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### Title

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# 1 Long-term Stability of Organic Carbon-stimulated Chromate Reduction in Contaminated 2 Soils, and its Relation to Manganese Redox Status

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## 11 12 **Abstract**

13 In-situ reduction of toxic Cr(VI) to less hazardous Cr(III) is becoming a popular strategy for  
14 remediating contaminated soils. However, the long term stability of reduced Cr remains to be  
15 understood, especially given the common presence of Mn(III,IV) oxides that reoxidize Cr(III).  
16 This 4.6 year laboratory study tracked Cr and Mn redox transformations in soils contaminated  
17 with Cr(VI) which were then treated with different amounts of organic carbon (OC). Changes in  
18 Cr and Mn oxidation states within soils were directly and nondestructively measured using micro  
19 X-ray absorption near edge structure spectroscopy. Chromate reduction was roughly 1<sup>st</sup>-order,  
20 and the extent of reduction was enhanced with higher OC additions. However, significant Cr(III)  
21 reoxidation occurred in soils exposed to the highest Cr(VI) concentrations (2,560 mg kg<sup>-1</sup>).  
22 Transient Cr(III) reoxidation up to 420 mg kg<sup>-1</sup> was measured at 1.1 years after OC treatment,  
23 followed by further reduction. Chromate concentrations increased by 220 mg kg<sup>-1</sup> at the end of  
24 the study (4.6 years) in one soil. The causal role that Mn oxidation state had in reoxidizing Cr  
25 was supported by trends in Mn K-edge energies. These results provide strong evidence for long-  
26 term dependence of soil Cr oxidation states on balances between OC availability and Mn redox  
27 status.

## 28 29 **Introduction**

30 Chromium is among the most common metal contaminants in soils, with elevated levels of the  
31 toxic hexavalent chromate species resulting from improper disposal of wastes from a variety of  
32 industrial operations including metal plating, wood preservation, and leather tanning (1). Soils  
33 and sediments at contaminated source sites can have very high Cr concentrations, exceeding  
34 10,000 mg kg<sup>-1</sup> (2-5). Commonly occurring Cr(VI) reductants in soils are organic matter and  
35 Fe(II). Under typical ranges of subsurface pH, reduction to Cr(III) substantially decreases this  
36 metal's solubility, mobility, and toxicity (6).

37 The strong oxidation state dependent toxicity of Cr has prompted research and  
38 development of remediation methods that stimulate in-situ Cr(VI) reduction in contaminated  
39 soils, sediments, and groundwaters. Primarily geochemical approaches tested include injection  
40 of Fe<sup>2+</sup> (7, 8), permeable reactive zero-valent Fe walls (4), and injection of H<sub>2</sub>S (9).  
41 Biogeochemical strategies rely on supplying organic carbon (OC) to stimulate direct microbial  
42 Cr(VI) reduction and indirectly microbially mediated reduction through Fe reduction (10-14).  
43 An outstanding issue associated with redox based remediation strategies for metals is that of  
44 long-term stability of the desired nonhazardous species. For reduction based Cr remediation, the  
45 relatively high *p<sub>e</sub>* of Cr(VI)/Cr(III) transformations works in favor of Cr(III) stability under  
46 many conditions. However, oxidation capacities of soils vary widely. The stability of reduced

47 Cr in the subsurface is primarily dependent on the redox status of manganese, with Mn(IV) and  
48 Mn(III) oxides being the only common soil minerals known to oxidize Cr(III) (15-20). Soils  
49 with relatively high Mn(IV,III) oxide concentrations tend to have high Cr oxidation capacities  
50 (21, 22).

51 Although a wide variety of reduction-based Cr remediation strategies have been  
52 investigated in soils, the majority of tests have been carried out over the course of only a few  
53 days to months. Relatively little information is currently available on the long-term stability of  
54 reduced Cr. Insights into the long-term behavior of reductively stabilized Cr in heavily  
55 contaminated soils is particularly important to obtain because the primary human exposure  
56 pathway of concern for Cr(VI) is that of inhalation (23). In order to better understand longer-  
57 term behavior of reductively stabilized Cr, we conducted a 4.6 year laboratory environmental  
58 simulation study on Cr(VI) contaminated soil treated with varying levels of OC.

59

## 60 **Materials and Methods**

61 **Soil.** The Altamont soil (Altamont Pass, CA) used in this study is typical of many semi-arid  
62 upland areas within California. Basic properties of this Aridic Haploxerert have been described  
63 previously (24, 25). Soil from the C horizon was sieved (250  $\mu\text{m}$ ), and homogenized prior to  
64 bulk physical and chemical analyses. This material is calcareous (2 to 4% calcite, pH 8.3),  
65 clayey (42% clay, 52% silt, 6% sand), and contains 1% organic carbon. The native Cr  
66 concentration of this soil is  $60 \pm 4 \text{ mg kg}^{-1}$ , and it has a total Mn concentration of  $1,370 \pm 60 \text{ mg}$   
67  $\text{kg}^{-1}$ , (X-ray fluorescence analysis).

