Denatonium Benzoate Removal from Water Sources Using Oxidation with Chlorine

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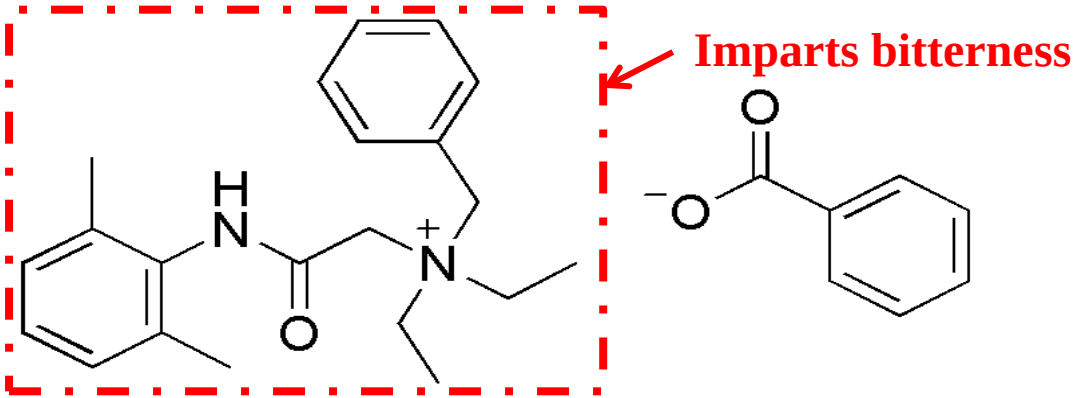
What is Denatonium Benzoate (DB)?

- Bittering Agent
  - Bitterest substance in existence
  - Taste threshold of 0.05 mg/L[(1)]
  - Unpalatable at concentrations of 30-100 mg/L
- DB is a quaternary ammonium salt, and its off-flavor is due to the denatonium ion
- Often added to common products like paint and nail polish
  - Ingestion deterrence
- Inexpensive additive
  - 1 tsp for 50 gallons
  - of antifreeze
  - $0.03-0.04/gallon



Source: upload.wikimedia.org/.../Denatonium_benzoate.png

Addition to Antifreeze

- According to Humane Society Legislative Fund at least 10,000 animals poisoned after ingesting ethylene glycol each year [2]
  - Ethylene Glycol = sweet taste but toxic
  - Biodegradable[4]
- Laws in several states mandate the addition of 30 ppm DB to antifreeze and engine coolant containing more than 10% ethylene glycol sold or manufactured in the state
  - California, Oregon, Arizona, Georgia, Illinois, Maine, Maryland, Massachusetts, New Jersey, New Mexico, Tennessee, Utah, Vermont, Virginia, Washington, West Virginia, and Wisconsin [1]

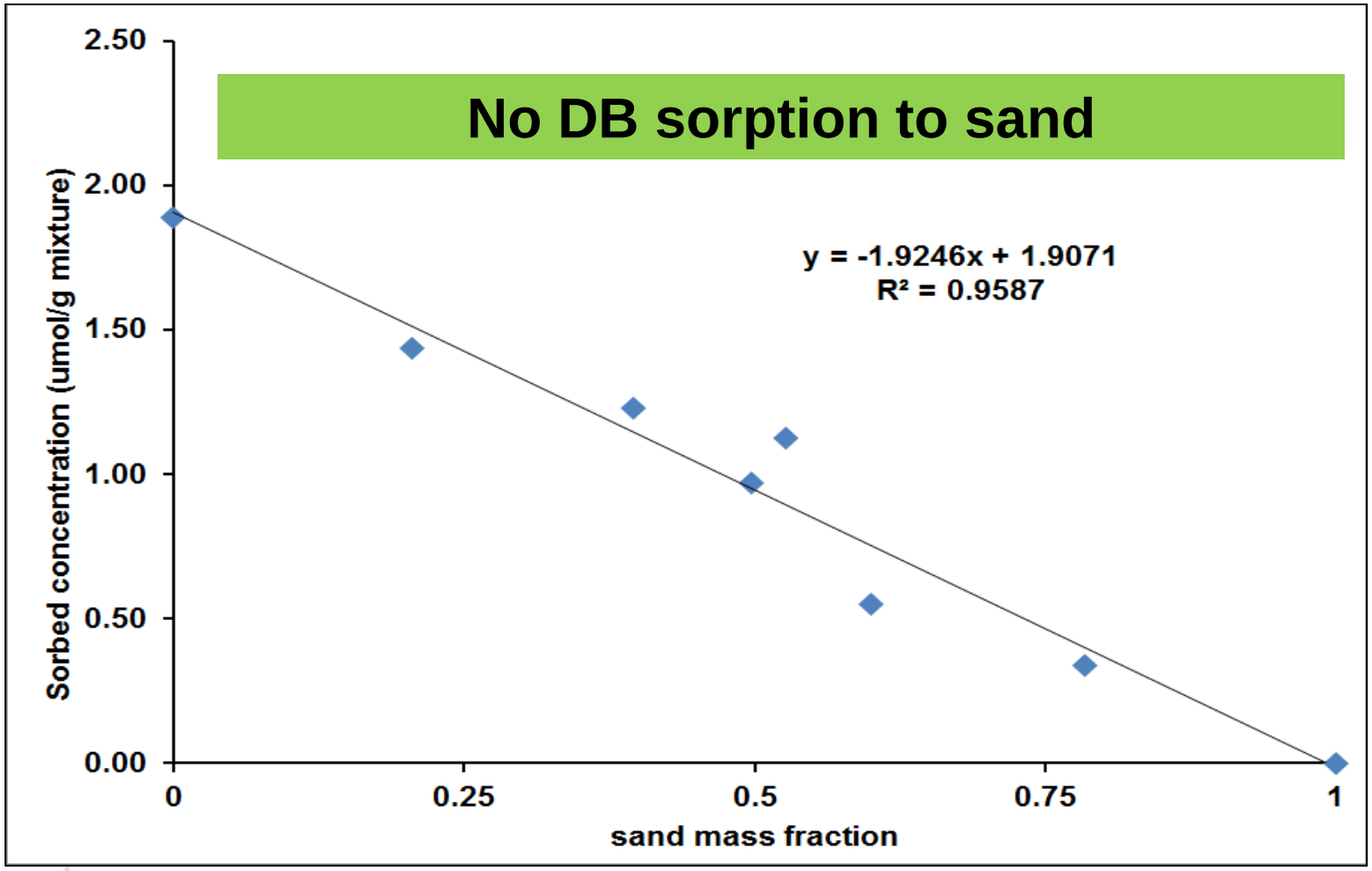
Addition to Antifreeze

- Consumer Specialty Products Association and Humane Society Legislative Fund (December 2012)[(2)]
  - DB added to antifreeze and engine coolant to prevent ingestion and accidental poisoning
  - All 50 States + District of Columbia
- Release of antifreeze into the environment (intentional or unintentional)
  - Improper disposal
  - Runoff and seepage





Research Significance



Clay fraction

Sorption/removal DB ion

Sand fraction

Crosson, G.S.; Crosson, K.M.; Thorpe, S.; MacPherson, L.M.; Murdock, M.M.; Smith, B. ***Activated Carbon and Clay Minerals for the Sorptive Removal of Denatonium Ions from Denatonium Benzoate Solutions*****. Journal of Water Resource and Protection. Accepted for publication.**

- Organic-free water, 100-1000 ppm denatonium benzoate
- 33,000 mg/L (0.8 g/24 mL) powdered activated carbon (PAC) dose
- 24-hr contact time, constant mixing at 60 rpm
- adsorption achieved 100% denatonium ion removal

