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Risk assessment of the utilization of Basic Oxygen Furnace Slag (BOFS) as soil liming material: oxidation risk and the chemical bioavailability of chromium species

Keywords (6): steel slag; chromate; chromium; soil; oxidation; liming

Highlights:

- Basic oxygen furnace slag (BOFS) is an effective liming material
- Liming with BOFS elevated field soil total Cr but not bioaccessible Cr^{III} or Cr^{IV}
- Oxidation risk of Cr^{III} in BOFS to Cr^{VI} by field soil MnO₂ was low
- In acidic soils a proportion of Cr in BOFS is potentially released

Abstract

Basic oxygen furnace slag (BOFS), a by-product of steel manufacturing, is efficient as liming material. It, however, contains trace amounts of heavy metal chromium (Cr). Under environmental conditions Cr exists in two stable oxidation states: +III and +VI. From those, Cr^{III} is an essential nutrient, whereas Cr^{VI} is highly toxic. In soils, soluble Cr^{III} is potentially oxidized to Cr^{VI} by manganese (hydr)oxides (MnO₂). We investigated the release of bioaccessible Cr^{III} or Cr^{VI} from BOFS to field soil. Prior to characterization of the bioaccessible, as well as less bioavailable Cr fractions, field soil was incubated with BOFS added in quantities equivalent to 10 and 100 t ha⁻¹ (7 weeks at 22°C, moisture content at 50% of water holding capacity). Liming with BOFS elevated soil acid soluble Cr (i.e. semi-total) but not the amount of bioaccessible Cr^{III} or Cr^{VI}. In addition, potential oxidation of initially soluble Cr^{III} (mimicking leachates of BOFS) was determined by a short-term net-oxidation test in soil suspension with 1 mM CrCl₃ (1:10 soil to solution). In field soil incubated with BOFS, the net-oxidation (oxidized Cr^{III} – Cr^{VI} reduced back to Cr^{III}) of added Cr^{III} into Cr^{VI} without MnO₂ was negligible. To produce highly oxidizing conditions, the test was further modified with excessive addition of synthetic Mn^{IV}O₂. Liming with BOFS diminished the

29 production of Cr^{VI} , whereas added $\text{Mn}^{\text{IV}}\text{O}_2$ notably promoted oxidation of Cr^{III} . Overall, the
30 oxidation risk of Cr^{III} in BOFS to Cr^{VI} by innate soil MnO_2 can be expected to be minimal
31 due to the low solubility of Cr^{III} in field soil.

32 **1. Introduction**

33 Basic oxygen furnace slag (BOFS), also known as converter slag, LD-slag, BOS-slag, or
34 steel slag, is a by-product of the steel industry. It is generated in massive quantities during
35 the conversion of raw iron (Fe) into crude steel. Conversion takes place in a blast oxygen
36 furnace where molten metal from a blast furnace is blown with oxygen at $\sim 1600^\circ\text{C}$. In this
37 process the impurities of the raw iron, mainly carbon (C), silicon (Si), phosphorus (P), and
38 manganese (Mn), are removed via oxidation (Shi, 2004). Oxidation of the non-gaseous
39 impurities is followed by slag formation with lime (CaO). Slag floats over the molten steel
40 from which it is tapped in a liquid form. Generally, tapping is followed by air-cooling
41 resulting in the formation of solid BOFS. Solid slag can be further crushed into practical
42 particle sizes, depending on its re-use purposes.

43 The production of BOFS per ton of crude steel varies from 50–220 kg (Szekely, 1995).
44 In 2015, the worldwide crude steel production was 1.62 billion tons (World Steel
45 Association, 2016). Consequently, 81–356 million tons of slag was simultaneously produced.
46 This amount of globally produced BOFS is massive, and it is expected to rise with the
47 increasing rates of steel production. Per the principles of circular economy, it is important to
48 either 1) recycle these substantial volumes of BOFS in the internal metallurgical processes of
49 steel manufacturing or 2) exploit them as new products. Not all BOFS produced is, however,
50 being utilized. For instance, in China, the largest steel production country, the re-use rate is
51 only 22% (Yi, et al., 2012).

BOFS is used in various applications, e.g. as construction material, a cementing component, road pavement material, raw material of glass production, and in mineral wool insulation. It mainly consists of calcium oxide (CaO), as well as the oxide and silicate minerals of Fe, Al (aluminum), Mg (magnesium), and Mn (Dahlin, et al., 2012; Waligora, et al., 2010). BOFS is strongly alkaline wherefore it can also be used for soil liming. Nonetheless, re-use should be sustainable from the environmental perspective. In the re-use of BOFS as liming material, a particular concern is its chromium (Cr) content. The proportion of Cr in BOFS varies between 0.1–0.5 %, depending on the composition of the ore and other primary materials used in the steel production (Shi, 2004). Chromium can be highly toxic to living organisms, although at low concentrations it is a vital micronutrient (Anderson, 1997). The toxicity of Cr, however, depends on its oxidation state as well as the amount chemically available for potential biological uptake (= bioaccessibility). In agricultural amendments, heavy metals are undesirable. However, in other re-use purposes of BOFS some trace elements can be beneficial (from technical perspective). For instance, the mechanical strength of BOFS is reported to enhance with increasing Cr levels (Sas et al. 2015). This is benign to road construction materials. In risk assessment, the re-use purpose of BOFS needs to be addressed. Furthermore, the ecological risk should be distinguished from that to human health. Proctor (et al. 2002) reported that BOFS used in e.g. fills, roadbases, landscaping, might have site-specific ecotoxicological impacts. Instead, no risk to human health was observed.

In soil, Cr exists in two stable oxidation states, +III and +VI. In small quantities, the trivalent form, Cr^{III}, is an essential nutrient for several organisms, including humans (Anderson, 1997). The hexavalent Cr^{VI} is merely a corrosive, carcinogenic, and mutagenic oxidant (Burke, et al., 1991; Cohen, et al., 1993; Costa, 2003). The ionic speciation of Cr^{III}

76 and Cr^{VI} is dissimilar and, consequently, the reactions dictating their mobility in soil also
77 differ. Thus, in addition to toxicity, redox reactions dictate the bioaccessibility of Cr. In this
78 study, roman numerals indicate the elemental oxidation number and the arabic numerals the
79 charge of ionic species.

80 In soil, inorganic Cr^{VI} exist as oxyanionic chromate (CrO_4^{2-}) or bichromate (HCrO_4^-)
81 (Saleh 1989). The mobility of the Cr^{VI} species is lowered by adsorption onto soil Fe- or
82 Al-(hydr)oxides by ligand exchange or reduction into less mobile Cr^{III} (Banks, et al., 2006;
83 Fendorf, 1995). In anoxic conditions, ferrous iron (Fe^{II}) and sulfides (S^{2-}) act as the main
84 electron donors in the reduction reaction with Cr^{VI} (Ye-Qing, et al., 2006). Instead, in oxic
85 conditions Cr^{VI} is mainly reduced by soil organic matter (SOM) (Park, et al., 2008). The
86 reduction of Cr^{VI} into Cr^{III} occurs via both abiotic and biological pathways. For instance,
87 *Pseudomonas dechromaticans* and *Bacillus subtilis* are bacteria that can mediate microbial
88 reduction of Cr^{VI} (Chen and Hao, 1998)

89 The trivalent Cr^{III} , on the other hand, exists as inorganic cationic species (Cr^{3+} ,
90 $\text{Cr}(\text{OH})^{2+}$ or $\text{Cr}(\text{OH})_2^+$), $\text{Cr}(\text{OH})_{3(\text{s})}$ precipitates or as organic complexes (Bartlett and
91 Kimble, 1976). At pH above ~5.5, the solubility of Cr^{III} is low due to the formation of
92 insoluble $\text{Cr}(\text{OH})_{3(\text{s})}$ (James, 1996; Saleh, et al., 1989). However, even at higher pHs, Cr^{III}
93 may remain soluble in the form of soluble organic complexes (Gustafsson, et al., 2014).

