Treatability Testing to Support Field Application of Ozone

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Uses for Ozone

- *In situ* remediation of contaminated groundwater or soil (saturated or unsaturated)
- *Ex situ* remediation of groundwater or surface water
- Treatment of plant process water
- Disinfection (of drinking water, produce, work surfaces, etc.)
- Odor or color removal

Pros and Cons of Ozone

- Pros
  - Ozone reacts with a wide range of compounds
  - Ozone can treat soil, water, or air
  - By-product (O_2) is safe
- Cons
  - Ozone is non-selective
  - Ozone has a short half-life
  - May have adverse secondary effects such as generation of hexavalent chromium [Cr(VI)] or bromate

Compounds Treated by O_3

- Organic
  - Chlorinated solvents (PCE, vinyl chloride)
  - 1,4-dioxane
  - Petroleum hydrocarbons (BTEX, gasoline, diesel)
  - Fuel Oxygenates (MTBE, TBA etc)
  - Pesticides (eg. DDT, toxaphene)
  - Polyaromatic hydrocarbons (PAHs)
  - Methyl salicylate (oil of wintergreen)
  - Biphenyl and Diphenyl ether (Dowtherm)
  - PCBs

Compounds Treated by O_3 -cont'd

- Inorganic
  - Ferrous iron
  - Sulfide
- Other
  - Odor
  - Dissolved organic matter
  - ***Emerging contaminants (pharmaceuticals?)***

Potential Secondary Effects

- Oxidation of soil chromium to Cr(VI)
  - amount of Cr(VI) depends upon amount of ozone applied
  - Cr(VI) often (but not always) attenuates
- Oxidation of naturally occurring bromide to bromate
  - May be controlled by adding H2O2 (appropriate O3:H2O2 ratio required) or adjusting pH
  - Attenuation of bromate uncertain
- Mobilization of metals
- Precipitation of iron and manganese
- SECONDARY EFFECTS ARE SITE-SPECIFIC

Treatability testing is laboratory testing performed on site soil and/or water to provide information beyond “what is the concentration of the contaminant?”

Why Perform Treatability Testing?

- Each site is different
  - Water quality may affect ozone dose requirements
  - Soil type may influence secondary effects
- Full-scale application is expensive
- Adverse secondary effects may off-set benefits
- May be required for regulatory approval of proposed ozone application

"Typical" Test Objectives

- Does ozone remove the contaminant?
  - Is removal due to destruction or volatilization?
  - Are intermediates formed?
- How much ozone is required (what is the soil or water ozone demand?)
- What are the secondary effects? Are they short-term or long-term?
- Find the answers by spending less money than a field pilot or full-scale test.

Ozone Batch Apparatus

Contaminant Removal-Batch

- Sparge with O_3 at ~25 mg/L (2% w/w) in air at 50 mL/min
- Collect off-gases if COCs are volatile
- If COCs non-volatile, sparge with N2 under same conditions as a control
- Destructively sample and analyze water and off-gases for COCs and/or secondary parameters

Contaminant Removal-Columns

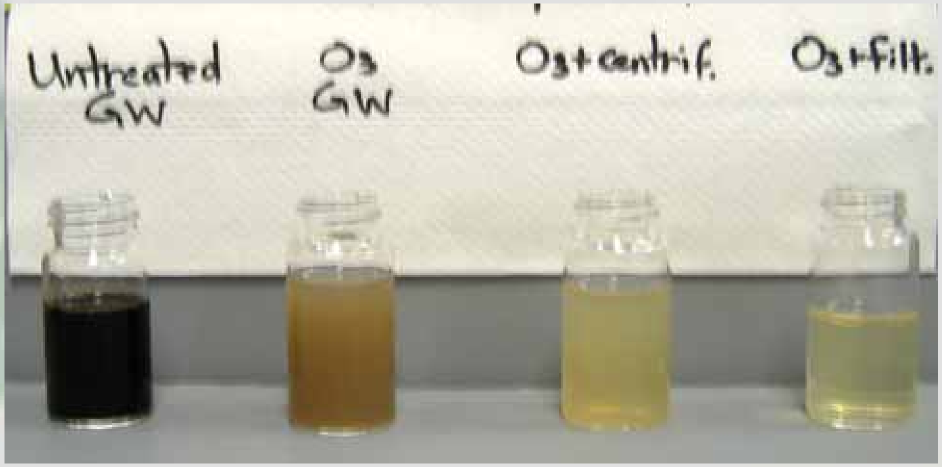
- Column tests conducted if COCs primarily in soil and are non-volatile and/or hydrophobic
- Humidified O_3 (~2% w/w in air) passed through each soil column
- Periodically, one column sampled and soil analyzed for COCs
- Correlate COC removed with amount of O_3 applied