- Organic-free water, 5-70 ppm denatonium benzoate
- 5 - 100 mg/L PAC dose
- 3-hrs or 24-hr contact time, constant mixing at 60 rpm
- Lower pH more favorable adsorption
- Langmuir model fit: S_m equals mg/g and K_L equals 0.0153 L/g, Langmuir separation factor r-value was 0.481
- Sorption of denatonium ion onto PAC was favorable, but adsorption achieved up to 50% DB removal with a 3-hour contact time
- not less than taste threshold

PAC treatment alone is insufficient

Oxidation with Chlorine

- American Water Works Association expressed concern that DB could be problematic for the drinking water industry and consumers
- DB exhibits limited to no biodegradability[3]
- Consumer Products Safety Commission reported that DB would likely be degraded by oxidants with no evidence to support the claim[5]
- **Research Objectives:**
  - To determine if oxidation (used separately or with PAC treatment) could suitably lower DB levels rendering water palatable
  - **Hypothesis:** Oxidation treatment will insufficiently lower denatonium ion concentrations, especially in natural waters

Materials and Methods

- Oxidation batch tests
  - 24-mL amber vials filled to no headspace
  - Water sample spiked to achieve proper concentration of DB
  - Cl_2 added to the samples as NaOCl

- Water Samples:

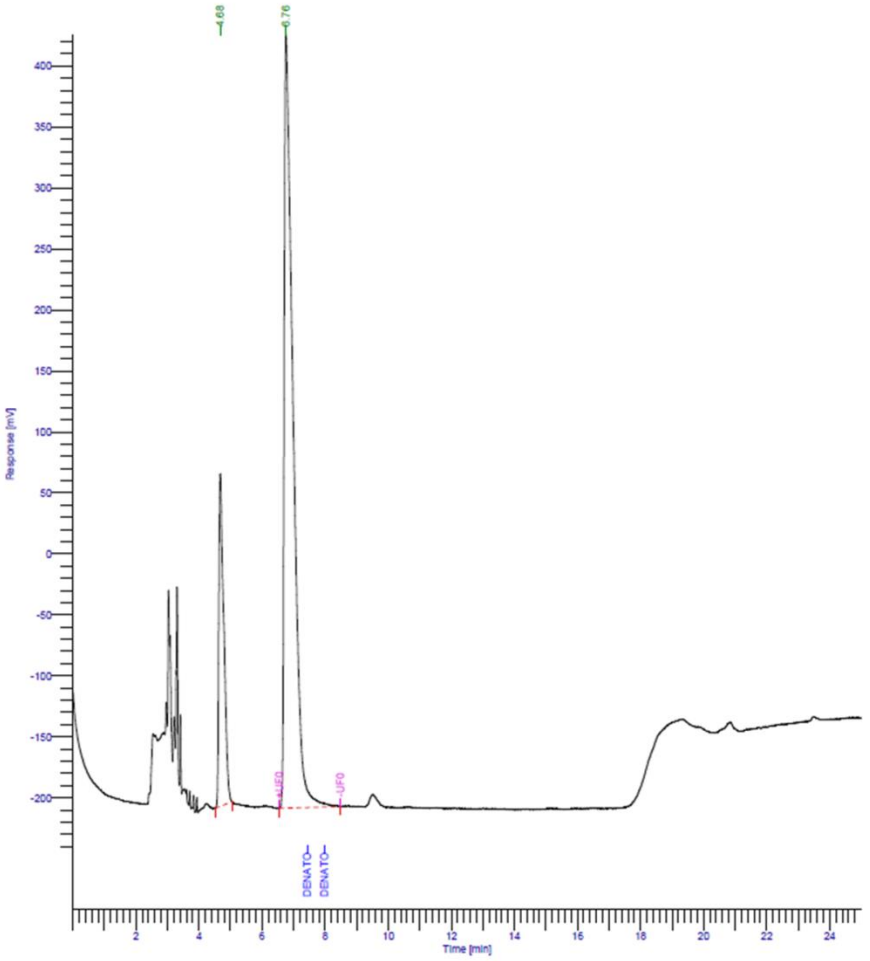
Table 1: Water Quality Characteristics		
Water Sample	Turbidity (NTU)	pH
Organic Free Water	-	~7
Groundwater	0.13	6.3
Softened Groundwater	165	9.3
Softened-Settled Groundwater	2.1	7.9

Materials and Methods

- Oxidation batch tests
  - Standards made with 5, 10, 30, 50, and 100 ppm DB
  - Blanks made that contained the water sample spiked with the same initial DB concentration
  - Redundancy: three replicates of samples
  - All samples mixed on a rotary shaker
  - After oxidation: Quantify remaining DB using high-performance liquid chromatography instrument (HPLC)

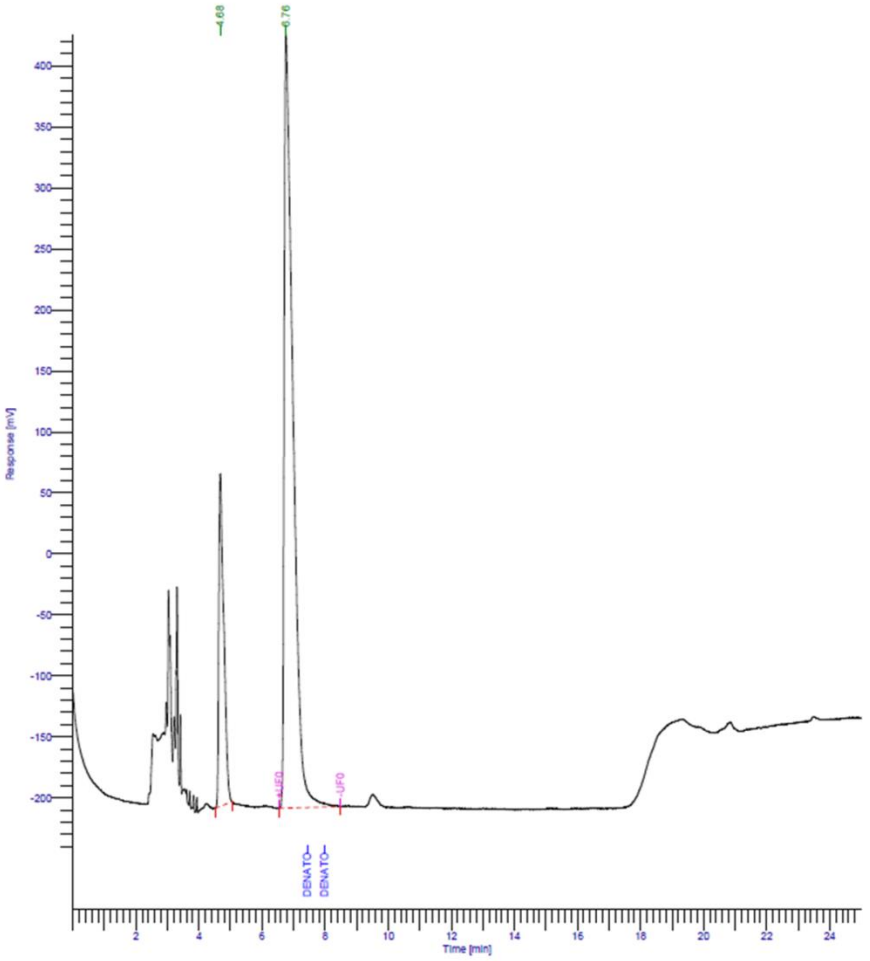
Materials and Methods

- After oxidation: Quantify remaining DB using high-performance liquid chromatography instrument (HPLC)
  - 2000 μL aliquots placed into vials
  - Quantified DB by passing solvent mix (mobile phase) and sample through chromatographic column at very high pressures
  - Instrument measured the retention time of the sample's components from the chromatographic column and these components were detected using a UV-VIS detector