94 Soluble species of Cr^{III} are susceptible to oxidation into hazardous Cr^{VI} by soil
95 manganese (hydr)oxides (MnO_2) (Bartlett and James, 1979). The oxidation reaction occurs
96 on the surfaces of MnO_2 after formation of an inner-sphere complex between Cr^{III} and Mn^{IV}
97 (Fendorf, 1995). Molecular oxygen (O_2) also acts an oxidizer of Cr^{III} , but only under highly
98 alkaline conditions (at pHs above 9) (Fendorf and Zasoski, 1992). Consequently, Mn^{IV} (or

99 Mn^{III}) (hydr)oxides are the main oxidizers of Cr under prevailing soil pH conditions (Bartlett
100 and James, 1979; Eary and Rai, 1987).

101 Our objective was assessment of potential environmental risks related to the utilization
102 of BOFS as a soil amendment or liming material. The experiments aimed to ascertain the risk
103 of oxidization of Cr^{III} in BOFS to Cr^{VI} by MnO_2 in field soil. Furthermore, we investigated
104 the potential leaching of both Cr^{III} and Cr^{VI} from BOFS into soil and their bioaccessibility
105 (chemical availability for potential biological uptake).

106 The potential pathways for the release of Cr species from BOFS to soil are described in
107 Scheme 1. The working hypotheses are based on the redox-reactions of Cr dictated by
108 $\text{Mn}^{\text{IV}}\text{O}_2$ as the oxidant for Cr^{III} and soil organic matter (SOM) as the reductant for Cr^{VI} . In
109 BOFS, Cr was considered to mainly exist as rather immobile Cr^{III} . Therefore, its risk to be
110 oxidized on the surfaces of MnO_2 was expected to be low in field soil. In addition to the
111 innate soil MnO_2 , the impact of Mn oxides in BOFS on the Cr^{III} oxidation risk was also
112 assessed. Furthermore, the potential formation of Cr^{VI} in field soil limed with BOFS was
113 investigated under extremely oxidizing conditions produced by extensive addition of
114 synthetic MnO_2 . The working hypothesis was that BOFS elevates the total Cr in the soil but

115 does not increase the amount of *bioaccessible* Cr^{III} or Cr^{VI} species.

116

117 *Scheme 1. Simplified pathways of Cr^{III} and Cr^{VI} release from BOFS to soil. The*
 118 *redox-reactions by MnO_2 and organic matter regulate the conversions in the oxidation state*
 119 *and, consequently, the environmental implications of Cr.*

2. Materials and methods

An incubation experiment followed by chemical fractionation tests was set up to investigate the potential release of chemically bioaccessible Cr^{III} and Cr^{VI} from BOFS added as a liming agent to a field soil. Potential reaction patterns in the oxidation of Cr^{III} to Cr^{VI} in the incubated subsamples were further investigated in a net-oxidation tests. The overall experiment design is illustrated in Scheme 2.

Scheme 2. Overall design of the experimental work.

Soil subsamples were incubated with or without BOFS at a constant temperature (22°C) and moisture content (at 50% of the water holding capacity) for seven weeks before chemical analyses. Furthermore, the impact of BOFS on the Cr fractions not readily bioavailable (amorphous Cr and semi-total Cr) was assessed. Various Mn fractions (amorphous or easily soluble Mn-oxides, water soluble Mn, and semi-total Mn) were also determined to assess the role of Mn on the Cr^{III} oxidation risk. The differences between the extraction results of the various treatments were tested statistically by variance analysis (ANOVA, at 0.05 level of significance) and Tukey's HSD as a post hoc test.

137   **2.1 Incubation experiment**

138   **2.1.1 Test soil**

139   Soil material was collected from the plough layer (0–30 cm) of arable land in Southern
140   Finland (60°.22'4140 N, 25°.03'6043 E), sieved through a polypropylene (PP) sieve
141   (Ø 4 mm), homogenized by thorough mixing, and stored at field capacity for incubation
142   experiments. Water holding capacity (WHC) was determined by measuring the total amount
143   of water (Milli-Q) retained by moist soil after being submerged for 24 h. The particle size
144   distribution determined by the pipette method (Elonen, 1971) was: 4% clay, 26% silt, and
145   70% sand. According to U.S.D.A (United States Department of Agriculture) classification
146   system it was *fine sand* by texture.

147   Soil pH was measured in 0.01 M calcium chloride (CaCl₂) suspension at a soil (in field
148   capacity) to solution ratio of 1:2.5 with a Schott BlueLine combination electrode. Air-dried
149   and powdered soil samples (500 mg) were used to analyze the total nitrogen (TN) and total
150   organic carbon (TOC) by dry combustion (C/N VarioMax analyzer) and to calculate the ratio
151   of C to N (C/N). Amorphous iron (Fe) and aluminum (Al) (hydr)oxides were extracted from
152   fresh soil by ammonium oxalate at the pH 3.3 ((COO)₂(NH₄)₂, 1:20 w/V, orbital shaking 250
153   rpm/2 h, centrifugation 3600 rpm/5min) (Niskanen, 1989). The extracts were filtered
154   (Blauband 589/3) and analyzed for Fe and Al by Inductively Coupled Plasma Optical
155   Emission Spectrometry (ICP-OES, λ_{Al} =309.3/396.2 nm and λ_{Fe} =238.2/259.9 nm).

156   Test soil was rather rich in organic carbon (OC) (Table 1). Soil sampling occurred after
157   winter before the growing season, wherefore the soil organic matter (SOM) mainly consisted
158   of humic or decomposed organic material. The C/N ratio (15:1) was typical to that in soils of

temperate regions and indicated a high degree of humification. Soil pH (5.6) was suitable to maintain normal microbial activity.

Table 1. Properties of the test soil expressed as means $\pm$ standard deviations (N=4).