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69 **Soil columns.** Several soil columns from an earlier Cr(VI) reduction study (25) were maintained  
70 for this much longer-term experiment. Six of the original 24 columns were used in the present  
71 study. Polycarbonate pipe (11.9 mm internal diameter) segments were cut into 50 mm lengths,  
72 with 30 mm by 5 mm wall sections cut away and covered with 2 layers of X-ray-transparent  
73 Kapton tape (Supporting Information, Figure S1). The inner layer of tape was cut to match the  
74 size of the wall opening, and taped to the outer layer such that the adhesive surfaces were  
75 sandwiched between Kapton films. This configuration avoided the possibility of redox reactions  
76 that could occur between soil components and the adhesive (26). Adhesive from the oversized  
77 outer layer of tape sealed the dual Kapton film windows to the polycarbonate pipe. Platinum  
78 wire electrodes were embedded along the length of each soil column for obtaining redox  
79 potential measurements (25). The columns were then packed with Altamont soil to a bulk density  
80 of  $1.26 \text{ Mg m}^{-3}$  (porosities and pore volumes of 0.52 and 1.74 mL, respectively) to a depth of 30  
81 mm. Soils were sequentially treated with 3 different solutions. First, deionized water was  
82 infiltrated into each column to achieve a soil water content of  $0.30 \text{ g g}^{-1}$  (equivalent to 70%  
83 saturation), and incubated for 8 days at room temperature to reactivate the microbial community  
84 while maintaining aerobic conditions. Next, 3 columns each received 1.10 mL of solutions  
85 containing  $1,000 \text{ mg L}^{-1}$  Cr(VI) added as  $\text{K}_2\text{CrO}_4$ , and the remaining 3 columns received  $10,000$   
86  $\text{mg L}^{-1}$  Cr(VI). These Cr(VI) solutions were infiltrated into the soils, with the initial soil pore  
87 waters discharged out of the bottom outlet port. Upon completion of this second infiltration step,  
88 the outflow port was sealed in each column for the remainder of the experiment, such that further  
89 transport was by diffusion only. At this stage, soils contained either 4.93 or 49.3  $\mu\text{mol}$  of added  
90 Cr(VI) per g soil, and the water content was  $0.40 \pm 0.02 \text{ g g}^{-1}$  ( $95 \pm 5\%$  saturation). Five days  
91 after the initial exposure to Cr(VI) solutions, columns were ponded with a third solution  
92 containing various concentrations of OC. Columns received 0.60 mL (0.345 pore volume) of

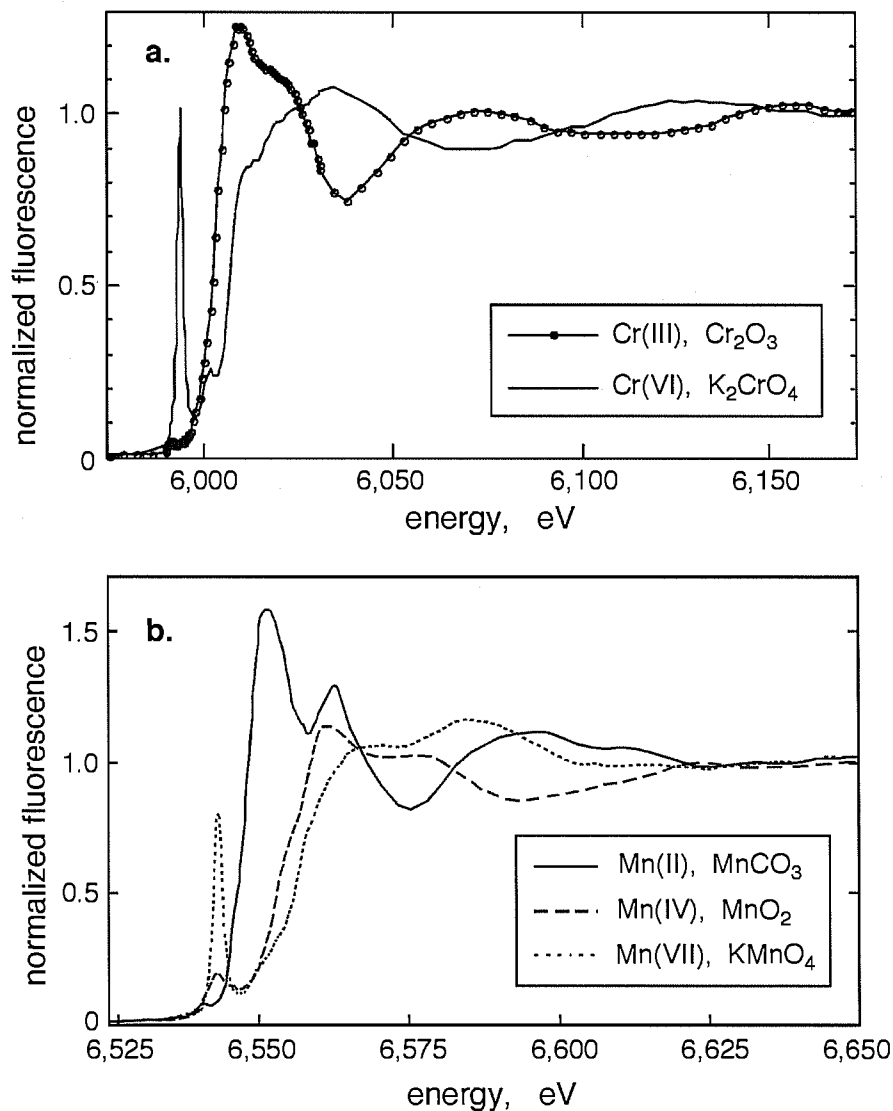
93 tryptic soy broth as the OC remediation agent. Solutions with 0, 800, or 4,000 mg L<sup>-1</sup> OC were  
94 applied to different columns, equivalent to adding 0, 9.3, or 47 μmol of OC per g soil (0, 112, or  
95 560 μg g<sup>-1</sup>). Tryptic soy broth was used as an OC source analog for decomposing plant tissue.  
96 The ponded surface of each column was capped to minimize evaporation, but vented through a  
97 segment of a hypodermic needle to maintain this boundary in equilibrium with atmospheric  
98 oxygen. Periodic uncapping for redox potential and pH measurements also help to maintain this  
99 aerated boundary condition. Soils were incubated at room temperature (21 ± 2 °C), within a  
100 humidified chamber. For the longer-term incubation (greater than 1 year), soil columns were  
101 also stored in the dark, with periodic small additions of water (≈ 0.1 mL per 3 months) to  
102 compensate for evaporative loss that occurred even in the humidified enclosure.

