

Toxicity in Wastewater Systems

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AQUAFIX Inc.

What will be covered?

**Symptoms
of toxicity**

**Causes of
toxicity**


**Aquafix
Quaternary
Ammonium
Cation
Research**

**Methods of
overcoming
toxicity**

Introduction



What is Toxicity?



What is the main problem with toxicity?

Symptoms of Toxicity

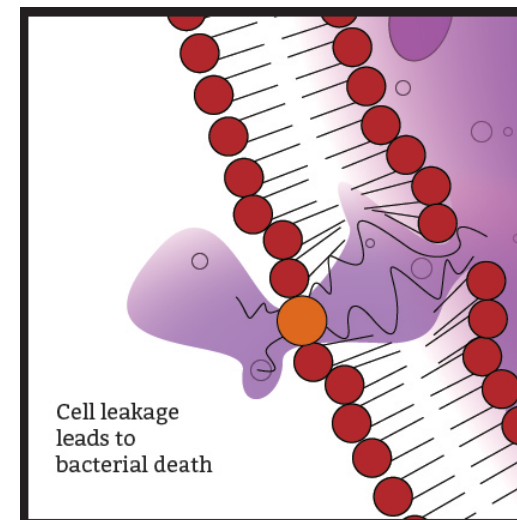
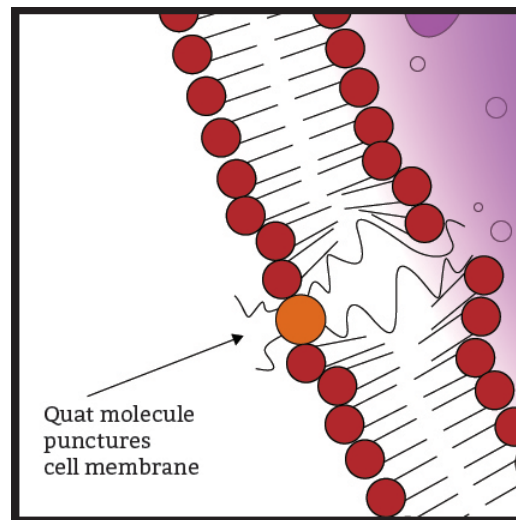
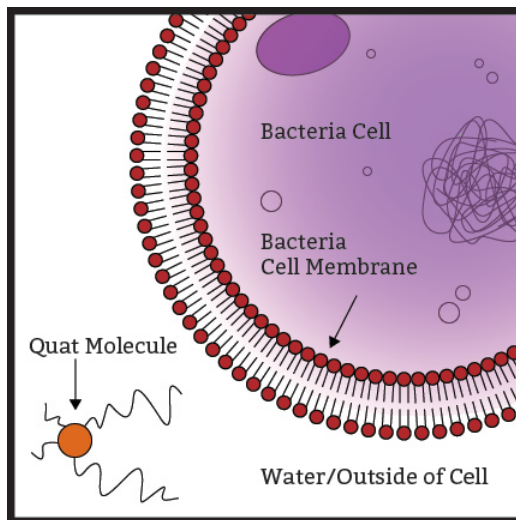
1. Difficult to confirm which symptoms are commonly caused by toxicity because it is difficult to confirm if problems are caused by toxicity, and what problems are caused by it
2. General signs of stress could be signs of toxicity
3. Increased extracellular polymeric substance (EPS) generation
4. Cloudy supernatant on settled sludge
5. Reduced prevalence of metazoan/protozoans, especially less resilient to stress varieties
6. Reduced filamentous bacteria, or selection of a specific strain of filamentous bacteria
7. Loss of nitrification
8. Others

Causes of Toxicity

1. Mild to Severe (Obviously not enough time to list every toxin today)
2. Excess septic waste
3. Chlorination (EX: when trying to get rid of filaments)
4. Sodium
5. “Non-Toxic” Metals
6. Antimicrobials (Antibiotics, alcohols, others)
 - Quats!
7. Other nastier stuff

