with BOFS equivalent to field dosages of 10 and 100 t ha$^{-1}$ (see chapter 3.3.1.). An additional soil subsample was incubated with potassium hydroxide (KOH) as a reference material to obtain the same pH as in soil limed with 10 t ha$^{-1}$ BOFS. All subsamples were incubated at constant
temperature (22°C) and moisture level (50% of WHC) for 7 weeks. The properties of the incubated soil subsamples are presented in Table 7.

Table 7. Mean values of pH, Eh and DOC in field soil subsamples (N=3) incubated (7 weeks at 22°C, moisture level of WHC 50%) without or with BOFS added in quantities equivalent to 10 or 100 t ha⁻¹ or with KOH (pH equivalent to lower BOFS dosage). Paper III.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extraction method</th>
<th>Environmental implication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water soluble Cr/Mn</td>
<td>Milli-Q water (1:10 soil to solution)</td>
<td>• Easily bioaccessible Cr (no speciation), leaching risk</td>
</tr>
<tr>
<td>绍兴</td>
<td>0.01 M Phosphate buffer (KH₂/H₂PO₄, pH 7.2, 1:10 soil to solution)</td>
<td>• Easily bioaccessible and highly toxic CrVI, leaching risk</td>
</tr>
<tr>
<td>Amorphous Cr/Mn (hydr)oxides</td>
<td>Ammonium oxalate (1:20 soil to solution (NH₄)₂C₂O₄, pH 3.3) (Niskanen 1989):</td>
<td>• Cr soluble under acidic soil conditions</td>
</tr>
<tr>
<td>绍兴</td>
<td>EPA₃₀₅₁A, microwave acid (3:1, nitric acid HNO₃: hydrochloride acid HCl) digestion</td>
<td>• Reluctantly soluble Cr</td>
</tr>
</tbody>
</table>

3.4.2 Chemical fractionation of soil Cr and Mn

The distribution of Cr into pools decisively differing in their bioaccessibility and ecotoxicity was determined by chemical fractionation of the incubated soil samples at 50% WHC (Paper II and III). Chemical fractions were analyzed also for Mn to assess its contribution to oxidation risk of CrIII. Methods used and the environmental implications for each chemical fraction are presented in Table 8. Details of analytical methods are described in paper II and III.

Table 8. Environmental implications and analysis methods of various Cr and Mn fractions in soil (Paper II and III).
3.4.3 The net-oxidation tests

Soil samples incubated at moisture level of 50% (Paper II and III) were tested for their ability to oxidize Cr\textsuperscript{III} to Cr\textsuperscript{VI}. The test was carried out according to method of Bartlett and James (1996) by using a 1 mM CrCl\textsubscript{3} suspension at soil to solution ratio of 1:10. Furthermore, the risk of Cr\textsuperscript{III} (leachates) being oxidized to Cr\textsuperscript{VI} under extremely oxidizing conditions was assessed in soils incubated with BOFS (Paper III). For this purpose, an enhanced net-oxidation test was introduced. In this procedure, oxidative MnO\textsubscript{2} powder is added to the soil suspensions after CrCl\textsubscript{3} as an additional step of the net-oxidation test. Details of the enhanced net-oxidation test (performed only with one type of BOFS slag) are described in paper III.

3.4.4 Chemical bioavailability of added Cr\textsuperscript{III} and Cr\textsuperscript{VI} produced via oxidation

The chemical bioavailability of added Cr\textsuperscript{III} and Cr\textsuperscript{VI} produced via oxidation, was further studied in net-oxidation tests carried out with field soil subsamples incubated with or without MnO\textsubscript{2} (Paper II). Soil samples were suspended to 1 mM CrCl\textsubscript{3} solution, allowed to react during orbital shaking, whereafter the supernatants obtained after centrifugation were analyzed for a) soluble (chemically bioavailable) Cr\textsuperscript{III} and Cr\textsuperscript{VI}, b) adsorbed, i.e. potentially available Cr\textsuperscript{VI} and c) reluctantly bioavailable adsorbed/precipitated Cr\textsuperscript{III}. The procedure for the chemical fractionation of Cr species is presented in detail in Paper II.

3.5 ELEMENTAL ANALYSES

Concentration of Al, Fe, Mn, Cr and V (without speciation) in soil extracts were analyzed by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrophotometer, Thermo iCAP 6000). In general, the reliability of the analysis was confirmed by using two wavelengths for each element: \(\lambda_{\text{Al}}=309.3/396.2\ \text{nm}\), \(\lambda_{\text{Fe}}=238.2/259.9\ \text{nm}\), \(\lambda_{\text{Mn}}=309.3/396.2\ \text{nm}\), \(\lambda_{\text{Cr}}=267.7/283.5\ \text{nm}\) and \(\lambda_{\text{V}}=290.8/292.4\ \text{nm}\). Radial view was used for concentrations above 1 mg L\textsuperscript{-1} and an axial one below that. Stability and validity of analyses were ensured with control samples (Quality control, QC samples: QC 0, QC 0.1 and QC 1 mg L\textsuperscript{-1}), and with spiked soil extracts (1 mg L\textsuperscript{-1}) prepared from different primary standard batches than standard solutions. Interval for QC’s was 10 samples. An inner reference sample of BOFS-treated field soil was used throughout all the experiments, in addition to control samples and two blank samples. Runoff water rich in metals (Virtanen, 2015) was used as an additional internal reference solution for the
ICP-OES analyses (Paper II). In the semi-total soil analyses, Montana Soil I (Mackey et al., 2010) served as the reference material.

The concentration of Cr\textsuperscript{VI} in soil extracts (Paper II and III) was determined by modified EPA 7196A method. In this method, Cr\textsuperscript{VI} is concomitantly reduced and complexed with diphenyl carbazide (DPC). The concentration of Cr\textsuperscript{VI}, as reduced Cr-DPC-complexes was easily measurable by a spectrophotometer (Shimadzu UVmini-1240) at $\lambda= 540$ nm. The limit of quantification (LOQ 40 $\mu$g L$^{-1}$) was determined from the background noise (x10). The modified version of EPA7196A method is thoroughly described in the Appendix of paper II.

### 3.6 STATISTICAL ANALYSES

The difference of group means (≥3) between the incubation treatments was tested using an analysis of variance (ANOVA) at the significance level of $0.05$. Tukey’s HSD followed as the post-hoc test. The means of two groups were compared using the independent $t$-test. The data expressed as relative values (%) were modified (via $\sqrt{\text{arc sin}}$) to achieve normality. The normality of the results was tested using kurtosis and skewness values. However, for the relative water solubility of V species, normality was assessed using the probability plot of residuals. Homogeneity of variance was analyzed by Levene’s test. In cases of unequal variance, Games-Howell with Welch’s correction (Paper II) or Kruskal-Wallis (Paper I) tests were used. Correlations between variables were determined by the Pearson correlation factor. Details of the statistical analyses on the chemical bioavailability of V species are presented in paper I and those related to Cr experiments in paper II. Statistical analyses were performed by R, SPSS22 and GraphPrism softwares.
RESULTS AND DISCUSSION

4.1 FACTORS CONTROLLING THE MOBILITY AND CHEMICAL BIOAVAILABILITY OF Cr AND V SPECIES

4.1.1 Soil pH

In soils, pH is a crucial variable connected with oxidation-reduction, precipitation-dissolution and adsorption-desorption reactions. These reactions were anticipated to control the chemical accessibility and bioavailability of Cr and V species. However, the pH-dependent reaction patterns of these metals in soils are very complex, with several chemical reactions occurring concomitantly. Systematic laboratory experiments were carried out to unravel the pH-dependency of the reaction patterns dictating the chemical bioavailability of Cr and V species in soils.

4.1.1.1 Chromium (Paper II)

Impact of pH on the chemical accessibility of Cr species

Field soil samples were incubated with or without MnO$_2$ (47 d at 22°C and 50% of WHC). After incubation, samples were suspended in 1 mM CrCl$_3$ (at soil to solution ratio 1:10). In field soil incubated without synthetic MnO$_2$, the added Cr$^{III}$ remained as its initial trivalent species (Figure 2). In the samples incubated with MnO$_2$, however, a small proportion of added Cr$^{III}$ had oxidized to oxyanionic Cr$^{VI}$. It is noteworthy, that at the lowest soil pH (4.4) oxidation was minor (0.4%), wherefore no Cr$^{VI}$ species are noticeable in Figure 2. The chemical bioavailability of both Cr species was dictated by soil pH (Figure 2). At elevated pH, the solubility of Cr$^{III}$ (and, thus, chemical bioavailability) in soil diminished, whereas that of Cr$^{VI}$ (produced by Cr$^{III}$ oxidation) increased. These results agree with the findings of Bolan & Thiagarajan (2001) that liming, as it raises soil pH, enhances the retention of Cr$^{III}$ but lowers that of Cr$^{VI}$ species. In addition, the MnO$_2$ amendment influenced the bioaccessibility of Cr in soil. The amount of soluble remaining Cr$^{III}$ was lower in soils incubated with MnO$_2$ than in those of the approximately same pH but without MnO$_2$. Thus, MnO$_2$ acted as an absorbent of soluble Cr$^{III}$. Under acidic soil conditions (pH ~4) this lowered the overall chemical bioavailability of Cr. At higher pH, the accessibility of Cr$^{III}$ was also reduced by MnO$_2$ but the overall availability of Cr increased. This was attributable to the oxidation of Cr$^{III}$ into more mobile Cr$^{VI}$ by MnO$_2$. 

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Chemical availability of Cr\textsuperscript{III} and that of the Cr\textsuperscript{VI} species produced in soil at various pHs in 1 mM CrCl\textsubscript{3} (1:10 w/V, suspension pHs are given in parentheses) (N=3, mean values). Soils were incubated with and without MnO\textsubscript{2} at +22 °C and 50% WHC capacity for 47 d. Paper II.

