International Symposium on Bioremediation and
Sustainable Environmental Technologies
Reno, Nevada, June 27-30, 2011

BIOLOGICAL BENCH-SCALE TREATABILITY TESTS FOR THE REDUCTION OF NATURALLY OCCURRING HEXAVALENT CHROMIUM

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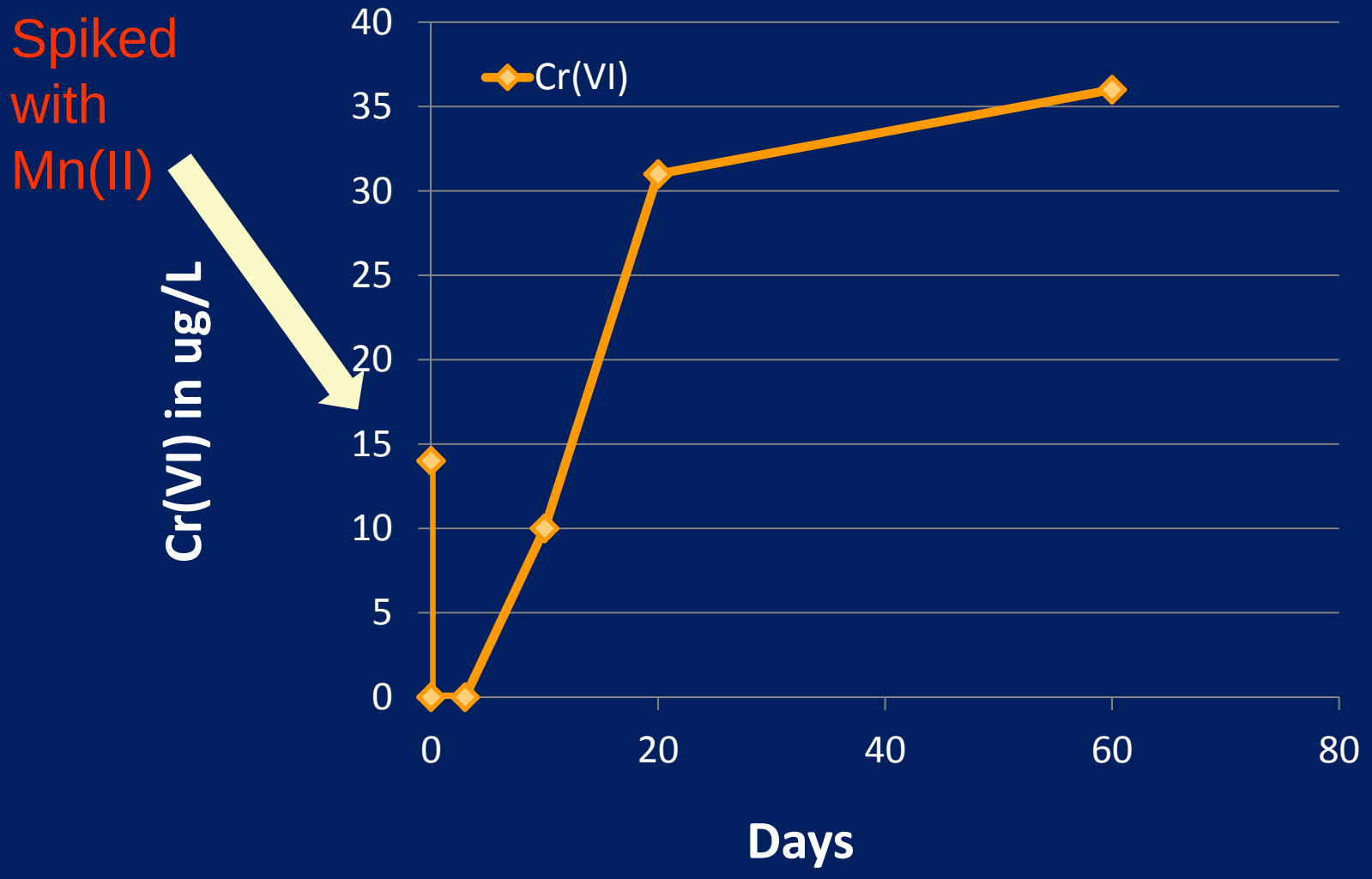
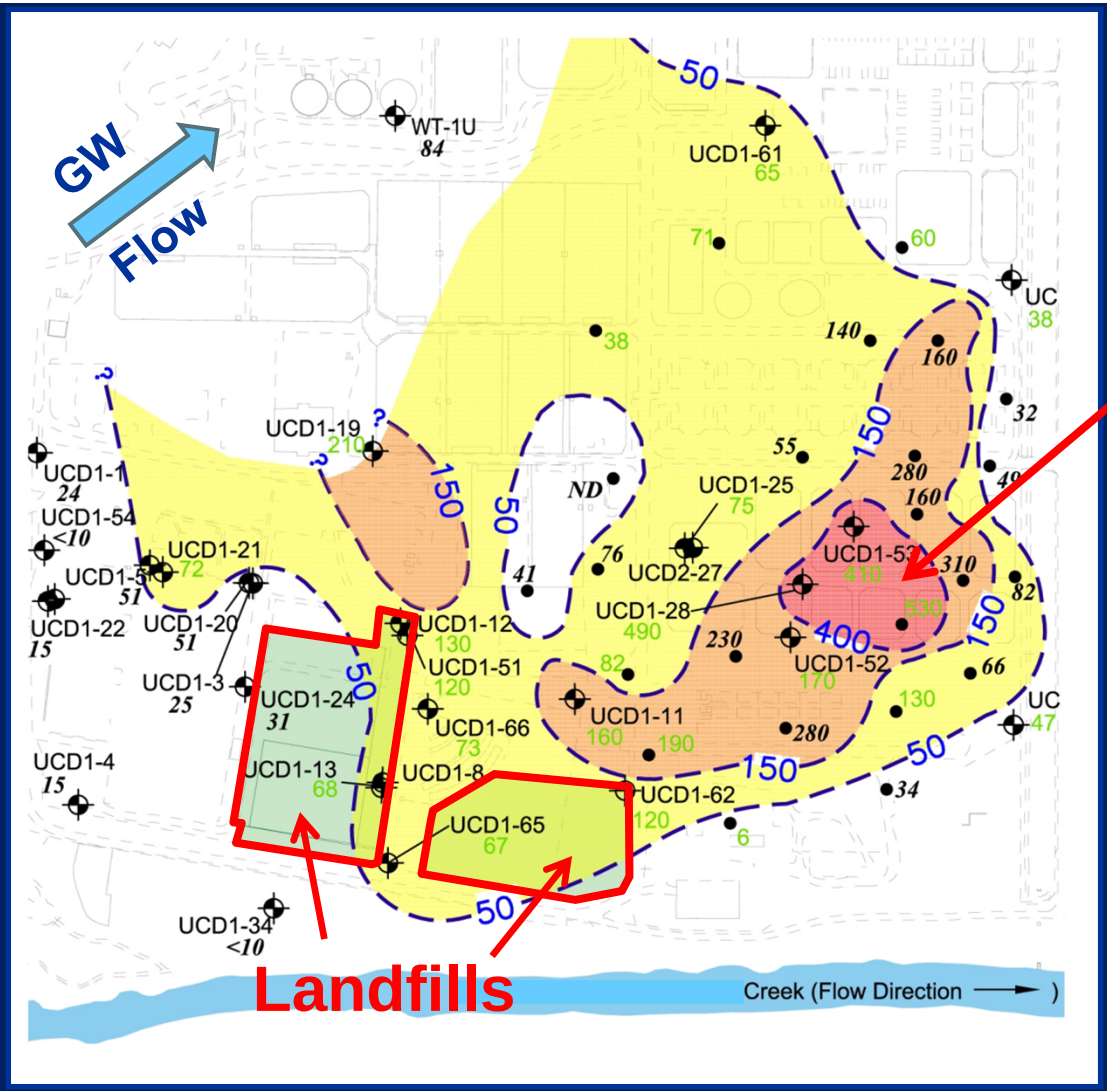
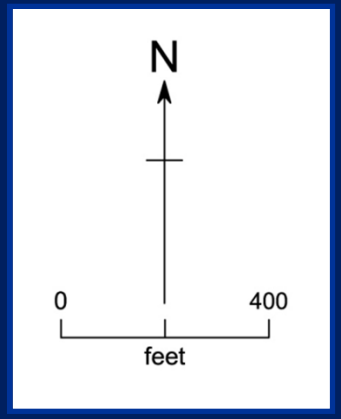
Major result: Mn can oxidize Cr(III) to Cr(VI) under aerobic conditions