103 **Micro-XANES spectroscopy.** Profiles of Cr and Mn oxidation states in soil columns were  
104 obtained at various times after exposure to Cr(VI) solutions, using micro- X-ray absorption near  
105 edge structure (μ-XANES) spectroscopy (27, 28). The μ-XANES measurements were obtained  
106 at beamline X26A of the National Synchrotron Light Source (NSLS, Brookhaven National  
107 Laboratory, Upton, NY), and the GeoSoilEnviroCARS beamline 13ID-C at the Advanced  
108 Photon Source (APS, Argonne National Laboratory, Argonne, IL). Large beam sizes of about  
109 300 μm were used in order to average over a large population of mineral grains and pores. It is  
110 also worth noting that because X-ray attenuation distances in soils are around 100 μm at the Cr  
111 and Mn K-edge energies, much finer spatial resolution in these thick samples could not be  
112 obtained using smaller spot sizes. The broad beam size also helped minimize X-ray beam-  
113 induced reduction, which was observed on Cr at the brighter GeoSoilEnviroCARS beamline. By  
114 using a large spot size and keeping exposure times to less than 15 s per sample location, beam-  
115 induced Cr(VI) reduction was kept to less than 6%, as determined by repeated analyses on  
116 selected locations. No X-ray induced Cr redox changes were detectable in samples measured at  
117 beamline X26A. Mn μ-XANES spectra were only collected on these soils at X26A, where a  
118 scanning procedure described below was used to avoid beam-induced reduction.

119 Oxidation state standards for Cr(III) and Cr(VI) were prepared by mixing Cr<sub>2</sub>O<sub>3</sub> and  
120 K<sub>2</sub>CrO<sub>4</sub> into dry Altamont clays, to obtain Cr concentrations of 10,000 mg kg<sup>-1</sup>. Chromium K-  
121 edge XANES spectra on these standards were collected at 0.2 to 0.5 eV steps through the pre-  
122 edge and edge regions, and 3 to 5 eV steps over the below- and above-edge regions. The energy  
123 of the pre-edge peak resulting from 1s-3d transitions allowed in tetrahedral Cr(VI) was calibrated  
124 to a value of 5,993.5 eV (29). The energy-calibrated Cr K-edge XANES spectra of the Cr(III)  
125 and Cr(VI) standards are shown in Figure 1a. Locations along the soil columns were measured  
126 with the monochromatic beam scanned below the absorption edge (5,970 to 5,988 eV, in 2 eV  
127 steps), through the pre-edge peak energy region (5,988 to 5,997 eV in 0.25 eV steps), and well  
128 above the absorption edge energy (6,170 to 6,200 eV in 5 eV steps). The background-subtracted  
129 Cr fluorescence in this latter energy range was used to normalize pre-edge peak fluorescence for  
130 calculating the Cr(VI)/[total Cr] fraction from the linear relation of Bajt et al. (30).

131 Manganese XANES standards consisted of MnCO<sub>3</sub> for defining the Mn(II) edge position,  
132 MnO<sub>2</sub> for defining the Mn(IV) edge position, and KMnO<sub>4</sub>, each mixed into SiO<sub>2</sub> powder to  
133 about 1% Mn. The KMnO<sub>4</sub> standard was run periodically for energy calibration, with its pre-  
134 edge peak energy set equal to 6,543.3 eV (31). Examples of these Mn K-edge spectra are shown  
135 in Figure 1b. Typical Mn K-edge scans on soils were obtained with coarse steps in the below  
136 edge region (6,530 to 6540 eV, in 2 eV step), finer steps in the edge region (6541 to 6565 eV, in  
137 0.5 eV steps), and coarse steps above the absorption edge (6,630 to 6,650 eV, in 5 eV steps).  
138 Preliminary tests showed some susceptibility for Mn redox changes under long exposures to X-