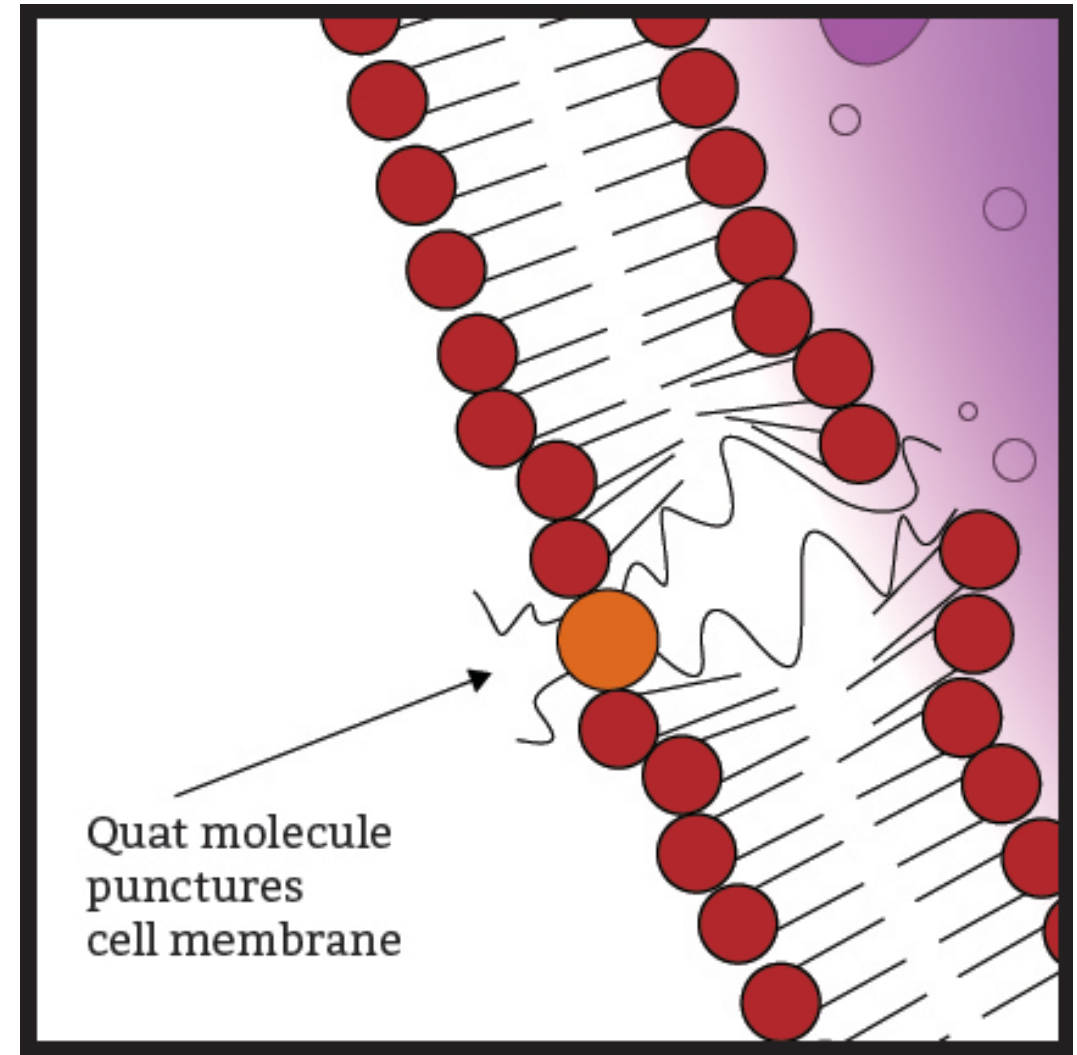
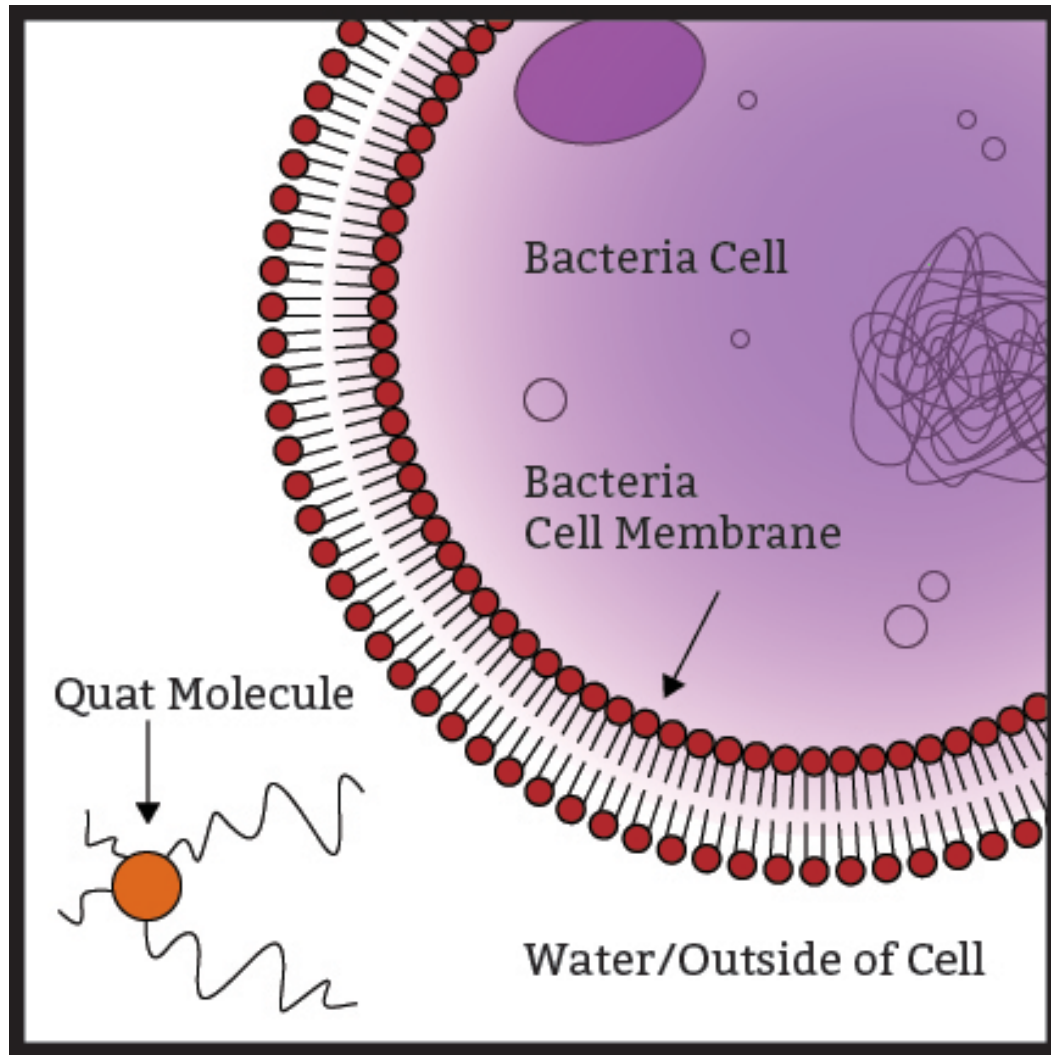
Quats! (Quaternary Ammonium Cations/QACs)

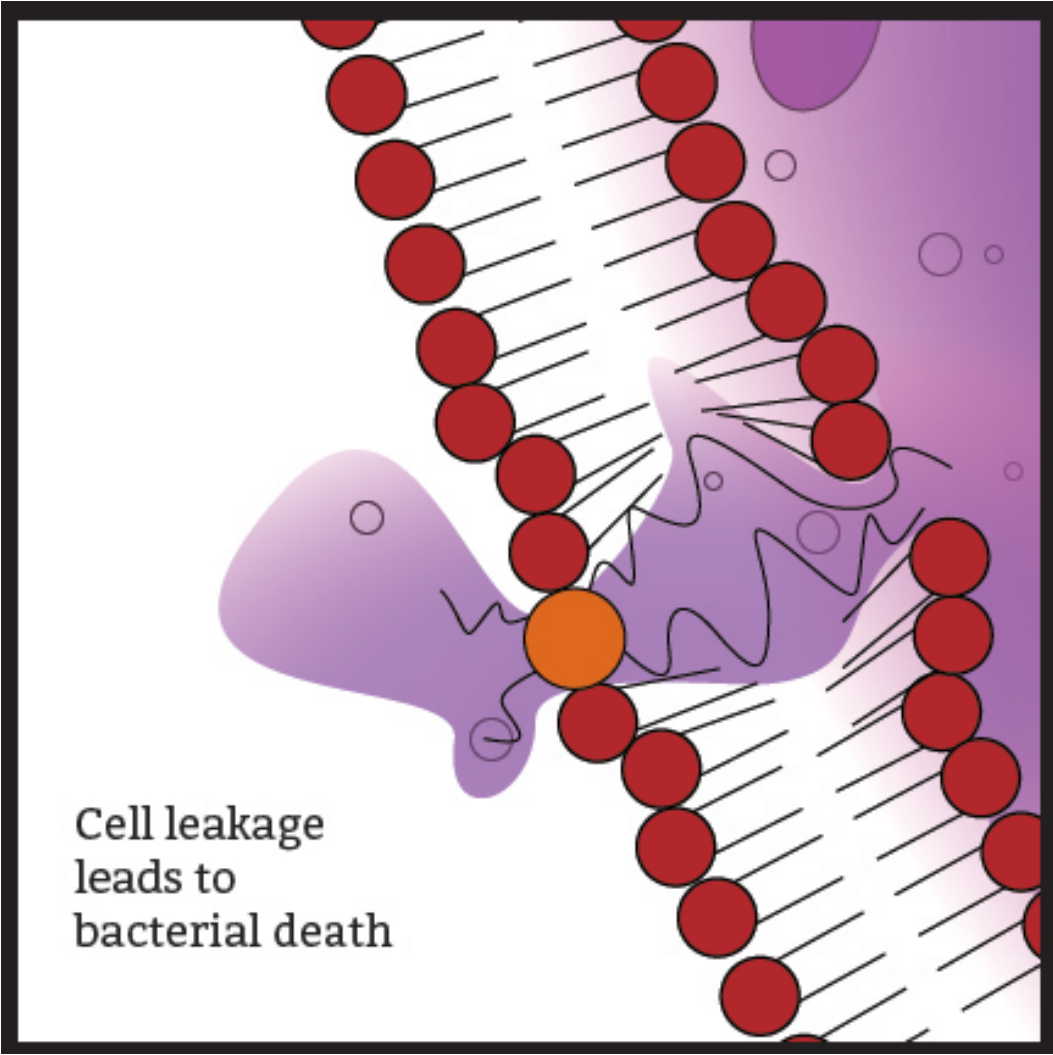
- Often used in food industries, therefore are often an antimicrobial concern for wastewater plants
- Very stable structure, likely to remain active from industry to wastewater plant
- Non-specific antimicrobial properties
- Near impossible to accurately measure in a wastewater sample



How Do Quats Work?