Site in Sacramento Valley: Cr Hotspot downgradient of two inactive landfills



Cr(VI) Hotspot
(400 - 613 µg/L)



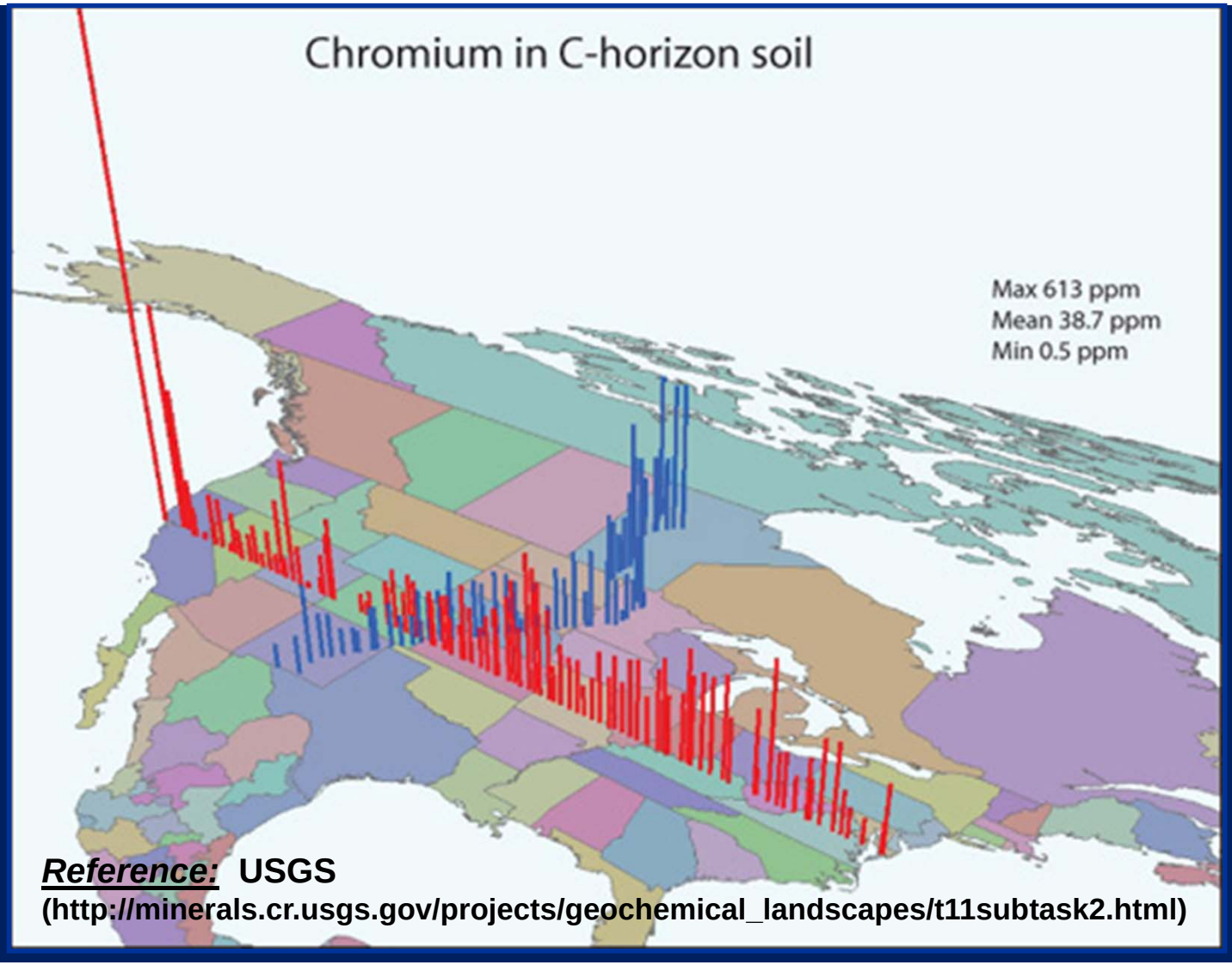
Is the Cr of anthropogenic origin?

