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 MnO_2 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 stabile 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 (MnO_2). 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 22ºC, 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 $CrCl_3$ (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 MnO_2 was negligible. To produce highly oxidizing conditions, the test was further modified with excessive addition of synthetic $Mn^{IV}O_2$. Liming with BOFS diminished the

29   production of Cr^{VI}, whereas added $Mn^{IV}O_2$ 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.

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 ~ 1600°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).

52   BOFS is used in various applications, e.g. as construction material, a cementing

53   component, road pavement material, raw material of glass production, and in mineral wool

54   insulation. It mainly consists of calcium oxide (CaO), as well as the oxide and silicate

55   minerals of Fe, Al (aluminum), Mg (magnesium), and Mn (Dahlin, et al., 2012; Waligora, et

56   al., 2010). BOFS is strongly alkaline wherefore it can also be used for soil liming.

57   Nonetheless, re-use should be sustainable from the environmental perspective. In the re-use

58   of BOFS as liming material, a particular concern is its chromium (Cr) content. The

59   proportion of Cr in BOFS varies between 0.1–0.5 %, depending on the composition of the

60   ore and other primary materials used in the steel production (Shi, 2004). Chromium can be

61   highly toxic to living organisms, although at low concentrations it is a vital micronutrient

62   (Anderson, 1997). The toxicity of Cr, however, depends on its oxidation state as well as the

63   amount chemically available for potential biological uptake (= bioaccessibility). In

64   agricultural amendments, heavy metals are undesirable. However, in other re-use purposes of

65   BOFS some trace elements can be beneficial (from technical perspective). For instance, the

66   mechanical strength of BOFS is reported to enhance with increasing Cr levels (Sas et al.

67   2015). This is benign to road construction materials. In risk assessment, the re-use purpose of

68   BOFS needs to be addressed. Furthermore, the ecological risk should be distinguished from

69   that to human health. Proctor (et al. 2002) reported that BOFS used in e.g. fills, roadbases,

70   landscaping, might have site-spesific ecotoxicological impacts. Instead, no risk to human

71   health was observed.

72   In soil, Cr exists in two stabile oxidation states, +III and +VI. In small quantities, the

73   trivalent form, Cr^{III}, is an essential nutrient for several organisms, including humans

74   (Anderson, 1997). The hexavalent Cr^{VI} is merely a corrosive, carcinogenic, and mutagenic

75   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 oxy*anionic* 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 subtilus* 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 $Cr(OH)^{2+}$ or $Cr(OH)_2^+$), $Cr(OH)_{3(s)}$ 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 $Cr(OH)_{3(s)}$ (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 (hyrd)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 bioaccesibility

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   $Mn^{IV}O_2$ 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.
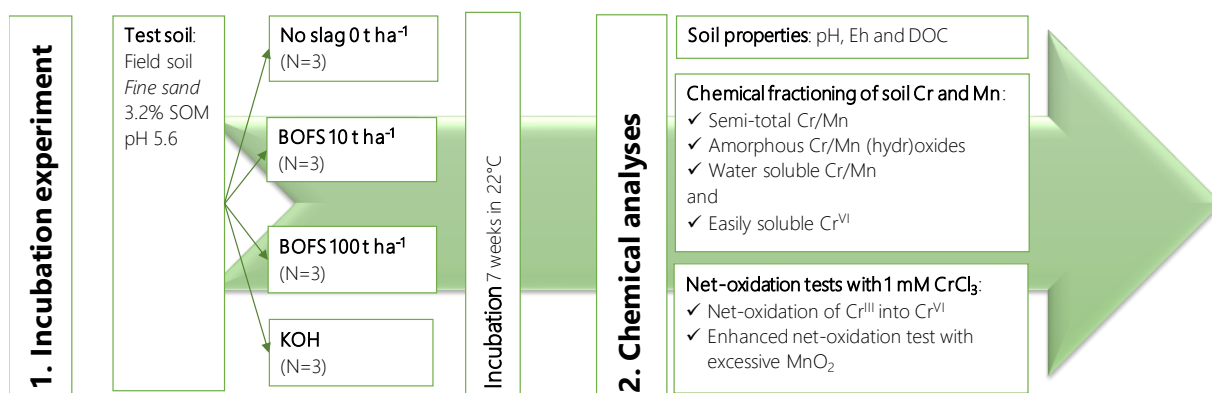

