There's Something in the Water: Reactive Synergies using Mixed Oxidants for Emerging Contaminant Removal

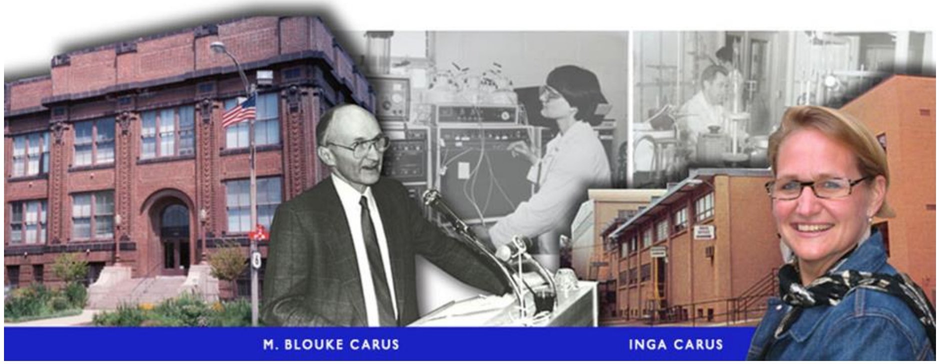
CARUS®

ONE COMPANY, ENDLESS SOLUTIONS

Pamela J. Dugan, Ph.D., P.G.
Carus Corporation;
Grant Walsom, XCG
Consulting Limited

About Us

- Privately Held; Founded in 1915
  - ➢ Headquarters in Peru, Illinois
  - ➢ About 400 Employees



- Five Manufacturing Sites in the United States
  - ➢ Warehouses in Europe
- International Sales and Distribution Organization
- Key Markets: Environmental
  - ➢ Water Treatment, Air Purification, and Remediation

Market Platforms

Water
Disinfection by-product
Taste/Odor
Fe / Mn
H_2S destruction
Sequestration
Corrosion Control
Adsorption
Oxidation
Disinfection

Air Purification
Catalyst for gas purification
CO destruction
Ozone destruction
Ethylene Oxide

Remediation
In Situ Chemical Oxidation
In Situ Chemical Reduction
Bioremediation
Metal Removal (uranium, arsenic, selenium, mercury)

Industrial
Electronics
Pharmaceuticals
Mining
Refinery
Cleaning
Pulp & Paper
Sugar Industry

Permanganates
Manganese Derivatives
Phosphates and Polymers
Chlorine Products
Specialty Chemicals

Agenda

- Background – Micropollutants and Emerging Contaminants
- Prevalence and Route
- Experimental Approach: Mixed Oxidant Systems
  - Permanganate with Persulfate (liquid mixtures and solid sustained-release (SR) technology)
  - Permanganate Decomposition Byproducts with Peroxymonosulfate (liquid mixtures)
  - “Activated” Permanganate (liquid mixtures)
- Results and Significance

Background

- Low levels of pharmaceuticals (PHCs), endocrine disrupting compounds (EDCs), personal care products (PCPs)
  - Present due to incomplete removal during conventional wastewater treatment plant (WWTP) processes
- Permanganate, ozone, chlorine, and chlorine dioxide are effective but…
  - Ozone and chlorine can react with bromide creating *harmful brominated disinfection byproducts* or generate *halogenated organic compounds* (*e.g.*, chloroform, trihalomethanes and haloacetic acids)

Background

- Emerging contaminants (e.g., 1,4 dioxane)
  - Dioxane is a reaction by-product produced during manufacturing of soaps, polyesters and plastics used primarily as a solvent stabilizer for 1,1,1-trichloroethane (Mohr, 2010)

"Should voters be asked to fund $30M cleanup of Gelman dioxane plume?"
Source: Mlive.com

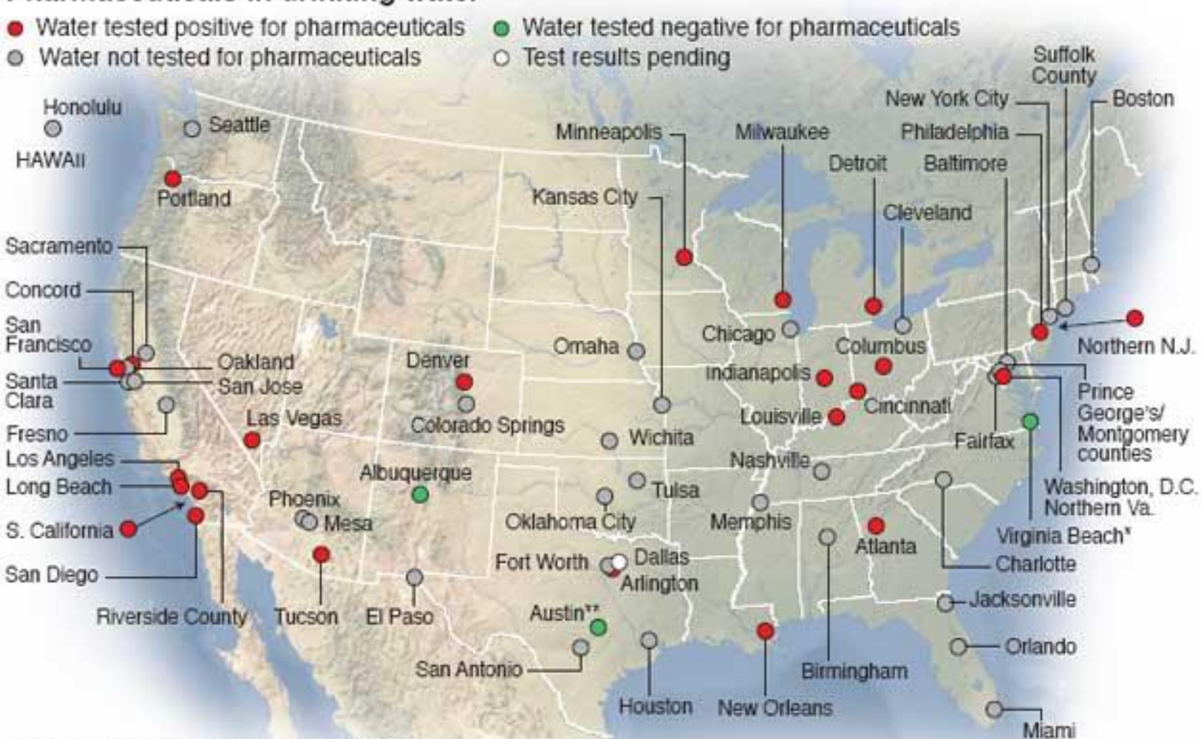
- *Recent research indicates free radicals and advanced oxidation processes (AOPs) can result from Mn-based oxidants* (e.g., Sun et al., 2016; Tratnyek 2016; Dugan 2016, Saptura et al., 2015)

Prevalence: Micropollutants

Major water sources positive for pharmaceuticals

At least one pharmaceutical was detected in tests of finished drinking water supplies for 24 metropolitan areas, according to an Associated Press survey of 62 major water providers. Only 28 tested finished drinking water. Test results vary widely. Some water systems said tests had been negative, but the AP found independent research showing otherwise.

Pharmaceuticals in drinking water



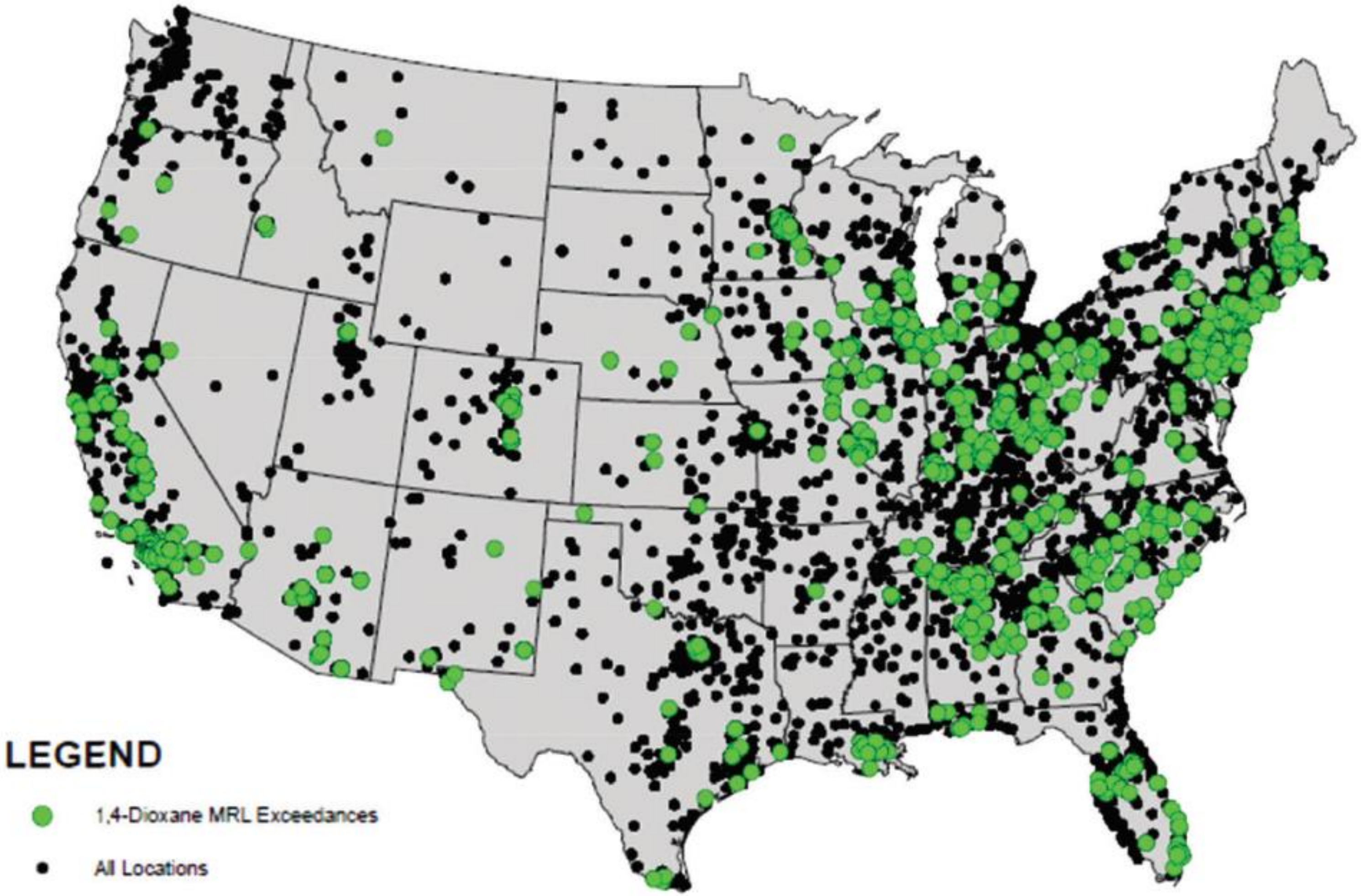
* In Virginia Beach, pharmaceuticals were found in source water but not in treated drinking water.
** Drinking water in Austin, Texas, was tested for only one prescription drug, a synthetic birth control chemical.

NOTE: All places include some surrounding areas except: Albuquerque, N.M.; Arlington, Texas; Fresno, Calif.; Long Beach, Calif.; Los Angeles; Memphis, Tenn.; New Orleans; New York City; and Orlando, Fla.