- Non-Polar (hydrophobic) side chains push into cell membrane, breaking up alignment of the lipid bilayer leading to cell leakage. Polar (hydrophilic) Ammonium end tends to stay on the outside of the cell
- Permanent positive charge of Quaternary Ammonium means its effectiveness is not impacted by pH
- Quats theoretically will remain active once a cell has died, but this tends to be too low level a release to cause problems





Cell leakage
leads to
bacterial death

Quat Studies: Overview, Goals, and Ideas

- Confirm what effects Quat can have on a wastewater process
- Determine if other forms of stress influence the toxicity of Quat
- Determine if long term exposure to moderate Quat dosages results in an accumulation of Quat in a system.

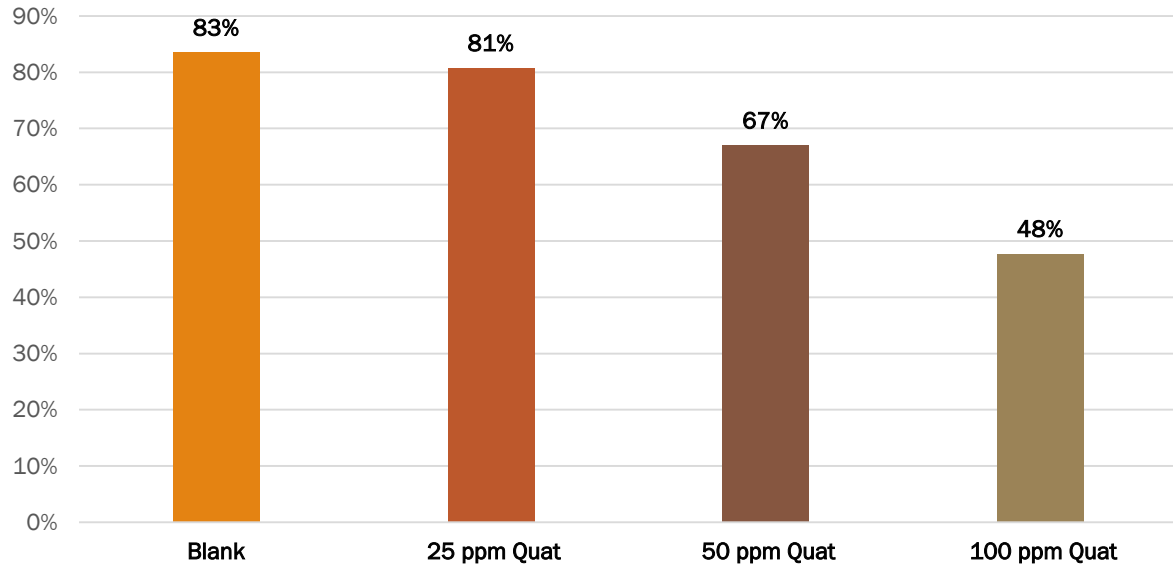
We tested Quats in a long term study, as well as several short term studies to get a rough idea what effects Quats can have in a process. More detailed studies are ongoing.

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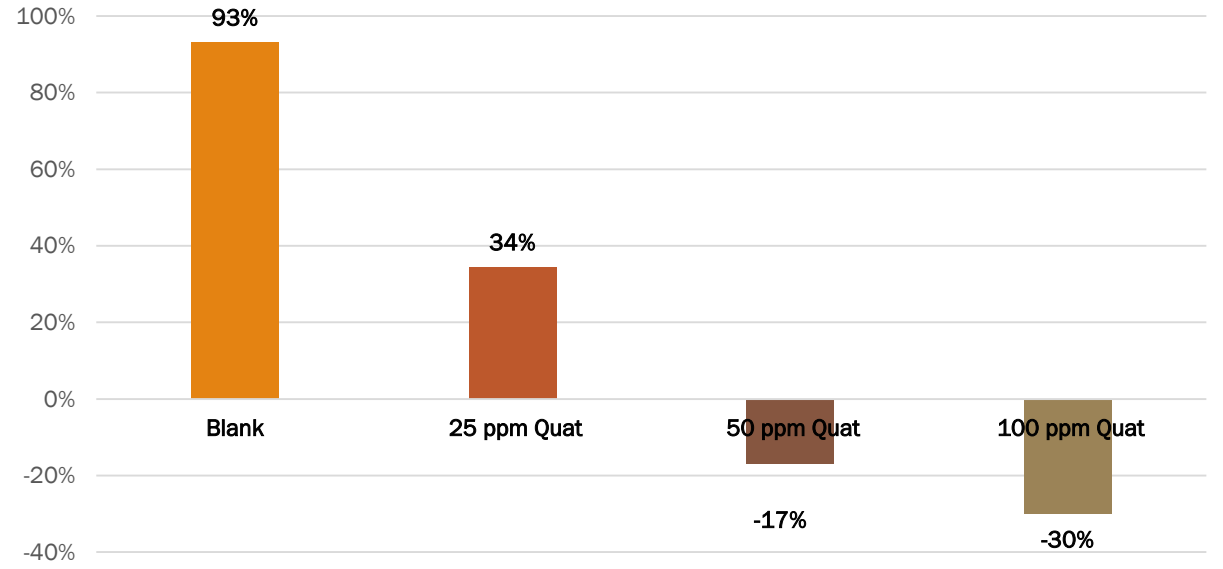
Acute Toxicity Overview

- In this study, we were attempting to determine a toxic dose rate for acute Quat exposure to a healthy wastewater sample.
- Used a known Quat concentration standard (product with listed Quat %)
- Mixed liquor for this testing is a healthy sludge sample we grow in the lab (for all testing)
- We used a slug dose of Quat, and analyzed the samples after mixing for 16 hours at 150 RPM on an orbital shaker plate