- Disposal of Cr-contaminated materials in the landfills
- Unlikely:
  - Only 7 of 930 Site soil samples > Site background Cr
  - Records, Site investigations suggest little Cr was disposed of

Or, is the Cr naturally occurring?

- Site background Cr: up to 306 mg/kg in soil
- Site background Mn: up to 1,900 mg/kg in soil
- Site sediments are derived from ultramafic rocks (e.g., serpentinite) of the Coast Range, which are especially high in Cr, Mn, Ni

USGS study found Cr soil concentrations in Sacramento Valley > 400 mg/kg…

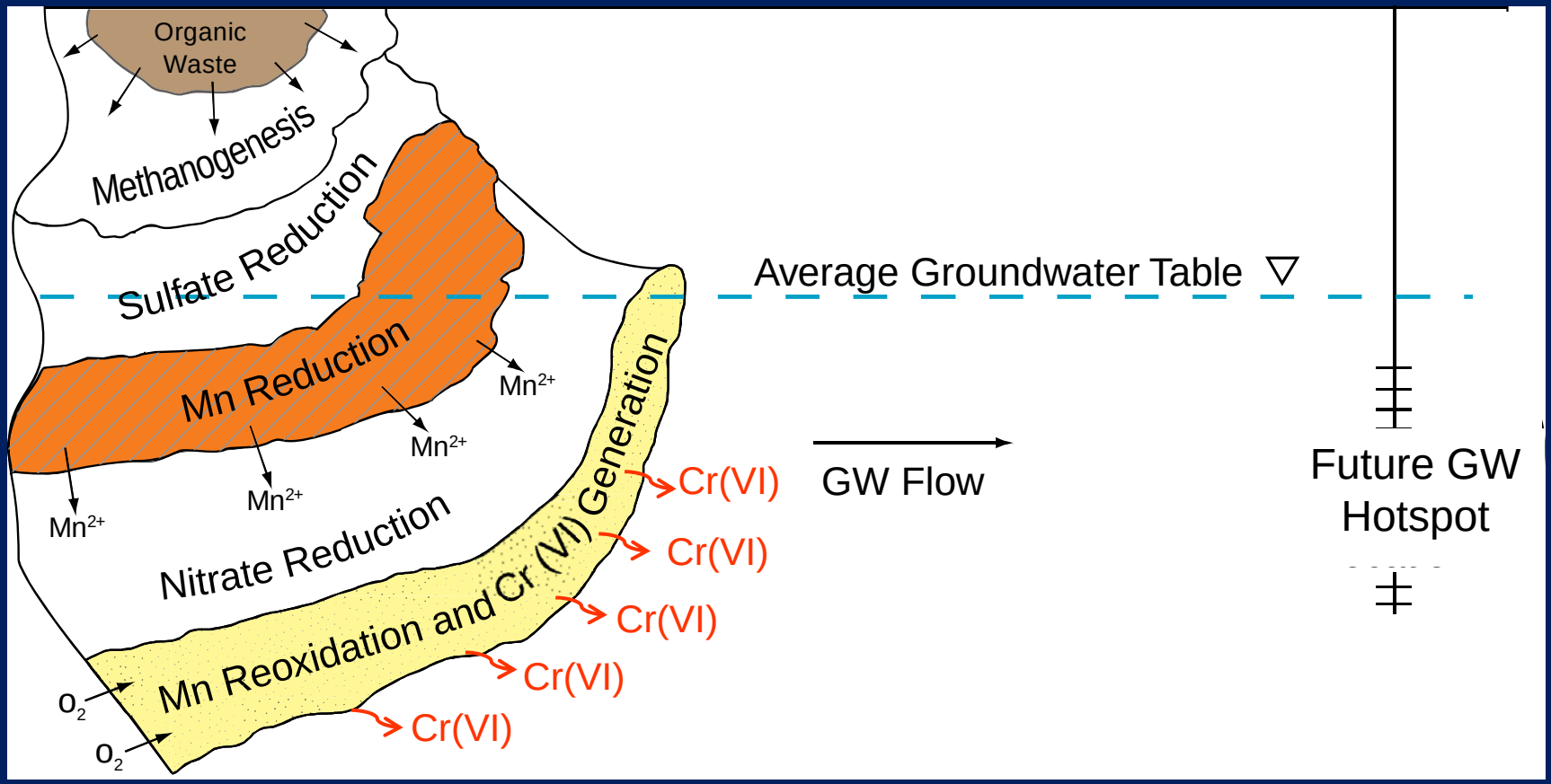


Reference: **USGS**
(http://minerals.cr.usgs.gov/projects/geochemical_landscapes/t11subtask2.html)

