



# Understanding the Natural Mechanisms for Hexavalent Chromium Mobilization in Groundwater



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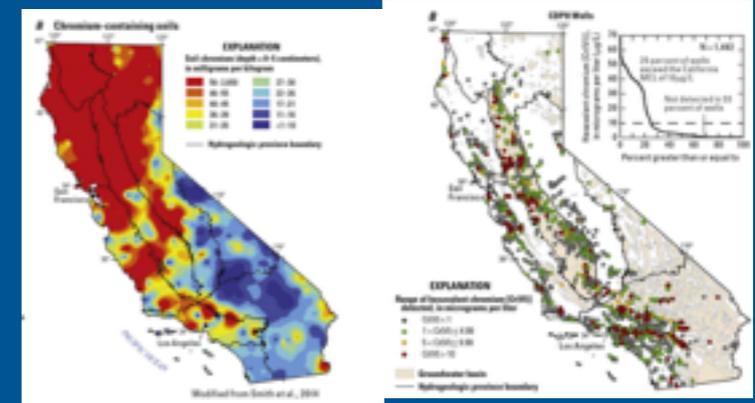
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## Research Question:

Does the presence of Mn(II) in groundwater affect the oxidation of Cr(III) to Cr(VI)? Does it affect the interaction of MnO<sub>2</sub> and Cr(III) containing minerals?

## Background:

- Hexavalent chromium, or Cr(VI), increases the risk of cancer, and kidney/ liver failure.
- Cr(VI) contamination in groundwater used to come from anthropogenic sources of Cr(VI)
- Natural sources of Cr(VI) in groundwater were not considered significant enough to cause concern. This is because:
  - Cr is found in abundance in certain soil and rock types, the vast majority of it is non-toxic Cr(III).
  - Manganese oxides are the primary oxidants of Cr(III) to Cr(VI) at environmentally relevant conditions.
  - Both manganese oxides and Cr(III) minerals' dissolution and subsequent reaction is kinetically unfavorable.
- In recent years elevated levels of Cr(VI) have been found far from predicted sources



Comparison between areas of high Cr in California soils with wells with Cr(VI) levels above the EPA limit

## Chromium Mineral:

$Cr_{0.25}Fe_{0.75}(OH)_3$	$Cr_{0.25}Fe_{0.75}(OH)_3$
$Cr(OH)_3$	$Cr(OH)_3$
$Cr_{0.25}Fe_{0.75}(OH)_3$	$Cr_{0.25}Fe_{0.75}(OH)_3$
$Cr(OH)_3$	$Cr(OH)_3$
$Cr_{0.25}Fe_{0.75}(OH)_3$	$Cr_{0.25}Fe_{0.75}(OH)_3$
$Cr(OH)_3$	$Cr(OH)_3$

## Treatment:

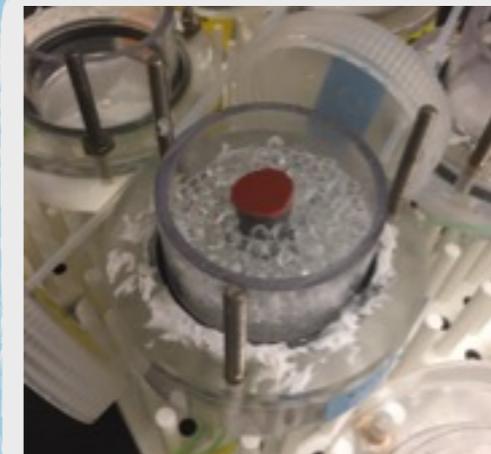
Birnessite in Aggregate  
No Mn(II) in Groundwater

No Birnessite in Aggregate  
Mn(II) in Groundwater

No Birnessite in Aggregate  
No Mn(II) in Groundwater  
(Control)