TOC (Tot. Organic Carbon)	3.24 $\pm$ 0.055%	WHC (Water Holding Capacity)	0.58 $\pm$ 0.008 ml g⁻¹
TN (Tot. Nitrogen)	0.22 $\pm$ 0.004%	Al_(hydr)oxides	1986 $\pm$ 6 mg kg ⁻¹
C/N	15:1	Fe_(hydr)oxides	2714 $\pm$ 24 mg kg ⁻¹
pH	5.6 $\pm$ 0.1	Soil classification (U.S.D.A)	<i>Fine sand</i>

2.1.2 Basic oxygen furnace slag (BOFS)

BOFS material used in the experiment originated from a northern European steel plant. Its particle size was <3 mm (detailed particle size distribution is presented in the Appendix, Table A1). Table 2 shows the chemical composition of BOFS analyzed by the X-ray fluorescence (XRF, Philips PW 2404) method. BOFS consisted mainly of Ca, Fe, Si and O. The total content of Cr amounted to 0.21% and Mn to 2.5%. The pH measured in the water at solid to solution ratio of 1:2 was 11.3.

Table 2. Chemical composition (%) of BOFS analyzed by XRF

O	36.4	Nb	0.031	F	< 0.05
Ca	33.7	K	0.025	As	< 0.002
Fe	16.7	Sr	0.020	Cl	< 0.002
Si	5.75	Ba	0.009	La	< 0.002
Mn	2.50	Sn	0.007	Sb	< 0.002
V	1.50	Zr	0.005	Ta	< 0.002
Mg	1.03	Ni	0.005	Bi	< 0.001
Al	0.85	Cs	0.004	Cu	< 0.001
Ti	0.78	Ce	0.003	Pb	< 0.001
P	0.35	Y	0.002	Rb	< 0.001
Cr	0.21	Mo	0.002	Th	< 0.001
S	0.090	Zn	0.001	U	< 0.001
Na	0.045				

The solubility of elements in BOFS were determined by water extraction (SFS-EN 12457-3: a 24 h shaking test without pH buffering: 1. step 2:1 and 2. step 8:1 L/S) (Table 3). Anionic elements were analyzed by ion chromatography and the others by inductively coupled plasma mass spectrometry (ICP-MS). Hexavalent Cr^{VI} was determined spectrophotometrically at $\lambda=540$ nm with LOD (Limit of Detection) equivalent to $12.5 \mu\text{g L}^{-1}$ (LOD=background noise 3σ , $N_{\text{blank}}=10$).

Total content of water soluble Cr (no speciation) in BOFS was 0.2 mg kg^{-1} and Cr^{VI} was 0.13 mg kg^{-1} . The amorphous Cr extracted (Niskanen, 1989) by 0.05 M oxalate (0.029 M (COO)₂(NH₄)₂ + 0.021 COOH, pH 3.3, 1:20 w/V) amounted to 16 mg kg^{-1} . The extract was analyzed for Cr by ICP-OES at $\lambda=267.7/283.5$ nm (LOD_{267.7 nm}= $10.0 \mu\text{g L}^{-1}$ and LOD_{283.5 nm}= $9.8 \mu\text{g L}^{-1}$).

Table 3. Water solubility of various elements in BOFS. Total concentration of water soluble Cr, and that of Cr^{VI} is indicated by underlining.

Water extraction (SFS-EN 12457-3)			
mg kg ⁻¹			
Br	< 0.1	Cu	< 0.01
Cl	4.9	Mo	0.07
F	< 0.1	Ni	0.1
NO₂	1.2	Pb	< 0.01
NO₃	< 0.1	V	0.04
PO₄	2.3	Sb	< 0.01
SO₄	32	Se	< 0.05
Cd	< 0.003	Sn	< 0.01
Co	< 0.03	Zn	0.01
<u>Cr</u>	<u>0.2</u>	As	< 0.006
Ba	1	<u>Cr^{VI}</u>	<u>0.13</u>

2.1.3 Experimental design

Prior to incubation, the moist test soil material at 50% water holding capacity (WHC) was divided into four subsamples equivalent to 300 g of dry soil. Three subsamples were

188 amended separately with 0 (control), 1.5, and 15 g of BOFS mixed in thoroughly. The doses
189 of slag were estimated to be equivalent to the additions of 10 and 100 t of BOFS ha⁻¹ (the
190 weight of a 20-cm soil layer per ha⁻¹ was assumed to be $2 \cdot 10^6$ kg). The recommended BOFS
191 dosage is 7–10 t ha⁻¹, followed by an addition of 4–6 t ha⁻¹ every three to five years. Thus,
192 the lower dosage corresponded to the common liming recommendation, whereas the higher
193 one to a tenfold addition.

194 To obtain a control treatment with the same pH as the treatment amended with the
195 “recommended” amount of BOFS (10 t ha⁻¹), one set of subsamples was treated separately
196 with a soluble alkali (0.16 M potassium hydroxide, KOH). The treatment with KOH was
197 included to distinguish between the chemical responses of Cr owing to increased alkalinity
198 from those attributable to the chemical characteristics of BOFS. All soil subsamples were
199 incubated as three replicates for 7 weeks at a constant temperature (22°C) and moisture level
200 equivalent to 50% of the soil WHC.

201 ***2.2 Chemical analyses of incubated soil samples***

202 The chemical analyses were conducted with the moist incubated soil samples, but the
203 results are given based on the dry weight (dw) determined by oven drying of 5.0 g soil at
204 105 °C (~22 h). The use of “fresh” incubated soil samples is important in analyses involving
205 redox-reactions of Cr or measurements of soluble Cr species. Soil drying can enhance the
206 solubility of organic Cr^{III} due to enhanced degradation of organic matter. Furthermore, drying
207 of SOM markedly changes the redox properties of soil leading to enhanced reduction of Cr^{VI}.

208 **2.2.1 Soil properties: pH, E_h and DOC**

209   **Soil pH and E_h** of all incubated subsamples were measured in soil suspended in
210 0.01 M CaCl₂ (1:2.5) (Mettler Toledo SP250 T-70, DG111-SC glass electrode). It is
211 noteworthy, however, that the redox potential measured by this method is a coarse estimate.
212 **Dissolved organic carbon (DOC)**, an estimate for soluble organic matter, was extracted
213 with Milli-Q water (1:10 dw/V, 250 rpm/15 min) from the moist incubated subsamples.
214 Extracts were filtered through a 0.45 µm Nuclepore syringe filter and the DOC in the filtrates
215 determined with a TOC-analyzer (Shimadzu TOC-V cph/TNM-1).

216 **2.2.2 Chemical fractionation of soil Cr and Mn**

217   **Content of semi-total Cr and Mn** was determined with by microwave (MarsXpress
218 CEM) acid digestion (EPA3051A) with a mixture of nitric and hydrochloric acids (3:1,
219 HNO₃:HCl). However, some minerals, particularly of Cr, will not dissolve by this method.
220 Thus, the amount of Mn and Cr in the extracts obtained can be taken to stand for semi-total
221 concentrations. As an exception to other chemical analysis on the moist incubated soil
222 samples, semi-total Cr and Mn were determined from air dry powdered soil.

223   **Poorly crystallized oxides of Cr and Mn** were extracted by an ammonium oxalate
224 solution of pH 3.3 as described above (Chapter 2.1.2). The extract was analyzed for Cr to
225 assess the solubility of Cr in BOFS under acidic soil conditions. The amorphous oxides of
226 Mn^{IV} concomitantly solubilized were measured to assess the oxidation potential of the
227 experimental soil as well as the impact of BOFS on it. Extraction of poorly crystalized
228 oxides of Mn^{IV} by ammonium oxalate is, however, not selective. Therefore soluble Mn
229 species and (hydr)oxides of Mn^{III} (or Mn^{II}) may be included in this fraction.