Oxidation of Cr\textsuperscript{III} and sorption of produced Cr\textsuperscript{VI} species

In field soil samples previously incubated with synthetic MnO\textsubscript{2}, soil pH notably influenced the net-oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} (that is, the oxidation of Cr\textsuperscript{III} minus subsequent reduction of the Cr\textsuperscript{VI} produced). The lowest net-oxidation yield (0.4%) was recorded in the most acidic soil sample (initial pH 4.4) (Figure 3). In the samples of higher initial pHs (5.5 and 6.2), the production of Cr\textsuperscript{VI} was more apparent (4.4% and 4.7%, respectively). In addition, the adsorption tendency of the produced Cr\textsuperscript{VI} was influenced by pH. The sorption was highest in the most acidic soil (initial pH 4.4), where all newly formed Cr\textsuperscript{VI} was adsorbed. Adsorption was significantly lower in soils of higher pHs (initial pHs 5.5 and 6.2).

Figure 2. Chemical availability of Cr\textsuperscript{III} and that of the Cr\textsuperscript{VI} species produced in soil at various pHs in 1 mM CrCl\textsubscript{3} (1:10 w/V, suspension pHs are given in parentheses) (N=3, mean values). Soils were incubated with and without MnO\textsubscript{2} at +22 °C and 50% WHC capacity for 47 d. Paper II.

Figure 3. Concentration of the total produced Cr\textsuperscript{VI} and adsorbed Cr\textsuperscript{VI} (mg L\textsuperscript{-1}) in the net-oxidation of added Cr\textsuperscript{III} (52 mg Cr\textsuperscript{III} L\textsuperscript{-1}) in 1 mM CrCl\textsubscript{3} suspensions with previously incubated MnO\textsubscript{2}-treated field soil samples at three pHs (1:10, w/V). Percentages stand for the proportion of the Cr\textsuperscript{III} net-oxidized. Error bars indicate standard errors (N=3). Paper II.
**The pH-dependent reaction patterns dictating the chemical bioavailability of Cr species**

**Redox-reactions and speciation of Cr.** The impact of Cr\(^{III}\) oxidation to Cr\(^{VI}\) on the overall chemical bioavailability of Cr in *field soil* was rather insignificant (Figure 2). In fact, without the specific addition of oxidative MnO\(_2\) no Cr\(^{VI}\) was produced. However, in the soil samples previously incubated with high amounts of oxidative MnO\(_2\), a small proportion (<5%) of added Cr\(^{III}\) was net-oxidized (Figure 3). At initial soil pH> 5.5, the oxidation reactions enhanced the chemical bioavailability of added Cr\(^{III}\). At low pH, their effect on the chemical availability of added Cr\(^{III}\) was negligible. This response was attributable to low production of Cr\(^{VI}\) and its efficient specific sorption onto Al- and Fe-(hydr)oxide surfaces.

In this work, the reduction reactions of *added* Cr\(^{VI}\) to Cr\(^{III}\) was not investigated. In the net-oxidation tests of Cr\(^{III}\), however, the subsequent reduction of the Cr\(^{VI}\) formed via oxidation by SOM was of importance. This reduction reaction limited the net-production of Cr\(^{VI}\). Particularly in acidic conditions, the Cr\(^{VI}\) produced appeared to be reduced back to Cr\(^{III}\). This conclusion is supported by previous studies showing that in oxic conditions the reduction of Cr\(^{VI}\) is favored by increasing acidity (James & Bartlett, 1983; Choppala *et al.*, 2013). However, the reduction of Cr\(^{VI}\) is reported to occur even under alkaline soil conditions at pH 8 (Choppala *et al.*, 2013). Wittbrodt and Palmer (1997), in turn, found that the capacity of humic organic substances to reduce Cr\(^{VI}\) diminished at circumneutral conditions.

**Sorption of various Cr species.** The chemical bioavailability of Cr\(^{III}\) in soil suspensions was mainly regulated by the sorption and precipitation reactions (Figure 2). At elevated pHs, the solubility of added Cr\(^{III}\) diminished as result of hydrolysis of Cr\(^{3+}\) to Cr(OH)\(^{2+}\)/Cr(OH)\(_2\)+ species able to adsorb onto Fe-, Mn- and Al-(hydr)oxides, or due to its precipitation as Cr(OH)\(_3\). In addition, it can be anticipated that binding to organic matter lowered the solubility of Cr\(^{III}\). However, in this study the sorption of Cr onto organic matter and oxides surfaces (i.e. sorption of hydrolyzed species) were not distinguished.

As expected, a low pH increased the sorption tendency of Cr\(^{VI}\) species (Figure 3). At soil pH 4.1, all Cr\(^{VI}\) produced via oxidation was retained onto the oxide surfaces by ligand exchange. At pHs higher than 5.5, the sorption diminished by roughly half. This reaction pattern was attributable to enhanced deprotonation of aqua groups in the hydration sphere of Fe- and Al- (hydr)oxides, which rendered their surface charge more negative. Consequently, the electrostatic repulsion between the sorption surface and oxyanionic Cr\(^{VI}\) species increased. These findings agree well with the reported pH-dependency of Cr\(^{VI}\) adsorption onto Al- and Fe-(hydr)oxides (Zachara *et al.*, 1987; Rai *et al.*, 1989; Fendorf *et al.*, 1997) and onto soil colloids in Ferrosols (Zhou *et al.*, 2001) and forest soils (Otero *et al.*, 2014).
4.1.1.2 Vanadium (I)

Impact of pH on the mobility and adsorption tendency of V species

Mobility of V^{IV} and V^{V} species (added as VOSO_{4} and NaVO_{3}, respectively) in surface soil and subsoil samples was determined by Milli-Q water extraction. Results in Figure 4 reveal that the relative water solubility of both species increased upon elevated pH. This response was similar in both soil samples despite the marked differences in their SOM content, which was high (3.2%) in surface soil and rather low (0.5%) in subsoil.

![Figure 4](image)

The relative water solubility (%) of a) V^{IV} added as VOSO_{4} and b) V^{V} added as NaVO_{3} (50; 100 and 500 mg V kg^{-1}) in fresh surface and subsoil (1:50 w/V water extraction) as a function of soil pH. Paper I.

The chemical sorption patterns of V species in the soil samples incubated with V^{IV} and V^{V} were investigated by sequential fractionation in the order of increasing binding strength (and decreasing chemical bioavailability): readily and easily soluble V < V bound by ligand exchange < V bound to solid organic matter < strongly bound V (Figure 5). Sorption mechanisms controlling the chemical bioavailability of V species (sorption of V^{V} onto oxide surfaces by ligand exchange and binding of V species to SOM) were demonstrated to be similar as suggested by Martin & Kaplan (1998) in their study with loamy sand soil.

Soil pH markedly dictated the sorption tendency of V species. Upon elevated pH, their binding to solid organic matter diminished, whereas the retention by the ligand exchange increased. Interestingly, the proportion of easily soluble V with elevated pH raised only in surface soil. In subsoil, this fraction showed no pH-dependency. Total recovery of V, calculated as the proportion of Σ V fractions (in the sequential extraction) to the added V, varied from 67 to 100%, with a median of 77%.
**Figure 5.** Recovery of added $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$ (50; 100 and 500 mg V kg$^{-1}$) extracted sequentially (1:10 w/V) from fresh surface soil and subsoil samples ($N=3$) after incubation at various soil pHs. Left side: $\text{V}^{\text{IV}}$ added as $\text{VOSO}_4$. Right side: $\text{V}^{\text{V}}$ added as $\text{NaVO}_3$. The error bars indicate standard errors. Paper I.

The pH-dependent reaction patterns dictating the chemical availability of V species

**Redox-reactions and speciation of V.** Soil redox-reactions controlled the distribution of added V into $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$ species, irrespective of its initial oxidation state. The chemical equilibrium between the concomitant oxidation and reduction reactions of V was dictated primarily by soil pH and SOM. Actually, the distribution of added $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$ between various chemical fractions in soils was rather similar. This indicates that the initial speciation of V in the added salts was of secondary importance.

Within the pH-range of the oxic test soils (4.0–6.9), the reduction $\text{V}^{\text{V}}$ to $\text{V}^{\text{IV}}$ by SOM diminished the chemical bioavailability of V (Figure 5). This reduction reaction promoted retention of V to SOM because $\text{V}^{\text{IV}}$ binds...
strongly to organic ligands. Acidic soil conditions favored this reaction pattern: the amount of V bound to SOM increased with lowering pH (Paper I). This outcome is in line with the previous findings that low pH enhanced the reduction of $V^V$ by fulvic acid, and that the $V^{IV}$ produced was subsequently bound to FA via complex formation (Wilson & Weber 1979).

Moreover, the comparison of the water extractable V in the surface soil and subsoil samples revealed the reduction reactions of $V^V$ to $V^{IV}$ by SOM to be significantly pH-dependent. Under acidic conditions, the solubility of added V was lower in surface soil. It seemed, however, that reduction by SOM diminished at circumneutral conditions (Figure 4). At pH ~6.5, the difference in the solubility of V between surface soil (high in SOM) and subsoil (low in SOM) levelled off. Similarly, in the reduction experiments carried out by Lu et al. (1998), solely with humic acid the reduction of $V^V$ to $V^{IV}$ diminished above pH 6.

A counteracting reaction, the oxidation of $V^{IV}$ to $V^V$ by molecular oxygen, notably enhanced the chemical bioavailability of added V. This reaction pattern was seen in subsoil low in OM. There the oxidation by $O_2$ dominated over the reduction by SOM and, consequently, the proportion of $V^V$ increased. As a result, the easily soluble and ligand exchangeable fractions of V (i.e. potentially bioavailable fractions) were greater in subsoil than in surface soil. Moreover, an increase in the proportion of ligand-exchangeable V upon elevated pH demonstrated that alkaline conditions favored the oxidation of $V^{IV}$ to $V^V$ in both soil types. The predominance of $V^V$ species upon elevated pH was indicated, in addition, by the increasing water solubility of added V at higher soil pHs (Figure 4).