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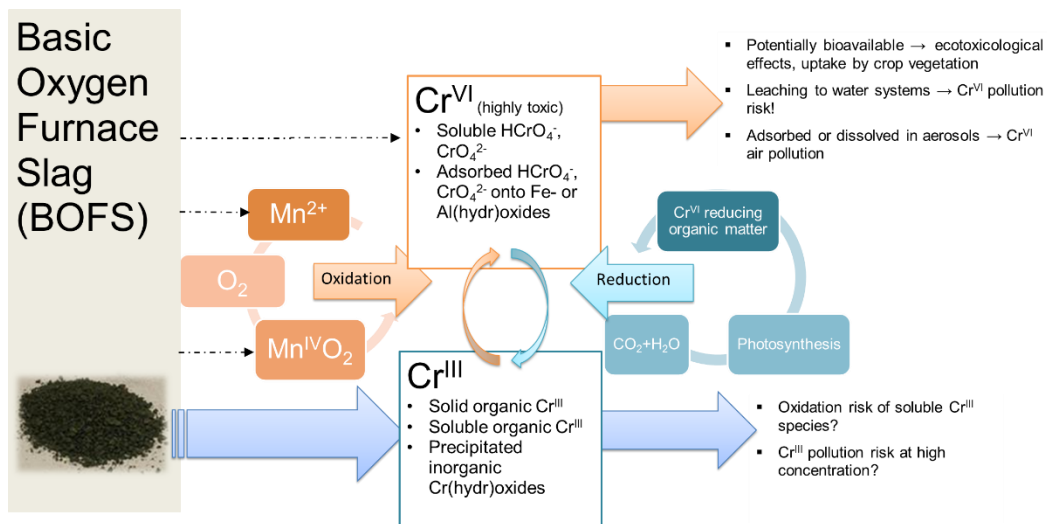
Scheme 1. Simplified pathways of Cr^{III} and Cr^{VI} release from BOFS to soil. The redox-reactions by MnO_2 and organic matter regulate the conversions in the oxidation state and, consequently, the environmental implications of Cr.

2. Materials and methods

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121

122   An incubation experiment followed by chemical fractionation tests was set up to

123   investigate the potential release of chemically bioaccessible Cr^{III} and Cr^{VI} from BOFS added

124   as a liming agent to a field soil. Potential reaction patterns in the oxidation of Cr^{III} to Cr^{VI} in

125   the incubated subsamples were further investigated in a net-oxidation tests. The overall

126   experiment design is illustrated in Scheme 2.

1. Incubation experiment

Test soil: Field soil *Fine sand* 3.2% SOM pH 5.6

- No slag 0 t ha^{-1} (N=3)
- BOFS 10 t ha^{-1} (N=3)
- BOFS 100 t ha^{-1} (N=3)
- KOH (N=3)

Incubation 7 weeks in 22°C

2. Chemical analyses

Soil properties: pH, Eh and DOC

Chemical fractioning of soil Cr and Mn:
- ✓ Semi-total Cr/Mn
- ✓ Amorphous Cr/Mn (hydr)oxides
- ✓ Water soluble Cr/Mn and
- ✓ Easily soluble Cr^{VI}

Net-oxidation tests with 1 mM CrCl$_3$:
- ✓ Net-oxidation of Cr^{III} into Cr^{VI}
- ✓ Enhanced net-oxidation test with excessive MnO$_2$

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128   *Scheme 2. Overall design of the experimental work.*

129   Soil subsamples were incubated with or without BOFS at a constant temperature

130   (22°C) and moisture content (at 50% of the water holding capacity) for seven weeks before

131   chemical analyses. Furthermore, the impact of BOFS on the Cr fractions not readily

132   bioavailable (amorphous Cr and semi-total Cr) was assessed. Various Mn fractions

133   (amorphous or easily soluble Mn-oxides, water soluble Mn, and semi-total Mn) were also

134   determined to assess the role of Mn on the Cr^{III} oxidation risk. The differences between the

135   extraction results of the various treatments were tested statistically by variance analysis

136   (ANOVA, at 0.05 level of significance) and Tukey's HSD as a post hoc test.