230   **Water-soluble Cr and Mn** were extracted by Milli-Q water (1:10 dw/V,
231 250 rpm/15 min orbital shaking, and centrifugation at 3600 rpm/5min) and filtered
232 (Blauband 589/3). The extracted Cr was estimated as the easily bioaccessible Cr in soil. In
233 soil, water soluble Mn consists mainly of Mn^{2+} or soluble organic species unable to oxidize
234 Cr. To assess the proportion of soluble Mn^{2+} (or soluble organic Mn complexes) of the
235 poorly crystallized Mn oxides of high oxidizing potential water soluble fraction of Mn was
236 measured.

237   **In addition to the chemical fractions of Cr without speciation, the easily soluble**
238 **Cr^{VI}** was determined to investigate the possible release of Cr^{VI} from BOFS (via oxidation of
239 Cr^{III} or dissolution of Cr^{VI}). This fraction was extracted from the soil at the ratio of
240 1:10 dw/V with phosphate buffer (0.01 M KH_2/K_2PO_4 at pH 7.2), 250 rpm/15 min orbital
241 shaking, centrifugation 3600 rpm/5min, and filtration (Blauband 589/3). The extracted
242 proportion represents the easily bioaccessible Cr^{VI} that is either readily soluble or easily
243 desorbed by ligand exchange from the Al/Fe (hydr)oxide surfaces.

244   **Concentrations of Cr and Mn (without speciation) in soil extracts were analyzed**
245 **by ICP-OES** (Thermo iCAP 6000, $\lambda_{Mn}=257.6/259.3$ nm, $\lambda_{Cr}=267.7/283.5$ nm). Prior to
246 analyses, the Milli-Q water and ammonium oxalate extracts were preserved with strong nitric
247 acid (20 mL of extract + 2 mL HNO_3). The filtrates (Blauband 589/3) obtained in the semi-
248 total analysis were diluted in 50 mL volumetric flask followed by a 1:10 dilution before ICP-
249 OES analysis. The minimum of 100 counts and relative standard deviation (RSD) less than
250 2% was accepted. Different reagent batches were used to prepare standard solutions and
251 quality control samples for Cr and Mn (QC 0, 0.5 and 1 mg L⁻¹).

252   **The easily soluble Cr^{VI} was measured with a modification of the EPA7196A**
253 **method** (Reijonen and Hartikainen, 2016). In this analysis, Cr^{VI} is detected

254 spectrophotometrically (by Shimadzu UVmini-1240, $\lambda=540$ nm). Prior to measurement, Cr^{VI}
255 is reduced and bound to a diphenylcarbazide (DPC) complex. Limit of quantification (LOQ)
256 was determined as a tenfold standard deviation of the background noise.

257 **2.2.3 Net-oxidation tests of Cr**

258 Incubated soil samples were tested for their ability to oxidize Cr^{III} into Cr^{VI} in a
259 *net-oxidation* shaking test with 1 mM CrCl_3 solution. In addition, to create extremely
260 oxidizing conditions, this test was carried out in a soil suspension by using synthetic MnO_2
261 as an oxidant for CrCl_3 . In other words, the *enhanced net-oxidation* of Cr^{III} in the suspension
262 was investigated in a hypothetical situation of “worst scenario” where soil is extremely rich
263 in an efficient oxidant. In the net-oxidation tests, the net-amount of Cr^{VI} produced is the
264 difference between the oxidation of Cr^{III} to Cr^{VI} and the subsequent reduction of Cr^{VI} back to
265 Cr^{III} . The idea of using initially soluble Cr^{III} in these experiments was to mimic leaching of
266 Cr^{III} from BOFS and to test its potential conversion into Cr^{VI} .

267 **Net-oxidation test of chromium.** Net-oxidation of Cr^{III} into Cr^{VI} was investigated with
268 a net-oxidation test (Scheme 2a) (Bartlett and James, 1996). Estimation of the oxidation
269 potential for Cr^{III} was based on the Cr^{VI} produced in soil suspensions (1:10 dw/V) with
270 1 mM chromium chloride ($\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$, Aldrich). The Cr^{VI} formed was further extracted by
271 phosphate buffer ($\text{KH}_2/\text{K}_2\text{HPO}_4$, at pH 7.2) and analyzed according to a modified
272 EPA7196A method. The background values for easily soluble Cr^{VI} were obtained by
273 replacing CrCl_3 in the net-oxidizing test (Scheme 2a) by Milli-Q water. Moreover, to assess
274 the chemical accessibility of the added Cr^{III} , the soluble remaining Cr in the soil suspension
275 with 1 mM CrCl_3 (Scheme 2b) was also analyzed by ICP-OES ($\lambda_{\text{Cr}}=267.7/283.5$ nm).

a) Net-oxidation test:
Total produced Cr^{VI}

b) Net-oxidation test:
Soluble remaining Cr (without
speciation)

276
277 *Scheme 3. Extraction protocol for a) easily soluble Cr^{VI} produced in the Cr net-oxidation test*
278 *and b) the total amount of soluble remaining Cr in the net-oxidation test with incubated field*
279 *soil samples.*

280 **Enhanced Cr net-oxidation test.** The Cr net-oxidation test was further modified to test
281 the theoretical ability of incubated soils to oxidize potential Cr^{III} in leachates under extremely
282 oxidizing conditions. This enhanced net-oxidation test (Scheme 4) resembles the net-
283 oxidation test, with the exception that after shaking the soil sample with CrCl_3 (250 rpm/15
284 min) the suspension is re-shaken with 300 mg of activated (highly oxidative) $\text{Mn}^{\text{IV}}\text{O}_2$ (Fluka)
285 (250 rpm/15 min). The easily soluble Cr^{VI} was extracted afterwards by phosphate buffer
286 ($\text{KH}_2/\text{K}_2\text{HPO}_4$ at pH 7.2) and after filtration, its concentration was determined by the
287 modified EPA7196A method.

Enhanced Cr net-oxidation test: Total produced Cr^{VI}

288

289 *Scheme 4. Extraction protocol for the determination of Cr^{VI} produced in the enhanced*
290 *net-oxidation test with excessive MnO₂ in soil suspension with 1 mM CrCl₃.*

291 **3. Results**

292 **3.1 Impact of BOFS and alkali additions on soil pH, Eh and** 293 **DOC**

294 Fine sand field soil samples incubated without (control 0) or amended with BOFS (10
295 or 100 t ha⁻¹) or a corresponding base amount as KOH (to 10 t BOFS ha⁻¹) were analyzed for
296 pH, E_h, and dissolved organic carbon (DOC). BOFS elevated pH and lowered E_h (Table 4).
297 The “recommended” BOFS dosage (10 t ha⁻¹) and the corresponding base amount added as
298 KOH raised pH from 5.8 to 6.5 and 6.3, respectively. Interestingly, the lower BOFS did not
299 significantly affect DOC but KOH almost duplicated it (Table 4). The tenfold BOFS addition
300 elevated pH to 8.4 and DOC to the same level as KOH.