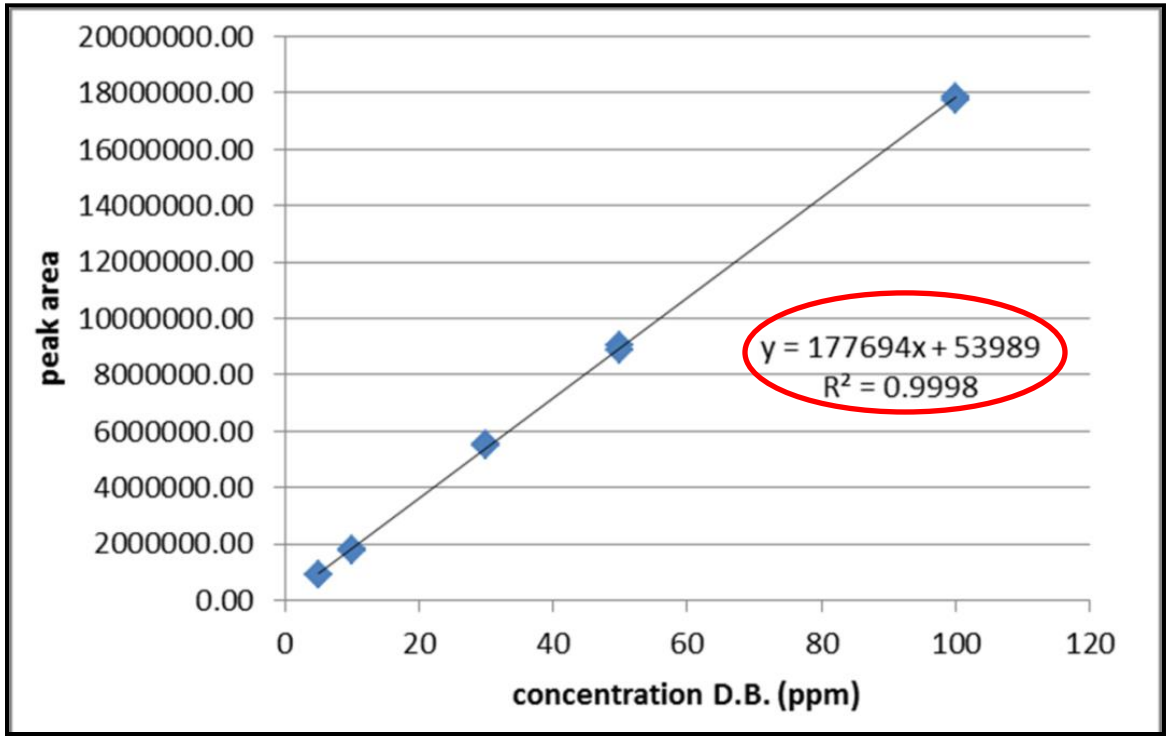
Materials and Methods

- After the analysis on HPLC
  - Chromatogram generated
  - Peak identified for each sample
  - Measured area underneath the curve
  - Use the standards to develop a correlation between the area and the concentration of denatonium in the sample



Materials and Methods

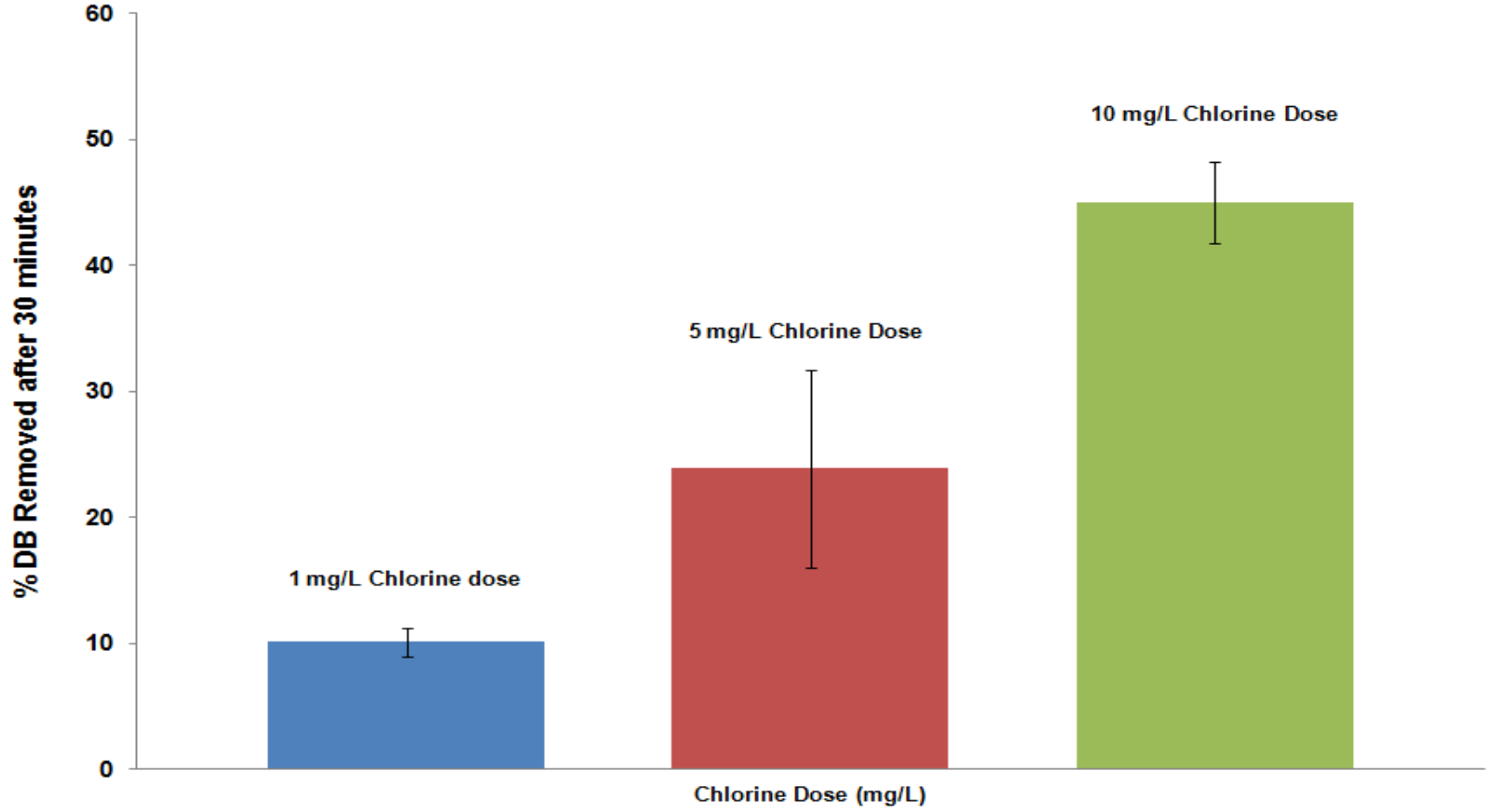
- Set of DB standards (5, 10, 30, 50, and 100 ppm DB) run with each set of samples analyzed
- Developed calibration curve
- Linear mathematical relationship between DB peak area (y-axis) and DB concentration (x-axis)
- Calibration curve equation used to determine the DB concentration in an experimental sample by using the sample's DB peak area