SOURCES: Drinking water providers' responses to Associated Press questions; AP review of scientific literature. AP

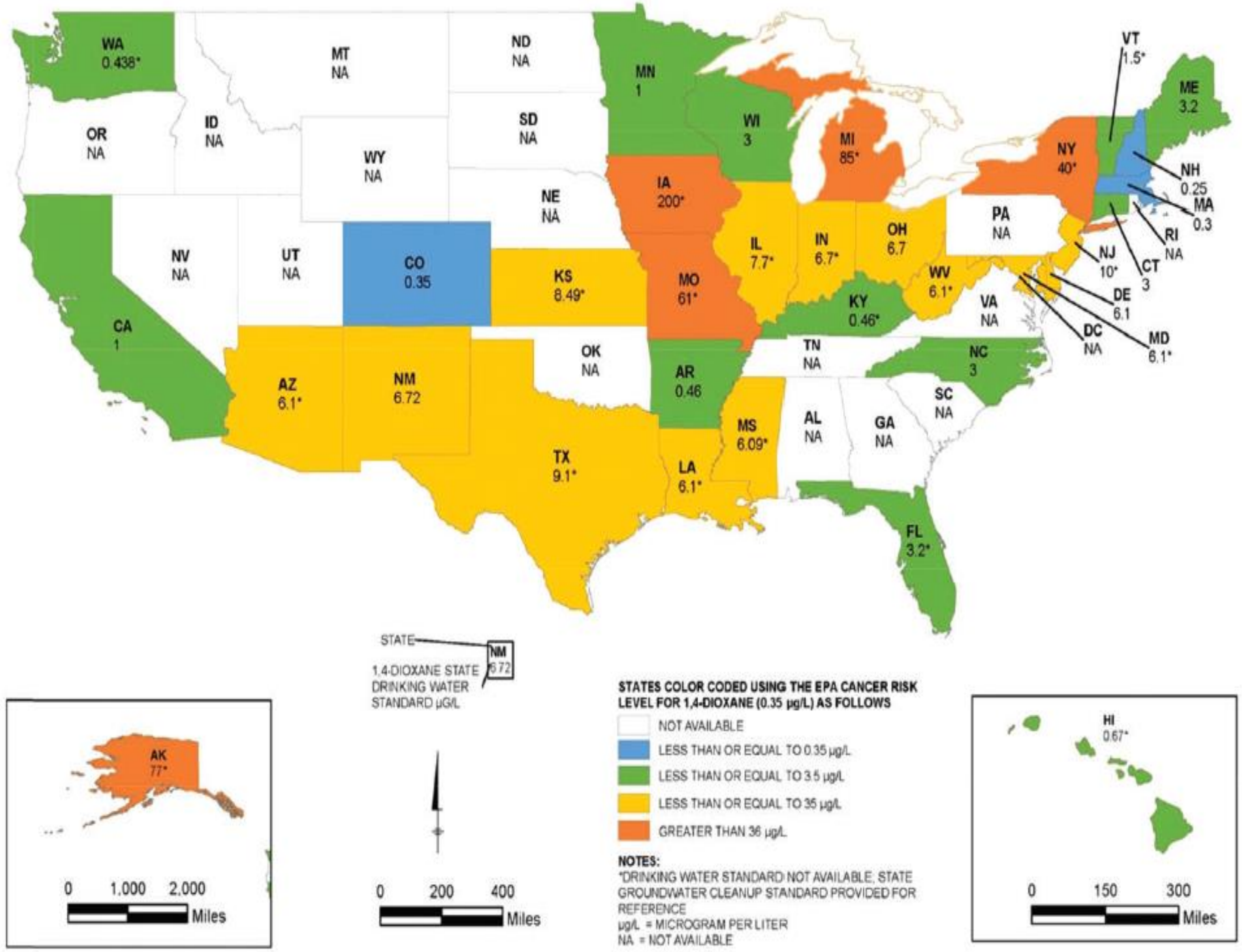
Associated Press 2008

Prevalence: 1,4 Dioxane



1,4-dioxane public water supply exceedances at nearly 7% of the facilities tested (USEPA 2015)

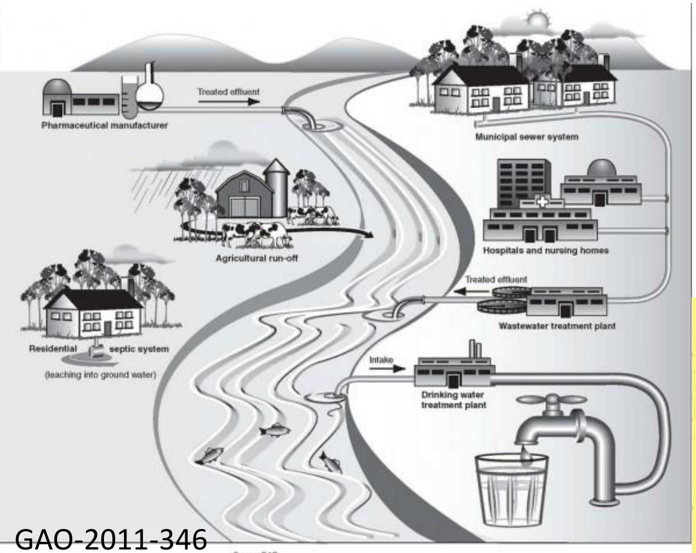
Prevalence: 1,4 Dioxane



33 states having established groundwater cleanup standards ranging from 200 µg/L in Iowa to 0.25 µg/L in New Hampshire (Suthersan et al., 2016)

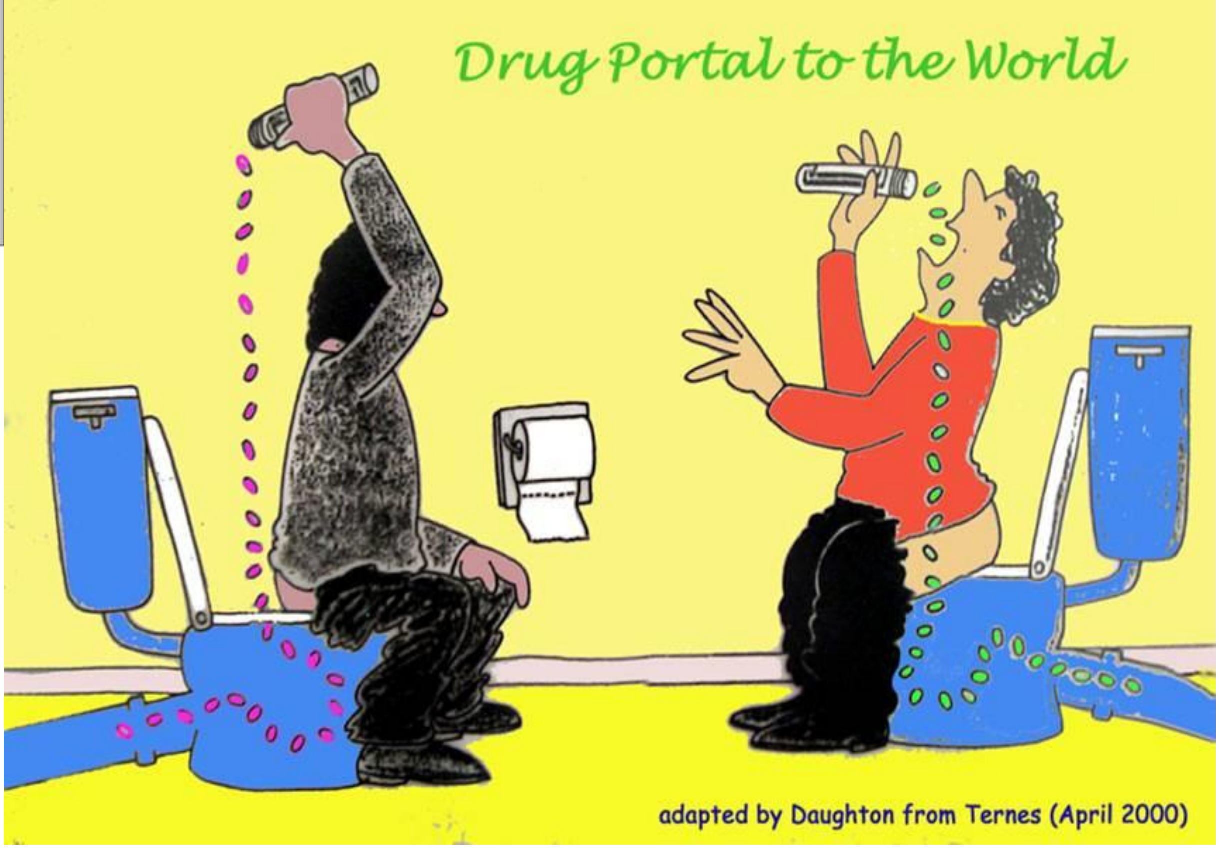
Route: Micropollutants

All pharmaceuticals, by design, are meant to elicit a biological response. We need to know what the environmental consequences are —Dana Kolpin, US Geological Survey

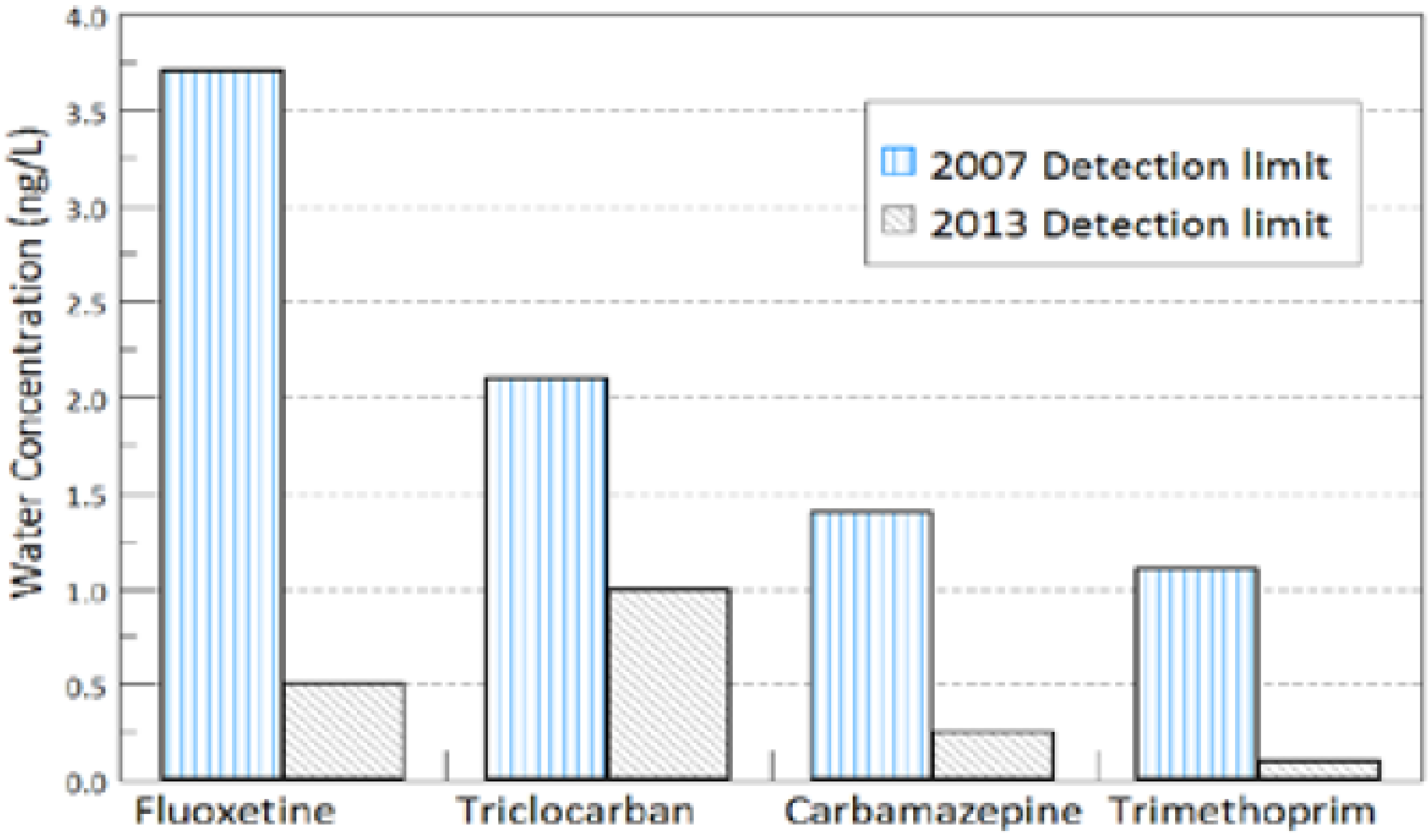


GAO-2011-346

Source: GAO.