139 ray beams, as previously reported by Ross et al. (32). In order to avoid X-ray beam induced  
140 shifts in Mn oxidation state, most measurements on soils were done with high resolution only  
141 along the main absorption edge. This allowed quantification of Mn K-edge energies for  
142 comparison with the range bounded by Mn(II) and Mn(IV) for assessing relative Mn redox  
143 status, but does not generally quantify fractions of Mn(II), Mn(III), and Mn(IV). Local Mn  
144 redox status was characterized by determining the energy along the absorption edge  
145 corresponding to half the absorption associated with the step height (22, 33), then comparing this  
146 half-height energy to those of Mn(II) and Mn(IV) standards. Because no significant spatial  
147 trends of Mn edge energies were detected along column lengths, results were summarized as  
148 time trends of column-averaged Mn edge energies. Both Cr and Mn K-edges were scanned  
149 sequentially at 0.5 to 5 mm depth intervals along each column.  
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**Figure 1.** (a) XANES spectra of chromium oxidation state standards. (b) XANES spectra of Mn oxidation state standards.

156 **Extractable Cr(VI) determination.** At the end of the experiment (4.6 years), soil from each  
157 column was emptied, homogenized, and split into sub-samples. Half of the sub-samples were  
158 used for microbial community analyses in a companion study (Chakraborty et al., in  
159 preparation). The remaining sub-samples were analyzed for extractable Cr(VI) using the hot  
160 carbonate/hydroxide method (34) directly (wet) and after air-drying. The extraction procedure  
161 was scaled down to  $\approx 0.8$  g of soil mass because of our small sample sizes. All final extractions  
162 were normalized to an oven-dry (105°C, 24 h) soil mass basis.

## 164 **Results and Discussion**

165 **General redox and pH conditions.** As noted in our earlier study, redox potentials in the soils  
166 exposed to Cr(VI) remained high (0.2 to 0.5 V), and pH values were in the range of 7.2 to 7.9  
167 (25). These redox and pH conditions persisted throughout the remainder of the experiment. It  
168 was also observed that gradients in Cr concentration and oxidation state within individual  
169 columns were insignificant at any given measurement time. Fairly homogeneous geochemical  
170 conditions continued to be observed within columns throughout the remainder of the study. For  
171 this reason, results are presented here in terms of column-averaged values of Cr and Mn  
172 oxidation states.

173 **Chromium oxidation state changes.** The normalized pre-edge peak intensity in the Cr  $\mu$ -  
174 XANES spectrum provided a measure of the fraction of the local total Cr occurring as Cr(VI),  
175 regardless of phase (aqueous, sorbed, solid). Overall, Cr  $\mu$ -XANES spectroscopy results showed  
176 decreases in Cr(VI) toward approximately steady-state values, or to detection limit ( $< 5$  mg kg<sup>-1</sup>).  
177 The observed trends reflect combined influences of initial Cr(VI) loading, OC addition, and  
178 oxidation of a fraction of the native soil organic carbon inventory (Figure 2). Chromate  
179 reduction occurred more rapidly and more completely with greater addition of OC, and less  
180 completely in the more heavily Cr(VI) loaded soil. Best fits to apparent first-order Cr(VI)  
181 reduction kinetics are shown in Figure 2, with parameters summarized in Table 1. Measured  
182 Cr(VI) fractions relative to their initial concentrations were least-squares fit to

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$$\frac{Cr(VI)}{Cr(VI)_0} = (Cr_{\infty}/Cr_0) + [1 - (Cr_{\infty}/Cr_0)] \exp(-kt) \quad (1)$$

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186 where  $k$  is the effective 1<sup>st</sup>-order rate constant,  $t$  is time, and  $Cr_{\infty}/Cr_0$  is the steady state fraction of  
187 unreduced Cr(VI). Simple first-order Cr(VI) reduction kinetics generally describe trends in the  
188 lower Cr soils better than in the heavily Cr loaded soils (Figure 2). All of the less contaminated  
189 soils had reduction to the point that Cr(VI) was undetectable by  $\mu$ -XANES ( $< 5$  mg kg<sup>-1</sup>) in 0.6  
190 to 3 years depending on the level of OC added (Figure 2a). The fact that complete reduction was  
191 observed even without OC addition suggests that this soil has the capacity to naturally attenuate  
192 Cr(VI) up to at least 256 mg kg<sup>-1</sup>. The ease with which soil organic matter reduces Cr(VI) has  
193 long been recognized, and is the basis of common assays for soil organic matter (35). In our  
194 previous work (25), Cr(VI) reduction in soils that receive no OC additions was attributed to  
195 about 3% of the native soil OC (1.0% of soil mass) that was oxidized through short-term Cr(VI)  
196 reduction reactions. However, it should be noted that the last data point from the  $\mu$ -XANES  
197 analyses of the +0 OC soil is suggestive of Cr(III) reoxidation. The average final Cr(VI)  
198 concentration measured in this soil by  $\mu$ -XANES spectroscopy is 8.7 mg kg<sup>-1</sup> (standard deviation  
199 = 12.8 mg kg<sup>-1</sup>), and this increase relative to the previously undetectable Cr(VI) levels at 3.2 and  
200 3.7 years is weakly significant ( $p = 0.25$ ). Although all of the soils with 256 mg kg<sup>-1</sup> Cr

201 exposure had relatively little Cr(VI) remaining at 4.6 years, the hot carbonate extractions still  
202 released 5 to 11% of the initially applied Cr(VI) (Table 2). The higher recovery of Cr(VI) from  
203 the lower Cr soils using the hot carbonate method might have resulted from oxidation of Cr(III)  
204 during the extraction by Mn(III,IV) (36), although lower extraction efficiency was observed in  
205 our higher Cr soils. The Cr(VI) fractions directly measured by  $\mu$ -XANES at the end of the  
206 experiment were lower for these soils, with the 4,000 mg L<sup>-1</sup> OC treatment having no detectable  
207 Cr(VI).