301 *Table 4. pH, E_h, and DOC in field soil samples incubated (7 weeks at 22°C, moisture content*
302 *at WHC 50%) without or with BOFS slag added 10 or 100 t ha⁻¹ or KOH (equivalent to*
303 *lower BOFS dosage). Values indicate means ±standard deviation and Tukey’s HSD (N=3).*

Field soil (<i>fine sand</i> , SOM 3.2%)				
	<i>BOFS 0 t ha⁻¹</i>	<i>KOH</i>	<i>BOFS 10 t ha⁻¹</i>	<i>BOFS 100 t ha⁻¹</i>
pH	5.8 ±0.3 ^a	6.3 ±0.1 ^b	6.5 ±0.1 ^b	8.4 ±0.1 ^c
E _h	547 ±6 ^a	493 ±1 ^b	455 ±12 ^c	438 ±0.5 ^c
DOC (mg L ⁻¹)	9.8±0.9 ^a	18.3 ±1.1 ^b	11.5 ±1.8 ^a	17.7 ±0.6 ^b

304 **3.2 Effect of added BOFS and KOH on chemical Cr fractions**
305 **in soil**

306 One third of the **semi-total Cr** occurred in **oxalate-extractable** (amorphous) form (

307 Table 5) in the control soil (BOFS 0 t ha⁻¹). The added BOFS markedly elevated the
308 semi-total Cr, at the low addition level 1.4-fold and at the high level 5-fold. It is noteworthy,
309 however, that the amorphous Cr did not increase in proportion to the increase in semi-total
310 Cr. The low BOFS dosage elevated the amorphous fraction 1.3-fold, but the 10-fold higher
311 dosage only 1.8-fold (Table 2). The experimental soil was very low in **water soluble Cr**
312 (0.08 mg kg⁻¹) and the BOFS additions did not significantly elevate it (Table 2).
313 Interestingly, the KOH addition equivalent to the lower BOFS dosage increased the
314 water-soluble Cr 3-fold. Regarding **easily soluble Cr^{VI}**, none of the samples contained
315 detectable quantities. Limit of quantification (LOQ) was 0.4 mg Cr^{VI} kg⁻¹.
316

317 *Table 5. Soil Cr fractions in field soil subsamples incubated (seven weeks at 22°C, moisture*
318 *content 50% WHC) without or with BOFS additions of 10 and 100 t ha⁻¹ or KOH. Values are*
319 *means ±standard deviations and Tukey's HSD groups (N=3).*

Field soil (Fine sand, SOM 3.2%)				
	<i>BOFS 0 t ha⁻¹</i>	<i>KOH</i>	<i>BOFS 10 t ha⁻¹</i>	<i>BOFS 100 t ha⁻¹</i>
Semi-total Cr (mg dw kg ⁻¹)	14.7±0.3^a	Not measured	20.1±2^b	73.2±24.9^c
Amorphous Cr (mg dw kg ⁻¹)	4.9±0.1^a	Not measured	6.2±0.1^b	9.0±0.2^c
Water soluble Cr (mg dw kg ⁻¹)	0.08±0.01^a	0.25±0.05^b	0.11±0.02^a	0.10±0.02^a
Easily soluble Cr^{VI} (mg dw kg ⁻¹)	< LOQ	< LOQ	< LOQ	< LOQ

320 **3.3 Effects of added BOFS and KOH on chemical fractions of** 321 **Mn in soil**

322 The incubation with the higher BOFS dosage notably elevated the **semi-total Mn** in
323 soil (

324   Table 6). The lower dosage increased it 75% and the higher one more than 800%.
325   Thus, a tenfold increment in BOFS addition resulted in an approximately tenfold increase in
326   the semi-total Mn. The BOFS treatments also elevated oxalate-extractable Mn assumed to
327   represent **amorphous Mn (hydr)oxides** (

328   Table 6). At the lower level BOFS it increased 2.2-fold and at the higher 5-fold. In
329   other words, a tenfold increase in the BOFS dosage practically duplicated the amorphous Mn
330   fraction.

331   **Water soluble Mn** in the soil subsamples varied between 0.2–0.63 mg kg⁻¹ (

332 Table 6). BOFS enhanced the solubility of Mn only at the addition level equivalent to
333 100 t ha⁻¹. The highest concentration of soluble Mn was, however, recorded in the subsample
334 treated with KOH.
335

336 *Table 6. Soil Mn fractions in field soil incubated (7 weeks at 22°C and moisture content*
337 *WHC 50%) with BOFS addition levels of 0, 10, and 100 t ha⁻¹ or KOH. Values indicate*
338 *means ±standard deviation and Tukey's HSD groups (N=3).*

	Field soil (<i>Fine sand</i> , SOM 3.2%)			
	BOFS 0 t ha ⁻¹	KOH	BOFS 10 t ha ⁻¹	BOFS 100 t ha ⁻¹
Semi-total Mn (mg dw kg ⁻¹)	93 ±10^a	83 ±6^a	163 ±28^b	863 ±289^c
Amorphous Mn (mg dw kg ⁻¹)	31.5 ±0.1^a	31.3 ±0.2^a	71.2 ±1.5^b	161.7 ±1.5^c
Water soluble Mn (mg dw kg ⁻¹)	0.2 ±0.03^a	0.63 ±0.14^b	0.36 ±0.05^{ac}	0.52 ±0.11^c

339 **3.4 Risk of Cr^{III} oxidation to Cr^{VI}: net-oxidation shaking tests** 340 **with 1 mM CrCl₃**

341   **The net-oxidation test** revealed the risk of the detrimental reaction pattern of Cr^{III}
342 oxidation (of the hypothetical leachates from BOFS) to Cr^{VI} by soil MnO₂ to be low (Figure
343 1). In the soil suspended in CrCl₃ solution, the net-oxidation (= oxidation of Cr^{III} –
344 subsequent reduction of formed Cr^{VI}) (see 2.2.3) was negligible. Only in the subsamples
345 incubated with a BOFS dosage equivalent to 10 t ha⁻¹ small amount (0.016 mg L⁻¹) of easily
346 soluble Cr^{VI}, i.e. dissolved or desorbable by ligand exchange) was recorded. This amount is
347 below LOQ (0.04 mg L⁻¹). Interestingly, the soluble Cr^{III} added was strongly retained by all
348 soil samples. Less than 1.5% of the added Cr^{III} (52 mg L⁻¹) remained soluble. Incubation
349 with BOFS or KOH further reduced the solubility of added Cr^{III}.

Figure 1. The total amount of remaining soluble Cr and easily soluble Cr^{VI} produced in the net-oxidation test (1:10 w/V, 1 mM CrCl₃) in soil samples incubated for 7 weeks at 22°C and moisture content of WHC 50%. Values indicate means and Tukey's HSD groups (N=3). Error bars indicate standard error.