It's in the water but… we couldn't detect it

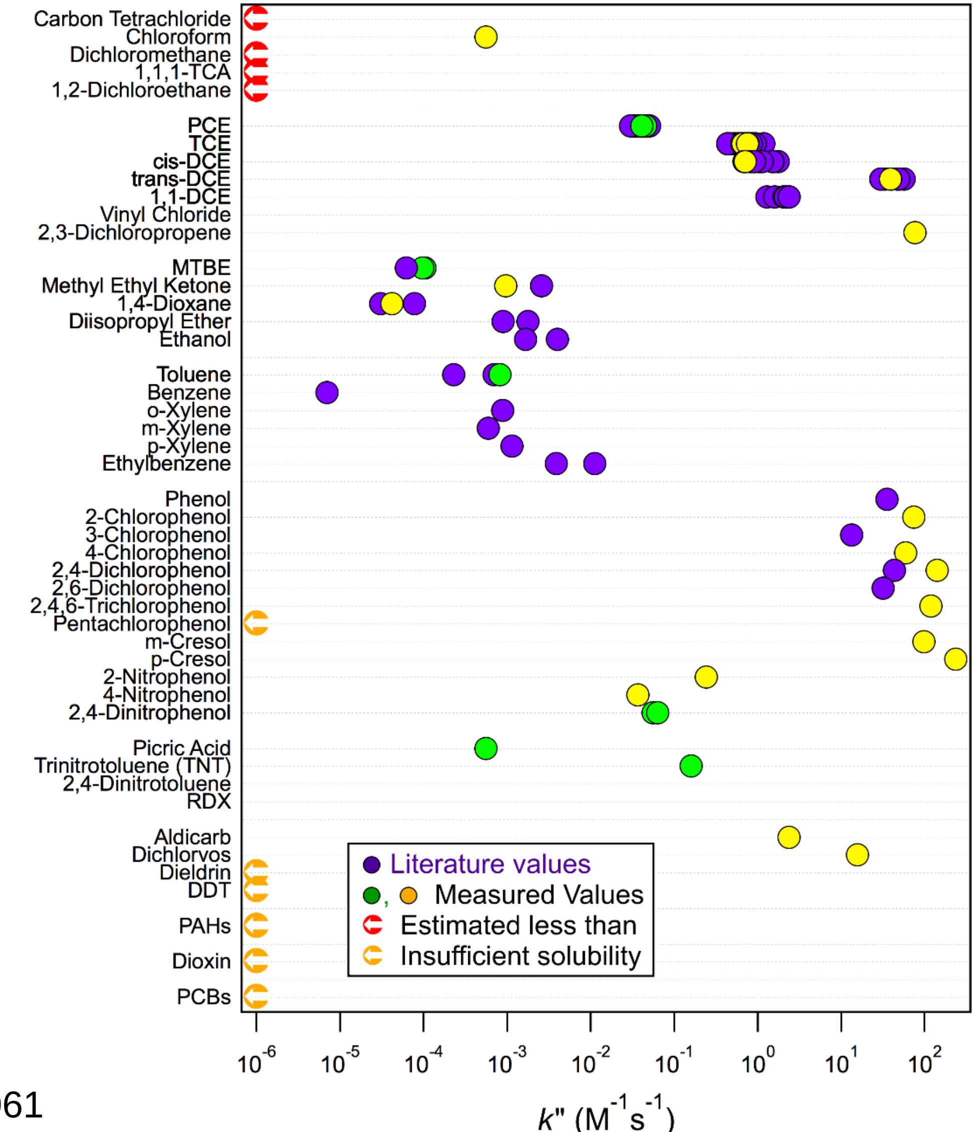


Data from EPA 2007, Anumol et al., 2013

- Prior to 1990, methods to detect chemicals in water at extremely low levels was not available
- Today, "state-of-the- art" equipment can detect micropollutants in water at much lower levels (e.g., ng/L) than just 5-6 years ago

Motivation: Kinetics of Permanganate Oxidation

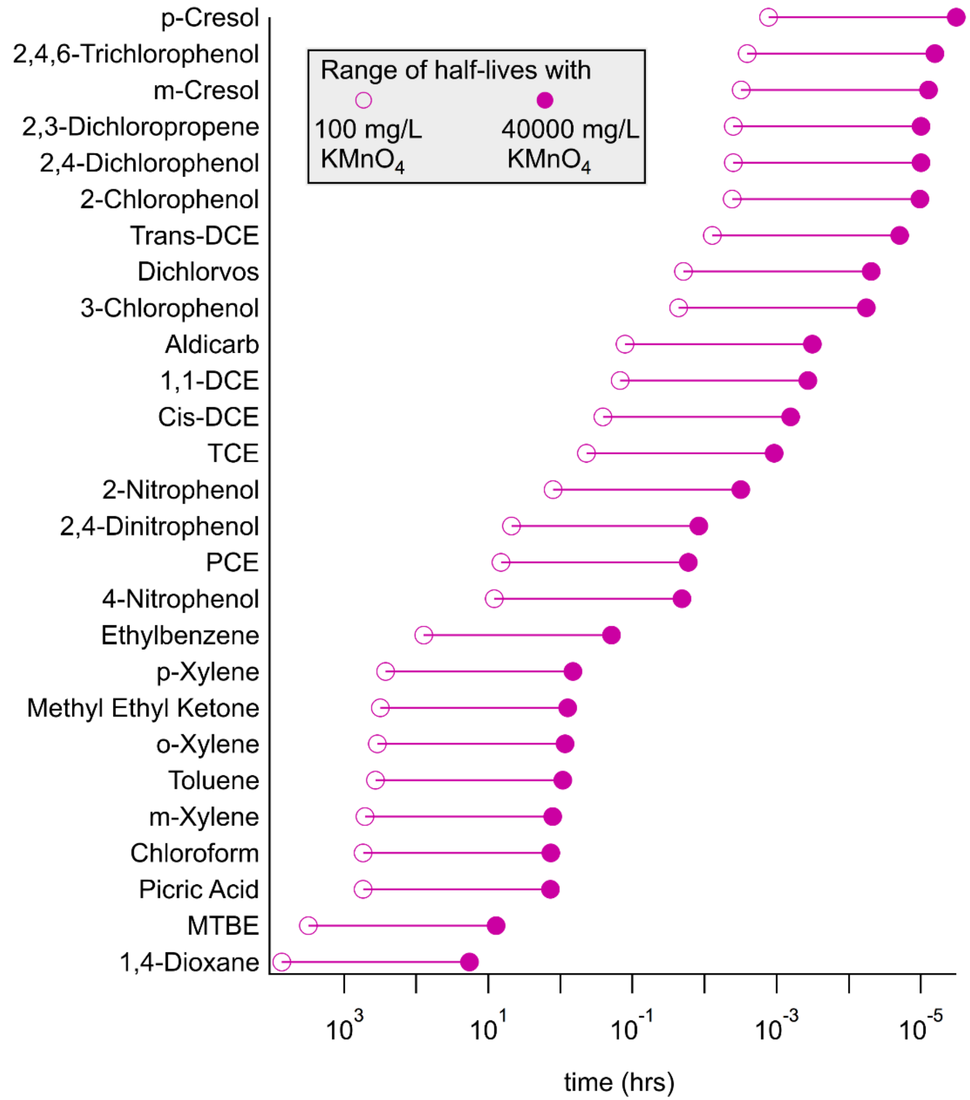
- Rate Constants (*k*″)
  - Compiled from many prior studies (ENVR and not)
  - New measured values
- Synthesis
  - Mostly good agreement across compounds and methods
  - Relatively fast: chloroethenes and phenols
  - Relatively slow: chloroalkanes and fuel compounds
- Implications
  - Permanganate reactivity varies greatly with contaminant



Waldemer and Tratnyek (2006) ES&T 40:1055-1061

Motivation: Kinetics of Permanganate Oxidation

- Rate Constants (k_{obs})
  - Using k'' from previous figure, calculated k_{obs} and half-life ($t_{1/2}$)
  - Assuming $[MnO_4^-]$ over a range relevant to treatment
  - Sorted from slow (bottom) to fast (top)
- Implications
  - Fast compounds can be very fast. Slow compounds can be too slow
  - High doses needed for many compounds



Waldemer and Tratnyek (2006) ES&T 40:1055-1061

Motivation: Permanganate and Persulfate Mixtures

- MnO_x can induce decomposition of peroxymonosulfate (PMS) producing sulfate radicals as shown in the following equations (Saptura et al., 2015):
  - $2HSO^{-5} + MnO_2 \rightarrow 2SO_5\bullet - + OH^- + Mn_2O_3$
  - $2HSO^{-5} + Mn_2O_3 \rightarrow SO_4\bullet - + H^+ + 2Mn$

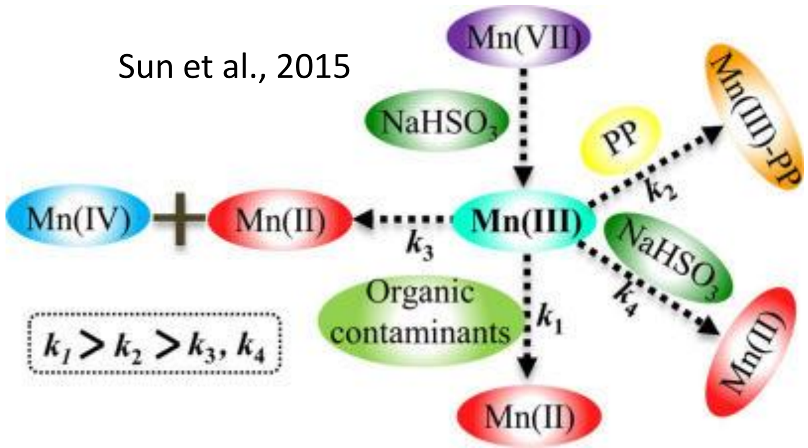
- Permanganate & persulfate reactive synergies with 1,4-dioxane (Dugan et al., 2016)

Oxidant	Matrix	Contaminant	Calculated Second Order Rate Constant ($M^{-1}s^{-1}$)
Persulfate (100 & 10,000 ppm)	Site Soil and Groundwater	Dioxane in a VOC mix	8.06E-06 (5ppm)
Permanganate (500 & 10,000 ppm)	Site Soil and Groundwater	Dioxane in a VOC mix	2.63E-05 (5ppm) 2.64E-05 (1ppm)
Mixed Oxidants (Permanganate) (500 & 5000 ppm)	Site Soil and Groundwater	Dioxane in a VOC Mix	2.85E-05 (8ppm) 2.62E-05 (2ppm)
Mixed Oxidants (Persulfate) (500 & 5000 ppm)	Site Soil and Groundwater	Dioxane in a VOC Mix	1.05E-04 (8ppm) 9.63E-05 (2ppm)

Motivation: "Activated" Permanganate

- Advanced oxidation processes (AOPs) can potentially be generated using Mn-based oxidants (e.g., Sun et al., 2015)