2.1 Incubation experiment

2.1.1 Test soil

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

Soil pH was measured in 0.01 M calcium chloride ($CaCl_2$) suspension at a soil (in field capacity) to solution ratio of 1:2.5 with a Schott Blueline combination electrode. Air-dried and powdered soil samples (500 mg) were used to analyze the total nitrogen (TN) and total organic carbon (TOC) by dry combustion (C/N VarioMax analyzer) and to calculate the ratio of C to N (C/N). Amorphous iron (Fe) and aluminum (Al) (hydr)oxides were extracted from fresh soil by ammonium oxalate at the pH 3.3 (($COO)_2(NH_4)_2$, 1:20 w/V, orbital shaking 250 rpm/2 h, centrifugation 3600 rpm/5min) (Niskanen, 1989). The extracts were filtered (Blauband 589/3) and analyzed for Fe and Al by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, λ_{Al}=309.3/396.2 nm and λ_{Fe} =238.2/259.9 nm).

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

159 temperate regions and indicated a high degree of humification. Soil pH (5.6) was suitable to

160 maintain normal microbial activity.

161 *Table 1. Properties of the test soil expressed as means ± standard deviations (N=4).*

TOC (Tot. Organic Carbon)	3.24 ± 0.055%	WHC (Water Holding Capacity)	0.58 ± 0.008 ml g^{-1}
TN (Tot. Nitrogen)	0.22 ± 0.004%	Al$_{(hydr)oxides}$	1986 ± 6 mg kg^{-1}
C/N	15:1	Fe$_{(hydr)oxides}$	2714 ± 24 mg kg^{-1}
pH	5.6±0.1	Soil classification (U.S.D.A)	*Fine sand*

2.1.2 Basic oxygen furnace slag (BOFS)

163 BOFS material used in the experiment originated from a northern European steel plant.

164 Its particle size was <3 mm (detailed particle size distribution is presented in the Appendix,

165 Table A1). Table 2 shows the chemical composition of BOFS analyzed by the X-ray

166 fluorescence (XRF, Philips PW 2404) method. BOFS consisted mainly of Ca, Fe, Si and O.

167 The total content of Cr amounted to 0.21% and Mn to 2.5%. The pH measured in the water at

168 solid to solution ratio of 1:2 was 11.3.

169 *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				

170

171   The solubility of elements in BOFS were determined by water extraction (SFS-EN

172   12457-3: a 24 h shaking test without pH buffering: 1. step 2:1 and 2. step 8:1 L/S) (Table 3).

173   Anionic elements were analyzed by ion chromatography and the others by inductively

174   coupled plasma mass spectrometry (ICP-MS). Hexavalent Cr^{VI} was determined

175   spectrophotometrically at $\lambda=540$ nm with LOD (Limit of Detection) equivalent to 12.5 µg L^{-}

176   ^{1}(LOD=background noise 3σ, $N_{blank}=10$).

177   Total content of water soluble Cr (no speciation) in BOFS was 0.2 mg kg^{-1} and Cr^{VI} was

178   0.13 mg kg^{-1}. The amorphous Cr extracted (Niskanen, 1989) by 0.05 M oxalate (0.029 M

179   $(COO)_2(NH_4)_2$ + 0.021 COOH, pH 3.3, 1:20 w/V) amounted to 16 mg kg^{-1}. The extract was

180   analyzed for Cr by ICP-OES at $\lambda=267.7/283.5$ nm (LOD$_{267.7\ nm}$= 10.0 µg L^{-1} and LOD$_{283.5}$

181   $_{nm}$= 9.8 µg L^{-1}).

182 *Table 3. Water solubility of various elements in BOFS. Total concentration of water soluble*
183 *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
Cr	*0.2*	**As**	< 0.006
Ba	1	*Cr^{VI}*	*0.13*

184

2.1.3 Experimental design

186   Prior to incubation, the moist test soil material at 50% water holding capacity (WHC) was

187   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.

2.2 Chemical analyses of incubated soil samples

201

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 ºC (~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}.

2.2.1 Soil properties: pH, E_h and DOC

Soil pH and E_h of all incubated subsamples were measured in soil suspended in 0.01 M $CaCl_2$ (1:2.5) (Mettler Toledo SP250 T-70, DG111-SC glass electrode). It is noteworthy, however, that the redox potential measured by this method is a coarse estimate. **Dissolved organic carbon (DOC)**, an estimate for soluble organic matter, was extracted with Milli-Q water (1:10 dw/V, 250 rpm/15 min) from the moist incubated subsamples. Extracts were filtered through a 0.45 µm Nuclepore syringe filter and the DOC in the filtrates determined with a TOC-analyzer (Shimadzu TOC-V cph/TNM-1).