**Sorption tendency of V species.** In studies with pure Fe-(hydr)oxides the adsorption of $V^V$ species is found to decrease at pHs above 3–4 (Peacock & Sherman, 2004; Naeem et al., 2007). Also in a recent modelling study carried out with batch experiments, Larsson et al. (2017) demonstrated the adsorption of $V^V$ onto mineral soils to decline upon elevated pH. In the present study, sorption reactions of both $V^{IV}$ and $V^V$ were controlled by soil pH (Figure 5). Interestingly, adsorption of $V^V$ species did not seem to diminish upon elevated soil pH (Figure 5). On the contrary, the amount of V bound onto oxide surfaces by ligand exchange increased with elevated pH. This outcome was, however, a result of the higher proportion of $V^V$ produced by oxidation reactions favored at higher pH.

The chemical bioaccessibility of $V^{IV}$ was mainly controlled by its binding to SOM and its oxidation to more mobile $V^V$ species by atmospheric oxygen. At elevated pH (pH range 4.0–6.7) the sorption of $V^{IV}$ to solid organic phase decreased as a result of its enhanced oxidation to $V^V$ (Figure 5). Consequently, the chemical availability and water solubility of initially added $V^{IV}$ increased at higher pHs (Figure 4 and Figure 5).
4.1.2 Soil organic matter

4.1.2.1 Reactions of Cr with SOM (Paper II)
The reactions of Cr with SOM have already been rather thoroughly explored and, thus, are not investigated during this study. On the basis of prior research, binding to soil insoluble organic phase lowers the chemical availability of Cr$^{III}$ (Bartlett & Kimble, 1976; Kyziol et al., 2006). Furthermore, binding of Cr$^{III}$ to soluble organics can decrease its solubility but only in case it contributes to the formation of insoluble aggregates. This mechanism is discussed, for example, in a review by Wood (1996).

It seems that the binding of Cr to SOM is limited to Cr$^{III}$ species. Retention of Cr$^{III}$ by soil humic substances is well established, whereas that of Cr$^{VI}$ is not described in the literature. Some weak chemical interaction between Cr$^{VI}$ and humic compounds, however, may exist (Gu et al., 2015). The dissimilarities in the retention of V$^V$ and Cr$^{VI}$ species by SOM may arise from differences in their speciation chemistry. It was previously demonstrated that before reduction, oxyanionic V$^V$ species decomposes to cationic VO$_2^+$ that is better retained by humic substances (Lu et al., 1998). However, Cr$^{VI}$ exists only as oxyanionic species, which explains its poor retention to organic soil components.

4.1.2.2 Reduction and binding of V by SOM (Paper I)
The chemical accessibility of V was notably lowered by SOM. In surface soil, most of the added V$^{IV}$ and V$^V$ (50 and 100 mg V kg$^{-1}$) was bound to solid organic matter (or precipitated to poorly soluble V$^{IV}$ hydroxides) (Figure 5). A strong tendency of V to be adsorbed onto SOM is reported also e.g. by Poledniok & Buhl (2003). In surface soil high in SOM (3.2%) the potentially bioavailable fractions (easily soluble V and V bound by ligand exchange) were notably smaller than in subsoil low in SOM (0.5%) (Figure 5). This outcome was governed by the ability of SOM to reduce V$^V$ to V$^{IV}$ and to retain both species. The contribution of solid organic matter to the retention of V was possibly further enhanced by the immobile humin fraction neither soluble in alkaline or acidic solutions. Binding of V to humin may explain the finding that part of the added V$^{IV}$ and V$^V$ remained unrecovered in the sequential extraction (Figure 5).

The results also indicated that SOM lowers the chemical availability of V beyond its reducing capacity. This conclusion is based on the finding that the sorption of added V$^V$ to SOM occurred even at pH as high as 6.4, although the reduction capacity of SOM under circumneutral conditions was consider to be diminished. Moreover, Lu et al. (1998) demonstrated in their ESR (Electron Spin Resonance) experiment that V$^V$ was bound to humic substances without being reduced. The chemical binding of this species,
however, can be considered significantly weaker than that of V\textsuperscript{IV}. Vanadium as V\textsuperscript{IV} species forms strong complexes, particularly with FAs or other organic compounds containing oxygen-donating sites (Cheshire \textit{et al.}, 1977). On the other hand, V\textsuperscript{V} (as monomeric vanadate species) has the potential to form organic esters or anhydrides similarly as its phosphate analog (Tracey & Crans, 1998). Overall, the formation of organic V\textsuperscript{V} species in soil cannot be neglected.

The solid fraction of SOM was considered to act as the main reductant of V\textsuperscript{V}. This outcome is supported by the work of Szalay \textit{et al.} (1967). In their research V\textsuperscript{V} was found to be reduced and subsequently retained as V\textsuperscript{IV} by insoluble humic acid. In this thesis, the reduction mechanism by SOM was investigated with \textit{surface soil} samples incubated with 0–500 mg V\textsuperscript{V} kg\textsuperscript{-1}. The results revealed that in a given pH, the amount of soluble organic C increased with greater V\textsuperscript{V} doses (Paper I). If soluble organic compounds acted as main reductants for added V\textsuperscript{V}, then the amount of DOC would have declined as a result of its oxidation to CO\textsubscript{2} (or remained unaltered if the oxidation products were non-gaseous). The increased solubility of SOM connected with the reduction of V\textsuperscript{V} can be explained by the oxidation-induced breakdown of solid humic or other organic substances. Humic compounds of large molecular weight oxidize to soluble compounds of small molecular weight, such as aliphatic carboxyls, phenolic acids and benzecarboxyls (Schnitzer & Khan, 1975).

Bolan \textit{et al.} (2003 & 2011) suggest that DOC acts as the main reductant in the microbial reduction of metal(loids).Soluble organic compounds might also reduce part of the added V\textsuperscript{V} in \textit{surface soil} in the present study. However, this reaction pattern was apparently less significant than that attributable to the solid organic matter in soil.

\textbf{4.1.2.3 The dual role of organic matter in controlling the potential ecotoxicity of Cr and V in soil}

The potential ecotoxic impacts of Cr and V were considered to diminish due to 1) reduction of Cr\textsuperscript{VI} and V\textsuperscript{V} by organic matter to less toxic Cr\textsuperscript{III} and V\textsuperscript{IV} species and 2) the binding of the Cr\textsuperscript{III} and V\textsuperscript{IV} (and V\textsuperscript{V}) produced to poorly bioavailable organic phases. Interestingly, SOM was able also to solubilize Cr\textsuperscript{III} and V\textsuperscript{IV} at the pH range where their inorganic counterparts exist as immobile surface bound hydrolyzed species or precipitates (Paper I and II). This response can be explained by the fact that as soluble organic complexes/chelates, the reduced Cr and V species are not hydrolyzed to solid hydroxides at elevated pH. Actually, upon increasing pH the solubility of organic Cr and V species is enhanced due to the deprotonation of the acidic functional groups of SOM. This was shown, for instance, in the increased solubility of natural Cr in \textit{field soil} treated with alkaline KOH (Paper III). This pH-dependent reaction pattern is thoroughly discussed in a previous study of Gustafsson \textit{et al.} (2014). Actually, the same response to elevated pH
was evident also for organic V species. In the *surface soil* high in organic V, the easily soluble V increased with increasing pH. In *subsoil*, this pattern was not observed, as it was significantly lower in organic V (Figure 5).

### 4.1.3 Concentration and bioaccessibility

Because oxyanionic Cr\(^{VI}\) is adsorbed by ligand exchange onto Al- and Fe-(hydr)oxide surfaces, its solubility will increase with elevated concentrations owing to increasing saturation of ligand exchange sites. The practical consequences of this reaction pattern are discussed e.g. by Palmer and Wittbrodt (1991) in a paper on remediation strategies. In paper II, the net-oxidation tests with Cr\(^{III}\) revealed another concentration-dependent mechanism associated to the production of Cr\(^{VI}\). The production of Cr\(^{VI}\) via oxidation by MnO\(_2\) appeared to be partially inhibited by the level of Cr\(^{III}\) added in the net-oxidation test. Precipitates of Cr(OH)\(_3\) were considered to form a physical barrier onto the surfaces of oxidative MnO\(_2\) but they were not specifically identified. This reaction pattern could be, however, ascertained for instance by EXAFS (Extended X-Ray Absorption Fine Structure) spectroscopy. Hitherto this inhibition mechanism is previously recognized with δ-MnO\(_2\) but without soil (Fendorf *et al.*, 1992).

In the present study, the chemical bioavailability of V species was not *directly* proportional to the amount of added V\(^{IV}\) or V\(^{V}\) (Paper I). Instead, the relative proportion of easily bioavailable (i.e. easily soluble) V increased with an elevated level of addition. In addition, the relative water solubility of the added V increased with increasing dosages of V\(^{IV}\) or V\(^{V}\). These findings were governed by two factors. First, the reduction capacity of SOM became exhausted. Consequently, the less retained V\(^{V}\) species predominated in soil. In a study on a Chinese agricultural soil, Tian et al., (2015) also reported that at higher V concentrations the proportion of V\(^{V}\) in soil increased at the expense of V\(^{IV}\). Second, adsorption of V\(^{V}\) declined with increasing saturation degree of ligand exchange sites. In other words, the relative sorption of V onto ligand exchange sites diminished at high V addition level (500 mg V kg\(^{-1}\)). This phenomena was particularly explicit in *subsoil* amended with V\(^{V}\). In the case of V, the formation of polymeric V\(^{V}\) species at higher concentration was expected to influence the chemical bioavailability of added V. For instance, the formation of inorganic decavanadate species (HV\(_{10}\)O\(_{28}\)^{5-}) is suggested to lowers the sorption of V\(^{V}\) onto Fe-oxides (Peacock & Sherman, 2004).
4.2 OXIDATION OF Cr\textsuperscript{III} TO Cr\textsuperscript{VI} IN FIELD SOIL

4.2.1 The mechanism of pH-dependent oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} by MnO\textsubscript{2} in field soil