Sun et al., 2015

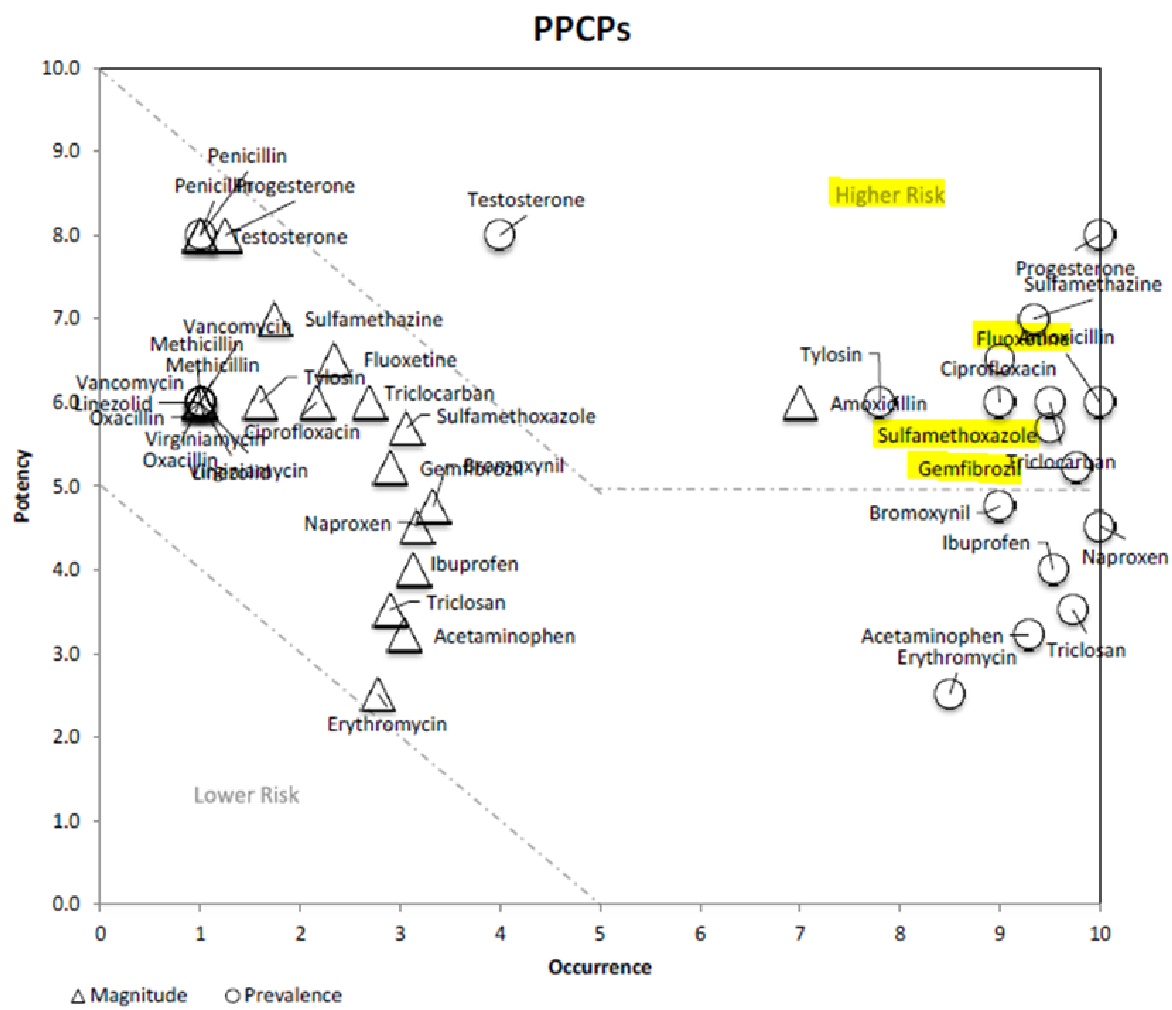


- Permanganate "activation" by bisulfite reduction produced highly reactive Mn (III) species

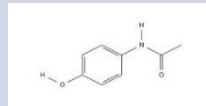
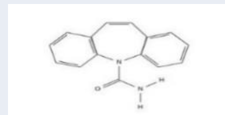
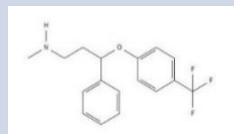
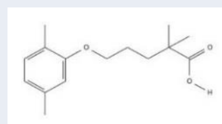
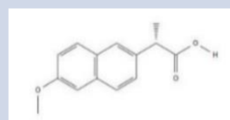
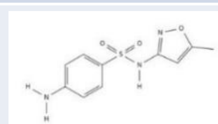
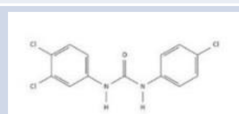
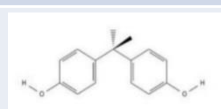
- Measured rates ($k_{obs} \approx 60-150\ s^{-1}$) 5−6 orders of magnitude faster than permanganate alone, and ~5-7 orders of magnitude faster than conventional AOP water treatment processes (Sun et al., 2015)

Approach: Micropollutants

- PHC compounds chosen based on American Water Works Association (AWWA) and the contaminant candidate list 4 (CCL4)
- Conducted series of batch experiments:
  - ➢ Batch Removal Efficiency Tests (8 compounds)
    - PHCs (6) , PCP (1), EDC (1)



Approach: Micropollutants

PHC/PCP/EDCs Compounds	Trade Name	Chemical Structure	Use
PHC Analgesic	**Paracetamol (Acetaminophen)**		Used to treat pain and fever
PHC Antiepileptic	**Carbamazepine (Tegretol)**		Treatment of epilepsy and neuropathic pain
PHC Antidepressant	**Fluoxetine (Prozac)**		Treatment of major depressive disorder, OCD, panic disorder, and bulimia nervosa
PHC Lipid-Regulator	**Gemfibrozil**		Gemfibrozil is the generic name used mainly to lower plasma lipid levels
PHC Anti-Inflammatory	**Naproxen (Aleve)**		Relief of pain, fever, swelling, and stiffness
PHC Antibiotic	**Sulfamethoxazole**		Antibiotic for bacterial infections such as bronchitis, and prostatitis
PCP Antibacterial/ Antiseptic	**Triclocarban**		Antibacterial agent commonly used in personal care products, such as soaps and lotions
EDC Bisphenol	**Bisphenol A (BPA)**		Used in the production of certain plastics, epoxy resins, flame retardants, and rubber chemicals

Approach: Removal Efficiencies

Target Compounds (500 ppb)
Acetaminophen Bisphenol A
Carbamapazine
Gemfibrozil
Fluoxetine Naproxen
Sulfamethoxazole
Triclocarban

Treatments
#1 Permanganate & Persulfate
#2 Hydrous Manganese Oxide (HMO) & PMS
#3 Permanganate

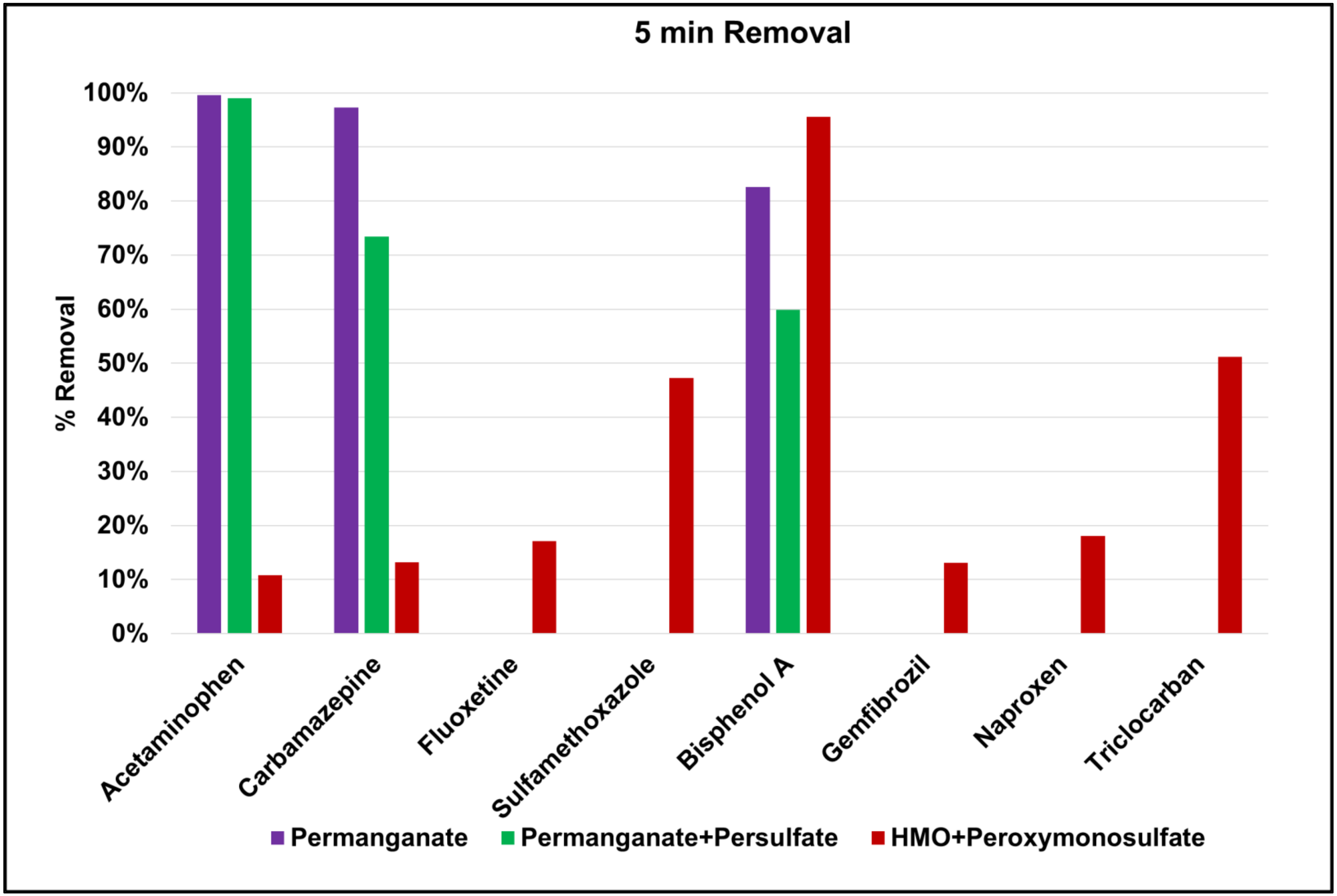
Analytical Methods
- Solid Phase Extraction
- LC-MS/MS
- Teerlink et al. (2012) Water Research, 46, 3261–3271

Treatment	Permanganate	Sodium Persulfate	HMO (Mn)	PMS
1	5 mg/L	5 mg/L	N/A	N/A
2	N/A	N/A	400 mg/L	20 mg/L
3	10 mg/L	N/A	N/A	N/A

Solutions made in Tertiary- Treated WWTP
Samples quenched at 5 min and 24 hours

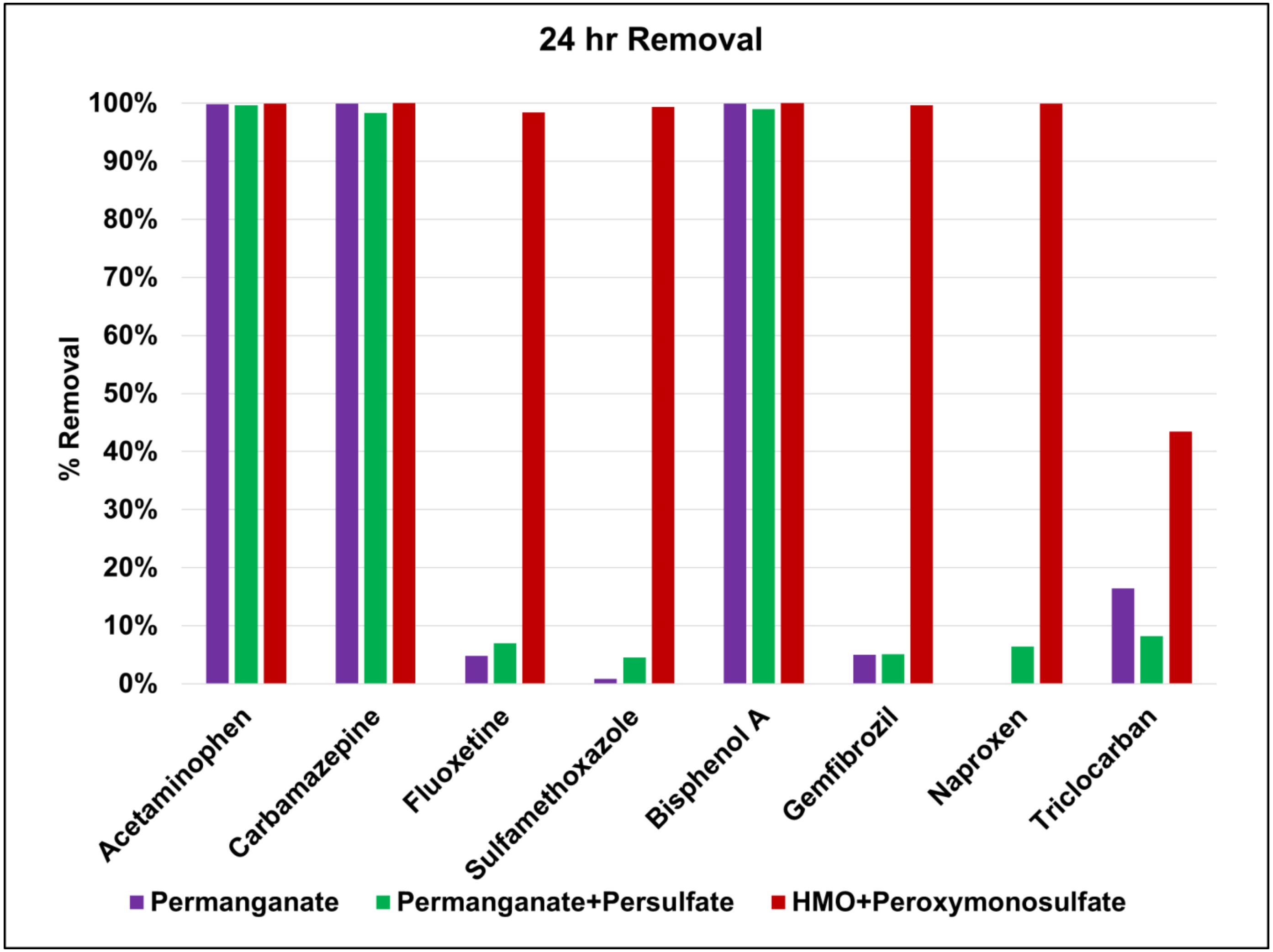
	ESI negative mode				ESI positive mode			
Detection limit [μg/L]	Bisphenol A 0.05	Gemfibrizol 0.01	Naproxen 0.01	Triclocarban 0.01	Acetominophen 0.01	Carbamazepine 0.025	Fluoxetine 0.005	Sulfamethoxazole 0.005