…and “particularly high” Cr in Western Sacramento Valley groundwater

- USGS (Morrison et al., 2009):
  - Average Cr = 16.4 µg/L Cr(VI)
  - 30-50 µg/L Cr common
- Cr(VI) up to 180 µg/L reported near, but not impacted by, the Site
- Significant variations in Cr concentrations reported over small distances

Previous work suggested landfills changed Site geochemistry, releasing naturally occurring Cr

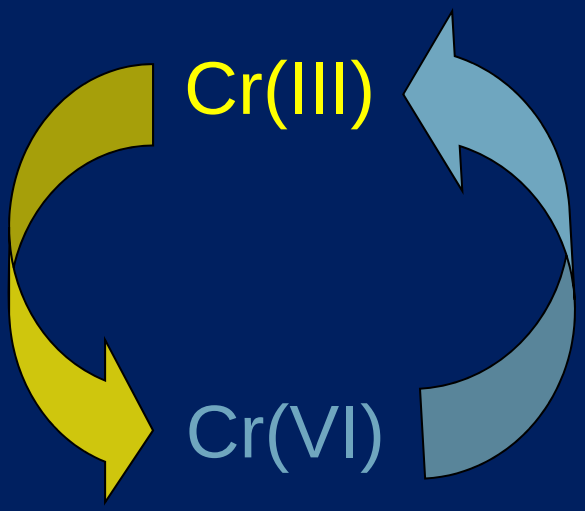


Time frame:1940's-1970's

Mn-oxides are the only major, naturally occurring oxidants of Cr(III)

Oxidation by:

- Mn-oxides
- O_2 at pH > 9.2



Reduction by:

- Organic matter
- Bacteria
- Ferrous iron/sulfides

The objectives of the present work were:

1. To determine feasibility of in situ, biological reduction of Cr(VI) at this Site
2. To determine if dissolved Mn produced under reducing conditions has the potential to re-oxidize naturally occurring Cr(III), when the aquifer returns to aerobic conditions.

Feasibility of biological reduction of Cr(VI) was evaluated in a microcosm study

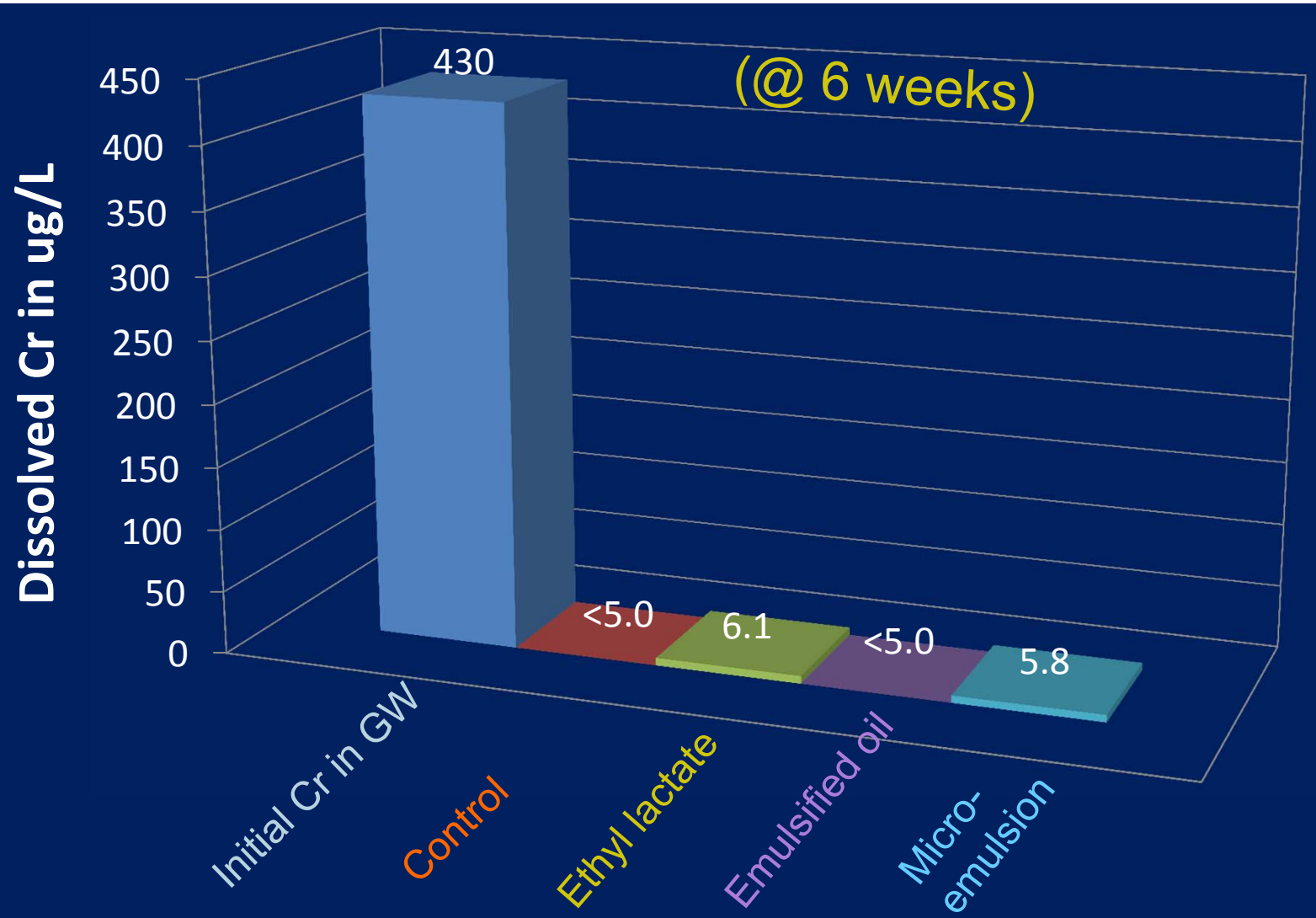
- All microcosms contained:
  - 530 mL Site groundwater (Cr=430 µg/L)
  - 177 g Site soil (Cr=150 mg/kg)
  - Resazurin redox indicator