208 Although first-order Cr(VI) reduction kinetics roughly describe overall trends in all soils,  
209 distinct departures from monotonic reduction stand out in the soils having higher Cr  
210 concentrations (Figure 2b). One major difference from approximately monotonic transformation  
211 toward complete reduction was the incomplete extent of reduction achieved in the soils exposed  
212 to highest Cr levels, even after nearly 5 years (Figure 2b). The very high concentration of Cr(VI)  
213 added (2,560 mg kg<sup>-1</sup>) clearly exceeded the reduction capacity of these soils, even with addition  
214 of the highest level of OC. However, extractable Cr concentrations were less than expected  
215 based on the final  $\mu$ -XANES measurements (Table 2). Conversely, as mentioned previously,  
216 more Cr was recovered in extractions of soils with lower initial Cr(VI) exposures than indicated  
217 by  $\mu$ -XANES spectroscopy. Although differences between final Cr(VI) concentrations  
218 determined by  $\mu$ -XANES spectroscopy and by hot carbonate/hydroxide extraction appear to  
219 depend on the level of initial Cr(VI) loading, an explanation for the disparity was not identified.  
220 The lower extraction-based recovery of Cr(VI) in the high Cr soils is especially puzzling because  
221 the hot carbonate digestion has been shown to yield good spike recoveries of very inert PbCrO<sub>4</sub>  
222 (34).

223 Another important variation from monotonic reduction demonstrated is Cr(III)  
224 reoxidation in the most heavily Cr-contaminated soils. In the higher Cr(VI) soils treated with 0  
225 and 800 mg L<sup>-1</sup> OC solutions, transient reoxidation of newly reduced Cr(III) was measured at 1.1  
226 years (data points encircled by dashed lines in Figure 2b). The reoxidation amounted to  
227 increases in Cr(VI) concentrations of 260 to 420 mg (kg soil)<sup>-1</sup>, and were highly significant ( $p =$   
228 0.001) in both soils. Reoxidation of Cr(III) was also measured at the end of the experiment in  
229 the high Cr soil treated with the 4,000 mg L<sup>-1</sup> OC solution. Although the variability in  
230 reoxidation was larger in this last data point (standard deviation = 320 mg (kg soil)<sup>-1</sup>), the  
231 increase in Cr(VI) concentration of 220 mg (kg soil)<sup>-1</sup> relative to the previous measurement at 3.8  
232 years was also highly significant ( $p = 0.001$ ). The apparent Cr(III) reoxidation measured at 2.26  
233 years in the high Cr soil treated with 0 and 800 mg L<sup>-1</sup> OC had weak ( $p = 0.1$ ), and no ( $p > 0.25$ )  
234 statistically significant, respectively. Given the low solubilities of stable Mn(IV) oxides and  
235 precipitated Cr(III) solids, and probably minimal direct contact between these solids, other  
236 factors must be operating when Cr(III) oxidation is observed. Other studies have shown that  
237 during microbially mediated Cr(VI) reduction, significant fractions of newly reduced Cr(III) can  
238 remain in solution in organo-complexes, and thereby diffuse to Mn(IV) surfaces and reoxidize  
239 (37, 38).

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	Cr(VI) <sub>0</sub> mg kg <sup>-1</sup>	<i>k</i> s <sup>-1</sup>	1 <sup>st</sup> -order reduction fitting		
			Cr(VI) <sub>∞</sub> mg kg <sup>-1</sup>	Cr <sub>∞</sub> /Cr <sub>0</sub>	rmsd
Low Cr, +0 OC	256	5.7x10 <sup>-8</sup>	8	0.03	0.059
Low Cr, +800 mg/L OC	256	8.4x10 <sup>-8</sup>	0	0.00	0.030
Low Cr, +4,000 mg/L OC	256	1.3x10 <sup>-7</sup>	0	0.00	0.044
High Cr, +0 OC	2,560	1.8x10 <sup>-8</sup>	1,590	0.62	0.064
High Cr, +800 mg/L OC	2,560	1.6x10 <sup>-8</sup>	1,450	0.57	0.077
High Cr, +4,000 mg/L OC	2,560	4.6x10 <sup>-8</sup>	294	0.12	0.046