In the field soil samples, at the pH range 3.9–6.3, the oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} was detected only in the subsamples incubated with synthetic MnO\textsubscript{2} (Figure 3). This reaction was dictated by soil pH, with the formation of Cr\textsuperscript{VI} being lowest in the most acidic soil samples (Paper II). It is known, however, that the production of Cr\textsuperscript{VI} depends on the difference between two counteracting reactions: total oxidation of Cr\textsuperscript{III} and the subsequent reduction of the Cr\textsuperscript{VI} formed. Therefore, the impact of pH must be considered as a net result of these reactions. According to Fendorf (1995), the end-product of the oxidation reaction of Cr\textsuperscript{III} (at pH 5) is Mn\textsuperscript{2+}:

$$\text{1.5 MnO}_2 + \text{Cr(OH)}^{2+} = \text{HCrO}_4^- + 1.5 \text{Mn}^{2+}$$

This reaction pattern was evident in the net-oxidation tests in the present study. In the soil samples previously incubated with MnO\textsubscript{2}, the amount of the soluble and adsorbed Mn\textsuperscript{2+} was recorded before and after addition of Cr\textsuperscript{III} in the net-oxidation test. Elevated concentration of Mn\textsuperscript{2+} revealed that in the acidic soil sample (pH 4.4) the oxidation of Cr\textsuperscript{III} by MnO\textsubscript{2} produced concomitantly substantial amounts of soluble Mn\textsuperscript{2+} (Paper II). However, in soil samples of higher pHs (above 5.5) no Mn\textsuperscript{2+} was produced. This outcome is in harmony with the theory that acidic soil conditions enhance the total oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} by MnO\textsubscript{2}. In addition, upon on the increasing solubility of Cr\textsuperscript{III} with lowering pH, also its total oxidation can be expected to increase. In a rather acidic soil (pH 4.4), one fourth of the added Cr\textsuperscript{III} (52 mg L\textsuperscript{-1}) remained soluble and, thus, prone to be potentially oxidized by MnO\textsubscript{2}. Instead, at higher soil pHs the hydrolysis of Cr\textsuperscript{3+}, followed by adsorption and precipitation reactions, diminished the solubility of Cr\textsuperscript{III}. At initial soil pH > 5.5, the amount of soluble Cr\textsuperscript{III}, susceptible to be oxidized on the MnO\textsubscript{2} surfaces, was very low (Paper II). The conclusion that acidic soil conditions enhance the total oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} is supported by previous studies, with pyrolusite (β-MnO\textsubscript{2}) and birnessite (δ-MnO\textsubscript{2}) (Eary & Rai, 1987; Fendorf & Zasoski, 1992).

Though acidic conditions indicated to promote total oxidation of Cr\textsuperscript{III}, the amount of produced Cr\textsuperscript{VI} was low. At soil pH 4.4, only 0.4% of the added Cr\textsuperscript{III} was net-oxidized by MnO\textsubscript{2}, whereas at pH 5.5 and 6.2 the yields were 4.4% and 4.7%, respectively. Thus, the net-oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} was actually enhanced at elevated pHs. This outcome was attributable to the fact that the increasing acidity also favored the reduction of the Cr\textsuperscript{VI} formed back to Cr\textsuperscript{III}. This conclusion is supported by the study of James \textit{et al.}, (1997) reporting a similar impact of low pH on the reduction of Cr\textsuperscript{VI} in the reaction with hydroquinone:

$$\text{1.5 C}_6\text{H}_6\text{O}_2 + \text{CrO}_4^{2-} + 2 \text{H}^+ = 0.5 \text{Cr}_2\text{O}_3 + 1.5 \text{C}_6\text{H}_4\text{O}_2 + 2.5 \text{H}_2\text{O}$$
Similar findings on the pH-dependency of Cr net-oxidation are proposed by Negra et al. (2005). In their study on various natural uncultivated soils, the net-oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI} was inferior in soils of lower pH.

The impact of pH on the production of Cr\textsuperscript{VI} via oxidation of Cr\textsuperscript{III} by MnO\textsubscript{2} in soil differs from that reported previously in experiments carried out without soil. This discrepancy is explained by the presence of organic matter (or other reducing components) in soils. In the present study with soil (Paper II), the formation of Cr\textsuperscript{VI} was lowered by SOM via two mechanisms. Firstly, the oxidized Cr\textsuperscript{VI} was reduced back to less mobile Cr\textsuperscript{III} by SOM. Secondly, in (acidic) soil the organic soil constituents reduced part of the added MnO\textsubscript{2} to Mn\textsuperscript{2+} that was not able to oxidize Cr\textsuperscript{III} added later to soil. Because of this reaction pattern, the oxidation capacity of MnO\textsubscript{2} decreased.

It is also noteworthy, that the reduction of Cr\textsuperscript{VI} is identified to take place both via abiotic and biotic pathways (Lovley, 1995; Tokunaga et al., 2003). Consequently, in experiments carried out with pure minerals or sterilized soils the contribution of biological activity (e.g. soil microbes) to redox reactions is neglected. In high OM soils, the microbial reduction of Cr\textsuperscript{VI} to Cr\textsuperscript{III} can be expected to be significant. Actually, microbial activity is linked also to the formation of biogenic MnO\textsubscript{2} (Tebo et al., 2004), that can further contribute to the oxidation yields of Cr\textsuperscript{III}. In this study, the impact of biological factors in the formation of Cr\textsuperscript{VI} in soil via oxidation were not separated from the abiotic ones. Thus, results are influenced by redox-reactions of both origins.

4.2.2 MnO\textsubscript{2}-induced oxidation risk of Cr\textsuperscript{III} to Cr\textsuperscript{VI} in the potential leachates of BOFS

The oxidation risk of Cr\textsuperscript{III} (mimicking Cr in the leachates from BOFS) by natural soil MnO\textsubscript{2} was low (Paper III). The net-oxidation tests with field soil samples incubated with BOFS revealed the formation of Cr\textsuperscript{VI} to be negligible. The Mn oxides in BOFS did not promote the Cr\textsuperscript{VI} production, although they elevated the total content of Mn oxides in soils. Even in soil amended with a very high amount of synthetic MnO\textsubscript{2} (equivalent to 8500 mg Mn\textsuperscript{IV} kg\textsuperscript{-1}), the formation of Cr\textsuperscript{VI} from initially soluble Cr\textsuperscript{III} remained minor. In the net-oxidation test the maximum net-oxidation yield was 5% of the added 52 mg Cr\textsuperscript{III} L\textsuperscript{-1} (Paper II).

Low production of Cr\textsuperscript{VI} via oxidation by MnO\textsubscript{2} can be attributed to 1) the precipitation of initially soluble Cr\textsuperscript{3+} into immobile Cr(OH)\textsubscript{3} and 2) the high organic C (3.2%) content of the experimental soil, which equates to 6.1% SOM (conversion coefficient 1.9 for non-calcareous soil). Consequently, the reduction capacity of the experimental soil to counteract the formation of Cr\textsuperscript{VI} can be considered high. In field soil samples incubated with BOFS, the Cr\textsuperscript{III} added initially as soluble was quickly immobilized (Paper III). Thus, in pH conditions of limed field soils (pH > pH 5) the potentially released Cr\textsuperscript{III}
from BOFS can be viewed as strongly retained (Paper III). In fact, the experiment indicated that the release of Cr from BOFS to field soil during the 3-month incubation was insignificant.

Interestingly, in the enhanced net-oxidation test the production of Cr\textsuperscript{VI} was apparent in the field soil samples incubated with or without BOFS (Figure 6). Without BOFS, 24% of the added Cr\textsuperscript{III} was net-oxidized to Cr\textsuperscript{VI}, while incubation with BOFS lowered the Cr\textsuperscript{VI} production. At the “recommended” BOFS dosage (equivalent to 10 t ha\textsuperscript{-1}) net-oxidation yield was 11%, whereas at the higher dosage (equivalent to 100 t ha\textsuperscript{-1}) only 1%.

Figure 6. Enhanced net-oxidation test: concentration of soluble remaining Cr (no speciation, mg L\textsuperscript{-1}) in 1 mM CrCl\textsubscript{3} (=52 mg Cr\textsuperscript{III} L\textsuperscript{-1}) suspension with field soil samples incubated without and with BOFS (1:10 w/V) and easily soluble Cr\textsuperscript{V} produced (mg L\textsuperscript{-1}) after addition of MnO\textsubscript{2}. Percentages indicate the mean production of Cr\textsuperscript{VI} from the added Cr\textsuperscript{III}. Error bars illustrate standard error (N=3). Paper III.

These results indicated that freshly precipitated Cr\textsuperscript{III} is susceptible to being oxidized by MnO\textsubscript{2} under extremely oxidizing conditions. In the enhanced net-oxidation test (Paper III), the added MnO\textsubscript{2} was equivalent to an extremely high soil Mn level (36 000 mg Mn kg\textsuperscript{-1}). Also, Mn\textsuperscript{IV}O\textsubscript{2} was added to soil suspension after the addition of Cr\textsuperscript{III} solution (52 mg Cr\textsuperscript{III} L\textsuperscript{-1}). Thus, prior incubation with soil had not altered the oxidative surfaces of MnO\textsubscript{2} by adsorption of metal hydroxide cations or organic substances. Moreover, the oxidizing capacity of MnO\textsubscript{2} was not lowered by its reduction to Mn\textsuperscript{2+} by SOM during previous incubation (as it was in the experiments of Paper II). In other words, the oxidation capacity of MnO\textsubscript{2} was extremely high and clearly exceeded the reduction capacity of organic matter. Thus, in the enhanced oxidation tests the production of Cr\textsuperscript{VI} was governed by the total oxidation by MnO\textsubscript{2}, whereas the role of the subsequent reduction of Cr\textsuperscript{VI} back to Cr\textsuperscript{III} was insignificant. Consequently, formation of Cr\textsuperscript{VI} diminished
upon increasing BOFS dosage as the elevated soil pH declined the *total* oxidation of Cr$^{\text{III}}$ by MnO$_2$. This outcome agrees with the pH-dependent oxidation mechanisms previously discussed (4.2.1). Overall, research on the oxidation mechanisms of slag-derived Cr in soils is practically non-existent, with no comparable reference literature available.