Results: Mn-Based Oxidant Systems



- Permanganate 99%-83% vs with Persulfate 98% - 60% (Acetaminophen, Carbamazepine, BPA)
- HMO/PMS – high reactivity BPA, low *initial* reactivity all others

Results: Mn-Based Oxidant Systems



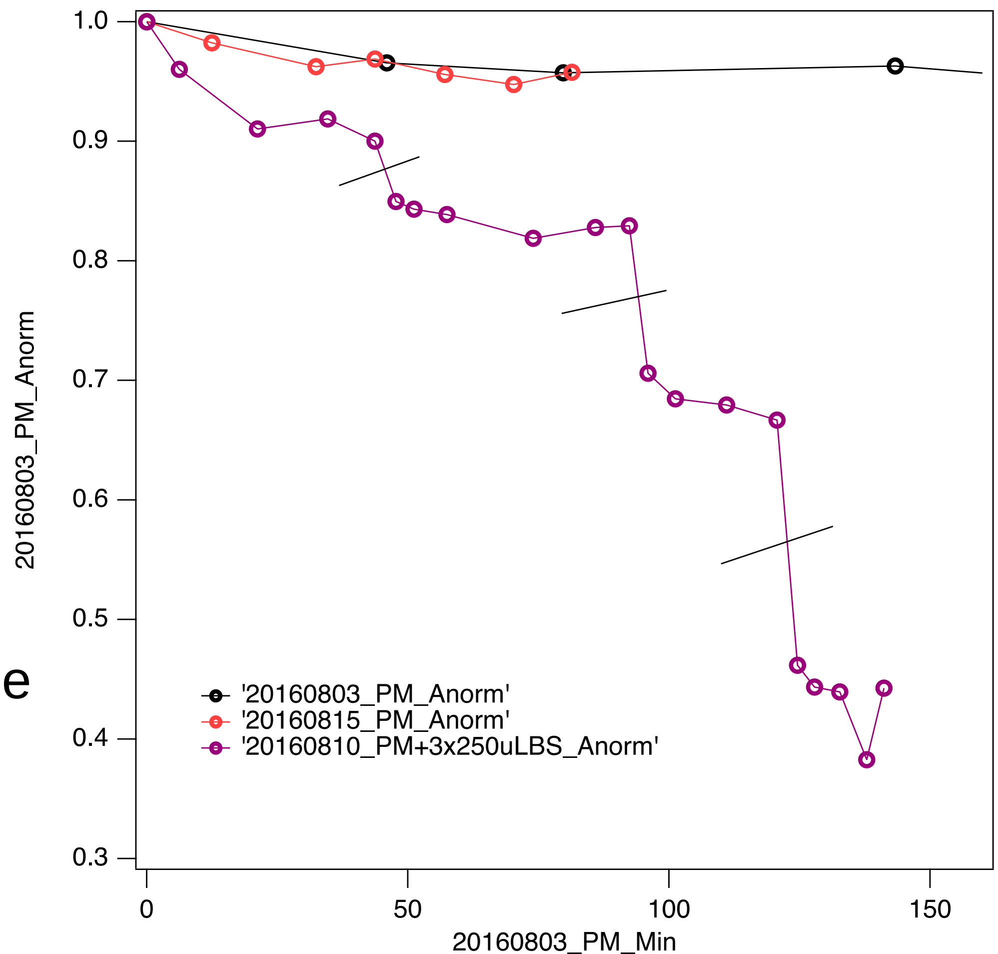
- Little change in permanganate alone or with persulfate (Acetaminophen, Carbamazepine, BPA)
- HMO/PMS – high reactivity with all compounds except Triclocarban

Results

- Of the 7 PHCs evaluated with permanganate alone 3 exhibited high reactivity at all sampling time points (5 min – 24 hr)
- Similar removals for permanganate with persulfate
- 7 out of 8 compounds evaluated had high reactivity with HMO-PMS (after 24 hours)

Approach/Preliminary Results: “Activated” Permanganate

- Experiments:
  - Exploratory experiments at OHSU and Carus
  - Various scenarios relevant to engineering applications
  - Batch tests with excess PM, re-spike with BS
  - Toluene in headspace by GC
- Preliminary Results:
  - Toluene oxidation by PM alone is slow
  - Upon each spike of BS, toluene drops immediately
  - Drops get bigger with each spike?



Sun, Guan, Fang, Tratnyek (2015) ES&T 49: 12414-12421

Sustained-Release (SR) Technology

Persulfate SR ISCO Reagent

- Persulfate in wax matrix (~73% w/w)

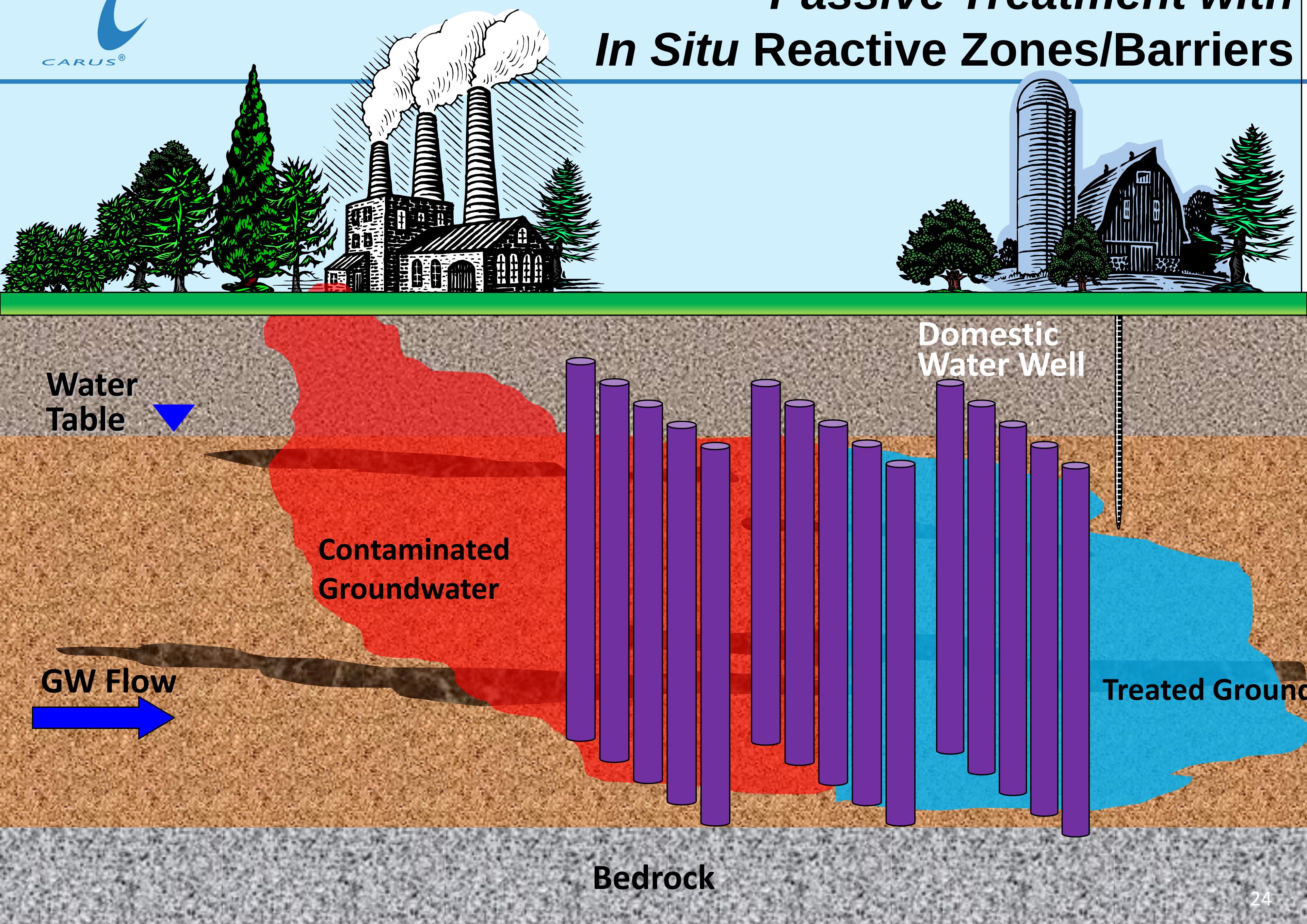
RemOx® SR+ ISCO Reagent

- Permanganate and persulfate in wax matrix (~83%)
- US Patent Pending PCT/US14/29247

Characteristics:

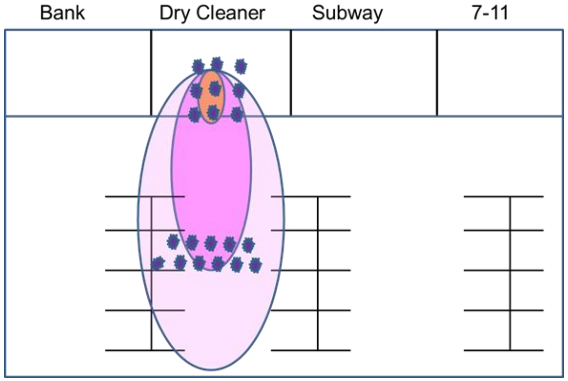
- Non-toxic and biodegradable wax
- Cylindrical shape: 6.4 cm diameter x 46 cm long

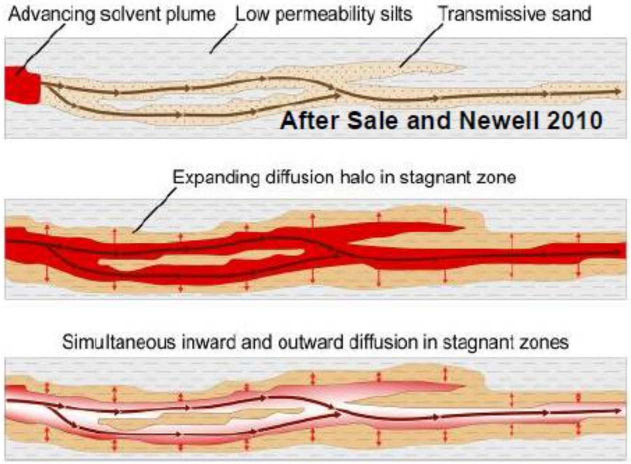
Passive Treatment with In Situ Reactive Zones/Barriers