2.2.2 Chemical fractionation of soil Cr and Mn

Content of semi-total Cr and Mn was determined with by microwave (MarsXpress CEM) acid digestion (EPA3051A) with a mixture of nitric and hydrochloric acids (3:1, HNO_3:HCl). However, some minerals, particularly of Cr, will not dissolve by this method. Thus, the amount of Mn and Cr in the extracts obtained can be taken to stand for semi-total concentrations. As an exception to other chemical analysis on the moist incubated soil samples, semi-total Cr and Mn were determined from air dry powdered soil.

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

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

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

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

The easily soluble Cr^{VI} was measured with a modification of the EPA7196A method (Reijonen and Hartikainen, 2016). In this analysis, Cr^{VI} is detected
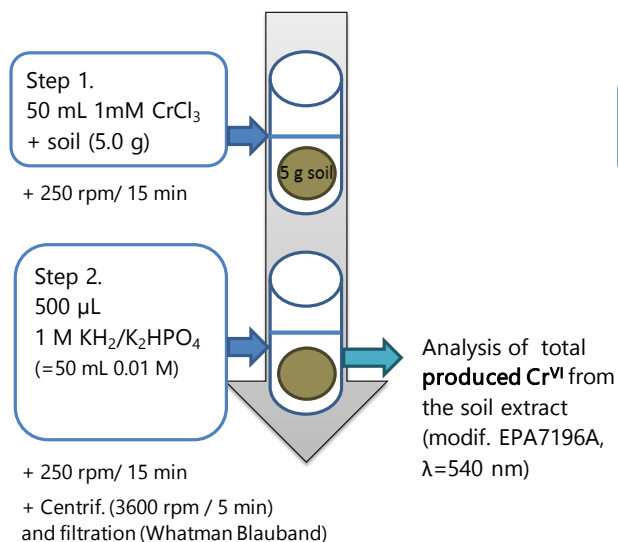
254   spectrophotometrically (by Shimadzu UVmini-1240, λ=540 nm). Prior to measurement, Cr^{VI}

255   is reduced and bound to a diphelnylcarbazide (DPC) complex. Limit of quantification (LOQ)

256   was determined as a tenfold standard deviation of the background noise.
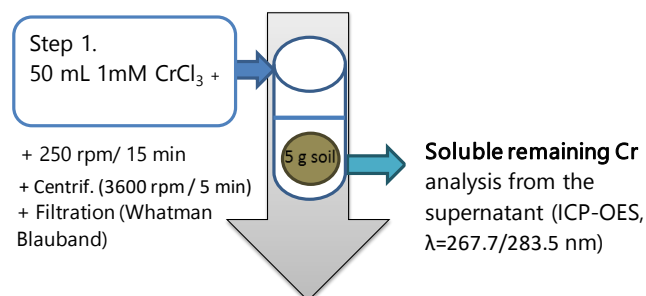

257 2.2.3 Net-oxidation tests of Cr

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 ($CrCl_3 \cdot 6\ H_2O$, Aldrich). The Cr^{VI} formed was further extracted by

271   phosphate buffer (KH_2/K_2HPO_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 (λ_{Cr}=267.7/283.5 nm).

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

Step 1.
50 mL 1mM CrCl$_3$
+ soil (5.0 g)

+ 250 rpm/ 15 min

Step 2.
500 µL
1 M KH$_2$/K$_2$HPO$_4$
(=50 mL 0.01 M)

+ 250 rpm/ 15 min
+ Centrif. (3600 rpm / 5 min)
and filtration (Whatman Blauband)

Analysis of total
produced Cr^{VI} from
the soil extract
(modif. EPA7196A,
λ=540 nm)

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

Step 1.
50 mL 1mM CrCl$_3$ +

+ 250 rpm/ 15 min
+ Centrif. (3600 rpm / 5 min)
+ Filtration (Whatman Blauband)

Soluble remaining Cr
analysis from the
supernatant (ICP-OES,
λ=267.7/283.5 nm)