### 4.2.3 Oxidation of Cr$^{\text{III}}$ in BOFS by atmospheric O$_2$

Trace amounts (0.1 mg kg$^{-1}$) of soluble Cr$^{\text{VI}}$ were detected in pure BOFS (Paper III). In the mineral structures of BOFS, Cr is reported to exist as Cr$^{\text{III}}$ (Chaurand *et al.*, 2006). Thus, it can be concluded that Cr$^{\text{VI}}$ is produced via oxidation after the formation of slag, not during its formation under high temperature. This indicates that a small portion of the Cr$^{\text{III}}$ in BOFS will be potentially oxidized by atmospheric oxygen. This mechanism is discussed in previous study by Pillay *et al.* (2003). In their experiments on alkaline EAF (Electric Arc Furnace) and CLU (Creusot–Loire–Uddeholm) steel industry slags, a maximum of 1% of the total Cr in slags was oxidized by atmospheric O$_2$ during the test period of 12 months.

Chromium in BOFS was poorly soluble in *field soil* samples (Paper III). Consequently, the oxidation of BOFS-derived Cr$^{\text{III}}$ to Cr$^{\text{VI}}$ by soil MnO$_2$ was considered very unlikely. Therefore, oxidation by molecular oxygen appears to be a more probable reaction pattern for the potential oxidation of Cr$^{\text{III}}$ to Cr$^{\text{VI}}$ in BOFS. However, oxidation of Cr$^{\text{III}}$ by O$_2$ is considered very slow and gradual in comparison to the oxidation by MnO$_2$ (Rai *et al.*, 1989). Oxidation of Cr$^{\text{III}}$ by atmospheric O$_2$ is also pH-dependent. Reaction is considered relevant only in alkaline conditions (Pillay *et al.*, 2003) and slags have the potential to produce highly alkaline soil conditions. The impact of slag amendment on soil pH depends on soil properties (e.g., initial pH, amount and composition of soil minerals, organic matter composition, biological activity) and, of course, on the amount and properties of the added slag.

Owing to its high CaO content, BOFS notably elevated the pH of the experimental soils (Table 7). However, in practice soils are spatially heterogeneous systems, wherein the pH of the soil solution does not stay constant when the seeping water moves throughout soil pores. In the vicinity of slag particles, conditions can be expected to be rather alkaline and, consequently, the Cr bearing minerals in BOFS may be exposed for oxidation by molecular oxygen. Thus, in theory, a minor proportion of Cr$^{\text{III}}$ may have the potential to be oxidized by atmospheric O$_2$ in oxic soils. Nonetheless, in the field soil samples incubated with BOFS (equivalent to 10 and 100 t ha$^{-1}$ additions) no easily soluble Cr$^{\text{VI}}$ was detected (Paper III). This means that the amount of soluble Cr$^{\text{VI}}$ released from BOFS was below the detection limit or reduced to Cr$^{\text{III}}$ by organic soil constituents. That said, whether this reaction mechanism is of real significance in soils remains unsolved. We need to
know, for example, to what extent can Cr\text{III} in BOFS be oxidized by atmospheric oxygen in soil, and if this Cr\text{VI} is available for biological uptake.

The partial pressure of oxygen in deeper soil layers is significantly lower than that above the soil surface. Therefore, the oxidation risk of Cr\text{III} in BOFS by atmospheric O\textsubscript{2} in soils might be lowered if BOFS particles are ploughed deeper into the soil. Furthermore, oxidation is counteracted by subsequent reduction of Cr\text{VI} to Cr\text{III} by soil organic matter. However, alkaline soil conditions favor the atmospheric oxidation of Cr\text{III}, but diminish the counteracting impact of Cr\text{VI} reduction reactions. In previous studies, the reduction of Cr\text{VI} by fulvic acids (FAs) is shown to fade out already at neutral conditions (Wittbrodt & Palmer, 1995).

4.3 SLAGS AS LIMING MATERIALS: BIOACCESSIBILITY AND MOBILITY OF VANADIUM AND CHROMIUM

4.3.1 Additional material: chemical bioavailability of V in slags

The distribution of V into fractions differing in their chemical bioavailability was investigated with surface soil and subsoil incubated with various slags (GBFS, BOFS and HVS) (Figure 7). Liming with GBFS resulted only in a slight increase in the strongly bound V fraction. BOFS and HVS, in turn, increased V in the potentially bioavailable (i.e. easily soluble and ligand-exchangeable fractions), as well as in the immobile fractions (i.e. V bound to solid organic matter and strongly bound V) in both soils (Figure 7). The V concentrations in all fractions were highest in the samples amended with HVS that was richest in total V and had the smallest particle size (i.e. the largest surface area) (chapter 3.2.1). Although HVS was higher in the sequentially extractable V than BOFS, the slags were rather similar in terms of the relative distribution of V between chemical fractions. This outcome is attributable to their chemical composition being rather similar, excluding their V concentration (Table 2).

It is noteworthy that at the “recommended” liming level (10 t ha\textsuperscript{-1}) both BOFS and HVS elevated the potentially bioavailable V significantly more in subsoil than in surface soil. Interestingly, at the higher dosages (100 t ha\textsuperscript{-1}) the impact of soil type (i.e. amount of organic matter) on the easily potentially bioavailable fractions levelled off. This change was attributable to the very alkaline conditions (soil pH 9.3–11.1) that diminished the reduction of V and, consequently, its tendency to be bound by SOM. High pH also promoted the solubilization of organic V bound to humic acid. Terrestrial HA will be solubilized at pH above 9 (e.g. Kipton et al., 1992).

The poorly soluble V fraction (i.e. strongly bound V) was considered to be still part of the slag mineral phase that had not been solubilized. Alternatively, this fraction might consist of released V subsequently
precipitated with Ca\(^{2+}\) to form calcium vanadate. Konnert and Evans (1975) describe the possible crystallization of inorganic V\(^V\) from aqueous solution with Ca\(^{2+}\) at pH 8–9. In the present study, most of V recovered at higher BOFS and HVS dosages was in the poorly soluble (strongly bound V) fraction.

In case V in the strongly bound fraction was not dissolved during incubation, the easily soluble and ligand exchangeable V fractions as well as that bound to organic matter can take to be released from slags. Thus, at the “recommended” slag dosages (10 t ha\(^{-1}\)) most of the V released was retained by solid organic matter. In subsoil, on the other hand, only about half of the released V was bound onto solid phase SOM. The other half remained soluble or adsorbed onto oxide surfaces by ligand exchange.

**Figure 7.** Recovery of V in various fractions extracted sequentially (1:10 w/V) from fresh surface soil and subsoil amended with slags (GBFS, BOFS and HVS). Upper part: a) surface soil and b) subsoil incubated with 10 t ha\(^{-1}\) slag dosage. Lower part: c) surface soil and d) subsoil incubated with 100 t ha\(^{-1}\) slag. The error bars indicate standard errors, N=3.
4.3.2 Additional material: mobility of V in soils limed with BOFS, GBFS and HVS

To determine the mobility of slag-derived V, the surface soil and subsoil samples incubated with slag amendments equivalent to 10 and 100 t ha$^{-1}$ were extracted using Milli-Q water (Figure 8). Both control soils incubated without slag were extremely low in water soluble V (<0.03 mg kg$^{-1}$). Solubility of V was also low in the GBFS-treated soils. Only <1% of the total V in GBFS was recovered in the water extraction. In contrast, BOFS- and HVS-treatment notably elevated water soluble V. At the lower dosage (10 t ha$^{-1}$) the water soluble V amounted to 6–12 mg kg$^{-1}$ and at the higher one (100 t ha$^{-1}$) it increased up to 20–80 mg kg$^{-1}$. The relative solubility of V was 2–3-fold higher at the lower (8–12%) than at the higher slag addition level (3–6%). It is noteworthy that the soil types did not differ in terms of the water solubility of V.

![Figure 8](image.png)

**Figure 8.** The mean water solubility of V in fresh surface and subsoil (1:50 w/V) incubated (3 months at 22 ºC and 60% WHC) with slag (GBFS, BOFS or HVS) dosages equivalent to a) 10 t ha$^{-1}$ and b) 100 t ha$^{-1}$ (N=3). Percentages indicate the proportion of soluble V of the total V content in slags.

4.3.3 Impact of soil organic matter on the chemical bioavailability of V released from BOFS and HVS

Organic matter decreased the chemical availability of V released from BOFS or HVS to soil, but only at the lower slag dosage (10 t ha$^{-1}$) (Figure 7). This response was indicated by the lower levels of easily soluble and ligand exchangable V but higher level of (solid) organic V in surface soil (SOM 3.5%) than in subsoil (SOM 0.5%). In surface soil, the binding of released V to SOM was considered to occur after the reduction of $V^{V}$ to $V^{IV}$ species. At higher slag dosages, the relative binding of slag-derived V to solid organic matter diminished upon increasing solubility of SOM as well as its diminished reduction capacity.
In a previous study, Chaurand and Rose (2006) demonstrated V in the BOFS leachates to exist as $V^{V}$ species. This supports conclusion that BOFS- and HVS-derived V in soil was retained by SOM after $V^{V}$ was reduced to $V^{IV}$ (Figure 7). However, it is possible that solid organic matter is also able to retain $V^{V}$ species. Both reaction pathways are depicted in Paper I.

Nevertheless, under the neutral or alkaline conditions in the slag-treated soils, SOM seemed not to lower the water-solubility of the slag-derived V. The surface soil and subsoil did not differ in terms of solubility of V (Figure 8). However, under acidic soil conditions (pH<6.5), the experiments with pure V chemicals proved the water solubility of added V to be lower in surface soil than in subsoil (Paper I). This indicates that the ability of SOM to lower the chemical bioaccessibility of V, also slag-derived V, is enhanced by low pH.