SR Technology Benefits

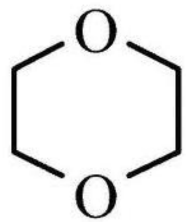
- **Passive ISCO technology**
- **Minimizes above-ground infrastructure**
- Cost-effective, and can be implemented as part of a **stepped-implementation** strategy
- Long-term presence of oxidants can mitigate the impacts of **"rebound", matrix diffusion, and vapor intrusion**
- Use **natural groundwater gradients** to deliver oxidants



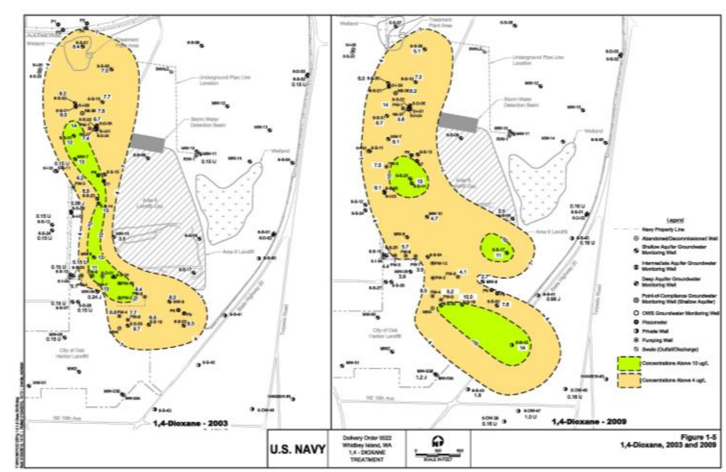


SR for Emerging Contaminant Remediation

- 1,4-Dioxane



  - Solvent stabilizer (e.g. TCA, TCE)
  - Carcinogenic
  - High miscibility creates long/dilute plume
  - Not biodegradable
  - ESTCP ER-201324 (Evans, Dugan, Crimi 2013)



SUSTAINED *IN SITU* CHEMICAL OXIDATION (ISCO) OF 1,4-DIOXANE USING SLOW-RELEASE OXIDANT CYLINDERS
ER-201324

Patrick J. Evans, Ph.D.
CDM Smith
Pamela Dugan, Ph.D., P.G.
Carus Corporation
Michelle Crimi, Ph.D.
Clarkson University

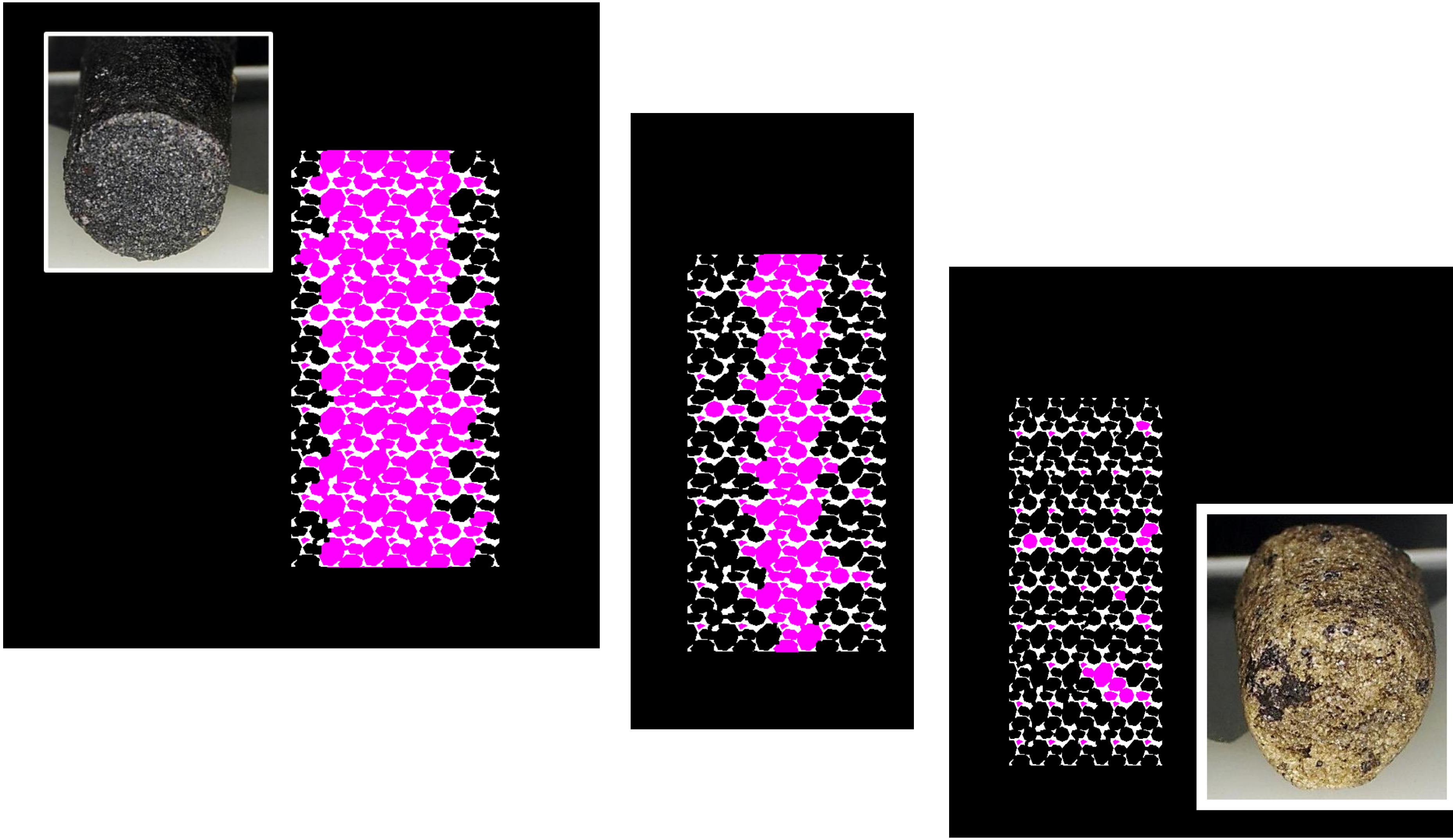
ESTCP

Direct Push Installation

- 8.25 cm tooling with disposable tip
- Lower cylinders within inner space of rods provides confirmation that cylinder placed at desired depth
- Rods retracted with cylinders remaining in place

Well Installation

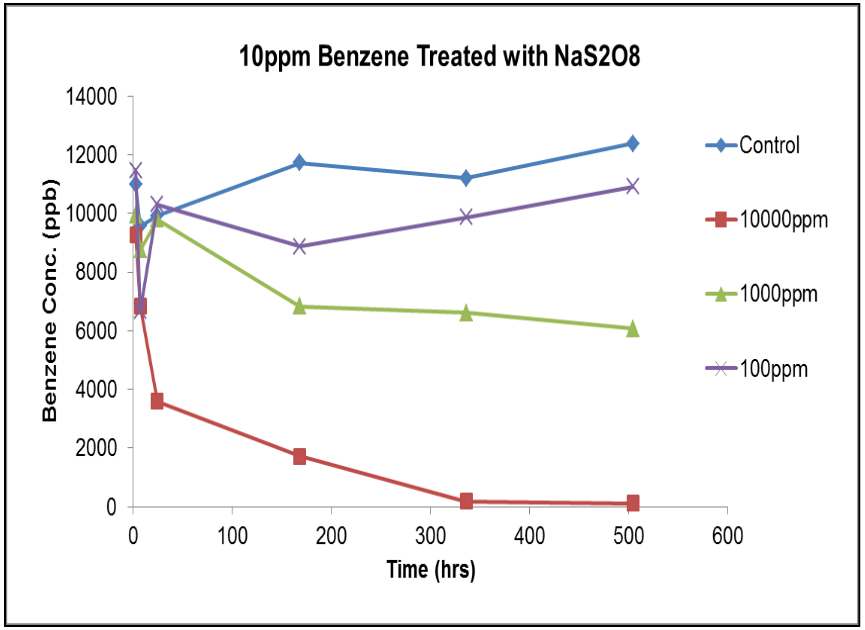
Oxidant Release Mechanism



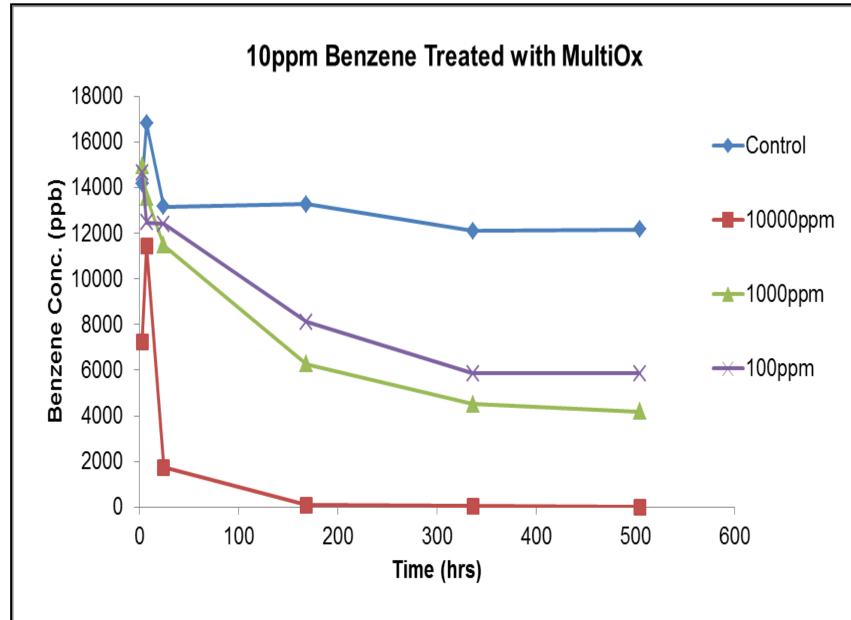
Persulfate SR and RemOx SR+: Batch and 1-D Column Results