For chlorine oxidation, optimal contact time was 30 minutes (significantly different at 80% confidence level). No other times statistically different (95% confidence level)

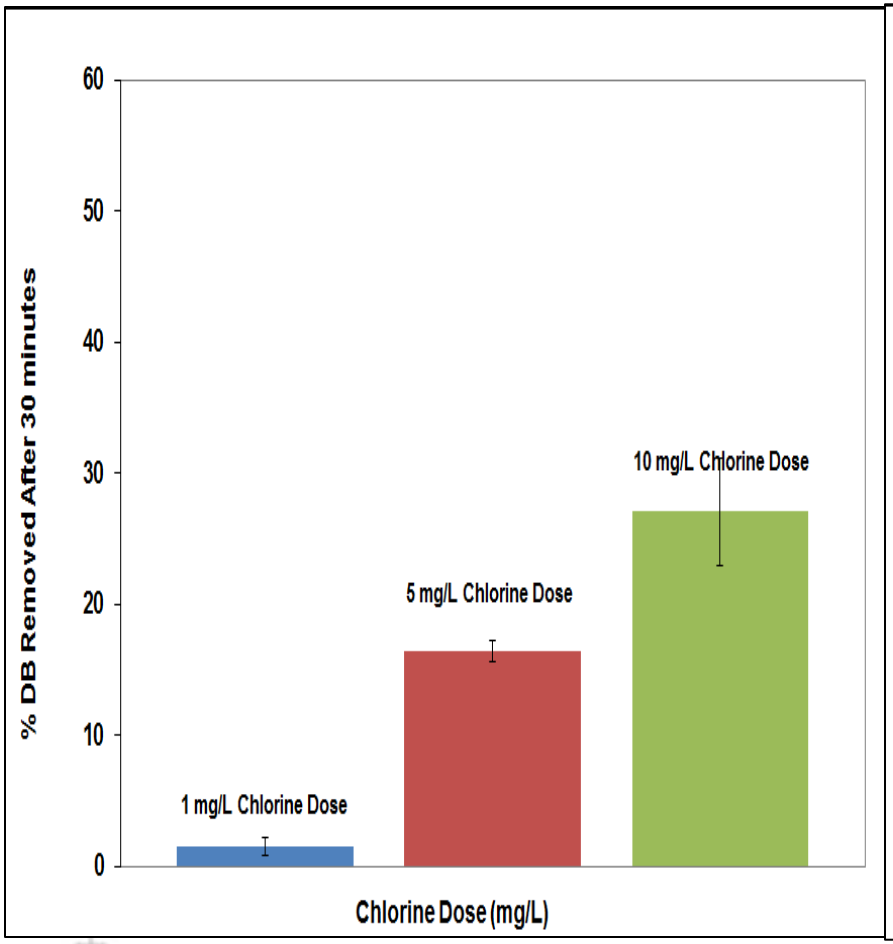
T test name	t test 10 min vs 20 min	t test 10 min vs 30 min	t test 10 min vs 40 min	t test 10 min vs 60 min	t test 20 min vs 30 min	t test 20 min vs 40 min	t test 20 min vs 60 min	t test 30 min vs 40 min	t test 30 min vs 60 min	t test 40 min vs 60 min
Statistically different to 80% Level?	NO	YES	NO	NO	NO	NO	NO	YES	YES	NO
Statistically different to 90% Level?	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO
Statistically different to 95% Level?	NO	NO	NO	NO	NO	NO	NO	NO	NO	NO

Impact of Chlorine on DB Removal (pH ~7) in Organic Free Water: Increased removal with increased dose; 7-44% removal

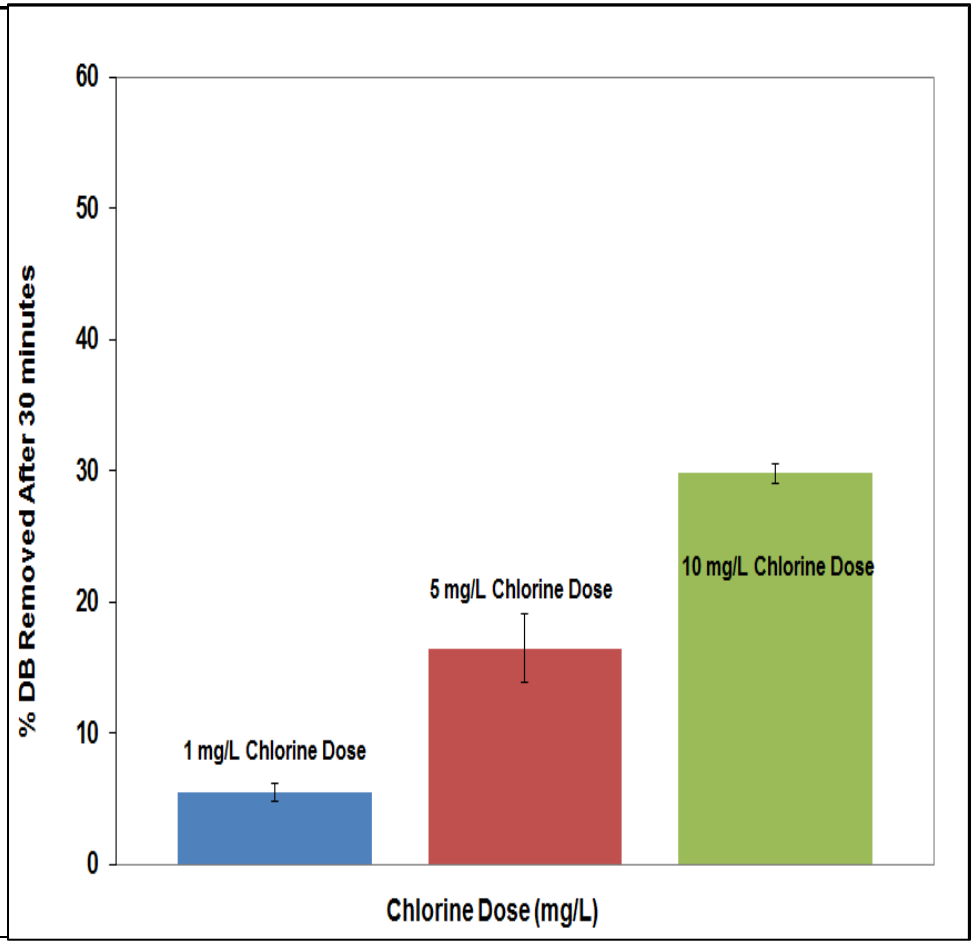


Impact of pH on DB Removal with Chlorine: Best removal at pH ~7

pH 8 (1.5-27% removal)