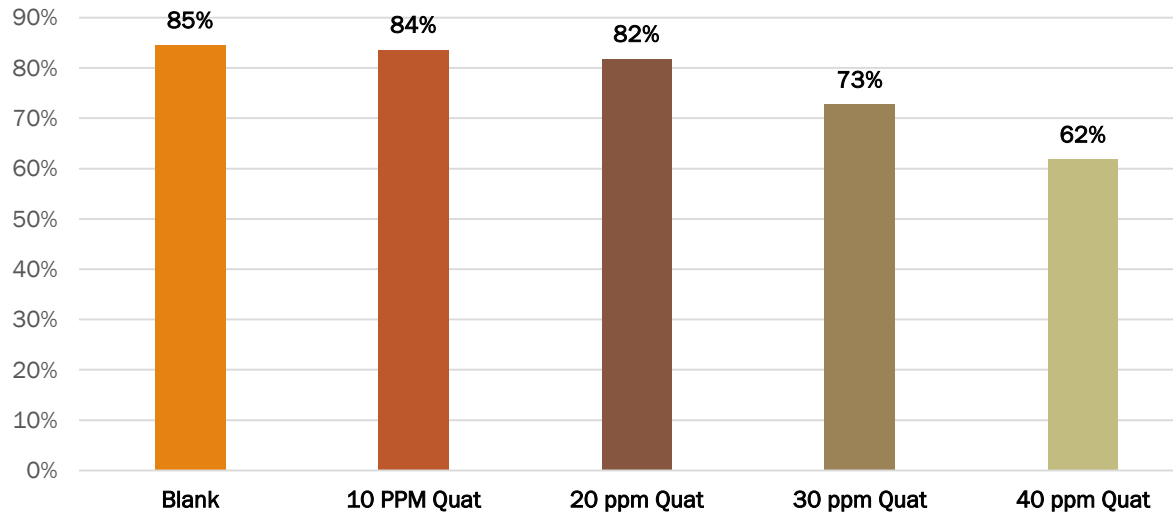
Percent COD Reduction MLSS 3000



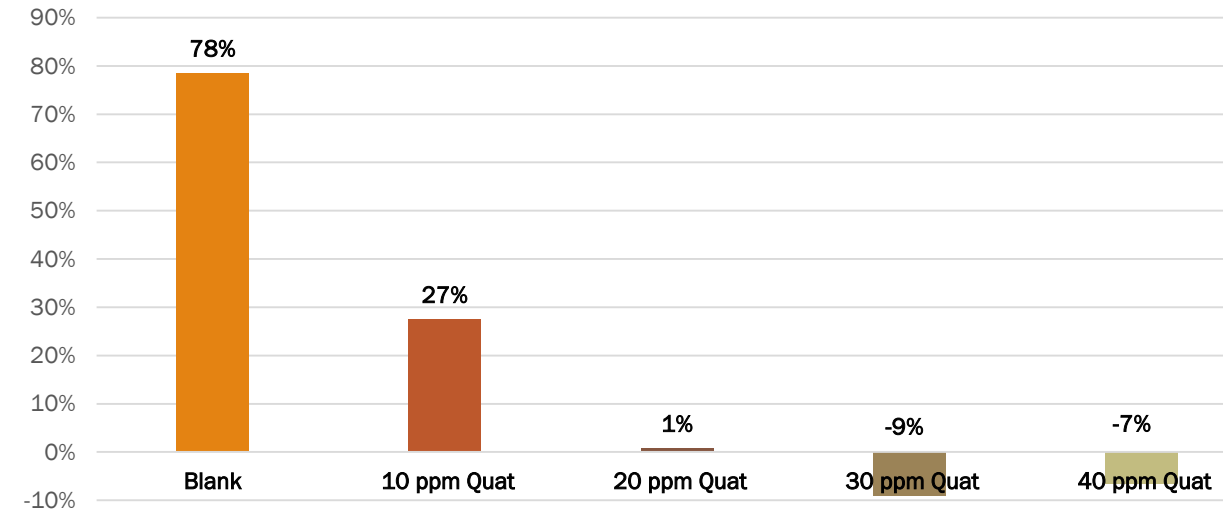
Percent Ammonia Reduction MLSS 3000



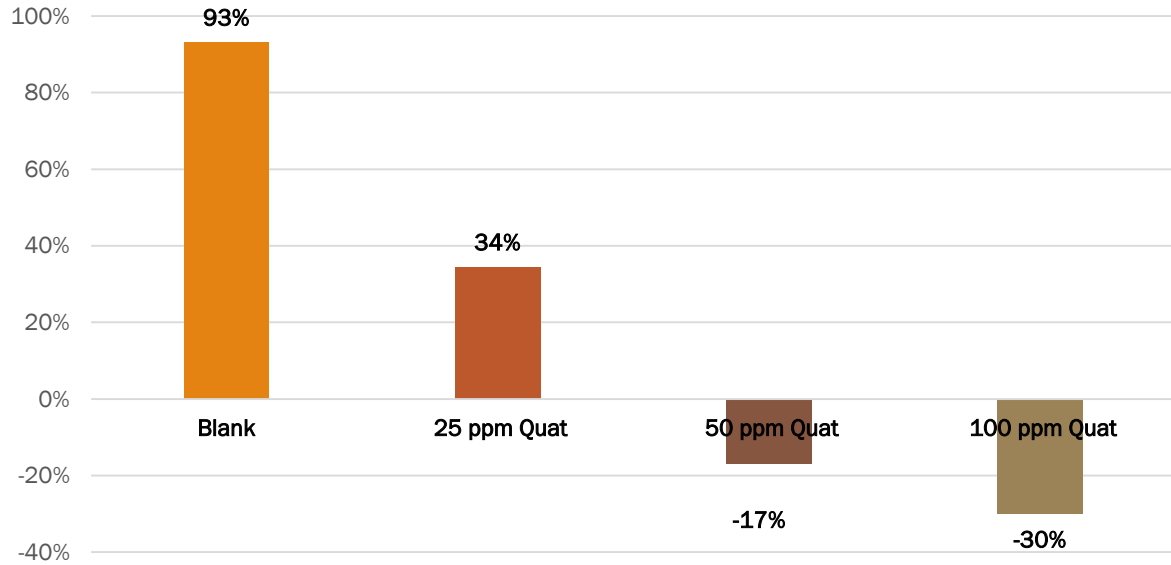
Percent COD Reduction MLSS 1800



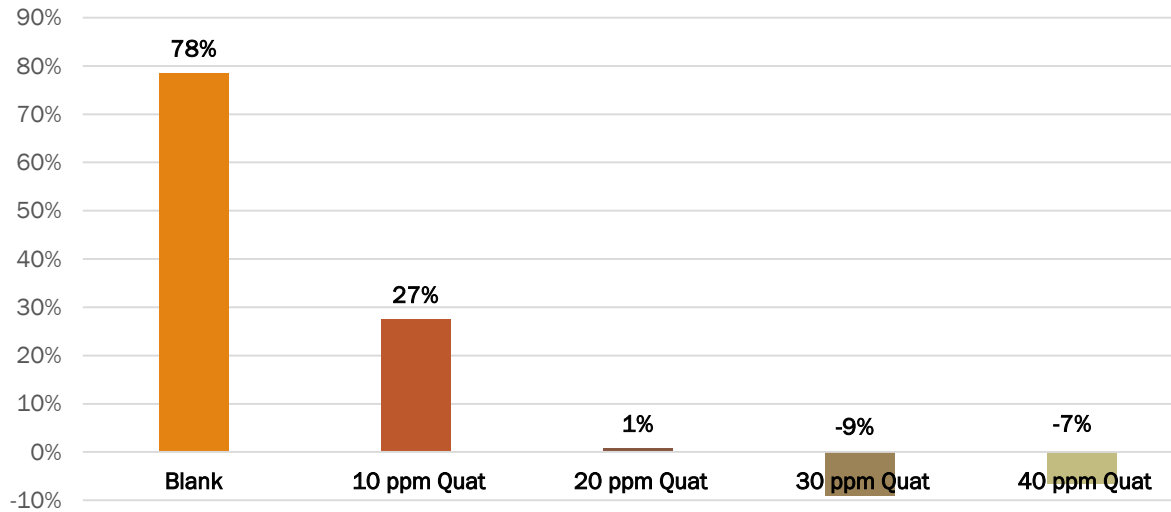
Percent Ammonia Reduction MLSS 1800



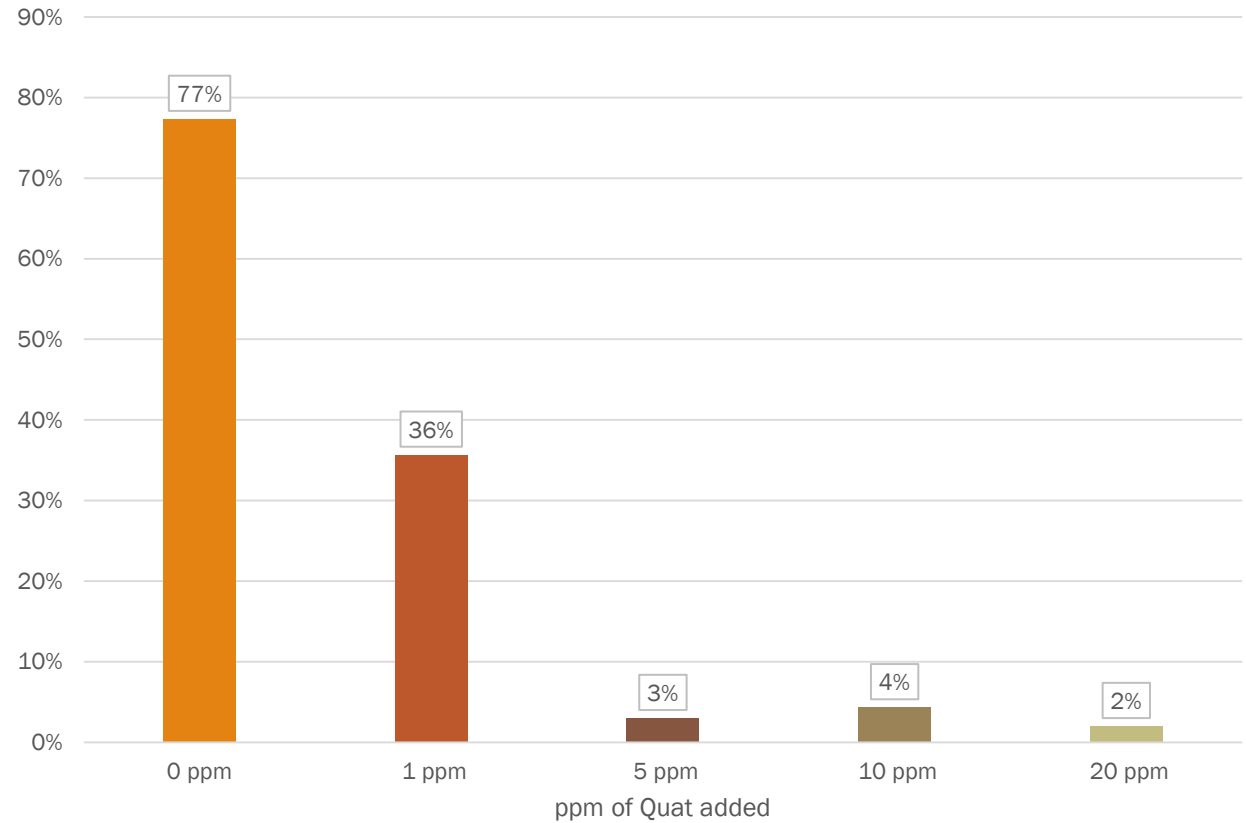
Percent Ammonia Reduction MLSS 3000



Percent Ammonia Reduction MLSS 1800



Percent Ammonia Reduction at Different levels of Quat



Test run with Lab nitrifiers on 9/19/18 – 9/20/18

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Acute study results

- We determined that higher MLSS levels caused Quat to be less toxic (assuming healthy sludge)