Duplicate microcosms were amended with commercially available substrates

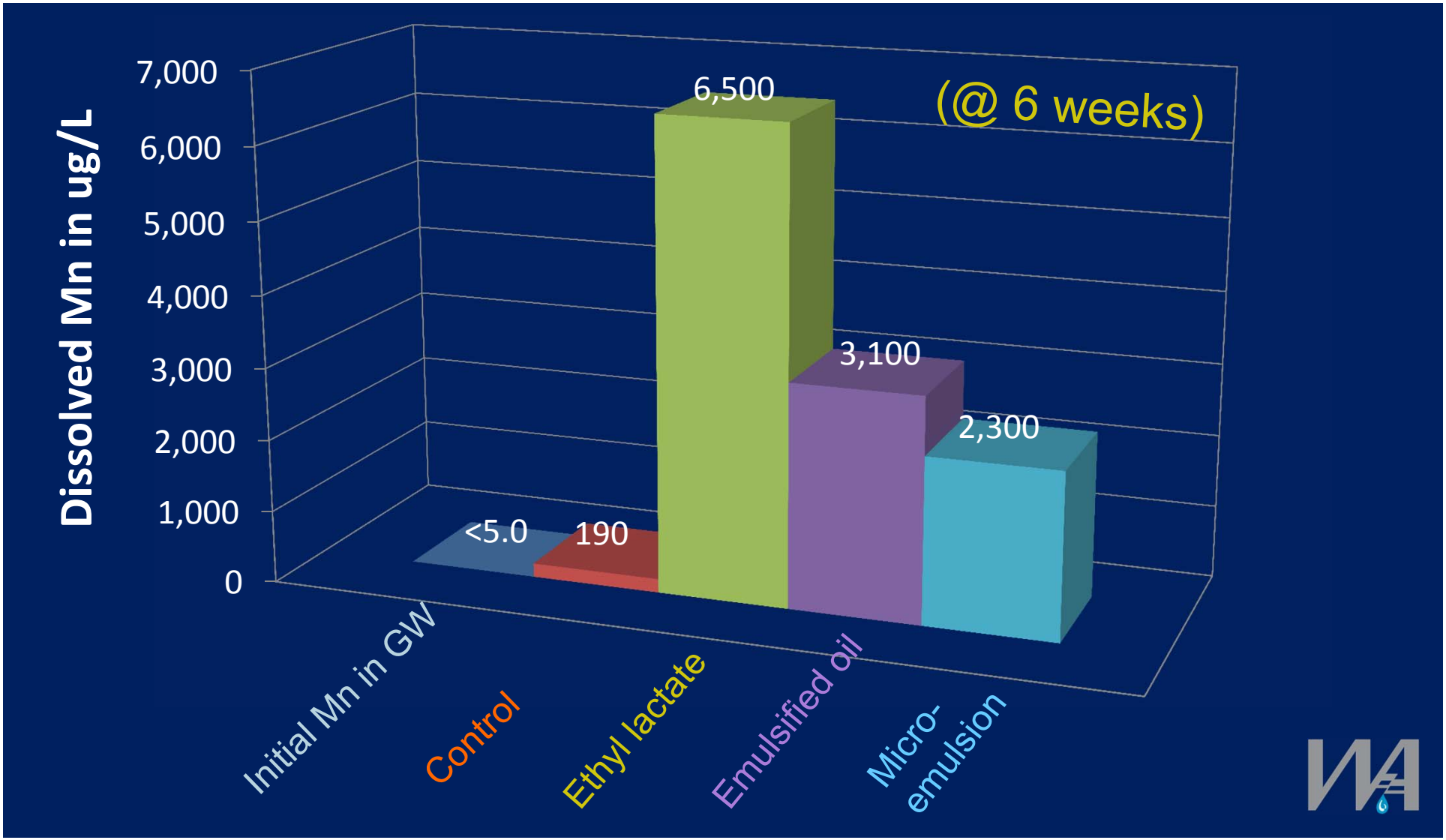
- Control: no carbon source (not sterilized)
- Ethyl lactate
- Emulsified Soybean oil
- Microemulsion