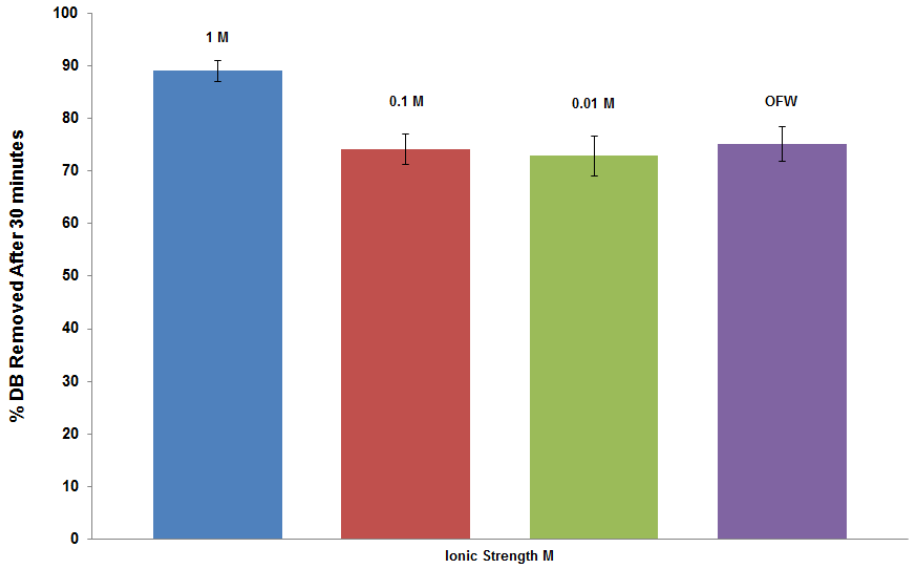
pH 10 (6-30% removal)



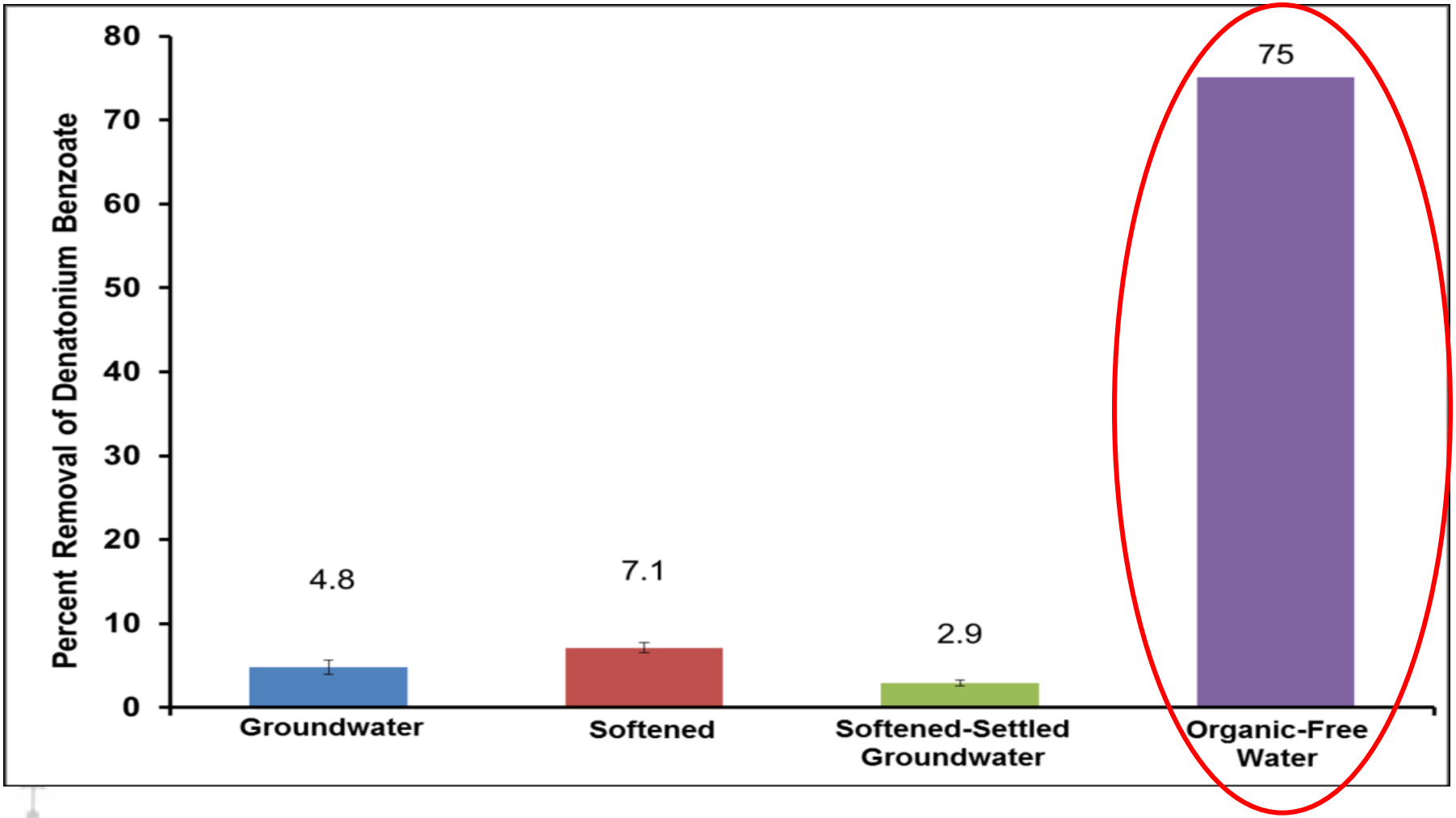
Optimal Conditions for Chlorine Oxidation of Denatonium Ion

Treatment Parameter	Optimal Treatment Condition
Contact time	30 minutes
pH	7
Ionic Strength	1 M (NaCl), 89% removal
Chlorine dose	2 mg/L (ppm); 75% removal

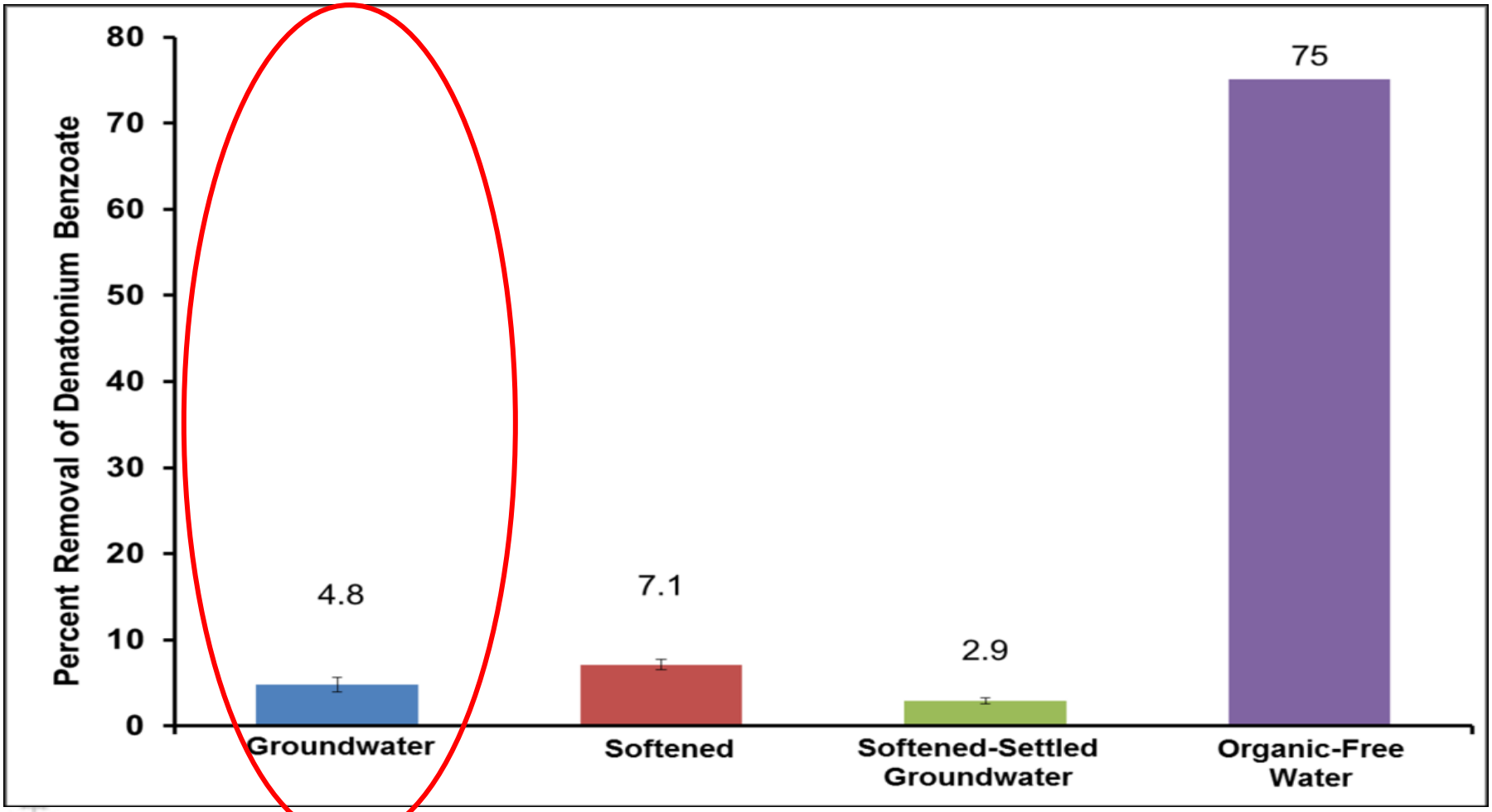
Remaining denatonium ion concentration is higher than 0.05 ppm taste threshold