Enhanced net-oxidation of Cr^{III} by active Mn^{IV}O₂. The theoretical possibility for the oxidation of initially dissolved Cr^{III} in field soil was investigated by using excessive amounts of synthetic MnO₂ as an oxidant. The results revealed that in the pure Cr^{III} solution without soil practically all Cr added (52 mg L⁻¹) remained soluble (Figure 2). After MnO₂ addition, 59% of this Cr^{III} was oxidized into easily soluble Cr^{VI} (i.e. readily soluble or easily replaced from oxide surfaces by ligand exchange). On the contrary, the solubility of the added Cr^{III} in field soils was very low. The response of Cr^{III} oxidation to added MnO₂, however, was apparent. This reaction pattern was most conspicuous in the unlimed field soil and became less prominent upon elevated BOFS dosage. In soil without BOFS, 24% of the added Cr^{III} was net-oxidized to easily soluble Cr^{VI}.

365 Interestingly, BOFS lowered the Cr^{VI} produced in the *enhanced* net-oxidation test. In
 366 soil subsamples incubated with BOFS dosage equivalent to 10 t ha^{-1} , only 11% of the added
 367 Cr^{III} was oxidized. When the BOFS dosage increased, the production of Cr^{VI} in the
 368 net-oxidation test diminished to 1%. The net-oxidation yield correlated positively with the
 369 solubility of Cr (Pearson's $r = 0.9$ with significance of 0.001). Because the *enhanced* net-
 370 oxidation test was only carried out with the control (no soil) and BOFS-treated soil
 371 subsamples, no comparison with the KOH-treated ones could be done.

372 **Figure 2.** The mean soluble remaining Cr (no speciation) after addition of $52 \text{ mg Cr}^{\text{III}} \text{ L}^{-1}$
 373 $(\text{soil:solution ratio } 1:10)$ and easily soluble Cr^{VI} produced from the further addition of
 374 MnO_2 in the enhanced net-oxidation test of field soil with and without BOFS and in
 375 suspension without soil. Percentage values indicate mean production of Cr^{VI} of the added
 376 Cr^{III} . Error bars illustrate standard error ($N=3$).

378 4. Discussion

379 4.1 Impact of BOFS on chemical properties of soil

380 BOFS acted as an effective liming agent due to its high CaO content (Table 2 and 4).
381 At the “recommended” application level (equivalent to 10 t ha⁻¹) it elevated the slightly
382 acidic soil pH (5.8) to the circumneutral level (6.5). A tenfold higher dosage (equivalent to
383 100 t ha⁻¹) raised pH to an alkaline level (8.4) not favorable to crop plants (Table 4). This
384 high soil pH, however, can be recorded in areas used as deposits of BOFS. As expected,
385 elevated pH lowered redox potential of the soil, but the ten-fold increase in BOFS dosage did
386 not further lower E_h (Table 4).

387 The “recommended” BOFS dosage did not significantly increase soluble organic
388 matter. This outcome was unexpected because the deprotonation of acidic functional (e.g.
389 carboxylic and phenolic) groups and, consequently, the solubility of organic matter tends to
390 increase with elevated pH. Actually, the expected response was recorded in the KOH-treated
391 samples, where pH was elevated to the same level as recorded in the “recommended “ BOFS
392 treatment but the solubility of organic matter doubled (Table 4). Actually, when using BOFS,
393 a 10 times higher dosage and pH as high as 8.4 were required to obtain this high increase in
394 DOC (Table 4). The lower solubility of organic matter in the BOFS-treated samples can be
395 explained by the fact that, in contrast to the monovalent K⁺, the divalent Ca²⁺ cation is
396 capable to form chemical bridges between dissociated functional groups of organic matter.
397 These linkages, in turn, increase the “apparent molecular size” and reduce the hydrophilicity
398 of organic matter. cation is capable to form chemical bridges between dissociated
399 functional groups of organic matter. These linkages, in turn, increase the “apparent molecular
400 size” and reduce the hydrophilicity of organic matter.

401 **4.2 Bioaccessibility of Cr^{III} and Cr^{VI} in BOFS**

402 Incubation with BOFS (containing 2100 mg Cr kg⁻¹) notably increased semi-total Cr in
403 the soil but did not affect soluble Cr (without speciation) or easily soluble Cr^{VI} fractions (

404 Table 5). This reveals that Cr was not released from BOFS during the incubation. On the
405 other hand, incubation with KOH slightly increased the water soluble Cr (without
406 speciation). This response supports the previous conclusion that the monovalent K^+ cation
407 favored the water-solubility of organic Cr complexes at higher pHs.

408 The negligible release of Cr from BOFS is likely attributable to its mineral
409 composition. The mineralogy of the slag material was not investigated but Cr in BOFS is
410 reported to occur as Cr^{III} in the brownmillerite and (partly oxidized) wustite type of minerals
411 that are reluctantly soluble (Chaurand, et al., 2006; De Windt, et al., 2011). The low
412 reactivity of Cr minerals of BOFS was also apparent in our experiments.

413 The analysis of semi-total Cr in the incubated soils samples revealed that about half of
414 Cr added with BOFS remained in the form not soluble in strong acid (1:3, $HNO_3:HCl$) in the
415 microwave digestion. Thus, the BOFS-derived increase in the soil semi-total Cr
416 corresponded only to about half of the Cr content determined by XRF (Appendix, Table A2).
417 This outcome reveals that minerals not solubilized in the semi-total analysis can be
418 considered rather inert in soils. The mineralogical properties of BOFS may, however, vary
419 depending on the composition of the raw materials (iron ore, limestone and coal) and on the
420 cooling conditions of slag. For instance, a high Mn/Fe ratio and a low crystallization degree
421 increases the solubility of Cr in BOFS minerals (Tossavainen, et al., 2007).

422 Furthermore, the potentially reactive Cr minerals are not necessarily the only ones
423 originally present in BOFS. Dewind *et al.* (2011) showed that weathering of the weakly
424 soluble primary minerals of Cr (wustite, brownmillerite) was followed by formation of
425 spinels. They were proposed to ultimately control the solubility of Cr^{III} in BOFS. In general,
426 the weathering and solubility of minerals, as well as the subsequent reactions of the released
427 Cr are known to depend on soil properties (e.g. moisture, temperature, pH, water fluxes, ion

428 composition of soil water). However, research conducted with BOFS in soil is scarce,
429 wherefore the number of reference studies on the bioaccessibility of Cr in BOF in terrestrial
430 environment is limited. However, in a study by (Proctor, et al., 2000) the soil to water
431 partition coefficient (K_d) for Cr in BOFS was estimated extremely high (856667 L kg^{-1}),
432 indicating a very low solubility. This is in agreement with our findings (

433 Table 5 and Figure 1).

434 ***4.3 Potential chemical availability of Cr in BOFS***

435 The *potential* risk of Cr release from BOFS to field soils was assessed under very
436 acidic conditions. The amorphous Cr extracted by acidic ammonium oxalate was considered
437 representative of the potentially chemically available in acidic soils. In BOFS its content was
438 only 16 mg kg⁻¹, wherefore its contribution to the ammonium oxalate extractable Cr in the
439 field soil was anticipated to be negligible. Incubation with BOF, however, did elevate the
440 amorphous Cr in soil (

441 Table 5).

442 The relative extractability of Cr by ammonium oxalate per kg of BOFS (conversion
443 calculations in Appendix, Table A3) increased in the following order: pure BOFS
444 (16 mg Cr kg^{-1}) < field soil incubated with BOFS equivalent of 100 t ha^{-1} (86 mg Cr kg^{-1}) <
445 field soil incubated with BOFS equivalent of 10 t ha^{-1} ($261 \text{ mg Cr kg}^{-1}$). In other words, the
446 higher the BOFS amount, the smaller the relative proportion of removed by a single
447 treatment. Extracted Cr was assumed to exist predominantly as Cr^{3+} , although no speciation
448 analysis was performed. According to the updated overview on Cr speciation (Ščančar and
449 Milačič, 2014), Cr^{3+} is the prevalent species below pH 4 (pK_a 4.1).