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

Enhanced Cr net-oxidation test. The Cr net-oxidation test was further modified to test the theoretical ability of incubated soils to oxidize potential Cr^{III} in leachates under extremely oxidizing conditions. This enhanced net-oxidation test (Scheme 4) resembles the net-oxidation test, with the exception that after shaking the soil sample with CrCl$_3$ (250 rpm/15 min) the suspension is re-shaken with 300 mg of activated (highly oxidative) Mn^{IV}O$_2$ (Fluka) (250 rpm/15 min). The easily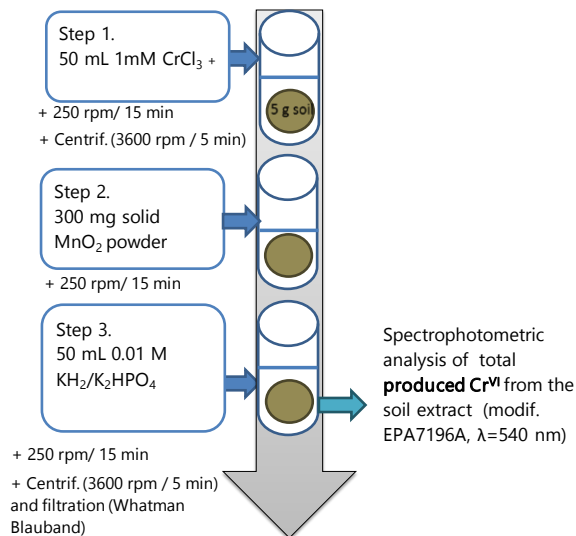 soluble Cr^{VI} was extracted afterwards by phosphate buffer (KH$_2$/K$_2$HPO$_4$ at pH 7.2) and after filtration, its concentration was determined by the modified EPA7196A method.

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

Step 1.
50 mL 1mM CrCl$_3$ +

+ 250 rpm/ 15 min
+ Centrif. (3600 rpm / 5 min)

5 g soil

Step 2.
300 mg solid
MnO$_2$ powder

+ 250 rpm/ 15 min

Step 3.
50 mL 0.01 M
KH$_2$/K$_2$HPO$_4$

+ 250 rpm/ 15 min
+ Centrif. (3600 rpm / 5 min)
and filtration (Whatman
Blauband)

Spectrophotometric
analysis of total
produced Cr^{VI} from the
soil extract (modif.
EPA7196A, λ=540 nm)

288

289 *Scheme 4. Extraction protocol for the determination of Cr^{VI} produced in the enhanced*
290 *net-oxidation test with excessive MnO$_2$ in soil suspension with 1 mM CrCl$_3$.*

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.

Table 4. pH, E_h, and DOC in field soil samples incubated (7 weeks at 22ºC, moisture content at WHC 50%) without or with BOFS slag added 10 or 100 t ha^{-1} or KOH (equivalent to lower BOFS dosage). Values indicate means ±standard deviation and Tukey's HSD (N=3).

	Field soil (*fine sand*, SOM 3.2%)			
	BOFS 0 t ha^{-1}	*KOH*	*BOFS 10 t ha^{-1}*	*BOFS 100 t ha^{-1}*
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]

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

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

17

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 22ºC, 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%)			
	BOFS 0 t ha^{-1}	*KOH*	*BOFS 10 t ha^{-1}*	*BOFS 100 t ha^{-1}*
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

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

	Field soil (*Fine sand*, 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]