Contaminant Removal Test

Analyte	Units	Time 0	Control		Ozone	
			Rep A	Rep B	Rep A	Rep B
		Aqueous Concentration				
GRO	mg/L	1.7	1.5	1.2	< 0.05	< 0.05
Benzene	µg/L	34	32	8.1	< 0.5	< 0.5
Toluene	µg/L	20	18	6.3	< 0.5	< 0.5
Ethylbenzene	µg/L	14	5.6	1.0	< 0.5	< 0.5
m,p-xylenes	µg/L	97	90	92	< 0.5	< 0.5
o-xylenes	µg/L	5.3	5.0	4.9	< 0.5	< 0.5
MTBE	µg/L	0.56	0.52	0.54	< 0.5	< 0.5
TBA	µg/L	< 10	< 10	< 10	< 10	< 10
Acetone	µg/L	< 20	< 20	< 20	120	150
Ozone applied	mg	0	0	0	420	2,490
volume	L		1.0	1.0	1.0	1.0
		Off-gas Concentration				
GRO	mg/L	n.a.	n.a.	n.a.	< 0.015	< 0.015
Benzene	µg/L	n.a.	n.a.	n.a.	< 0.15	< 0.15
Toluene	µg/L	n.a.	n.a.	n.a.	< 0.15	< 0.15
Ethylbenzene	µg/L	n.a.	n.a.	n.a.	< 0.15	< 0.15
m,p-xylenes	µg/L	n.a.	n.a.	n.a.	< 0.15	< 0.15
o-xylenes	µg/L	n.a.	n.a.	n.a.	< 0.15	< 0.15
MTBE	µg/L	n.a.	n.a.	n.a.	< 0.15	< 0.15
TBA	µg/L	n.a.	n.a.	n.a.	< 7.5	< 7.5
Acetone	µg/L	n.a.	n.a.	n.a.	< 3	< 3
volume	L	n.a.	n.a.	n.a.	12	71

Effect of Ozone on TOC/Color

- 2L Groundwater sparged with O3 for 3.9 days (5,200 mg O3 applied)
- Initial TOC = 2,900 mg/L
- Final TOC = 1,600 mg/L (filtered)



Secondary Effects

Test Conditions
- BTEX/gasoline
- 90 g soil
- 900 mL GW
- 1,080 mg O3 applied

Pink—decreased

Yellow--increased

Analyte	Units	Control-Low	Ozone-Low	Control-High	Ozone-High
Alkalinity	mg/L $CaCO_3$	n.m.	n.m.	602	558
Bromate	**µg/L**	**n.m.**	**n.m.**	**< 25**	**542**
Bromide	**µg/L**	**n.m.**	**n.m.**	**574**	**263**
Chloride	mg/L	n.m.	n.m.	39	39
Conductivity	µS	1,300	621	1291	1250
Cr(VI)	**ppb**	**< 1**	**30**	**< 1**	**79.6**
Metals					
beryllium	ppb	n.m.	n.m.	< 4	< 4
sodium	ppb	n.m.	n.m.	110,000	100,000
magnesium	ppb	n.m.	n.m.	69,000	67,000
aluminum	ppb	n.m.	n.m.	< 200	< 200
potassium	ppb	n.m.	n.m.	3,900	3,800
calcium	ppb	n.m.	n.m.	89,000	86,000
vanadium	**ppb**	**n.m.**	**n.m.**	**23**	**33**
chromium (total)	**ppb**	**n.m.**	**n.m.**	**< 5**	**79**
manganese	**ppb**	**n.m.**	**n.m.**	**3,500**	**220**
iron	ppb	n.m.	n.m.	580	560
cobalt	ppb	n.m.	n.m.	< 5	< 5
nickel	**ppb**	**n.m.**	**n.m.**	**8.4**	**< 5**
copper	ppb	n.m.	n.m.	< 10	12
zinc	ppb	n.m.	n.m.	< 100	< 100
arsenic	**ppb**	**n.m.**	**n.m.**	**8.7**	**17**
selenium	ppb	n.m.	n.m.	< 5	< 5
molybdenum	ppb	n.m.	n.m.	13	11
silver	ppb	n.m.	n.m.	< 5	< 5
cadmium	ppb	n.m.	n.m.	< 5	< 5
antimony	ppb	n.m.	n.m.	< 5	< 5
barium	**ppb**	**n.m.**	**n.m.**	**170**	**110**
tungsten	**ppb**	**n.m.**	**n.m.**	**12**	**< 5**
mercury	ppb	n.m.	n.m.	< 1	< 1
thallium	ppb	n.m.	n.m.	< 5	< 5
lead	ppb	n.m.	n.m.	< 5	< 5
ORP	mV	262	283	286	277
pH	--	7.45	7.98	7.51	8.23
sulfate	mg/L	n.m.	n.m.	24	26
TDS	mg/L	n.m.	n.m.	819	814

SUMMARY

- Treatability testing can show whether ozone treatment is effective under site conditions
- Estimate the amount of ozone needed to remove contaminants
- Determine whether use of ozone may have adverse secondary effects
- Raise the comfort level of you, regulators, clients, and stakeholders

Summary

- What treatability testing CANNOT do (in situ applications)
  - Perfectly simulate field conditions
  - Determine exact amount of reagent needed
  - Predict the exact degree of change in a secondary parameter [eg. Cr(VI), metals mobilization] or how long they last
  - **promise you treatment will work in the field** (successful treatment depends strongly on how treatment is implemented)

Designing a Treatability Test

- Discuss problem/goals of testing your lab
- Agree upon approach, procedures, costs
  - sources of procedures
    - PRIMA
    - You
    - Reports or scientific literature (eg., *Methods of Soil Analysis*)
  - costs—if necessary, modify scope to keep within your budget
- Receive samples from client

Contact Information

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