- It takes very high levels of Quat to inhibit COD removal
- In a healthy sample, it takes high levels of Quat to cause toxicity to nitrifiers

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Long Term Studies Overview

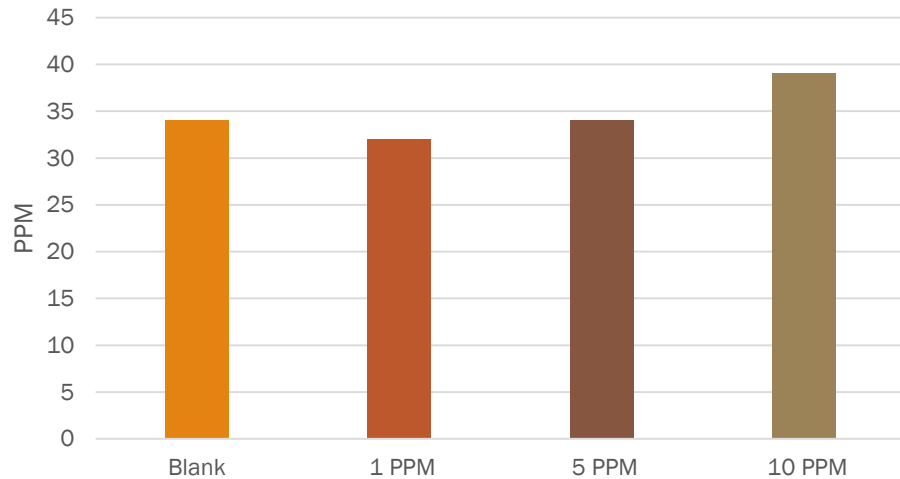
- This study was conducted with the same methods as the acute study, only reactors were analyzed each week for 1 month
- This study was designed to determine if Quats accumulate in a wastewater system leading to toxicity at lower dose rates
- This test was run with a daily addition of 0 PPM, 1 PPM, 5 PPM and 10 PPM of Quat

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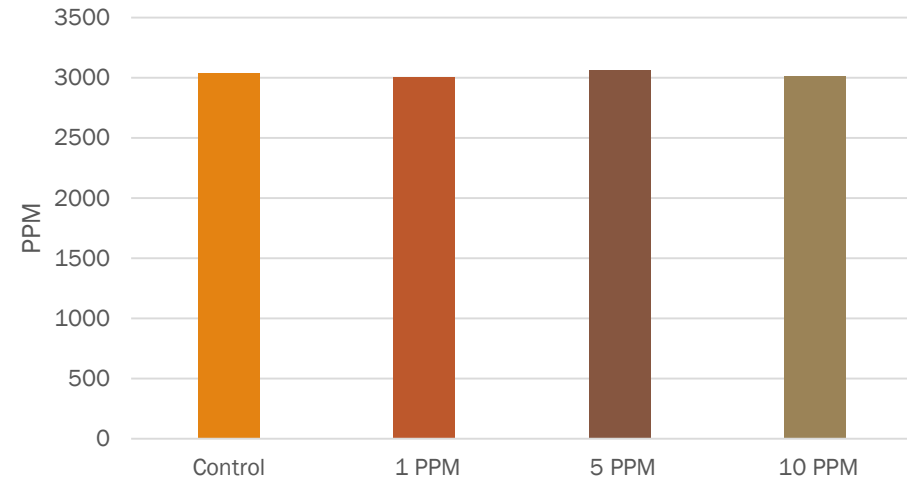
Long Term Studies Results