3.4 Risk of Cr^{III} oxidation to Cr^{VI}: net-oxidation shaking tests with 1 mM CrCl$_3$

The net-oxidation test revealed the risk of the detrimental reaction pattern of Cr^{III} oxidation (of the hypothetical leachates from BOFS) to Cr^{VI} by soil MnO$_2$ to be low (Figure 1). In the soil suspended in CrCl$_3$ solution, the net-oxidation (= oxidation of Cr^{III} – subsequent reduction of formed Cr^{VI}) (see 2.2.3) was negligible. Only in the subsamples incubated with a BOFS dosage equivalent to 10 t ha⁻¹ small amount (0.016 mg L⁻¹) of easily soluble Cr^{VI}, i.e. dissolved or desorbable by ligand exchange) was recorded. This amount is below LOQ (0.04 mg L⁻¹). Interestingly, the soluble Cr^{III} added was strongly retained by all soil samples. Less than 1.5% of the added Cr^{III} (52 mg L⁻¹) remained soluble. Incubation with BOFS or KOH further reduced the solubility of added Cr^{III}.
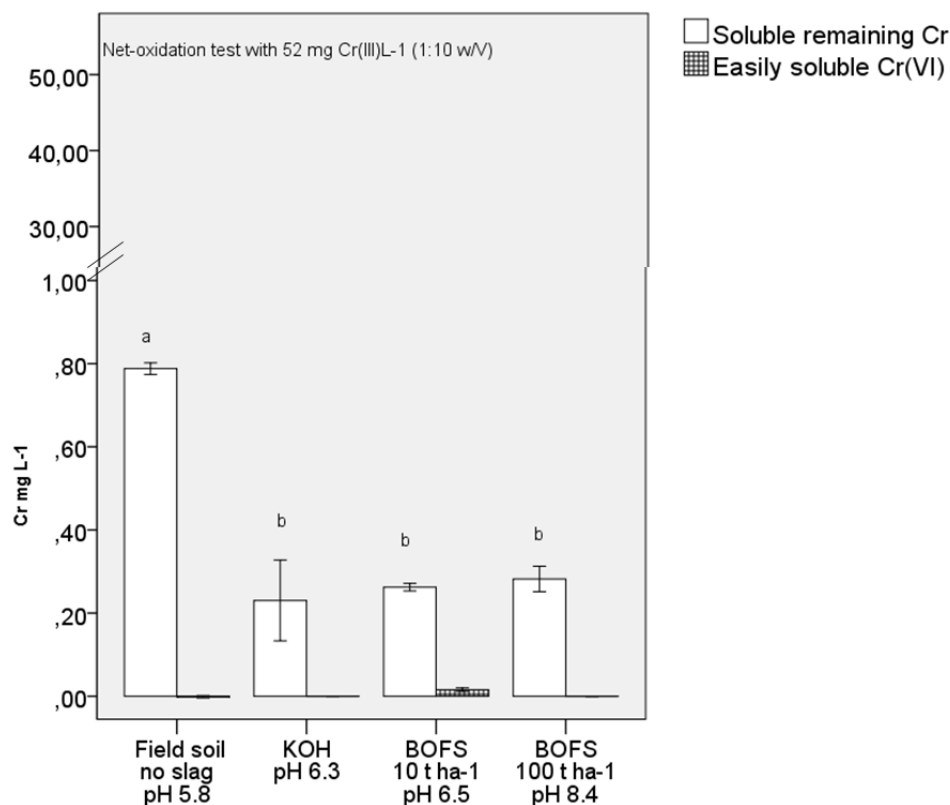
Figure 1. *The total amount of remaining soluble Cr and easily soluble Cr^{VI} produced in the net-oxidation test (1:10 w/V, 1 mM $CrCl_3$) in soil samples incubated for 7 weeks at 22ºC and moisture content of WHC 50%. Values indicate means and Tukey's HSD groups (N=3). Error bars indicate standard error.*

Enhanced net-oxidation of Cr^{III} by active $Mn^{IV}O_2$. The theoretical possibility for the oxidation of initially dissolved Cr^{III} in field soil was investigated by using excessive amounts of synthetic MnO_2 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 MnO_2 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 MnO_2, 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}.

24

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.
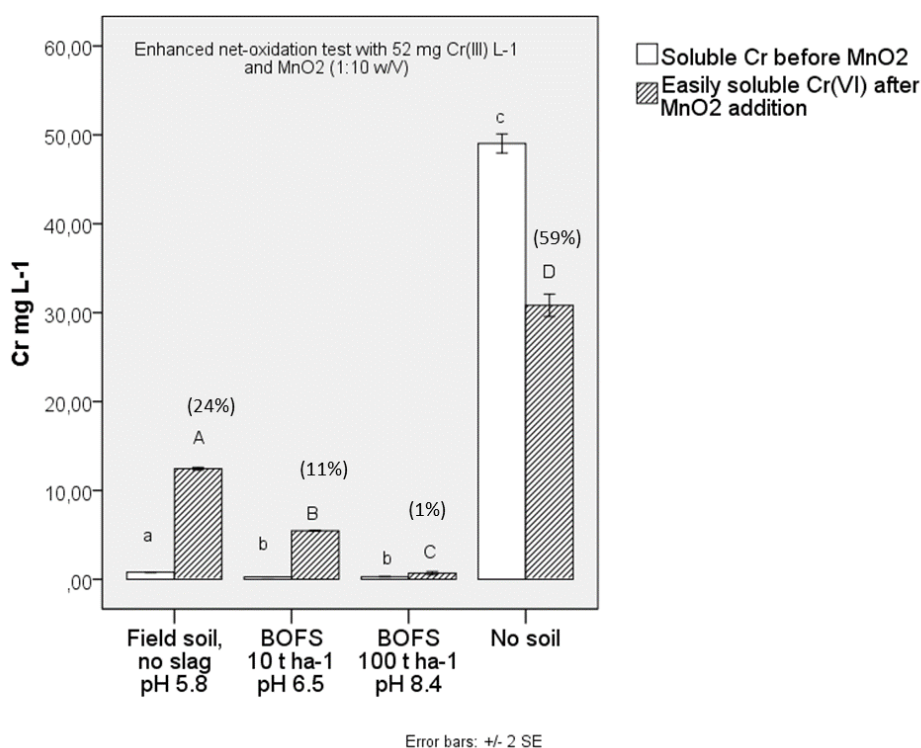
372
373   *Figure 2*. *The mean soluble remaining Cr (no speciation) after addition of 52 mg $Cr^{III}L^{-}$*
374   *^{1}(soil:solution ratio 1:10) and easily soluble Cr^{VI} produced from the further addition of*
375   *MnO2 in the enhanced net-oxidation test of field soil with and without BOFS and in*
376   *suspension without soil. Percentage values indicate mean production of Cr^{VI} of the added*
377   *Cr^{III}. Error bars illustrate standard error (N=3).*