BTEX Batch Kinetic Oxidation Results

Unactivated Persulfate Oxidation



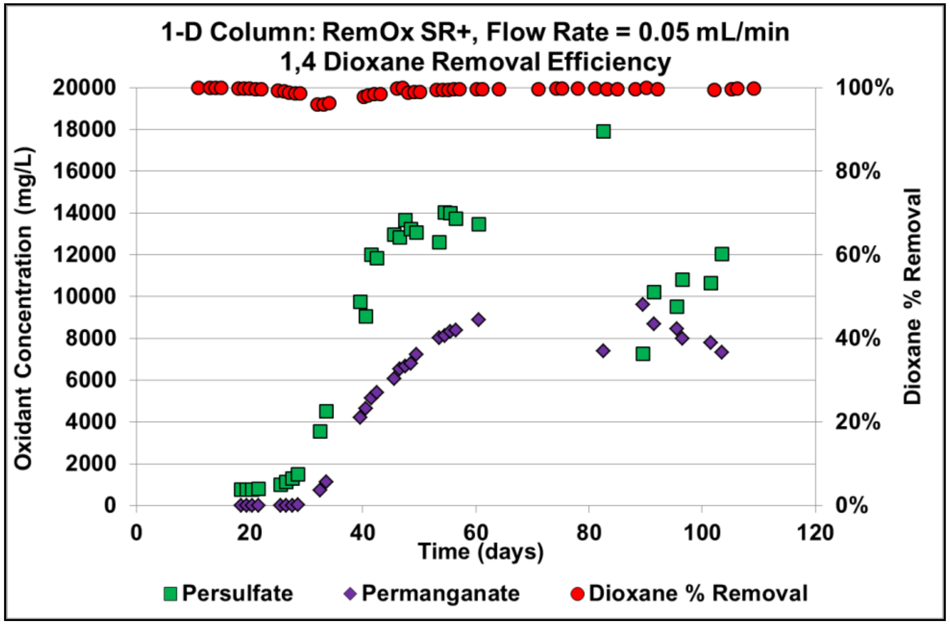
RemOx SR+ Oxidation

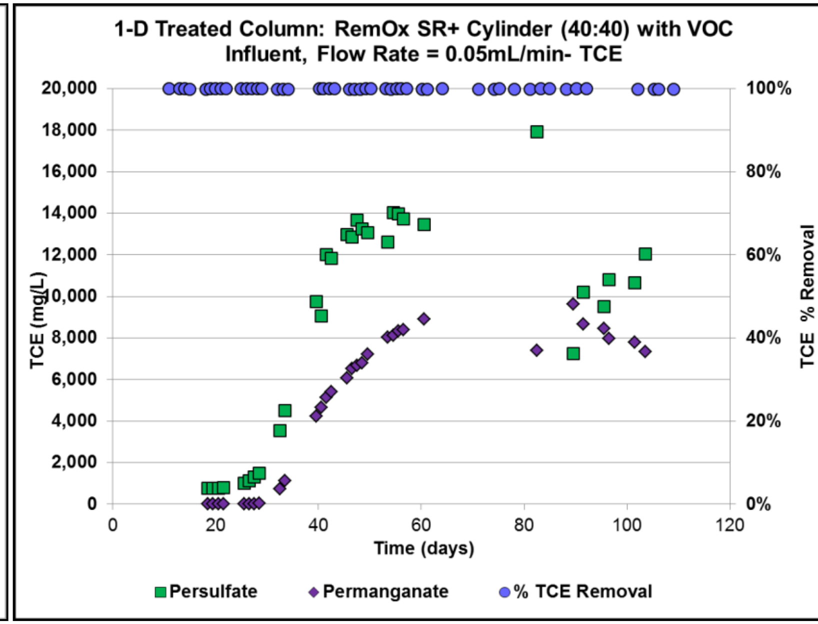


Second Order Oxidation Rate Constants ($M^{-1}s^{-1}$)			
	Permanganate	**Persulfate**	**SR+**
Benzene	Neglible	5.72E-5[2]	1.1E-4[2]
Toluene	5.74E-4[1]	5.63E-5[2]	3.2E-4[2]
Ethylbenzene	7.07E-3[1]	5.91E-5[2]	1.9E-3[2]
Xylene(s)	2.22E-3[1]	4.81E-5[2]	4.0E-3[2]
MTBE	8.82E-5[1]	Neglible	7.6E-5[2]

[1]ISCO-kin Database
[2]This study

Permanganate & Persulfate Reactive Synergies: 1, 4 Dioxane

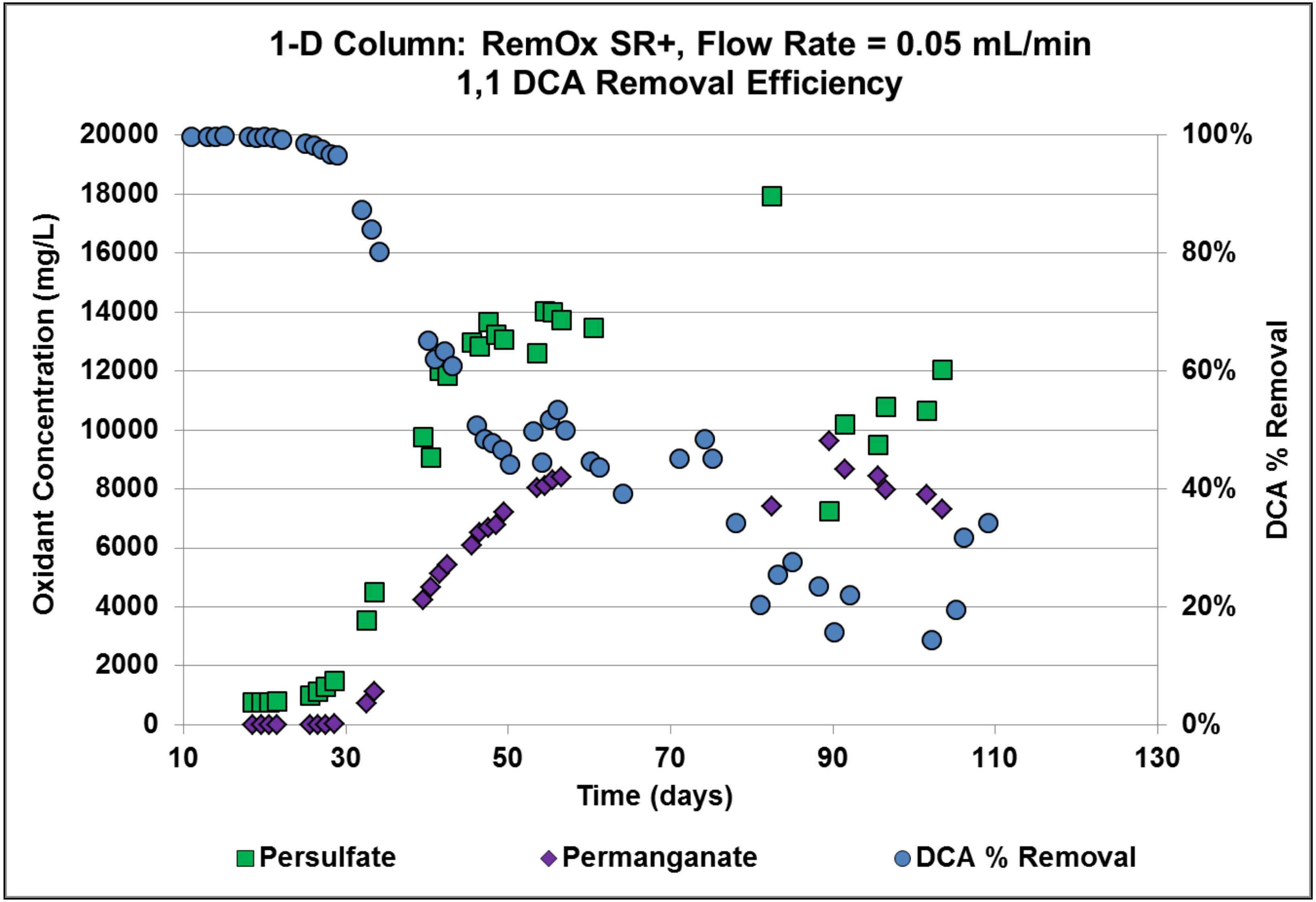




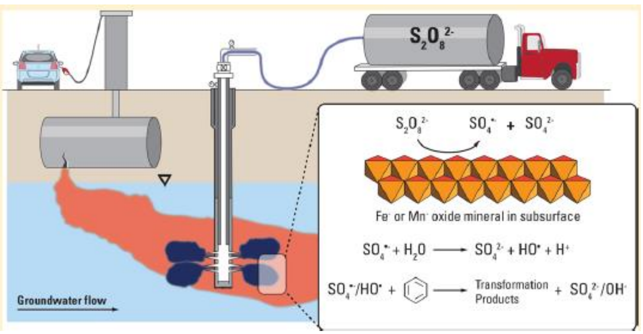
> 99.9% Removal of 1,4-dioxane and chlorinated ethenes ~ 12 months

1,4 Dioxane Reaction Rate Constants (k)		
1,4 Dioxane Concentration (mg/L)	***RemOx® S ISCO Reagent***	***Persulfate SR ISCO Reagent***
100	6.76E-07 L mol^{-1} s^{-1}	5.88E-04 L mol^{-1} s^{-1}
14	8.80E-07 L mol^{-1} s^{-1}	3.05E-04 L mol^{-1} s^{-1}
RemOx® SR+ ISCO Reagent	***Permanganate***	***Unactivated Persulfate***
100	1.16E-03 L mol^{-1} s^{-1}	1.96E-04 L mol^{-1} s^{-1}
14	1.47E-03 L mol^{-1} s^{-1}	2.49E-04 L mol^{-1} s^{-1}

SR+ Treated Column - 1,1 DCA Removal



Fe(III) and Mn (IV) Catalyzed Persulfate Radical Formation



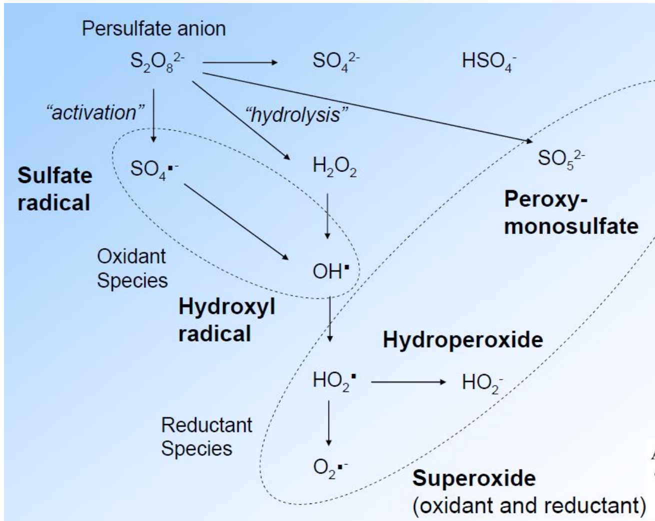
$$2HSO_5^- + 2MnO_2 \rightarrow 2SO_5^{\bullet-} + H_2O + Mn_2O_3$$

$$2HSO_5^- + Mn_2O_3 \rightarrow 2SO_4^{\bullet-} + H_2O + 2MnO_2$$

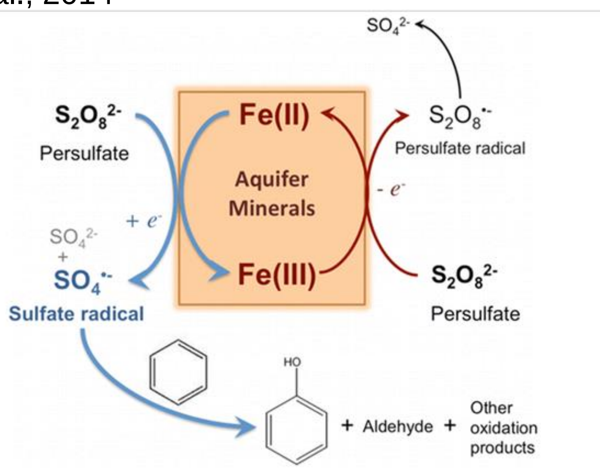
$$Org + SO_4^{\bullet-} \rightarrow ... \rightarrow CO_2 + H_2O + SO_4^{2-}$$

Liu et al., 2014

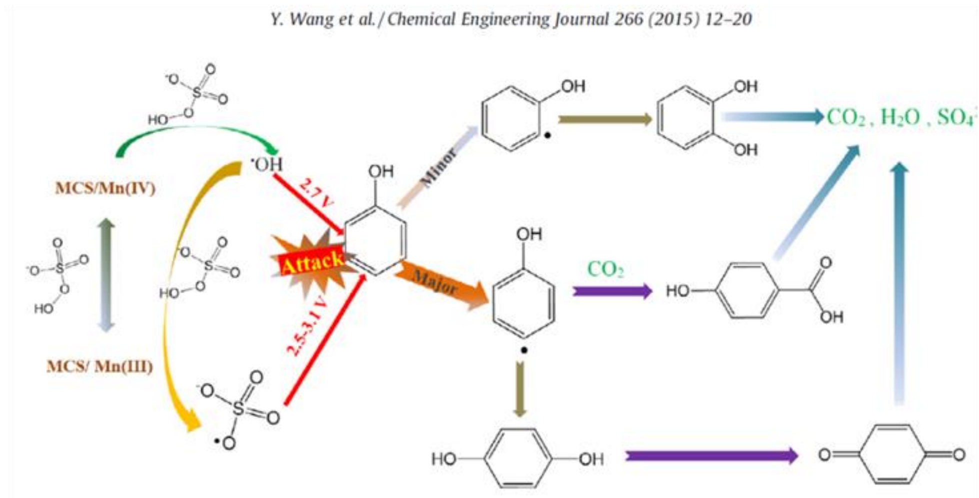
- *Fe(III)- and Mn(IV)-oxides catalytically convert persulfate into sulfate radical ($SO_4^{\bullet-}$) and hydroxyl radicals ($HO^{\bullet}$)*