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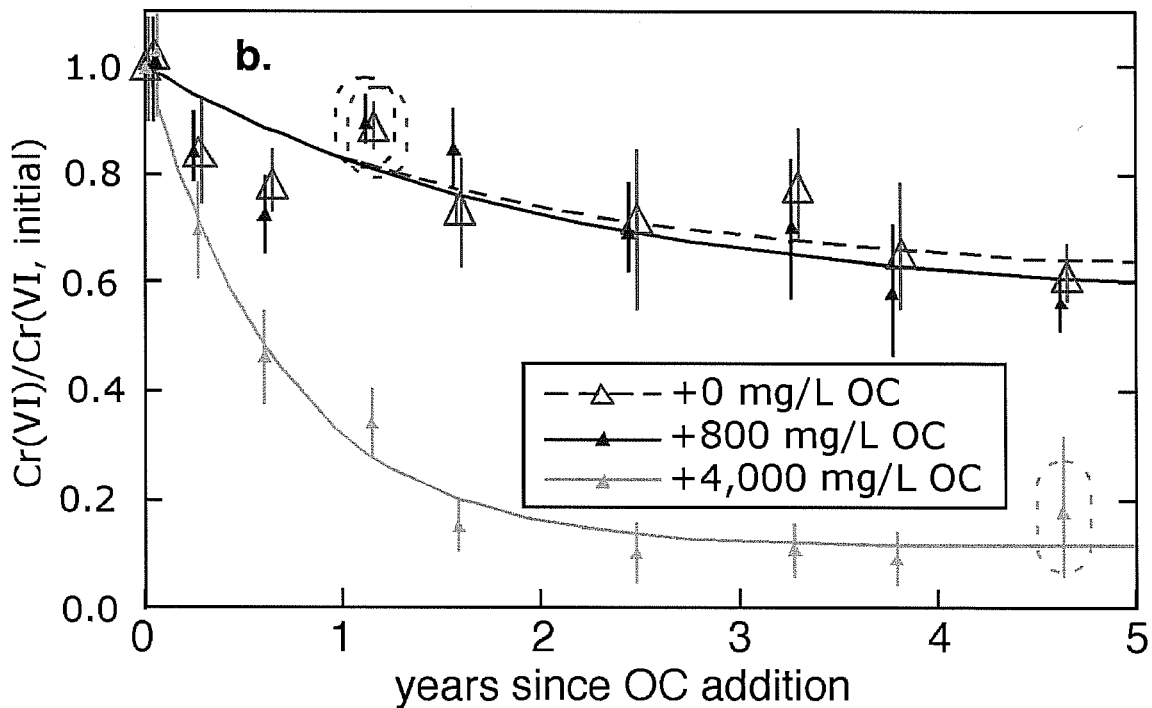
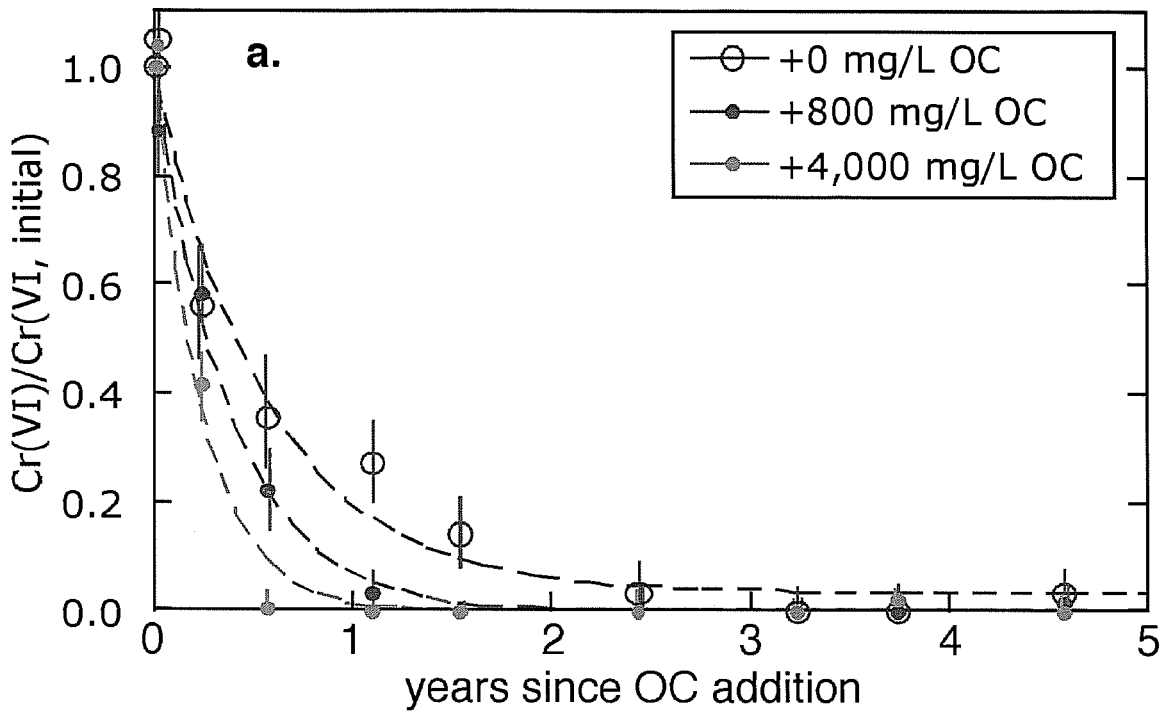
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**Table 1.** Fits of 1<sup>st</sup>-order Cr(VI) reduction rates to time trends in soils measured by  $\mu$ -XANES spectroscopy. Cr(VI)<sub>0</sub> denotes the initial Cr(VI) concentration in soils, *k* is the effective 1<sup>st</sup>-order rate constant (s<sup>-1</sup>), Cr(VI)<sub>∞</sub> is the fitted steady-state Cr(VI) concentration, Cr<sub>∞</sub>/Cr<sub>0</sub> is the fitted steady-state relative Cr(VI) concentration, and rmsd is the root mean square deviation between measured and fit Cr(VI) concentrations relative to Cr(VI)<sub>0</sub>.