25

4. Discussion

4.1 Impact of BOFS on chemical properties of soil

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

The "recommended" BOFS dosage did not significantly increase soluble organic matter. This outcome was unexpected because the deprotonation of acidic functional (e.g. carboxylic and phenolic) groups and, consequently, the solubility of organic matter tends to increase with elevated pH. Actually, the expected response was recorded in the KOH-treated samples, where pH was elevated to the same level as recorded in the "recommended " BOFS treatment but the solubility of organic matter doubled (Table 4 Actually, when using BOFS, a 10 times higher dosage and pH as high as 8.4 were required to obtain this high increase in DOC (Table 4). The lower solubility of organic matter in the BOFS-treated samples can be explained by the fact that, in contrast to the monovalent K$^+$, the divalent Ca^{2+} cation is capable to form chemical bridges between dissociated functional groups of organic matter. These linkages, in turn, increase the "apparent molecular size" and reduce the hydrophilicity of organic matter.   cation is capable to form chemical bridges between dissociated functional groups of organic matter. These linkages, in turn, increase the "apparent molecular size" and reduce the hydrophilicity of organic matter.

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

Incubation with BOFS (containing 2100 mg Cr kg^{-1}) notably increased semi-total Cr in 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 browmillerite 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).

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 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 (pKa 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.

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

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

The oxidation risk of Cr^{III} (mimicking Cr in the leachates from BOFS) to Cr^{VI}, assessed by net-oxidation shaking tests (Figure 1), was seemingly negligible in all samples, irrespective of BOFS incubation (Figure 1). The low net-oxidation yield was considered to be attributable to the low solubility of Cr^{III}. In all samples the proportion of soluble residual Cr^{III} was very small (Fig. 1). This fraction is susceptible to be retained onto the oxidizing surfaces of soil MnO_2. In field soil, BOFS as well as the KOH addition diminished the solubility of added Cr^{III} (Figure 1). This indicates that the elevated pH diminished the solubility of Cr^{III} by enhancing the precipitation of soluble Cr^{3+} into immobile $Cr(OH)_3$.

4.4.2 Contribution of manganese in BOFS in the Cr oxidation reactions

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

483   Table 6) but the production of Cr^{VI} in the net-oxidation test was very low (Figure 1). It

484   is noteworthy that in previous studies with soils the (net)oxidation of Cr^{III} is demonstrated to

485   correlate positively with the total amount of Mn oxides (Bartlett and James, 1979). This

486   indicates that the oxidation potential of Mn in BOFS was low. Yildirim and Prezzi (2011)

487   reported that in BOFS, Mn is mainly in the divalent form as a constituent of wustite type of

488   minerals (MnO). Consequently, the prerequisite for the oxidation of Cr^{III} to Cr^{VI} would be

489   that the Mn^{II} in BOFS is first oxidized to Mn^{IV}. In addition, the Cr^{III} in BOFS should be first

490   dissolved to become capable to form an inner-sphere complex with MnO_2. Furthermore, the

491   dissolution reactions of Cr^{III} minerals and the oxidation of Mn^{II} to Mn^{IV} do not occur at the

492   same pHs. Therefore, in BOFS the oxidation of Cr^{III} by Mn^{II} can be considered implausible.