} @ 5x stoichiometric demand

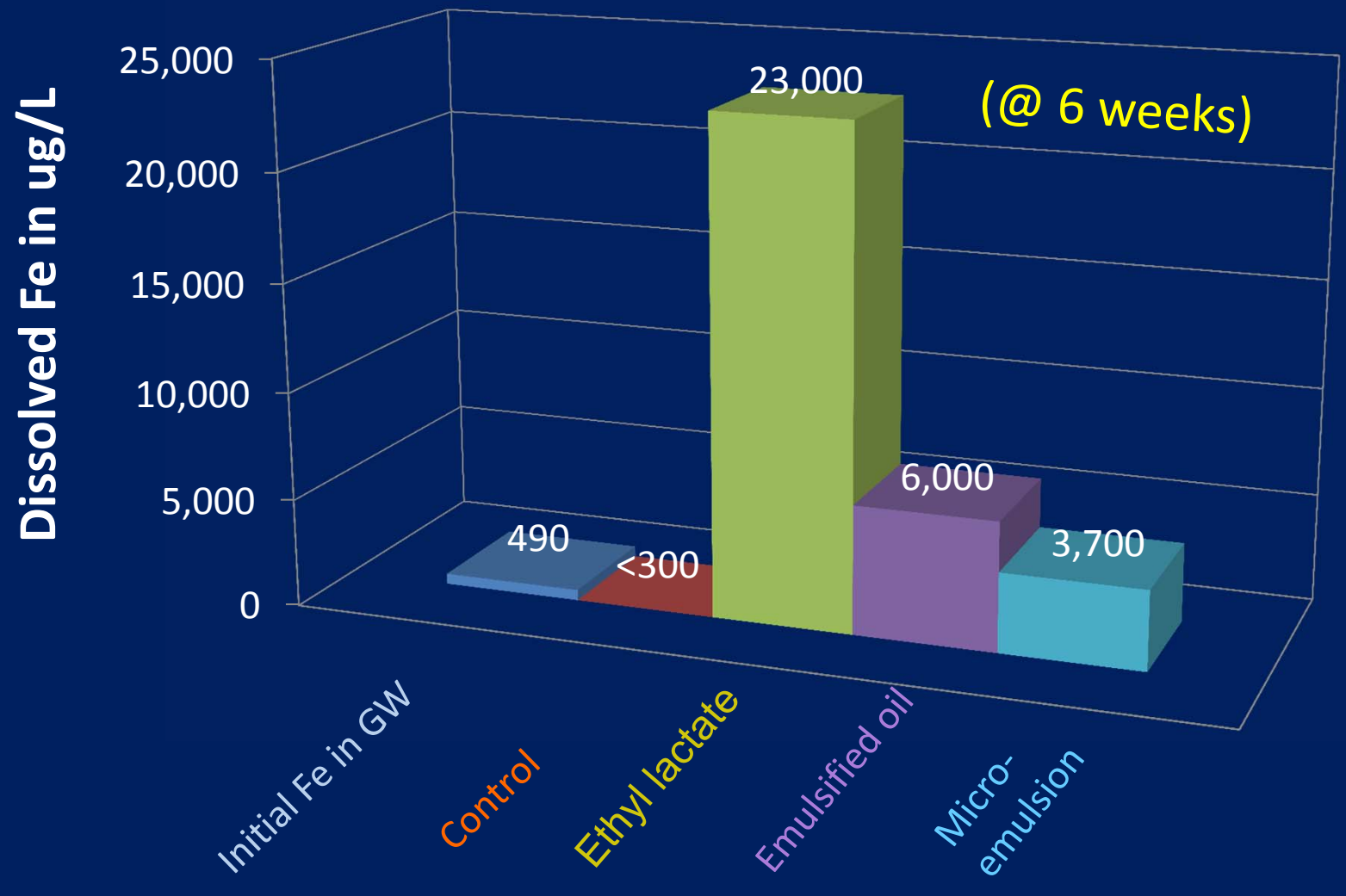
All substrates promoted Cr reduction, but Cr was also reduced in control



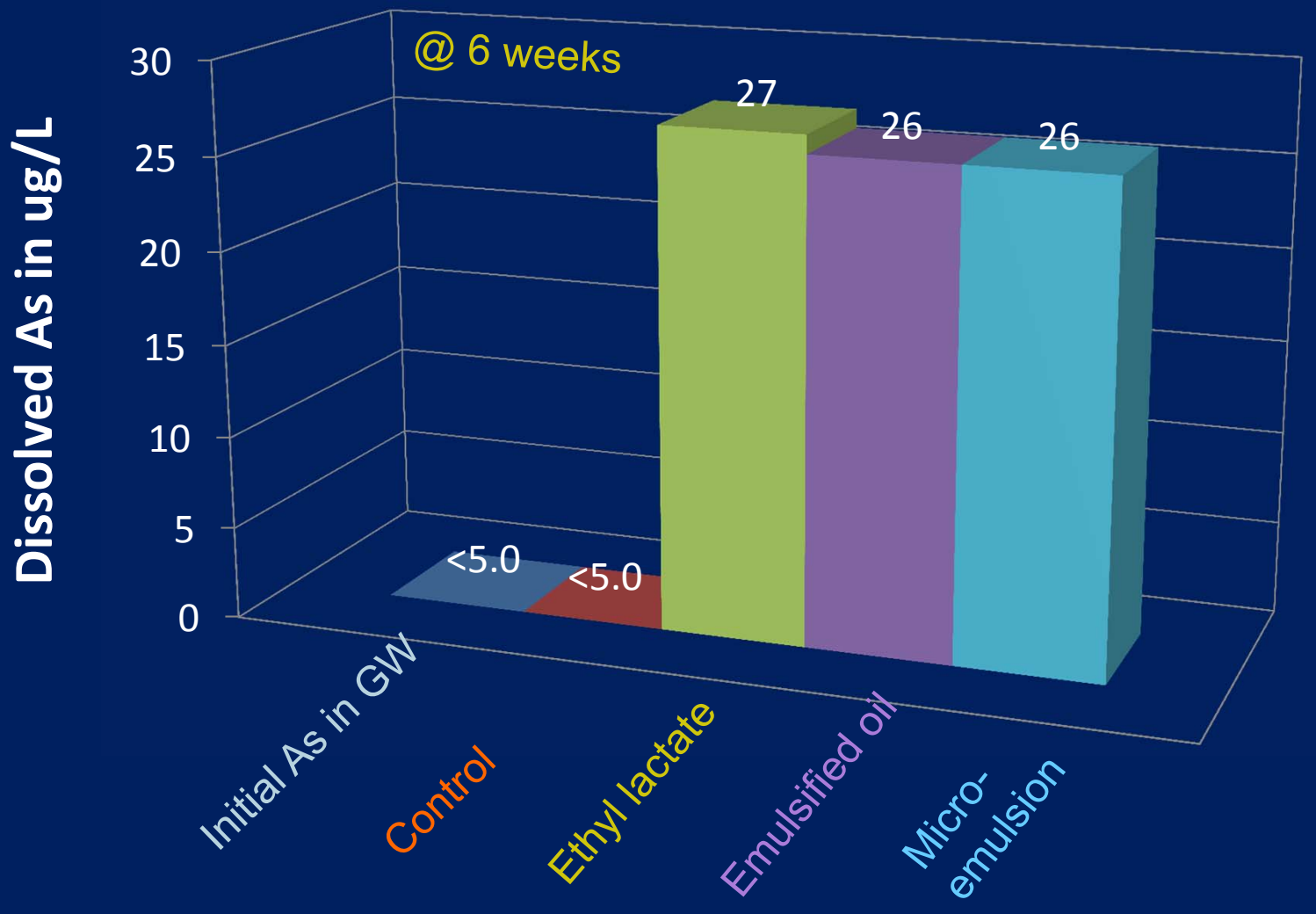
Manganese was solubilized in all treatments receiving substrates…