75% DB removal in organic-free water (pH 7; 2 ppm chlorine; C_o= 70 ppm)

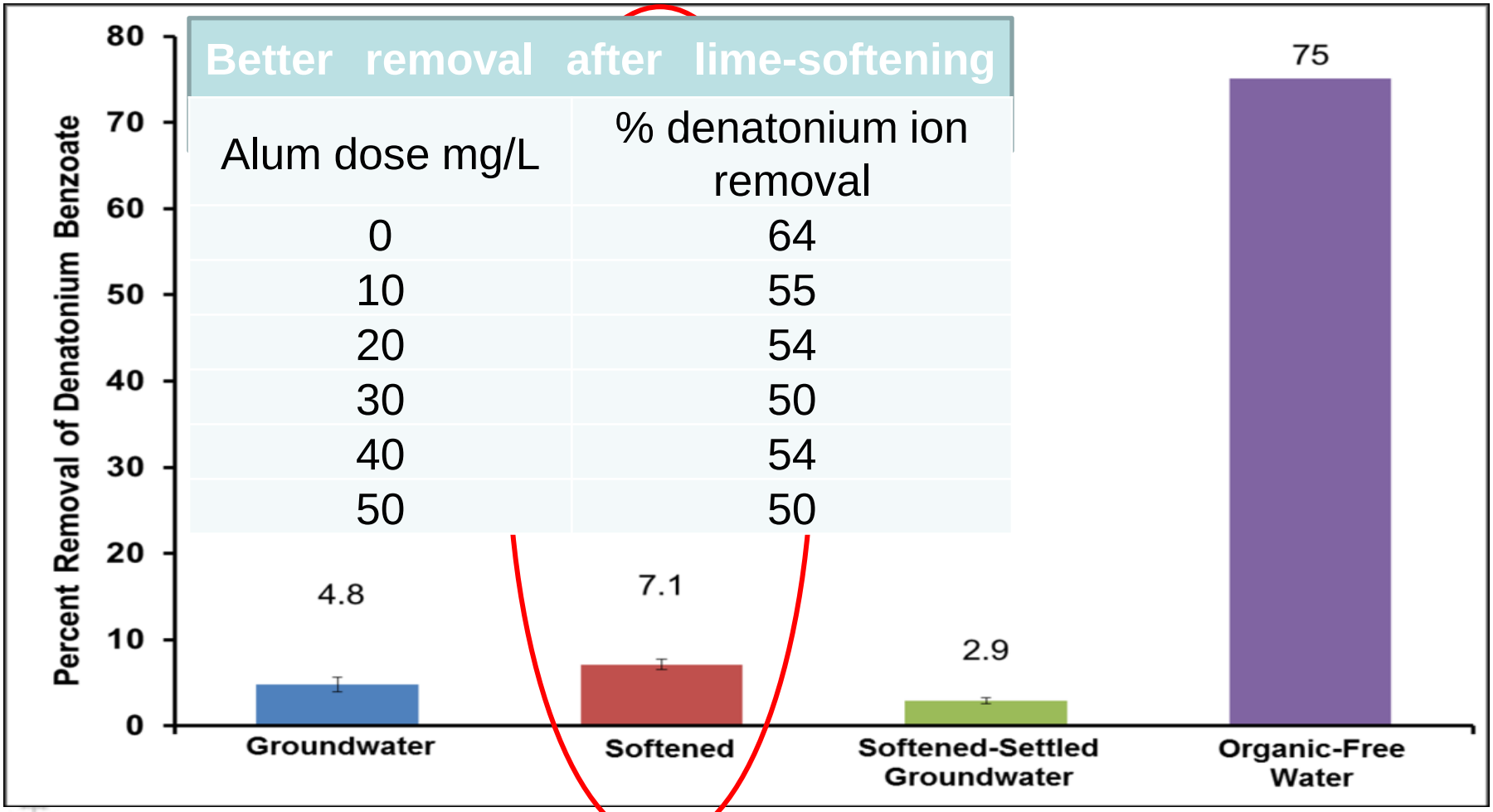


4.8%DB removal in groundwater (pH 6.3; 2 ppm chlorine; C_o= 70 ppm)