Gao et al., 2015

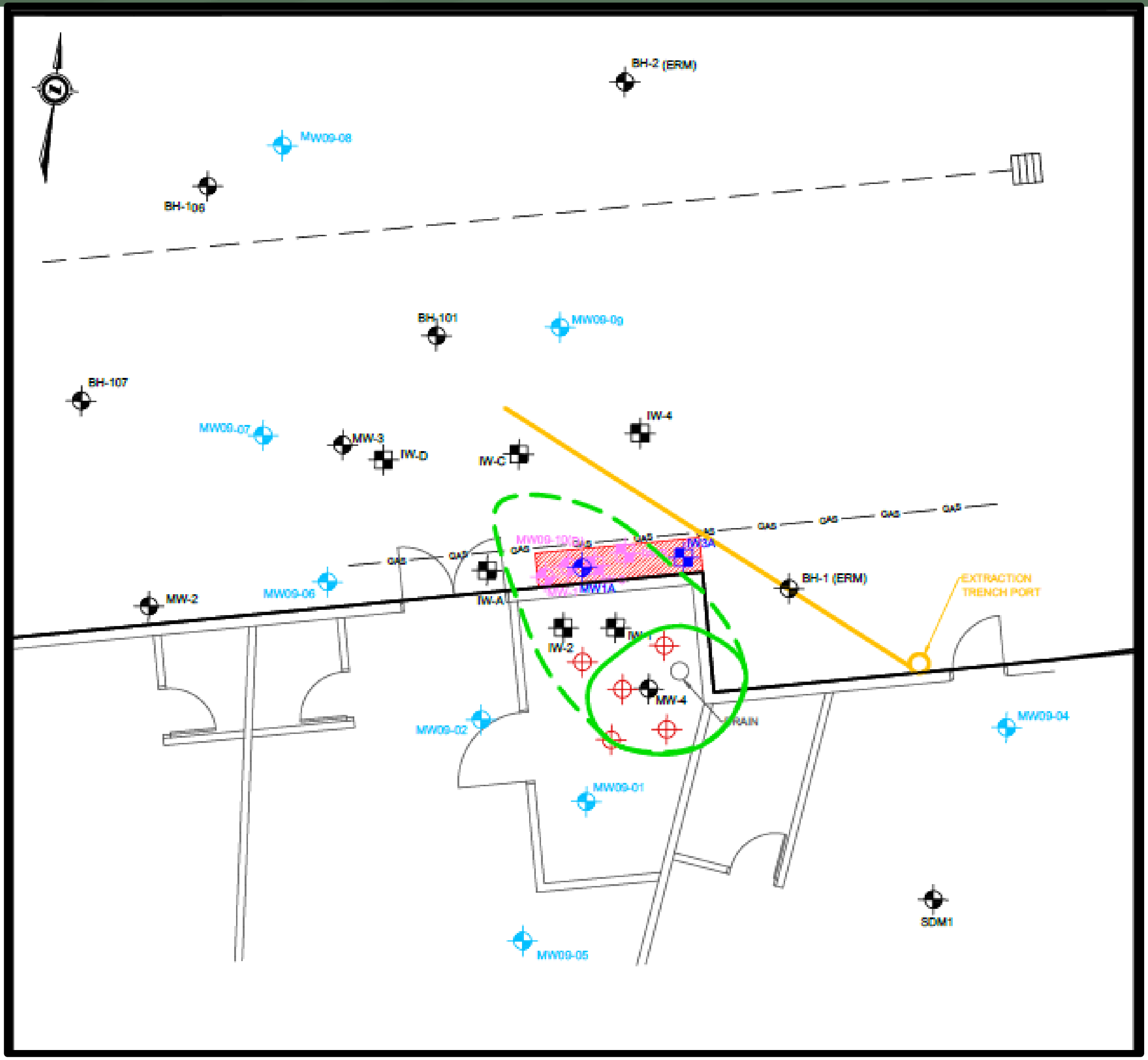


Liu et al., 2016



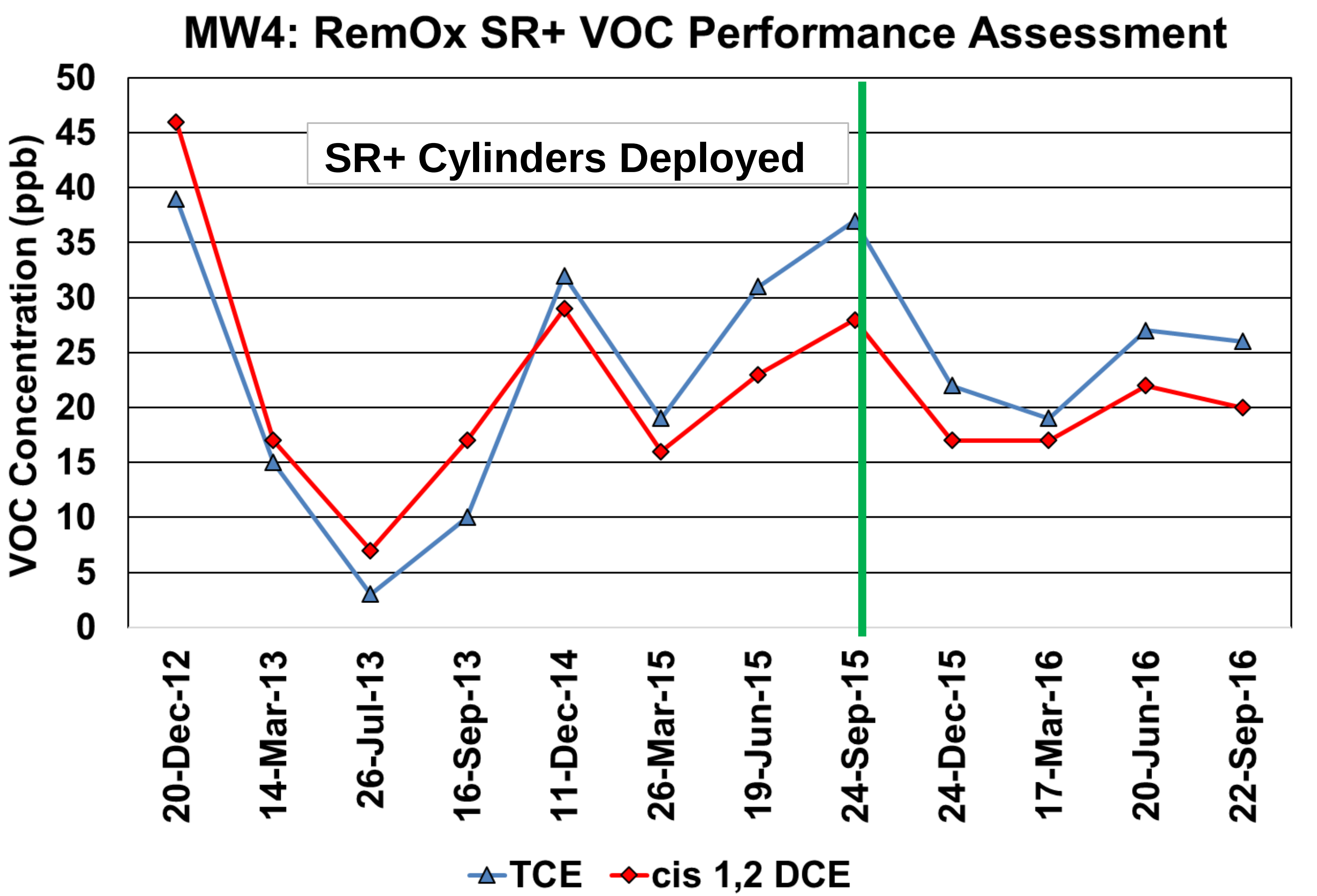
Wang et al., 2015

Field Results: RemOx SR+



- 10 SR+ cylinders installed

Field Results: RemOx SR+



Significance: Micropollutants

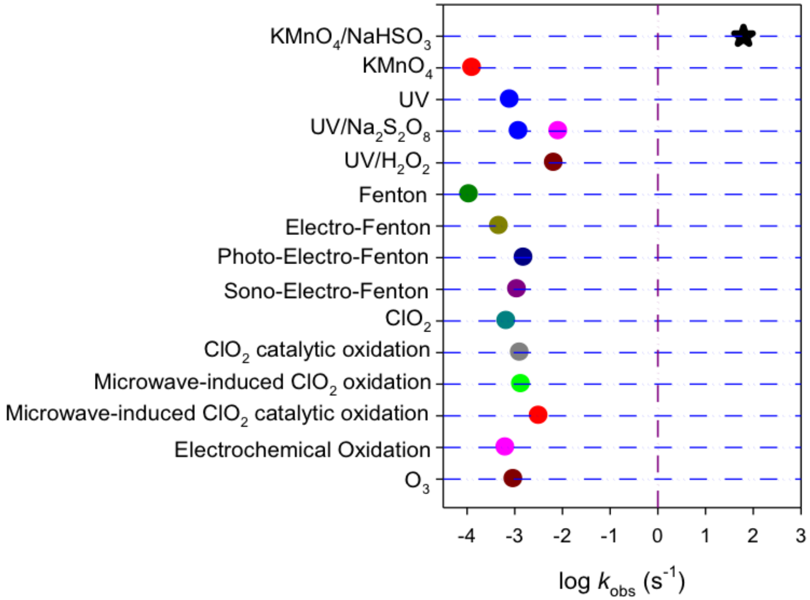
- Permanganate highly reactive with compounds that possess olefin (carbamazepine) and phenolic (acetaminophen, BPA) moieties in their structures

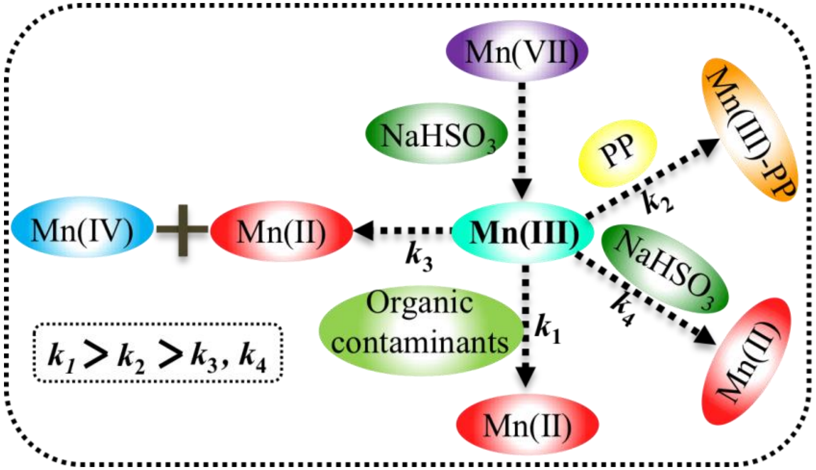
- Compounds exhibiting high reactivity with HMO-PMS possess secondary/tertiary aliphatic or aromatic amine groups in their structures (e.g., sulfamethoxazole)

- PMS activation through permanganate decomposition generates highly reactive radical species

Significance: "Activated" Permanganate

- "Activated permanganate" process causes very rapid oxidation of contaminants
- System has the characteristics of an AOP, with Mn activated to some reactive intermediate
- Translation to a new type of AOP seems possible





Permanganate-Based Oxidant Systems Summary

- Novel treatment strategy for removing a variety of micropollutants and emerging contaminants
- SR cylinder technology can help address “rebound” and back-diffusion
- Mn-based oxidant strategies can be applied with direct push or in wells (SR technology) or liquid pressurized injections
- Two-for-one injection liquid injection followed by SR deployment for long-term passive treatment

Must Attend Friday Talks!

- Manganese Activated Persulfate (MnAP) for the Treatment of Recalcitrant Organics: Development and Commercialization, Bruce Marvin, Geosyntec Consultants
  - Beatty Conference Room (9:55-10:25 AM)

- ISCO Reingeneered, Robert Luhrs, Raytheon Company
  - Beatty Conference Room (11:25-11:55 AM)

Thank You!
Questions?

pamela.dugan@caruscorporation.com

815-224-6870