…as was iron…


Dissolved Fe in ug/L
25,000
20,000
15,000
10,000
5,000
0
490
<300
23,000
6,000
3,700
(@ 6 weeks)
Initial Fe in GW
Control
Ethyl lactate
Emulsified oil
Micro-emulsion

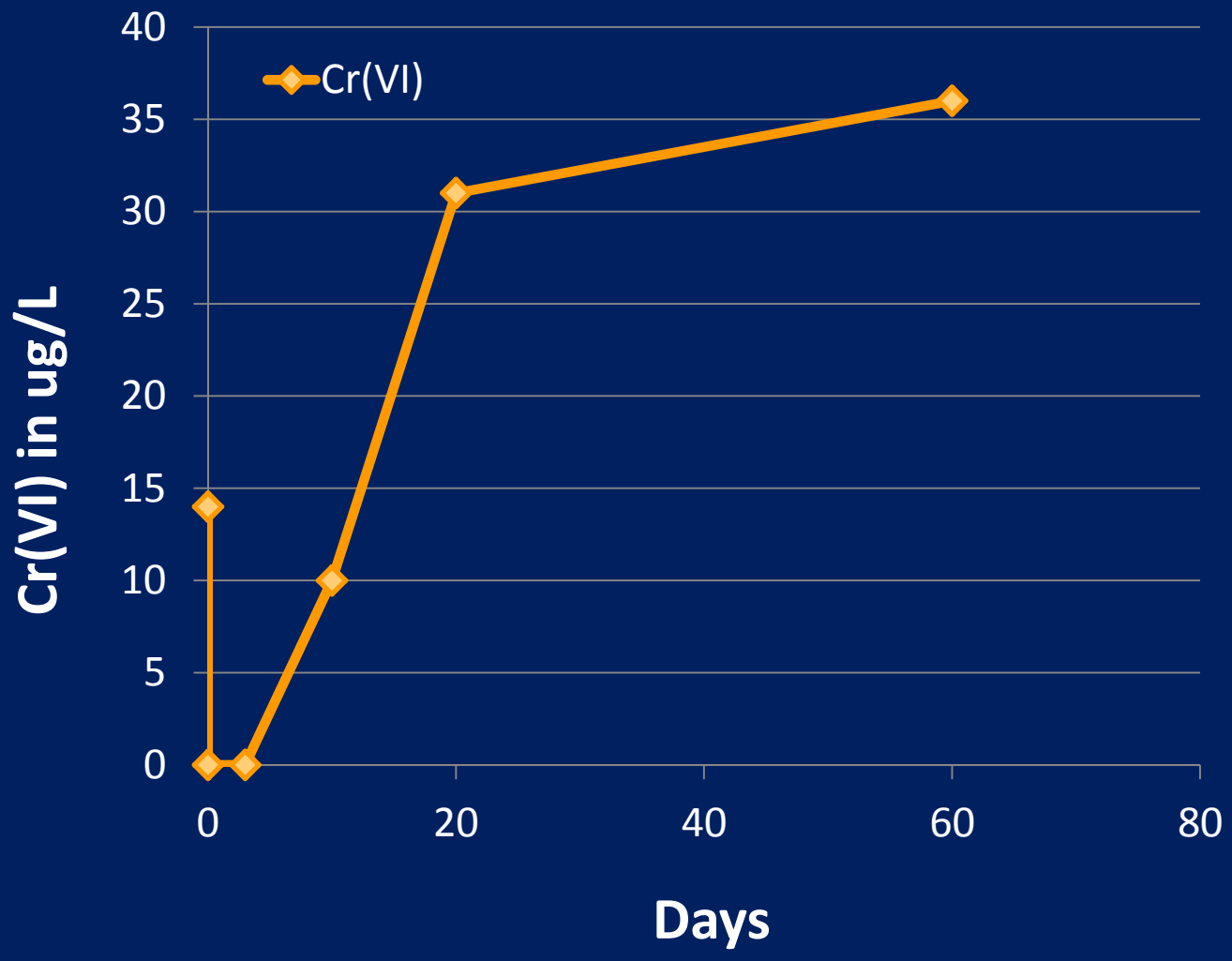
…and arsenic


@ 6 weeks
Dissolved As in ug/L
30
25
20
15
10
5
0
27
26
26
<5.0
<5.0
Initial As in GW
Control
Ethyl lactate
Emulsified oil
Micro-emulsion