No Problems Occurred in any reactor

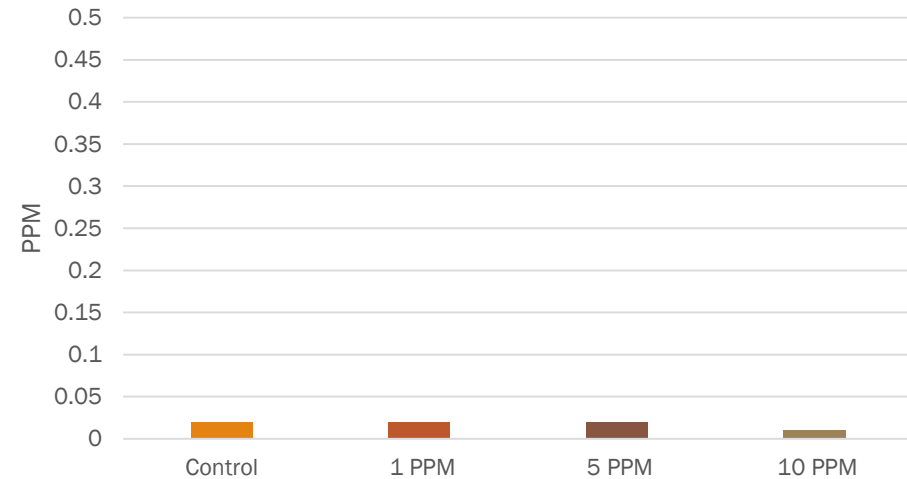
COD Average Over 1 Month



MLSS Average Over 1 Month



Ammonia Average Over 1 Month

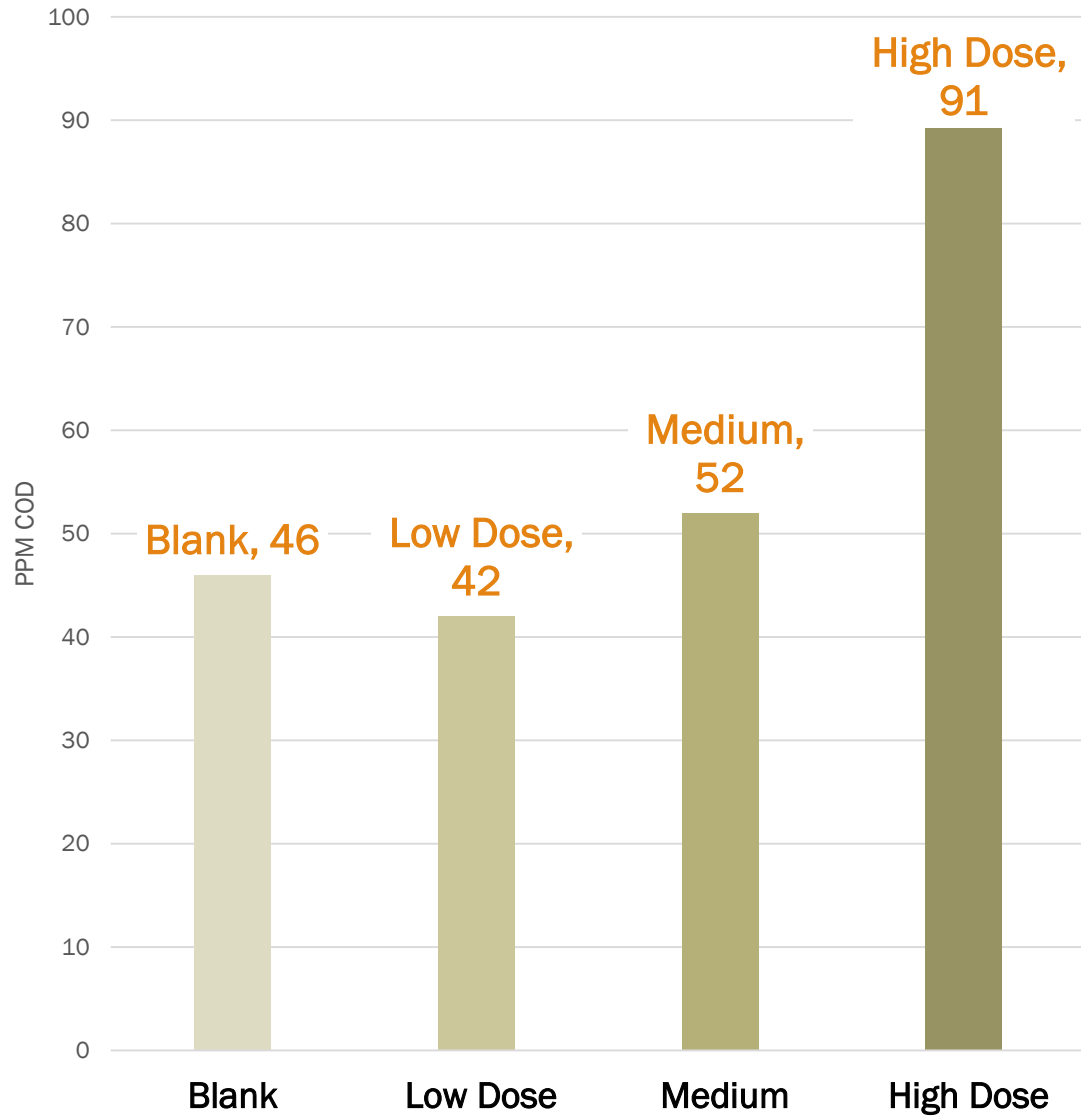


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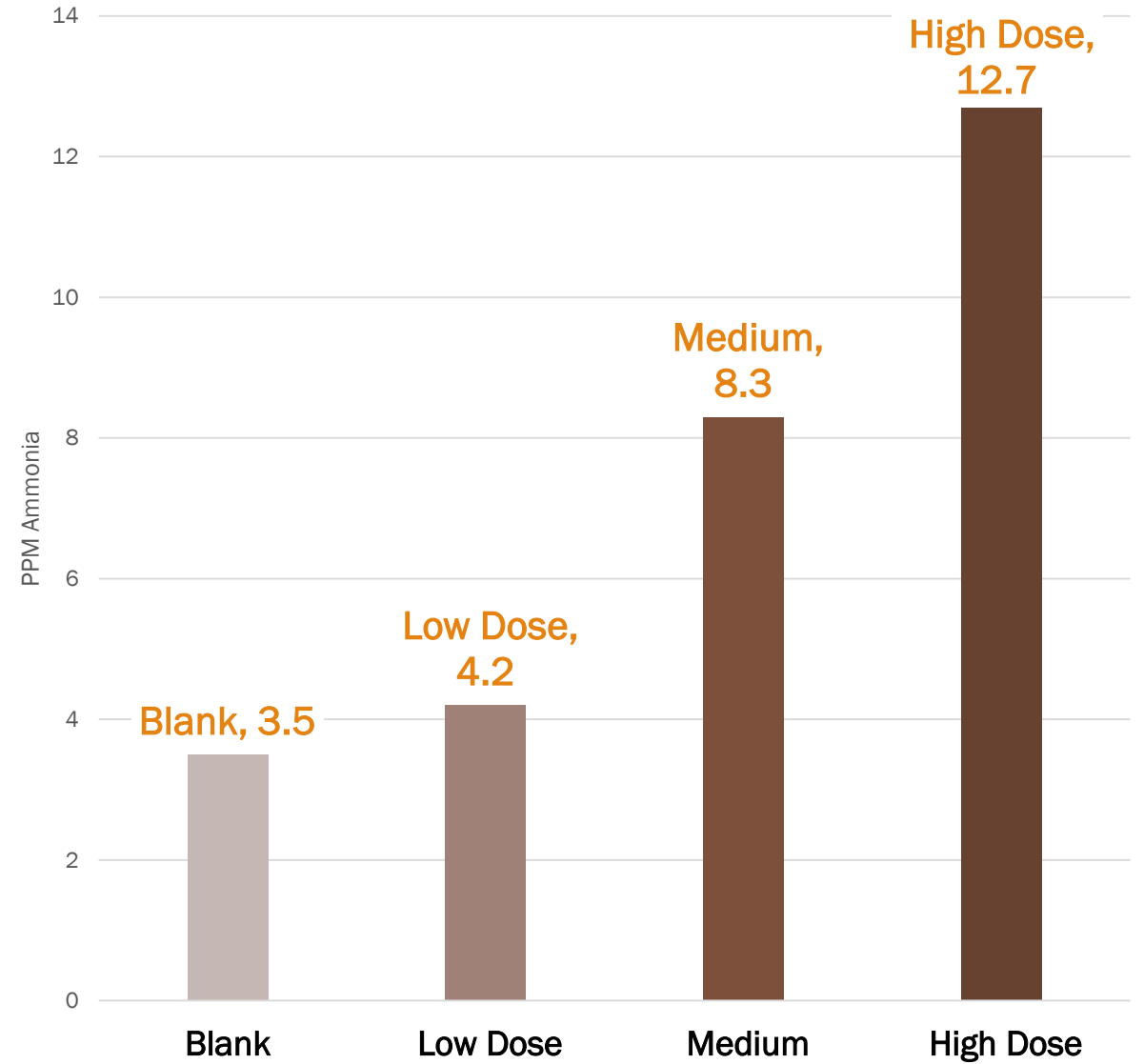
Quats and Temperature Shock Studies Overview