## Materials and Methods:

- Synthesized two types of chromium minerals commonly found in the environment:  $Cr(OH)_3$  and  $Cr_{0.25}Fe_{0.75}(OH)_3$ , and birnessite ( $MnO_2$ )
- Minerals were then coated onto fine quartz sand grains, rinsed, and allowed to dry
- Chromium minerals were suspended with birnessite in a cylindrical agar gel aggregate in a molar ratio of 10:1.
- This cylinder was surrounded by 4.5mm glass beads in a flow-through reactor. The beads simulated advective flow regions in porous media.
- Groundwater media was pumped through the reactors at 0.6mL per hour
- Each chromium mineral was run in duplicate, and each mineral was treated with Mn in one of three ways: in four reactors, birnessite powder was mixed directly into the aggregate, in the next four, 0.23mM Mn(II) was present in the groundwater media, and in the last four Mn was not present in either the aggregate or the groundwater media. The reaction was allowed to proceed for 20 days, with Cr(VI) diffusing out of the aggregate, where the oxidation was taking place, and into the advective flow. Samples were taken every 4 hours for the first 40 time-points, then reduced to once a day for a total of 20 days.
- These samples were then diluted by a factor of 3 in 2% Nitric Acid and analyzed for several redox active metals, including Cr, on an ICP-OES.

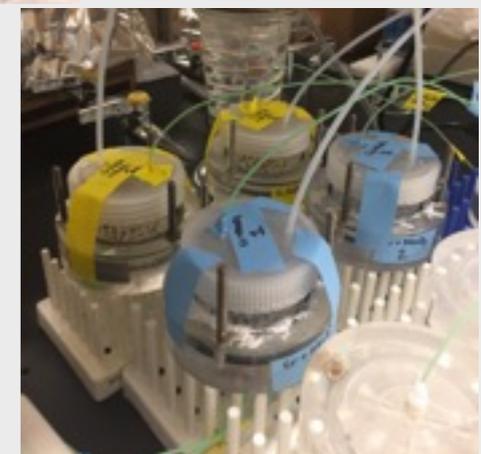


View of the inside of a reactor:

- Red dot is the cap of the aggregate
- Beads surround aggregate to provide structural support

4 aggregates once fully set up:

- White tube going into top provides aeration
- Green tube pulls sample out at same rate as is being pumped in





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## Results:

Our analysis focuses on the second and third treatments: they are directly comparable because the sands used in those aggregates were made at the same time.

- There was an initial spikes in Cr(VI) in every reactor
- Spikes in reactors that had Cr(OH)<sub>3</sub> spiked (4.5μm and 3.5μm peaks for Mn(II) reactors and No Mn(II) reactors respectively) much higher than the reactors with Cr<sub>0.25</sub>Fe<sub>0.75</sub>(OH)<sub>3</sub> (1.6μm and 2.1μm peaks for Mn(II) reactors and No Mn(II) reactors respectively).
  - This is largely due to the difference in solubility between the two minerals. Cr(OH)<sub>3</sub> has a higher solubility than Cr<sub>0.25</sub>Fe<sub>0.75</sub>(OH)<sub>3</sub>, allowing it to dissolve and subsequently oxidize at a higher rate than the Cr<sub>0.25</sub>Fe<sub>0.75</sub>(OH)<sub>3</sub> minerals.

- Cr(OH)<sub>3</sub> reactors:
  - Ones without Mn(II) had a lower peak of Cr(VI) than the reactors with Mn(II) in the groundwater.
  - This was as expected, as we predicted that Mn(II) could be oxidizing and driving some oxidation of the Cr minerals.
- Cr<sub>0.25</sub>Fe<sub>0.75</sub>(OH)<sub>3</sub> reactors:
  - the exact opposite trend was seen: the reactors without Mn(II) peaked higher than the reactors with Mn(II).
  - We hypothesize that this is due to surface passivation (or the reduction of a mineral surface's reactivity) caused by a precipitation of manganese carbonates, which are produced by a reaction with the Mn(II) with carbonates in the groundwater media.