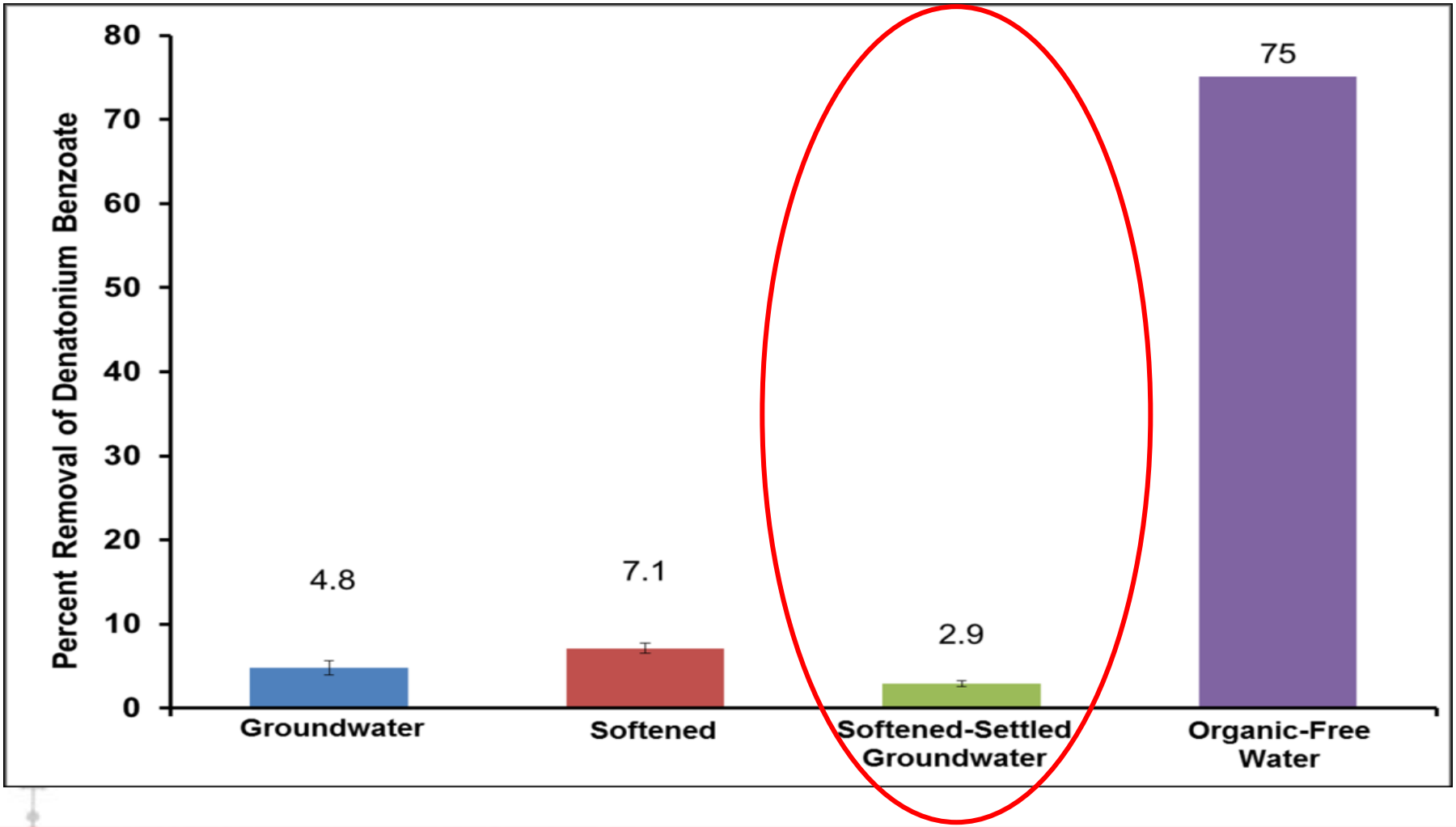


7.1% DB removal in softened water (pH 9.3; 2 ppm chlorine; C_o= 70 ppm)

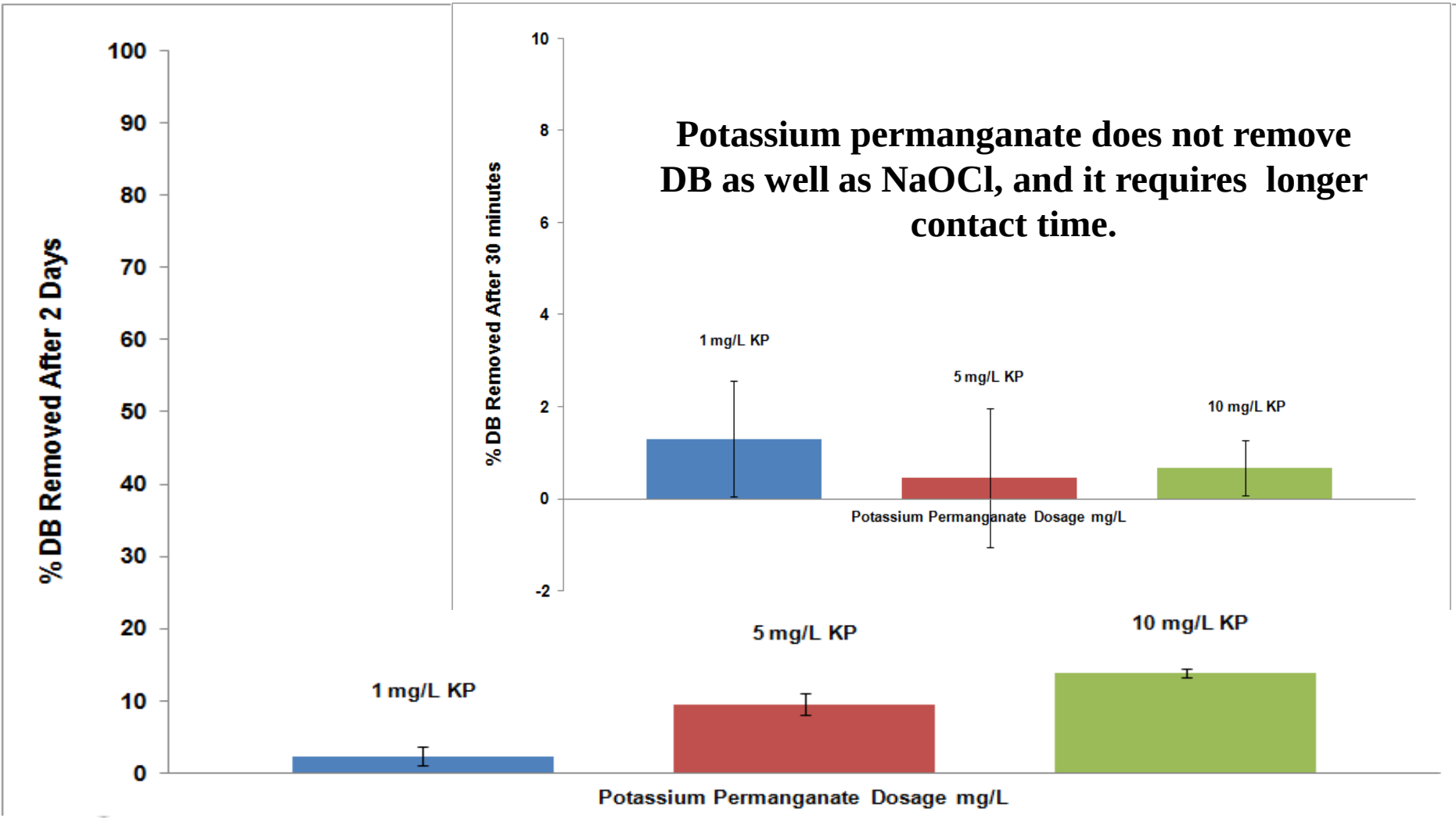
Better removal after lime-softening	
Alum dose mg/L	% denatonium ion removal
0	64
10	55
20	54
30	50
40	54
50	50



2.9% DB removal in soften-settled water (pH 7.9; 2 ppm chlorine; C_o= 70 ppm)