- This testing was designed to determine if a common alternative form of stress could make Quat toxicity more potent
- Quat was dosed as a sludge dose at 0, 5, 10 and 20 ppm
- Temperature was also decreased from 20°C to 7°C
- Results were recorded after 16 hours

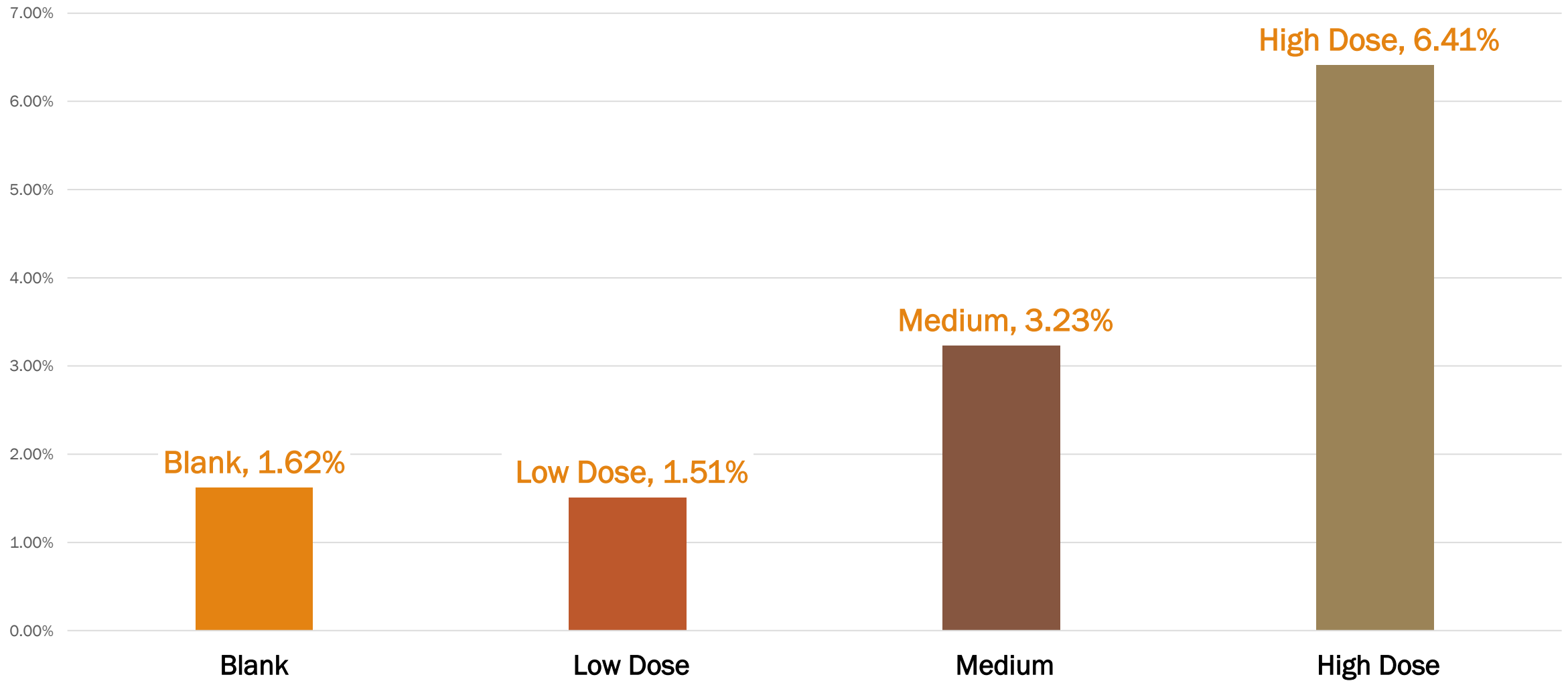
Temperature Shock COD



Temperature Shock Ammonia



Temperature Shock Biological Stress Index (BSI%)



**higher BSI% indicates higher bacterial stress

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Quats and Temperature Shock Studies Results

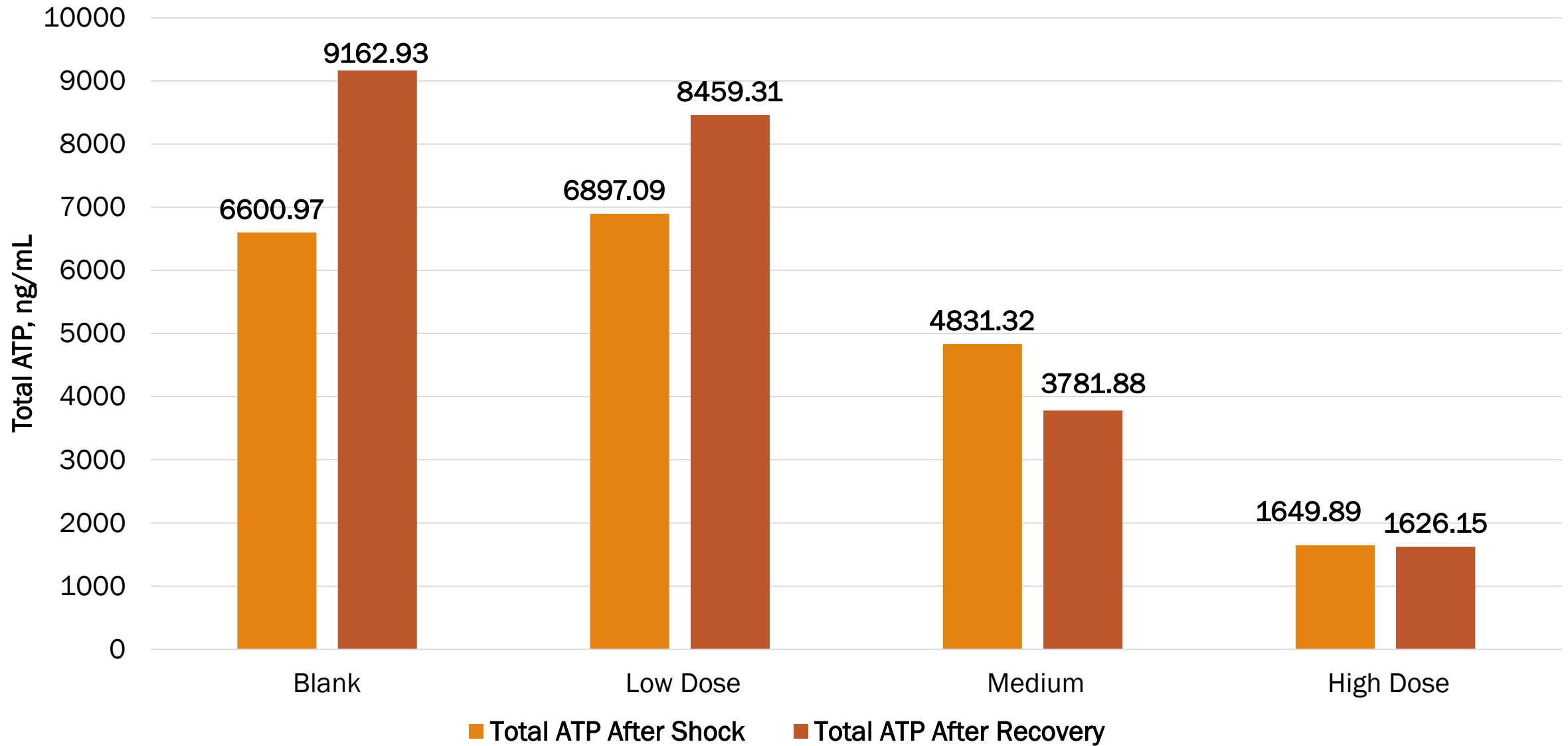
- The combination of temperature shock and Quat was more inhibitory to bacteria than either individually
- Temperature shock alone had a larger negative effect than Quat alone
- Our assumption is these observations would be consistent with other alternative forms of stress on a system