450 The elevated extractability of amorphous Cr in BOFS-treated field soil (

451 Table 5) indicates that under acidic conditions its release is enhanced. Thus, in soils
452 that are naturally highly acidic, such as boreal forest soils (pH 3–5) or coastal acid sulfate
453 soils (pH < 2), part of the Cr in BOFS is in theory at risk to be leached. However, liming
454 with BOFS elevates soil pH, wherefore a prerequisite for the enhanced release of Cr^{3+} from
455 BOFS is the reinstatement of acidic soil conditions.

456 The differences in the relative extractability of amorphous Cr likely arises from
457 changes in the pH of the ammonium oxalate extract. The pHs of the extracts were not
458 measured, but the initial pH (3.3) of the extractant was likely increased with the elevated
459 BOFS dosages and, consequently, less Cr was solubilized. Interaction between BOFS and
460 soil can be taken to further promote the release of Cr from BOFS. When Cr dissolved from
461 BOFS is (ad)sorbed onto soil particles, its concentration in the solution decreases. To
462 maintain a given equilibrium between solution and solid phase, more Cr is dissolved from
463 BOFS. Consequently, dissolution of Cr from BOFS continues with its progressing sorption
464 onto soil particles. In practice, biological processes such as uptake of Cr^{3+} by roots also alter
465 the chemical equilibrium between BOFS and soil solution. Furthermore, the dissolution of Cr
466 minerals in BOFS is regulated by soil pH. Therefore, it is not only essential to investigate the
467 potential release of Cr from BOFS but also the subsequent reactions of Cr in actual soil. Risk
468 assessment that solely relies on properties of the deposited material is not scientifically
469 sound.

470 **4.4 Oxidation risk of Cr^{III} in BOFS into Cr^{VI}**

471 **4.4.1 Oxidation of Cr^{III} to Cr^{VI} species in potential leachates from BOFS**

472 The oxidation risk of Cr^{III} (mimicking Cr in the leachates from BOFS) to Cr^{VI}, assessed
473 by net-oxidation shaking tests (Figure 1), was seemingly negligible in all samples,
474 irrespective of BOFS incubation (Figure 1). The low net-oxidation yield was considered to
475 be attributable to the low solubility of Cr^{III}. In all samples the proportion of soluble residual
476 Cr^{III} was very small (Fig. 1). This fraction is susceptible to be retained onto the oxidizing
477 surfaces of soil MnO₂. In field soil, BOFS as well as the KOH addition diminished the
478 solubility of added Cr^{III} (Figure 1). This indicates that the elevated pH diminished the
479 solubility of Cr^{III} by enhancing the precipitation of soluble Cr³⁺ into immobile Cr(OH)₃.

480 **4.4.2 Contribution of manganese in BOFS in the Cr oxidation reactions**

481 Incubation with BOFS notably elevated the content of semi-total and amorphous Mn in
482 soil (

Table 6) but the production of Cr^{VI} in the net-oxidation test was very low (Figure 1). It is noteworthy that in previous studies with soils the (net)oxidation of Cr^{III} is demonstrated to correlate positively with the total amount of Mn oxides (Bartlett and James, 1979). This indicates that the oxidation potential of Mn in BOFS was low. Yildirim and Prezzi (2011) reported that in BOFS, Mn is mainly in the divalent form as a constituent of wustite type of minerals (MnO). Consequently, the prerequisite for the oxidation of Cr^{III} to Cr^{VI} would be that the Mn^{II} in BOFS is first oxidized to Mn^{IV} . In addition, the Cr^{III} in BOFS should be first dissolved to become capable to form an inner-sphere complex with MnO_2 . Furthermore, the dissolution reactions of Cr^{III} minerals and the oxidation of Mn^{II} to Mn^{IV} do not occur at the same pHs. Therefore, in BOFS the oxidation of Cr^{III} by Mn^{II} can be considered implausible.

4.4.3 The enhanced net-oxidation of Cr

The *enhanced* Cr net-oxidation tests revealed that in the presence of oxidative $\text{Mn}^{\text{IV}}\text{O}_2$, the oxidation of Cr^{III} into Cr^{VI} was evident in all soil samples (Figure 2), whereas without added $\text{Mn}^{\text{IV}}\text{O}_2$ the production of Cr^{VI} was negligible (Figure 1). Thus, it seems that the net-oxidation of Cr^{III} in field soils limed or not limed is also limited by the low amount of the tetravalent Mn^{IV} needed in Cr oxidation. Nonetheless, the *enhanced* net-oxidation of Cr^{III} to Cr^{VI} was lowered when the field soil was incubated with BOFS. This is likely attributable to the elevated pH that lowered the solubility of Cr^{III} . Furthermore, the tendency of Mn^{IV} to accept electrons and, consequently, its ability to oxidize Cr^{III} diminishes with elevated pH. Interestingly, a low soil pH can also diminish the net-oxidation of Cr (= oxidation of Cr^{III} – reduction of Cr^{VI}) (Reijonen and Hartikainen, 2016). In acidic conditions, e.g. soil organic matter can subsequently reduce the produced Cr^{VI} back to Cr^{III} . An optimal balance for the formation of Cr^{VI} via oxidation of Cr^{III} by $\delta\text{-MnO}_2$ may occur within the soil pH range of 4–6

506 (Stepniewska, et al., 2004). In the soil pH range 5.5-8.4, acidity increased the overall
507 oxidation of Cr^{III} to Cr^{VI} (Figure 2). BOFS increased soil pH, which in turn lowered the
508 oxidation of Cr^{III} by MnO_2 . Thus, oxidation of Cr in BOFS by MnO_2 appears to be self-
509 restricted – even if the Cr^{III} in slag would be more soluble. However, as the oxidation risk of
510 Cr^{III} to Cr^{VI} is demonstrated to depend on soil pH it should be noted that the liming impact of
511 BOFS is not continuous. In naturally acidic soils, initial conditions will eventually return if
512 liming is discontinued.

513 Interestingly, Fendorf (et al. 1992) reported that in their laboratory experiments
514 without soil, oxidation of Cr^{III} by $\delta\text{-MnO}_2$ was inhibited above pH 4. This oxidation reaction
515 is, however, demonstrated to occur at various soil pHs – even under neutral conditions (e.g.
516 James & Bartlett 1983, Kozuh et al. 2000). Oxidation of and added Cr^{III} by MnO_2 also
517 demonstrated in our enhanced net-oxidation test (Figure 2). These results demonstrate the
518 importance of studies with actual soil.