4.3.4 Chemical availability of V species at different extraction ratios

The water extraction test showed the ability of SOM to reduce and retain added V to diminish at pH above ~6.5 (Paper I). This explains that SOM did not affect the water solubility of V derived from BOFS or HVS because the conditions of slag treated soils were neutral or highly alkaline (Figure 8). However, according to the sequential extraction, SOM reduced $V^{V}$ to $V^{IV}$ and bound both species even under neutral conditions (Paper I and Additional material, Figure 7). These somewhat contrasting impacts of SOM on the retention of V (above circumneutral conditions) are attributable to dissimilar soil:solution ratios used. In the fractionation procedure, the extraction ratio was small (1:10). Thus, the capacity of SOM to reduce $V^{V}$ to $V^{IV}$ remained relatively high. In the water extraction, in turn, the reduction (and sorption) capacity of SOM was lower because the amount of soil was smaller in respect to soluble $V^{V}$ at the larger extraction ratio (1:50).

At a given concentration ($c$), the amount ($n$) of soluble element is higher when the amount of solution (V) increases ($c=n/V$). At an extraction ratio of 1:50, the greater extractant volume means that a higher amount ($n$) of $V^{V}$ is needed to reach a given concentration. Thus, at a soil to solution ratio of 1:50 of the water extraction, the amount of soluble $V^{V}$ prone to be reduced by SOM is greater than at ratio of 1:10. Consequently, the reduction capacity of SOM was exhausted in the water extraction but not in the sequential extraction. In the latter, SOM was still able to reduce $V^{V}$ to $V^{IV}$ that was strongly bound to solid organic matter. To obtain an equilibrium concentration in the soil solution, $V^{V}$ is either adsorbed to or desorbed from ligand exchange sites. In water extraction, $V^{V}$ will be released from ligand exchange sites to the surrounding solution (initially free of $V^{V}$) to obtain an equilibrium corresponding to the degree of saturation on sorbent surface. Upon increasing solid:solution ratio, the desorption continues until a new
equilibrium between the solution concentration and the quantity of the V sorbed onto the solid phase is reached.

In the water extraction test, the desorption of V\textsuperscript{V} species from sorption sites to solution was favored by the very low ionic strength (I) of Milli-Q water used as an extractant. In the fractionation procedure, however, the easily soluble species were extracted by 0.25 M KCl having a rather high I which decreases the extractability of V\textsuperscript{V}. Moreover, the extraction time used in water extraction was longer than that used in the chemical fractionation procedure.

As for the soil to solution ratio, the experimental conditions in the sequential extraction were more comparable to those in actual soils. Thus, the results indicate that retention of V species to SOM in soil is relevant even in circumneutral conditions. The organic chelates expand the pH range of stable V\textsuperscript{IV} species from acidic conditions to pH 7–8 (Wehrli & Stumm, 1989).

The increased chemical bioavailability of V upon decreasing soil to solution ratio is of relevance in terms of aquatic ecosystems. For instance, V in the erosion material from slag-amended fields can be anticipated to be efficiently released in recipient waters owing to the enormous volume of solution in proportion to the eroded particles. Moreover, the surface runoff from slag-amended fields increases the risk of V release. This is attributable to the fact, that desorption of V from the particle surfaces is favored by increasing the solution to soil ratio. The same holds true for release of V pure slags, i.e. the total release of V increases when the water to slag ratio increases. De Windt et al. (2011) reported that the relative dissolution rates of V from BOFS at the solid to solution ratios of 1:10 and 1:100 were 0.06% and 1.7%, respectively.

### 4.3.5 Experiments with actual soils – prerequisite of risk assessment

Reactions with soil enhanced the dissolution and release of V from HVS and BOFS and that of Cr from BOFS (Paper III and Additional material). As for V in slags, water extracted it more from incubated soils than from pure slags. On the basis of the solubility of V in pure slags (0.16 mg kg\textsuperscript{-1} in BOFS and 52 mg kg\textsuperscript{-1} in HVS), the water soluble V in limed soils was estimated to increase from <0.001 up to 2.6 mg kg\textsuperscript{-1}. The increment was, however, remarkably higher than expected: the water soluble V increased up to 80 mg V kg\textsuperscript{-1} (Figure 8).

After a 3-month incubation with the “recommended” liming dosage, up to 9-12% of V in BOFS/HVS was recovered in water extraction. This proportion is notably higher than that (below 1.7%) reported in previous experiments with BOFS without soil (De Windt et al., 2011). In soil, the subsequent sorption of solubilized V onto soil particles enhanced the gradual release of V from slags. An attempt to maintain a given equilibrium concentration in the
solution phase means that the sorption of released V in soil contributes to a continuous release of V from the slags, which results in its gradual accumulation in the ligand-exchangeable and organically bound fractions (Figure 7). In other words, soil acts as a sink for V and, consequently, promotes the further release of V from slags to maintain a chemical equilibrium between solid and solution phase. In case the equilibrium was not reached during the 3-month incubation period, it is possible that extended incubation could have resulted in greater dissolution of V from slags to soil.

Moreover, in soils incubated with 10 t ha\(^{-1}\) dosage of BOFS or HVS, pH (7.0–7.9) was lower than in pure water suspension (above pH 11) (Table 2 and Table 5). The pH being lower in these soil samples may have influenced the dissolution of V from slags. In the soils amended with the higher dosage of BOFS/HVS, pH (9.3–11.1) did not notably differ from that in the water suspensions of slags. According to a technical report of Technical Research Centre of Finland (Wahlström & Laine-Ylijoki, 1997), the water solubility of V from BOFS, however, increased when pH was elevated from 4.5 to 9.5. Interestingly, in highly alkaline conditions (pH 9.5–12) its solubility again declined.

As for Cr, the contribution of soil reactions in enhancing its release from BOFS was detected only under acidic conditions (Paper III). In fact, at pH above circumneutral the solubility of Cr from BOFS was negligible (the water soluble Cr in soil with or without slag amounting to 0.1 mg kg\(^{-1}\)). No Cr was released to soil as chemically bioavailable Cr\(^{\text{III}}\) or Cr\(^{\text{VI}}\) species. However, the ammonium oxalate extraction (at initial solution pH 3.3) indicated that a proportion of the Cr in BOFS is potentially solubilized in acidic soils (Paper III). Similar to V, the solubility of Cr appeared to be enhanced in the presence of soil that acted as a sink for the Cr released. In other words, when Cr dissolved from BOFS is (ad)sorbed onto soil particles, its concentration in the solution decreases. To maintain a given equilibrium between solution and solid phase, more Cr is dissolved from BOFS. This was seen in the elative extractability of Cr by ammonium oxalate (Cr per kg of BOFS) increasing in the order: pure BOFS (16 mg Cr kg\(^{-1}\)) < field soil incubated with BOFS equivalent of 100 t ha\(^{-1}\) (86 mg Cr kg\(^{-1}\)) < field soil incubated with BOFS equivalent of 10 t ha\(^{-1}\) (261 mg Cr kg\(^{-1}\)).

Furthermore, the decrease in soluble Cr\(^{\text{III}}\) upon elevated BOFS dosage was also considered to result from the ability of BOFS to elevate the initial pH of the extractant (Paper III). Although ammonium oxalate is a buffer solution, the high alkalinity of BOFS challenged its ability to maintain pH at 3.3. Thus, the extraction conditions with soil samples incubated with higher BOFS dosage might have been more alkaline than intended. This was obviously the case in the extraction of pure slag. Consequently, upon increasing alkalinity less Cr was released from BOFS. Unfortunately, pH of the soil/BOFS suspended to ammonium oxalate solution was not measured. It is noteworthy, that in the ammonium oxalate extraction the dissolution of
Cr from slags might be enhanced also by the formation of Cr-oxalate complexes.

Results clearly demonstrate that in terms of risk assessment, the experiments with actual soil are of crucial importance. Release of Cr and V from pure slags to water solution differs from their release to soil solution. In practice, the release of these metals was governed by soil properties such as pH and amount and quality of soil organic matter. The solubilization of Cr and V from slags can be further enhanced by their leaching into deeper soil layers or as surface run-off to recipient waters. Moreover, soil biological processes, such as uptake by plant roots, can increase the release of these metals from slags. All these phenomena lower the concentration of Cr and V in soil solution and, thus, promote further solubilization from slags.

In soils, the release of Cr and V from slag can also be enhanced by microbial activity as described in the review by Ehrlich (1997). The contribution of biotic release of V from slags can be assumed more probable in the surface soil than in the deeper soil layers.

The impact of SOM on the solubility of slag-derived V is dependent on soil pH. In highly alkaline conditions, SOM is not able to reduce the bioaccessibility of released V (Paper I and Additional material). Thus, in areas where slags are being deposited in large amounts onto soil (e.g. landfills, BOFS piling areas), soluble V exists mainly as V\textsuperscript{v} species. Thus, the chemical availability of V released from HVS or BOFS can be expected to be regulated by the adsorption-desorption reactions of V\textsuperscript{v}. However, the adsorption of this oxyanionic species decreases at elevated pHs (chapter 4.1.1.1.). In neutral soil conditions, part of the V released from BOFS or HVS can still be bound to SOM (Figure 7). The ability of humic matter to strongly retain V derived from BOFS is actually demonstrated in the acidic (pH <4.6) upper layers of Swedish forest soil (Larsson et al., 2015b). Overall, it can be concluded that the assessment of the environmental risks of slags as liming materials solely based on their chemical properties is not scientifically sound.

4.3.6 Speciation of Cr and V in slags

The mineralogy and speciation of Cr and V influences their dissolution rates in soil. In this study, however, the initial oxidation state of these metals in slags was not investigated. A general conclusion is that unlike V, the release of Cr from BOFS to field soil is negligible (Additional material and Paper III). This is attributable to the minerology of Cr in BOFS. Previous studies have demonstrated that the solubility of Cr is controlled by the reluctantly soluble Cr\textsuperscript{III} in brownmillerite and wustite minerals (Chaurand et al., 2006).

As for V, the results obtained in the present study revealed that the impact of GBFS on the potentially bioavailable proportion of V was negligible both in surface soil and subsoil (Figure 7). Larsson et al. (2015a) obtained similar results with their test soil. They suggested that V in GBFS minerals initially
exists as trivalent $\text{V}^{\text{III}}$. This could explain the insignificant release of V from GBFS to soil.