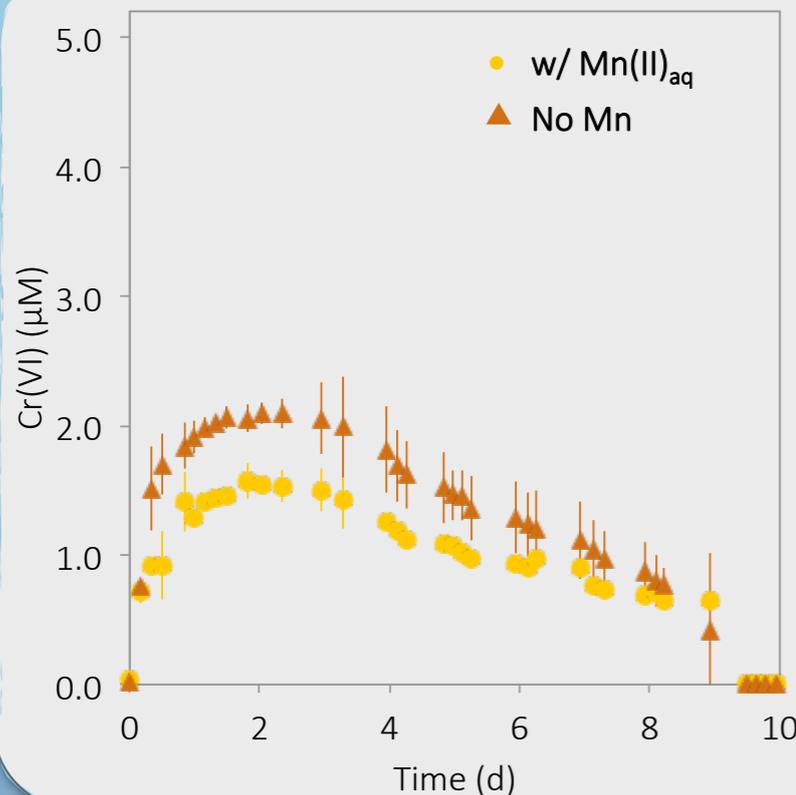


Figure 4: Mobilization of Cr(VI) over time in reactors with Cr<sub>0.25</sub>Fe<sub>0.75</sub>(OH)<sub>3</sub> coated sands

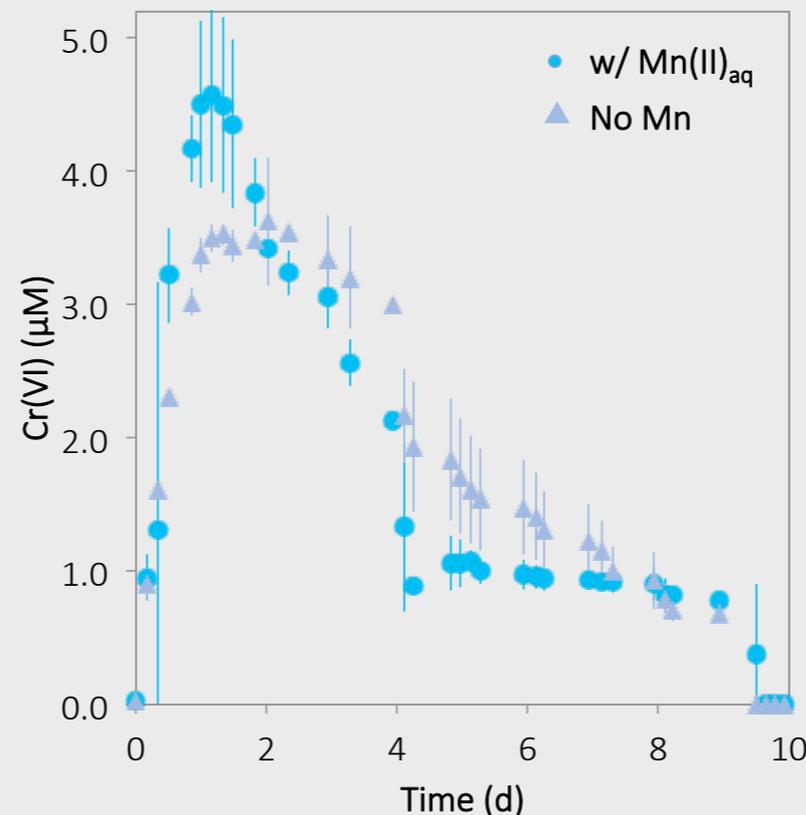


Figure 5: Mobilization of Cr(VI) over time in reactors with Cr(OH)<sub>3</sub> coated sands

## Future Work:

- We want to determine the unintended source of the Cr(VI) being oxidized
  - We have tested for the pH of the agarose, the temperature of the agarose, and the presence of light
  - Light has the biggest affect on how much Cr(VI) was mobilized in the aggregate
- We are currently running tests with a similar set-up to the tests done this summer.
  - One batch (which is a set of 4 reactors, two with Cr<sub>0.25</sub>Fe<sub>0.75</sub>(OH)<sub>3</sub> and two with Cr(OH)<sub>3</sub>) has birnessite, and the other set has only birnessite.
  - We are also running controls that have iron minerals, but no Mn in the reactors
- These experiments will be re-run in dark conditions, which better simulate the conditions of an aquifer