519 The oxidizing conditions in the *enhanced* net-oxidation test were extreme and are not
520 present in typical soils. The amount of added MnO_2 was equivalent to almost 36 000 mg Mn
521 soil kg^{-1} (see Appendix, page A2), which is excessive in comparison to natural soil Mn levels
522 of 20–3000 mg kg^{-1} (Krauskopf, 1972). At an extremely high concentration of $\text{Mn}^{\text{IV}}\text{O}_2$ the
523 amount of Cr^{VI} produced via oxidation can also be expected to be beyond the reducing
524 capacity of SOM in the oxic field soil. Consequently, the net-oxidation yields were very
525 high (Figure 2). The MnO_2 added to soil was fresh and, thus, prior reactions with soil it had
526 not used its oxidation potential or its oxidizing surfaces were not inhibited e.g. by adsorbed
527 metal hydroxide cations or organic compounds.

528 **4.4.4 Oxidation of Cr^{III} in BOFS to Cr^{VI} by atmospheric oxygen**

529   Prior to its addition to soil samples the pure BOFS was determined to contain water
530 soluble Cr^{VI}, although in very low amounts (Table 3). The conditions in the production of
531 BOFS (~1600 °C) favor the formation of Cr^{III} minerals. Thus, it can be concluded that a
532 small portion of it will be oxidized to Cr^{VI} afterwards, potentially by atmospheric oxygen.
533 This mechanism is discussed in a study on EAF (Electric Arc Furnace) and CLU (Creusot–
534 Loire–Uddeholm) slags (Pillay, et al., 2003). However, in the soil samples incubated with
535 BOFS no easily soluble Cr^{VI} (i.e. readily soluble or adsorbed onto oxide surfaces by ligand
536 exchange) was detected (

Table 5). This reveals that the minor amount of soluble Cr^{VI} potentially released from BOFS into soil was present in concentrations below the detectable level and/or Cr^{VI} was reduced into less toxic Cr^{III} by SOM. The ability of various soil organic compounds to reduce Cr^{VI} has previously been well established (Fendorf, 1995). The content of organic C in our test soil was rather high (3.2%) and, thus, its reducing capacity can also be expected to be high.

5. Conclusions

BOFS is powerful as a liming material as it efficiently increases soil pH. Although incubation of soil with BOFS elevated semi-total Cr, no release of bioaccessible Cr^{III} or Cr^{VI} was detected. Thus, under pH conditions prevalent in field soil, ecotoxic effects of BOFS-derived Cr can be considered to be negligible. In acidic conditions, however, some Cr is potentially dissolved as inorganic forms of Cr^{3+} . This soluble species is theoretically bioavailable and prone to be leached. Moreover, in such acidic conditions other metals, e.g. Al and Mn, can also be solubilized from the inherent soil constituents in concentrations toxic to biota.

The net-oxidation test revealed that the oxidation risk of potentially solubilized Cr^{III} to Cr^{VI} by soil innate MnO_2 is low. Furthermore, the Mn-bearing minerals in BOFS did not increase the net-oxidation yield in soil. Oxidation was limited by the low solubility of Cr^{III} and the limited availability of the oxidizing surfaces of $\text{Mn}^{\text{IV}}\text{O}_2$. A more plausible reaction pattern is oxidation of Cr^{III} in BOFS by atmospheric oxygen on the surfaces of the alkaline slag. This type of oxidation of Cr^{III} by O_2 , however, can be expected to be slow and to occur only to a minor extent. On the other hand, the enhanced net-oxidation demonstrated that in the

559 presence of excessive amounts of MnO_2 the oxidation of Cr^{III} to Cr^{VI} is apparent. The
560 oxidation of Cr^{III} in BOFS to Cr^{VI} by Mn^{IV} appears relevant only in extremely oxidizing
561 conditions, *i.e.*, in soils rich in MnO_2 and low in reducing SOM. As for the use of BOFS as a
562 liming material in agricultural soils high in SOM, this scenario is unlikely. Because the
563 environmental impacts of Cr ending up to soil with BOFS are dictated by dissolution-
564 precipitation, oxidation-reduction and adsorption-desorption reactions, soil properties critical
565 in terms of Cr chemistry should be included in the risk assessment. This research focused on
566 Cr in BOFS. Slags contain also other trace elements, such as vanadium. The solubility and
567 bioavailability of these elements in soil may be exceed that of Cr.

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673

Appendix

Table A1. Particle size distribution of BOFS

Sieve (mm)	Distribution (%)
4	99.8
2	91.2
1	74.4
0.5	57.5
0.3	45.5
0.15	29.2

Conversion equations and results:

Table A2. Estimation of BOFS-derived increase in semi-total Cr of soil and that actually detected.

	Semi-total Cr (mg kg ⁻¹)	Detected BOFS- derived increase in semi-total Cr* (mg kg ⁻¹)	Estimated BOFS- derived increase in semi-total Cr (on the basis of Cr in BOFS by XRF)** (mg kg ⁻¹)
Field soil without BOFS	14.7	-	-
Field soil with 10 t ha ⁻¹ BOFS equivalent	20.1	5.4	10.4
Field soil with 100 t ha ⁻¹ BOFS equivalent	73.2	58.5	100

* **Detected BOFS-derived increase** = $\frac{\text{Cr composition in BOFS (0.21\%)} \times m(\text{BOFS})}{m(\text{BOFS}) + m(\text{soil})}$

** **Estimated BOFS-derived increase** = $c(\text{semitotal Cr in BOFS incubated soil}) - c(\text{background, i.e. soil without BOFS})$

Table A3. The relative extractability of Cr by ammonium oxalate per BOFS kilogram

	Amorphous Cr (amm.oxalate extraction) (mg kg ⁻¹)	Conversion to extractability of Cr by amm.oxalate in BOFS kilogram* (mg kg ⁻¹)
Pure BOFS	16	16
Field soil without BOFS	4.9	
Field soil with 10 t ha ⁻¹ BOFS equivalent	6.2	86
Field soil with 100 t ha ⁻¹ BOFS equivalent	9	261

* **Extractability in BOFS** = $\frac{(c(\text{amorph.Cr in BOFS incubated soil}) - c(\text{amorph. Cr background, i.e. soil without BOFS})) \times (m(\text{BOFS}) + m(\text{soil}))}{m(\text{BOFS})}$

686 Conversion of the added MnO_2 used in the enhanced net-oxidation test into total Mn with
687 respect to soil:

$$688 \quad c(\text{Mn in soil}) = \frac{m(\text{Mn})}{m(\text{soil} + \text{added MnO}_2)} = \frac{m(\text{MnO}_2) \div M(\text{MnO}_2) \times M(\text{Mn})}{m(\text{soil} + \text{MnO}_2)} = 35\,770 \text{ mg Mn/kg}$$

$$689 \quad m(\text{MnO}_2) = 300 \text{ mg} = 0.0003 \text{ kg}$$

$$690 \quad M(\text{MnO}_2) = 86.9368 \text{ mg/mmol}$$

$$691 \quad m(\text{soil}) = 0.005 \text{ kg}$$

$$692 \quad M(\text{Mn}) = 54.938 \text{ mg/mmol}$$

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