493   4.4.3 The enhanced net-oxidation of Cr

494   The *enhanced* Cr net-oxidation tests revealed that in the presence of oxidative $Mn^{IV}O_2$, the

495   oxidation of Cr^{III} into Cr^{VI} was evident in all soil samples (Figure 2), whereas without added

496     $Mn^{IV}O_2$ the production of Cr^{VI} was negligible (Figure 1). Thus, it seems that the

497   net-oxidation of Cr^{III} in field soils limed or not limed is also limited by the low amount of the

498   tetravalent Mn^{IV} needed in Cr oxidation. Nonetheless, the *enhanced* net-oxidation of Cr^{III} to

499   Cr^{VI} was lowered when the field soil was incubated with BOFS. This is likely attributable to

500   the elevated pH that lowered the solubility of Cr^{III}. Furthermore, the tendency of Mn^{IV} to

501   accept electrons and, consequently, its ability to oxidize Cr^{III} diminishes with elevated pH.

502   Interestingly, a low soil pH can also diminish the net-oxidation of Cr (= oxidation of Cr^{III} –

503   reduction of Cr^{VI}) (Reijonen and Hartikainen, 2016). In acidic conditions, e.g. soil organic

504   matter can subsequently reduce the produced Cr^{VI} back to Cr^{III}. An optimal balance for the

505   formation of Cr^{VI} via oxidation of Cr^{III} by δ-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 δ-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 & Bartlett1983, 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 $Mn^{IV}O_2$ 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.

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

528

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

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536

537   Table 5). This reveals that the minor amount of soluble Cr^{VI} potentially released from

538   BOFS into soil was present in concentrations below the detectable level and/or Cr^{VI} was

539   reduced into less toxic Cr^{III} by SOM. The ability of various soil organic compounds to reduce

540   Cr^{VI} has previously been well established (Fendorf, 1995). The content of organic C in our

541   test soil was rather high (3.2%) and, thus, its reducing capacity can also be expected to be

542   high.

543 5. Conclusions

544   BOFS is powerful as a liming material as it efficiently increases soil pH. Although

545   incubation of soil with BOFS elevated semi-total Cr, no release of bioaccessible Cr^{III} or Cr^{VI}

546   was detected. Thus, under pH conditions prevalent in field soil, ecotoxic effects of BOFS-

547   derived Cr can be considered to be negligible. In acidic conditions, however, some Cr is

548   potentially dissolved as inorganic forms of Cr^{3+}. This soluble species is theoretically

549   bioavailable and prone to be leached. Moreover, in such acidic conditions other metals, e.g.

550   Al and Mn, can also be solubilized from the inherent soil constituents in concentrations toxic

551   to biota.

552   The net-oxidation test revealed that the oxidation risk of potentially solubilized Cr^{III} to Cr^{VI}

553   by soil innate MnO_2 is low. Furthermore, the Mn-bearing minerals in BOFS did not increase

554   the net-oxidation yield in soil. Oxidation was limited by the low solubility of Cr^{III} and the

555   limited availability of the oxidizing surfaces of $Mn^{IV}O_2$. A more plausible reaction pattern is

556   oxidation of Cr^{III} in BOFS by atmospheric oxygen on the surfaces of the alkaline slag. This

557   type of oxidation of Cr^{III} by O_2, however, can be expected to be slow and to occur only to a

558   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.

568   ACKNOWLEDGMENTS

571

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673

674 # **Appendix**

675

676 ***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

677 ## **Conversion equations and results:**

678

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

	Semi-total Cr	Detected BOFS-derived increase in semi-total Cr*	Estimated BOFS-derived increase in semi-total Cr (on the basis of Cr in BOFS by XRF)**
	(mg kg^{-1})	(mg kg^{-1})	(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

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

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

683

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

	Amorphous Cr (amm.oxalate extraction)	Conversion to extractability of Cr by amm.oxalate in BOFS kilogram*
	(mg kg^{-1})	(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** $= \frac{(c\ (amorph.Cr\ in\ BOFS\ incubated\ soil - c\ (amorph.\ Cr\ background,\ i.e.\ soil\ without\ BOFS)) \times (m(BOFS) + m(soil))}{m\ (BOFS)}$

685

686   Conversion of the added MnO₂ used in the enhanced net-oxidation test into total Mn with

687   respect to soil:

688    $$c\ (Mn\ in\ soil) = \frac{m(Mn)}{m\ (soil + added\ MnO2)} = \frac{m(MnO2) \div M(MnO2) \times M(Mn)}{m\ (soil + MnO2)} = 35\ 770\ mg\ Mn/kg$$

689    $m(MnO2) = 300\ mg = 0.0003\ kg$

690    $M(MnO2) = 86.9368\ mg/mmol$

691    $m(soil) =\ 0.005\ kg$

692    $M(Mn) = 54.938\ mg/mmol$

693