On the contrary, V in BOFS and HVS was rather soluble. During a 3-month incubation of surface soil and subsoil samples, up to 9% of V in BOFS and 12% of that in HVS were recovered in the mobile fraction (Figure 8). The significantly higher solubility of V is likely associated to the oxidation state of V in slags formed in blast oxygen furnace. According to Chaurand et al. (2006) V in BOFS initially exists as $\text{V}^{\text{IV}}$ in dicalciumferrite minerals which control the dissolution of V from BOFS. De Windt et al. (2011) concluded the dissolved species to exist as $\text{V}^{\text{IV}}$ that will be oxidized to $\text{V}^{\text{V}}$. These findings support our conclusion that under alkaline conditions the chemical bioavailability of V is regulated by sorption reactions of $\text{V}^{\text{V}}$ species.

### 4.3.7 Release of Cr and V from BOFS to soil – chemical reaction patterns

The reactions controlling the release of Cr and V from BOFS and the potential reaction pathways in soils are depicted in Scheme 5. As for Cr and V in GBFS, the reactions of Cr were not investigated, and the release of V to soil showed to be insignificant. The reaction patterns of Cr and V in HVS can be taken to be comparable to those of BOFS because both slags are formed in blast oxygen furnace and, consequently, their composition is rather similar.

The release of $\text{Cr}^{\text{III}}$ and $\text{Cr}^{\text{VI}}$ from BOFS was negligible at field soil pH. Owing to the low solubility of $\text{Cr}^{\text{III}}$, the risk of its oxidation to hazardous $\text{Cr}^{\text{VI}}$ by $\text{MnO}_2$ was considered insignificant. Instead in highly alkaline conditions, a small portion of the $\text{Cr}^{\text{III}}$ in BOFS may be oxidized by atmospheric oxygen. A more probable risk is, however, the release of $\text{Cr}^{\text{III}}$ under acidic soil conditions. At low soil pH its conversion to $\text{Cr}^{\text{VI}}$ is, nonetheless, unlikely as the capacity of SOM to reduce $\text{Cr}^{\text{VI}}$ to $\text{Cr}^{\text{III}}$ is very high.

On the contrary, the solubilization of V from BOFS in soil was notable. However, SOM lowers the potential bioavailability of the released V (assumed to exist as $\text{V}^{\text{IV}}$) by reducing a part of $\text{V}^{\text{V}}$ to $\text{V}^{\text{IV}}$, whereafter both species are bound onto the soil organic matter. The contribution of SOM diminishes under alkaline conditions, where at high pHs, the bioavailability of V is mainly controlled by adsorption-desorption of $\text{V}^{\text{V}}$ species by ligand exchange onto Fe- and Al- hydroxides.

The distinct solubility of Cr and V released from slag to soil is attributable to their dissimilar oxidation reactions. In oxic soils, soluble as well as immobile $\text{V}^{\text{IV}}$ can be oxidized to more mobile $\text{V}^{\text{V}}$ by atmospheric oxygen, whereas the oxidation of $\text{Cr}^{\text{III}}$ by $\text{O}_2$ is plausible only at very high pH. Oxidation of $\text{Cr}^{\text{III}}$ to $\text{Cr}^{\text{VI}}$, in turn, was shown to be governed by reactions of soluble $\text{Cr}^{\text{III}}$ with soil $\text{MnO}_2$. This reaction pattern seemed to be insignificant for BOFS. Consequently, the impact of oxidation reactions on the chemical bioavailability in soil was more pronounced with V than it was with Cr.
Scheme 5. Summary of the simplified pH-dependent reaction patterns of Cr and V derived from BOFS in soil.
4.4 ENVIRONMENTAL IMPLICATIONS: SLAGS AS LIMING MATERIALS

4.4.1 Chromium

In terms of bioaccessibility of Cr\textsuperscript{III} or Cr\textsuperscript{VI}, the use of BOFS as liming material did not cause any changes in field soil (Paper III). This finding agrees with the results of Proctor et al. (2000) and De Windt et al. (2011) showing the leaching of Cr from BOFS to be insignificant. Thus, in pH conditions typical of agricultural soils, the impact of Cr in BOFS on terrestrial ecosystems can be expected to be negligible. Also the contamination of ground waters by BOFS-derived Cr is unlikely owing to the reluctantly soluble Cr minerals in BOFS.

Due to the poor solubility of Cr\textsuperscript{III} in slags, the risk of its oxidation to hazardous Cr\textsuperscript{VI} by MnO\textsubscript{2} in field soil was low (Paper II and III). However, in extremely oxidizing soils rich in MnO\textsubscript{2} and low in reducing organic matter, even precipitated Cr\textsuperscript{III} is susceptible to be oxidized to Cr\textsuperscript{VI} (Paper III). In most soils, however, the atmospheric oxidation of Cr\textsuperscript{III} on the slag surface appears to be a more plausible pathway for the formation of Cr\textsuperscript{VI} (Paper III). However, the relevance of this reaction in soils remains unknown.

In acidic soils a proportion of Cr\textsuperscript{III} in BOFS is potentially solubilized (Paper III). This may be of significance if BOFS is used as a liming material, e.g. in acidic boreal forest soils where pH does not rise sufficiently to prevent solubilization. However, a low soil pH that promotes the release of Cr\textsuperscript{III} from BOFS, concomitantly diminishes the risk of the Cr\textsuperscript{VI} formation via oxidation (Paper II and III). Consequently, the environmental impacts of the released Cr\textsuperscript{III} under acidic conditions mainly rest on the proportion remaining available for biological uptake.

Solubilized (initially inorganic) Cr\textsuperscript{III} can be anticipated to form both soluble and immobile organic complexes in acidic soils high in organic matter. The soluble organic Cr species are potentially bioavailable. However, the cellular uptake of the soluble organic Cr\textsuperscript{III} species is further influenced by several factors, e.g. their molecular size and structure, as well as by the properties of the biological receptor organism. Although the large dissolved organic Cr\textsuperscript{III} complexes are not bioavailable, they still may leach from soil to water systems.
4.4.2 Vanadium

In contrast to Cr, the BOFS-derived V was rather soluble in soil (Figure 7 and Figure 8). This was considered to be attributable to the oxidation of V^{IV} to more mobile V^{V} by atmospheric oxygen. Similar conclusions are reported in experiments on pure BOFS without soil (Chaurand et al., 2006). The fate of released V depends on soil pH and organic matter content (Paper I and Additional material). A high soil pH and low organic carbon content promote the chemical bioavailability of V (Paper I). The mobility of V^{V} species is limited by their adsorption onto oxide surfaces by ligand exchange (Paper I). Thus, also the bioavailability of V released from BOFS can be anticipated to correlate with the content of amorphous Fe- and Al-(hydr)oxides in soil. This conclusion is supported by finding of Wang & Liu (1999) that the uptake of added V^{V} by soybean seedlings from Oxisol soil (high in Fe-oxides) was negligible. The pH-dependency of V sorption recorded in this study (Paper I) agrees with the results of earlier batch experiments of Mikkonen & Tumnnavuori (1994) on the sorption of V^{V} onto Finnish mineral soils. However, they suggested sorption mechanisms differing from those in this research. In the present work, the formation of organic (soluble and insoluble) V species was also demonstrated.

Overall, it is clear that a significant proportion of the V in BOFS is potentially bioavailable or susceptible to be leached into recipient water systems. This possibly precludes the use of BOFS as liming material of agricultural soils. Moreover, in non-acidic soils the soluble V exists predominantly as a V^{V} species considered more harmful to biota than V^{IV}. The risk limits given for V in soil are defined in a report by National Institute for Public Health and the Environment of Netherlands (Van Vlaardingen et al., 2005). In soil with a background concentration of 42 mg V kg^{-1}, addition of 25 mg V kg^{-1} (total concentration of 67 mg kg^{-1}) was considered a serious risk for terrestrial ecosystems. A minor increment of 0.03 mg V kg^{-1} was estimated to be permissible without inducing a significant ecological risk. On this scale, V in BOFS poses a severe threat to soil organisms.

Present research available on the ecotoxicity of V in terrestrial ecosystems is somewhat limited. Therefore, it is difficult to assess the actual impacts of the BOFS-derived V on terrestrial organisms. Vanadium gradually released from BOFS can be expected to be less toxic than in the case that soil biota is rapidly exposed to an equivalent amount of V. However, in many ecotoxicity experiments, test organisms are subjected to a given concentration of soluble V chemicals all at once. Further research on the release rate of V on its ecotoxicity in soil is urgently needed.

Moreover, as previously discussed, soil properties (particularly pH and content of SOM) further dictate the bioavailability of V from BOFS (Paper I and Additional material). Thus, also the ecotoxicological effects of V in BOFS are dependent on the soil type. These conclusions agree well with previous findings in toxicity experiments with collards (Brassica oleracea) (Kaplan...
et al., 1990) and soil microbes (Larsson et al., 2013). In these studies, the toxicity of V was influenced by soil type. Furthermore, direct ingestion of BOFS by animals also has hazardous consequences. In northern Sweden, poisoning of grazing cattle was associated to the V content (3%) of BOFS used as liming material (Frank et al., 1996). Levels of V in tissues of the dead animals were high, but one could imagine that the toxicity may have also been attributable to the high alkalinity of slags affecting the cattle digestive system.

On the other hand, in the present study GBFS did not elevate the chemically bioavailable fraction of V in soil. Larsson et al. (2015a) reported comparable results in their study on similar blast furnace slag used for liming of Swedish soils. It is noteworthy, however, that GBFS is notably lower (0.05%) in total V than BOFS and HVS (1.7% and 2.6%, respectively). Moreover, the liming effect (ability to elevate soil pH) of GBFS is substantially lower than that of blast oxygen furnace slags. Consequently, higher volumes of GBFS are needed to obtain the same increase in soil pH than when using BOFS. Nonetheless, the ecotoxicological risk related to use of GBFS as a liming material can take to be negligible in terms of its V content.