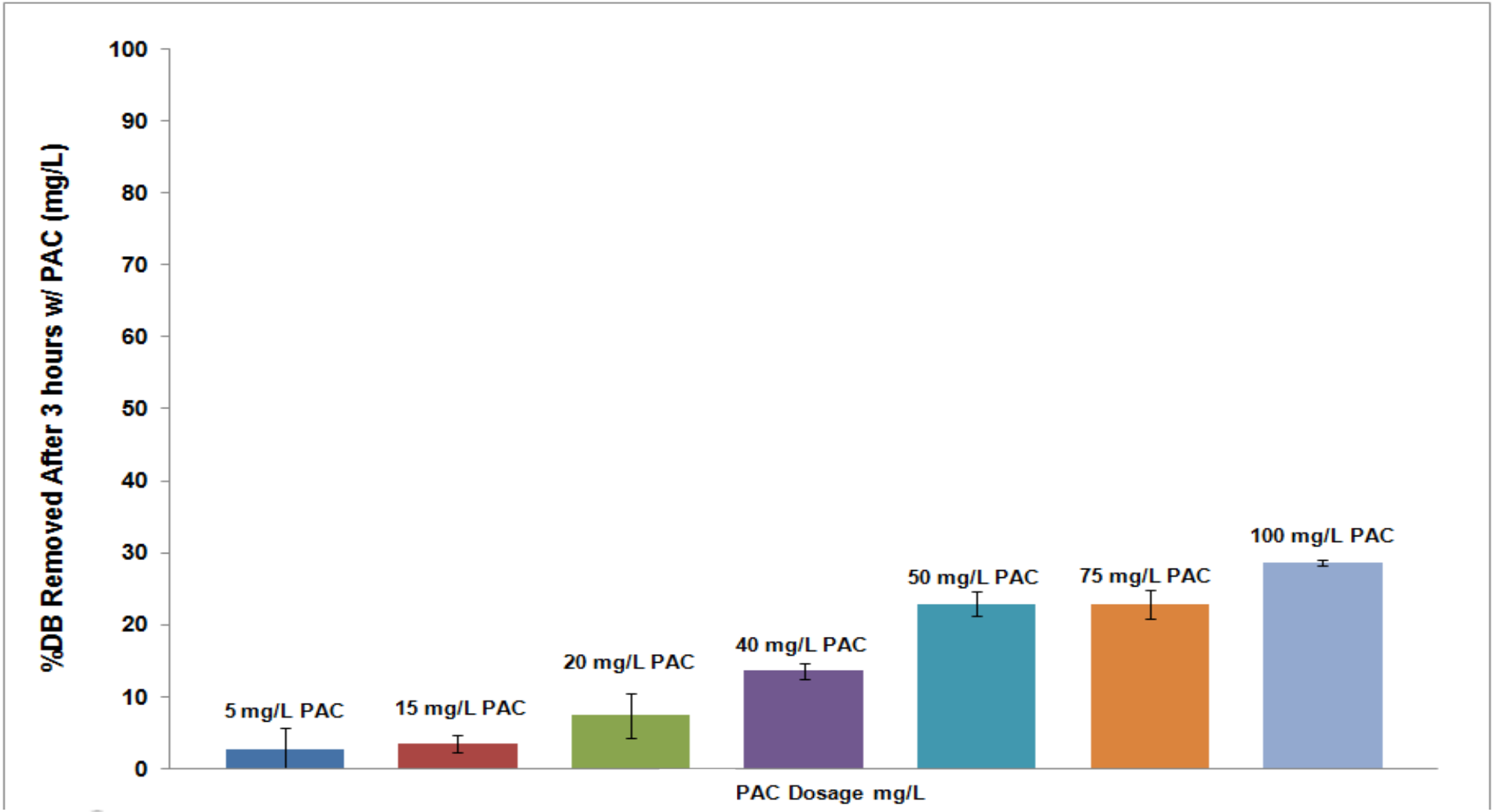


Impact of Potassium Permanganate on DB Removal

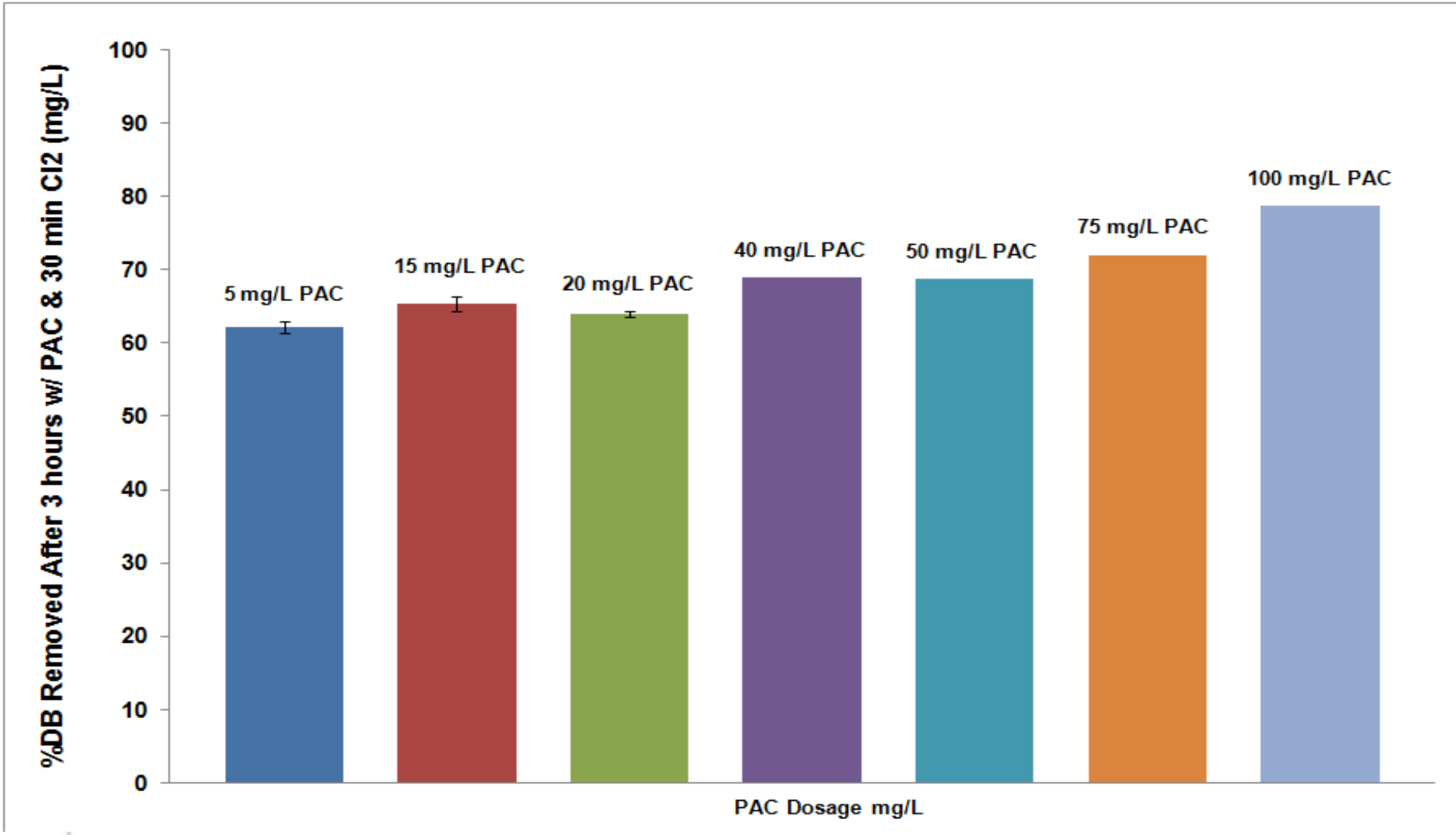


Potassium permanganate does not remove DB as well as NaOCl, and it requires longer contact time.

DB removal with PAC Treatment (3 hrs)



DB removal with PAC and then Oxidation Treatment (2 mg/L chlorine)



Conclusion

- Water pH conditions higher than 7 result in lower DB removal via chlorine oxidation
  - Cl_2 added to water forms a stronger oxidizer at pH 6-7.5 than higher pH values
- Softened Groundwater samples:
  - DB possibly sorbed to softening precipitates and flocs formed in the softened groundwater sample, thereby yielding higher DB removal despite the water sample's high pH (9.3)
  - Softening precipitates = higher turbidity for the softened groundwater sample
- Oxidation treatment with chlorine was **not successful** in lowering the DB concentration below the taste threshold of 0.05 ppm to make water palatable

Conclusion

- Future research will examine:
  - Temperature effects on chlorine oxidation
  - Denatonium ion removal using flocculation and sedimentation treatment
  - More powder activated carbon adsorption with oxidation

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Questions?