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**Figure 2.** Time trends of Cr(VI) concentrations, relative to the initial contamination level in soils with initial Cr(VI) concentrations of (a) 256 mg kg<sup>-1</sup>, and (b) 2,560 mg kg<sup>-1</sup>. Data points encircled by dashed lines are for Cr(III) reoxidation significant at p = 0.001. Curves are least-squares fits for 1<sup>st</sup>-order Cr(VI) reduction toward final (finite or zero) concentrations.

	Cr(VI) <sub>0</sub>	$\mu$ -XANES	Cr(VI)/Cr(VI) <sub>0</sub>	
	mg/kg		Extract, wet	Extract, dry
Low Cr, +0 OC	256	0.03	0.07	0.07
Low Cr, +800 mg/L OC	256	0.02	0.11	0.09
Low Cr, +4,000 mg/L OC	256	0.00	0.08	0.05
High Cr, +0 OC	2,560	0.61	0.27	0.24
High Cr, +800 mg/L OC	2,560	0.57	0.24	0.22
High Cr, +4,000 mg/L OC	2,560	0.18	0.05	0.04

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**Table 2.** Chromium (VI) fractions in soils at the end of the experiment (4.62 years), relative to initially added Cr(VI). Cr(VI)<sub>0</sub> denotes the initial soil Cr(VI) concentration. Methods used are  $\mu$ -XANES spectroscopy (normalized Cr(VI) pre-edge peak height) and the hot carbonate/hydroxide extraction (applied on wet and air-dried samples).

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**Manganese redox changes.** The possibility that soils in these columns had Mn(IV) available to reoxidize Cr(III) was examined through Mn K-edge  $\mu$ -XANES measurements obtained during later stages of this study (1.5 to 4.6 years). For comparison,  $\mu$ -XANES spectra were also collected on moist Altamont soil incubated over 0.9 years without exposure to Cr(VI) or additional OC. This latter sample was considered representative of Mn redox status in the original uncontaminated soil. Comparisons among all Mn K-edge spectra, despite measurements obtained at different times, was permitted through consistent calibration with the Mn(VII) pre-edge peak energy, as described previously.