4.5 CRITICAL EVALUATION OF ANALYTICAL METHODS

4.5.1 Net-oxidation tests of Cr\textsuperscript{III} to Cr\textsuperscript{VI}

**Net-oxidation tests and suspension pH.** The potential formation of Cr\textsuperscript{VI} in soil samples was investigated by net-oxidation tests (= oxidation of Cr\textsuperscript{III} – subsequent reduction of Cr\textsuperscript{VI} back to Cr\textsuperscript{III}) with soil suspended with 1 mM CrCl\textsubscript{3} (Paper II). During the experiments, added Cr\textsuperscript{3+} encountered hydrolysis reactions, leading to acidification of soil suspension. The decrease in soil pH depended on the degree of Cr\textsuperscript{3+} hydrolysis. In soils of initially higher pHs, it is higher than in those of lower pHs. Consequently, the acidifying impact of Cr\textsuperscript{3+} hydrolysis was more pronounced at higher pHs.

The lowered pH in the soil suspended with Cr\textsuperscript{III} solution can be anticipated to influence the net-oxidation of Cr\textsuperscript{III} to Cr\textsuperscript{VI}. In paper II it was suggested that in acidic conditions the production of Cr\textsuperscript{VI} was diminished by its intensive reduction back to Cr\textsuperscript{III}. Therefore, in less acidic conditions the net-oxidation yields of Cr\textsuperscript{III} to Cr\textsuperscript{V} could be expected to be higher. However, also high pH was concluded to limit formation of Cr\textsuperscript{VI} (Paper II). To find optimal conditions favoring the production of Cr\textsuperscript{VI}, net-oxidation of Cr\textsuperscript{III} should be studied at a pH range wider than that in the present study. To obtain various (and constant) acidity conditions, further experiments should be conducted with buffered Cr\textsuperscript{III} solutions.
**Oxidation products and inhibition mechanisms.** Paper I indicated that under acidic conditions, the end-product of the reduction of MnO$_2$ (owing to oxidation of Cr$^{III}$) is Mn$^{2+}$. The possible formation of Mn$^{III}$$(OOH)$ as an end-product at higher pHs was discussed. Potential formation of both, soluble Mn$^{2+}$ and Mn$^{III}$$(OOH)$ precipitates, are described in the literature (Fendorf, 1995; Guha et al., 2001). To confirm the actual speciation of Mn produced as end-product in the soil samples, the analytical protocol should be supplemented by additional methods. For instance, the formation of Mn$^{III}$$(OOH)$ could be discovered by means of EXAFS (Extended X-Ray Absorption Fine Structure) spectroscopy. The same analysis method could be used also to study formation of Cr$^{III}$ hydroxides that inhibit the oxidizing surfaces of MnO$_2$.

### 4.5.2 Extraction methods and speciation of V

The chemical bioavailability of V species in soils was investigated by a sequential extraction procedure (Paper I). The chemical reaction patterns and speciation of V were assessed on the basis of the dissimilar sorption mechanisms of V$^{IV}$ and V$^{V}$ species at soil pH range of ~4—7. Moreover, to assess the role of organic matter in the reaction patterns of added V$^{IV}$ and V$^{V}$, the experiment was carried out with soils differing mainly in their organic matter content. Sequential extraction provided valuable information on the pH-dependent reaction mechanisms dictating the chemical bioavailability of V species. However, speciation of V in soil extracts was not further analyzed.

To provide further information on the potentially chemically bioavailable V in the easily soluble fractions (extracted by KCl or Milli-Q water), they should be subjected to speciation analyses. Furthermore, molecular scale analysis of the V species is needed, for example, to distinguish between the reactions of polymeric and monomeric V$^{V}$ species. It is also noteworthy that there is practically no research on the environmental impacts of different organic V species in soils. Speciation of V dissolved by disruptive extractants (i.e. by NaOH and H$_2$SO$_4$) is inappropriate, because the soil conditions will be drastically altered. For instance, XANES (X-ray absorption near edge structure) spectroscopy is used to analyze solid phase but this method is applicable for the mean speciation of elements. As for the soluble V species in soil, speciation methods have some uncertainties. One of them is the stability of species in the soil extracts. In analysis of water samples by HPLC-ICP-MS (High Performance Liquid Chromatography-Inductively Coupled Mass Spectrometry) method, the stability issues are confronted with the chelation of V species with EDTA (Minelli et al., 2000; Aureli et al., 2008). According to Baken et al. (2012) this method is suitable to soil samples.
4.5.3 Use of “fresh” soil samples in chemical analyses

The use of fresh and moist samples is particularly important in the case of redox-sensitive elements such as Cr and V. Soil drying can interfere with redox-reactions dictating speciation of metals. This impact is shown in earlier studies e.g. as inability of soils to net-oxidize Cr$^{\text{III}}$ to Cr$^{\text{VI}}$ (Bartlett & James, 1980). Therefore, in this work almost all analyses were conducted with soil samples at a constant moisture level (used during prior incubation). As an exception, powdered dry soil was used for elemental semi-total analyses.

Air-drying can solubilize soil organic matter as result of its disruptive oxidation e.g. by MnO$_2$. The simultaneous reduction of Mn$^{\text{IV}}$ to Mn$^{2+}$ (or Mn$^{\text{III}}$(OOH)) can be expected to lower the capacity of soil to oxidize Cr$^{\text{III}}$. In dry soil, the high solubility of organic matter is also suggested to result from degradation of microbial biomass (Raveh & Avnimelech, 1978). This process may increase the proportion of organic carbon available to act as a reductant. Overall, soil drying can lower the chemical bioavailability of Cr$^{\text{VI}}$ and V$^{V}$ by promoting their reduction into less mobile Cr$^{\text{III}}$ and V$^{IV}$. On the other hand, the increased solubility of organic matter enhances the solubility of organic Cr and V species.
5 CONCLUSIONS

Various reactions occur in soils concomitantly. Redox-reactions regulate the speciation both of Cr and V. Speciation, in turn, influence the chemical availability and mobility of Cr and V in soils. Under the typical pH conditions of agricultural soils, the mobility of oxidized Cr\textsubscript{VI} and V\textsubscript{V} exceeds that of reduced Cr\textsubscript{III} and V\textsubscript{IV} species. Thus, findings of this thesis well agree with the original working hypotheses. Overall, it can be concluded that:

- Soil pH dictates the chemical bioavailability of Cr and V species (Paper I and II). In oxic conditions the potential bioavailability of V increases with elevated soil pH, irrespective of its initial speciation. Conversely, the solubility of Cr\textsubscript{III} that accumulates in soil is diminished at higher pHs, whereas that of Cr\textsubscript{VI} formed via oxidation increased. Moreover, the chemical bioavailability of V in oxic soils notably exceeds that of Cr because V\textsubscript{IV} can be oxidized to V\textsubscript{V} by molecular oxygen. The speciation of Cr and V and their availability is notably influenced by the pH-dependent reactions with SOM. Organic matter acts as a reductant of Cr\textsubscript{VI} and V\textsubscript{V} and, therefore lowers the stability of these oxidized species. Furthermore, this influences the distribution of Cr and V into fraction differing in their chemical bioavailability. Cr\textsubscript{III} and V\textsubscript{IV} are found in the fractions strongly retained by soil (particularly solid organic matter), whereas Cr\textsubscript{VI} and V\textsubscript{IV} are more mobile. Although, under highly acidic conditions the dissolution of hydroxide precipitates solubilizes also Cr\textsubscript{III} and V\textsubscript{IV} species.

- Risk of the formation of Cr\textsubscript{VI} via oxidation of (initially inorganic) Cr\textsubscript{III} by MnO\textsubscript{2} in field soil is low. This reaction pattern is controlled by soil pH. In typical agricultural soil conditions, the solubility of Cr\textsubscript{III} is limited, which holds down its oxidation to Cr\textsubscript{VI} by MnO\textsubscript{2}. Furthermore, the organic soil constituents can reduce Cr\textsubscript{VI} back to Cr\textsubscript{III}. However, in highly oxidizing conditions in soils rich in MnO\textsubscript{2} and low in organic matter inorganic Cr\textsubscript{III} deposits are susceptible to oxidation to Cr\textsubscript{VI} (Paper II and III).

- As a result of the low solubility Cr in BOFS, its use as a liming material in field soil is not a risk in terms of oxidation of Cr\textsubscript{III} to Cr\textsubscript{VI} by MnO\textsubscript{2}. Ecotoxicological risks due to enhanced uptake of Cr\textsubscript{III} by organisms is also negligible. Nevertheless, in acidic soils, such as boreal forest soils, a proportion of Cr\textsubscript{III} in BOFS is potentially solubilized.

- However, V is susceptible to be released from BOFS to soil (Paper I and Additional material). Furthermore, substantial part of the released V can be expected to be available for biological uptake. Although soil organic matter reduces the bioavailability of V, this impact is leveled off above pH neutral conditions. In contrast to slags from blast oxygen furnace, the solubility of V from GBFS is negligible.
The total concentrations of Cr and V in soil are not indicative of their chemical bioavailability (Paper I, II, III and Additional material). Therefore, soil properties as well as the actual concentration of Cr and V potentially available for biological uptake, should be considered in the ecological risk assessment. Particularly soil acidity, and the content and quality of organic matter should be taken into account. These factors control the distribution of Cr and V between less toxic (Cr$^{III}$/V$^{IV}$) and hazardous (V$^{V}$/Cr$^{VI}$) species. In contaminated sites, the actual determination the speciation of these metals is of importance.

The novelty of this work relies particularly on the scrutiny of the soil chemistry of V as well as on the research on the pH-dependent oxidation mechanism of Cr$^{III}$ to Cr$^{VI}$ by MnO$_2$ not previously investigated in soil. However, as the research on the environmental chemistry of V is generally rather scarce, it is clear that further studies are needed to unravel the complex speciation chemistry of inorganic and organic V as well as the toxicological impacts of various V species in soils.

Furthermore, there is little research data available on the chemical behaviour of Cr and V in slags deposited to soil. Therefore the contribution of this thesis in the risk assessment of steel industry slags as liming material can be considered significant. Research results can also be applied in the environmental risk assessment of slags used for other purposes. In addition, information provided in this thesis can be used when developing new environmentally sustainable slag products.
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