Ability of dissolved Mn to re-oxidize Cr(III) was evaluated in a separate microcosm test

- All microcosms contained:
  - 300 mL Site groundwater (Cr(VI)=14 µg/L)
  - 100 g Site soil (Cr=150 mg/kg)
- Microcosms spiked with:
  - 10,000 µg/L Mn(II)
  - 23,000 µg/L Fe(II)
  - 27 µg/L As(III)
- Incubated under oxic conditions

Results indicate Mn can re-oxidize Cr(III) to Cr(VI) under aerobic conditions



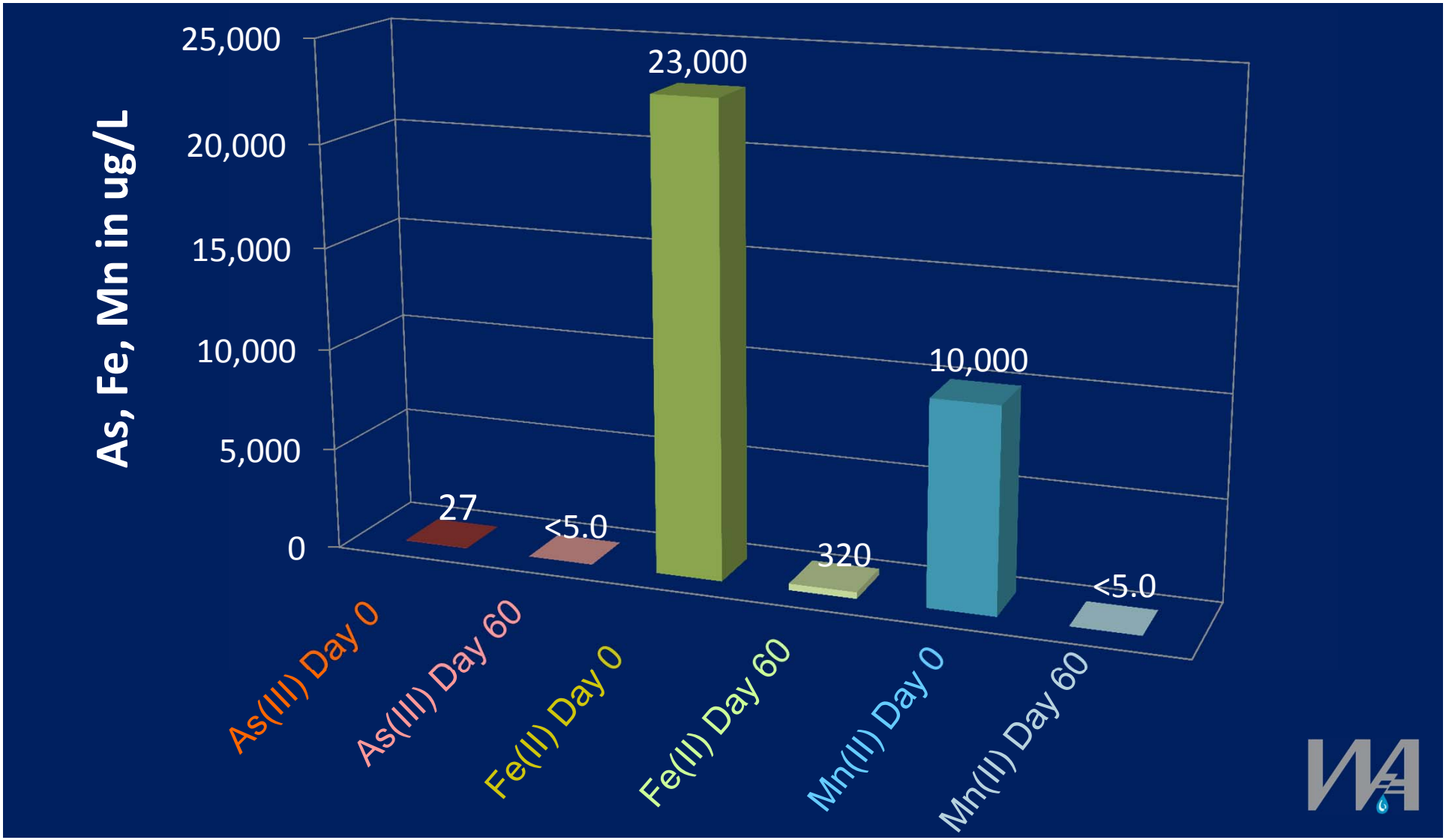
Day 0:

- DO: 6.9 mg/L
- ORP: -157 mV
- pH: 7.31

Days 3-60:

- DO: 7.5- 8.5 mg/L
- ORP: 76-210 mV
- pH: 7.9-8.2

However, manganese, iron, and arsenic significantly attenuate under aerobic conditions



Summary of results

- Strictly speaking, the effect of organic substrate on Cr(VI) reduction was inconclusive, because Cr(VI) also was completely removed in control reactor
- Substrate addition also solubilized arsenic, manganese, and iron
- Mn produced under reducing conditions has the potential to re-oxidize naturally occurring Cr(III), when it migrates into aerobic regions of the aquifer

Conclusions

- Promoting in situ, biological reduction of chromium was not recommended for this Site, because of:
  - The potential to solubilize arsenic
  - The potential of solubilized Mn to oxidize Cr(III) to Cr(VI) when the aquifer returns to aerobic conditions