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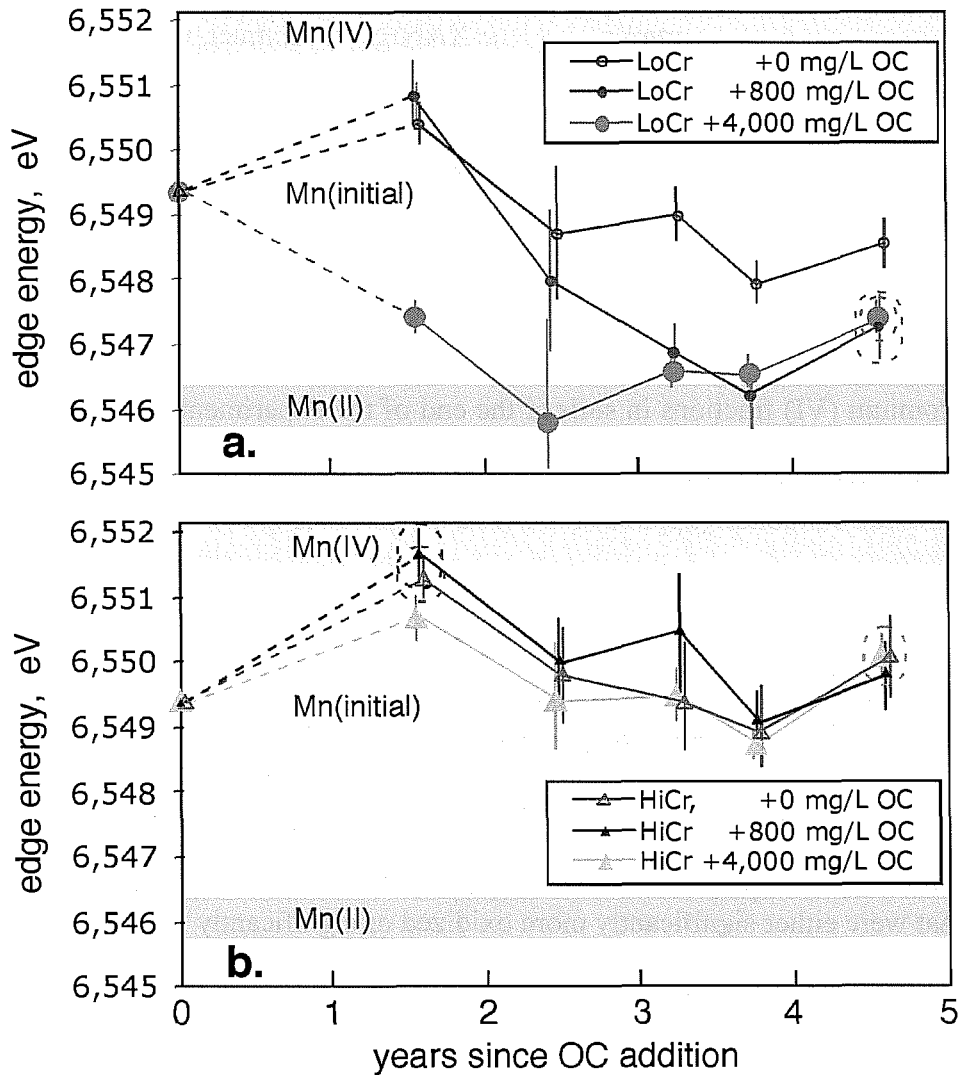
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Relative to the unexposed Altamont soil, the Cr-contaminated soils had Mn redox states at 1.5 years that were either significantly more oxidized or significantly more reduced (Figure 3). Most of the soils were in the group with Mn K-edge energies shifted higher than those of the original soil, indicating net Mn oxidation resulted from Cr(VI) exposure. The two soils showing greatest Mn(IV) fractions were those with high Cr that received no or intermediate levels of OC. These high Cr soils with highest Mn(IV) fractions were in fact the only soils in which Cr(III) reoxidation was detected during the previous set of Cr  $\mu$ -XANES analyses (1.1 years), and exemplify the importance of tracking the redox status of both elements. The stability of reduced Cr requires supply of electron donor sufficient to also reduce Mn(IV). The one exception to the net Mn oxidation measured at 1.5 years was found in the soil that received the lower Cr(VI) exposure and highest OC input. The Mn  $\mu$ -XANES spectra in that soil were shifted to significantly lower absorption edge energies, showing that the high level of added OC not only effectively reduced Cr(VI), but also reduced Mn to Mn(II). Subsequent  $\mu$ -XANES measurements showed that this low Cr(VI) soil with highest OC had its Mn fully reduced to Mn(II) by 2.4 years. However, Mn in this soil gradually reoxidized back toward its original intermediate redox status. Mn  $\mu$ -XANES of the low Cr soil treated with the intermediate level of OC showed a gradual reduction to Mn(II) by 3.7 years, followed by Mn reoxidation. The collective set of Mn  $\mu$ -XANES measurements on all soils appears to indicate a gradual stabilization of Mn redox status toward intermediate values similar to that of the original soil. The labile nature of Mn redox status, with sensitivity to oxidation by dissolved O<sub>2</sub> (39) and transformations that are accelerated by microbes (40-42), will thus exert controls on long-term Cr redox cycling in soils.

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296 **Figure 3.** Time trends of Mn K-edge energies of (a.) low Cr, and (b.) high Cr-contaminated soils  
 297 treated with different amounts of OC. The time zero value is for the original soil, without  
 298 exposure to Cr or additional OC. Edge energies are taken at the half step height, and compared  
 299 with values from Mn(II) and Mn(IV) standards. The ranges of Mn K-edge energies measured on  
 300 standards and on the original soil are indicated by the vertical ranges of the horizontal bands.  
 301 Error bars on data points represent  $\pm 1$  standard deviation. Data points circled at 1.5 years  
 302 are associated with soils that showed Cr(III) reoxidation at 1.1 years. Data points circled at 4.6 years  
 303 show Mn reoxidation significant at  $p = 0.001$ , relative to the preceding measurement (3.8 years).  
 304

305 **Implications for long-term stability of Cr(III).** Although the transformations of Cr(VI) in  
 306 contaminated soils is known to depend on Mn and available OC (6, 43, 44), this study shows that  
 307 changes in redox status can exhibit reversals and require years to stabilize. Extrapolation from  
 308 short-term reduction rates can yield overestimates of the extent to Cr reduction, particularly  
 309 when the level of Cr(VI) contamination is high. In heavily Cr-contaminated soils, the quantities  
 310 of OC or other reducing agents required to stabilize Cr(III) also need to reduce Mn(IV,III). Over

311 long time scales, sustained Cr and Mn reduction in soils can require a large supply of electron  
312 donor, perhaps most practically in the form of decomposing plant biomass (45). When the  
313 electron donor supply becomes limiting, Mn reoxidation back to conditions characteristic of the  
314 given soil environment can drive Cr reoxidation. When oxidizing conditions are established, a  
315 broad range of long term conditions are possible for Cr(VI) depending on prevailing  
316 biogeochemical and hydrological conditions. Possible solubility-controlling Cr(VI) phases  
317 include coprecipitates with barite (21, 46), and precipitation of chromate jarosite (47). When  
318 such solubility controls are lacking, the high capacity of Mn(IV,III) oxides to oxidize Cr(III) and  
319 releasing moderately high levels of Cr(VI) into porewaters becomes possible (48). Ultimately,  
320 magnitudes and directions of soil water fluxes will determine potential Cr exposure pathways by  
321 transporting reoxidized Cr(VI) down into underlying groundwaters or up to the soil surface.

322

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341

### 342 **Supporting Information Available**

343 A diagram of the soil column is presented in Figure S1. This material is available free of charge  
344 via the Internet at <http://pubs.acs.org>.

345

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