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Recovery from Quat Toxicity Study Overview

- This testing was to determine if Quat adversely impacted plant acclimation to cold temperature
- Quat dose rates were reduced to 1, 5 and 10 ppm daily
- Temperature was held at a constant 7° C

ATP After Temperature Shock and After Recovery



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Recovery from Quat Toxicity Study Results

- Quat clearly had a negative impact on the ability of my wastewater reactors to acclimate to cold temperatures
- At the low dose, recovery was slowed, at the medium and high dose rates, no recovery appeared to be occurring, conditions were still getting worse

Summary of Results

- In a healthy system, it takes quite high doses of Quat to lead to toxicity symptoms
- Quat may accumulate in a system, but does not appear to move to new bacteria quickly enough to cause chronic toxicity problems
- Impacts of Quat are made worse by alternative forms of stress such as temperature shock
- Quats slow down a wastewater plant's ability to recover from an upset

Anaerobic QAC Testing: University of Wisconsin Oshkosh

- Worked with UW Oshkosh to design an anaerobic study to allow us to compare the toxicity of Quats in aerobic and anaerobic systems.
- UW-Oshkosh performed a 28 day treatability study measure methane, carbon dioxide, and hydrogen sulfide generation with the addition of Quats.
- All reactors were run in triplicate, given a standard feeding, and had QAC applied at 0 ppm, 1 ppm, 10 ppm and 40 ppm.



This study was completed by the Environmental Research and Innovation Center at UW-Oshkosh.

More about UW-Oshkosh's Environmental Research and Innovation Center

- UW-Oshkosh lab's main focus is on drinking water testing
- Oshkosh also performs extensive testing in surface waters/beach remediation projects
- They perform biomethane potential testing to determine the feasibility of treating different feedstocks in anaerobic systems



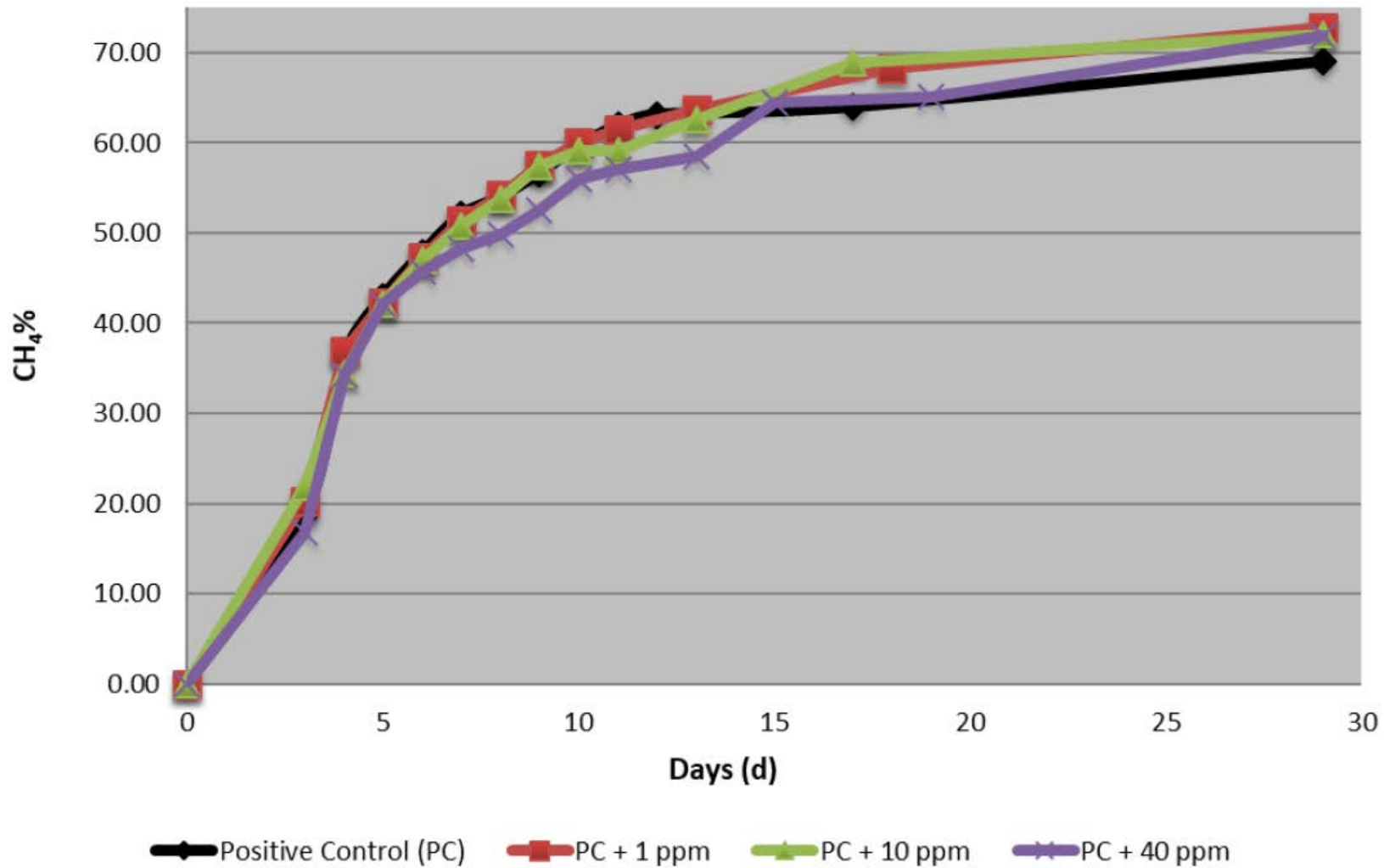


Figure 1. Represents the % CH₄ (NI biogas/kg volatile solids) over the duration of the 28-day experiment for the positive control and each spike of Quat Ammonia.

Table 3. Biogas production results from the BMP study. Biogas production values are averages from duplicate samples taken on the last day of the study (Day 28).

| Analysis | | Result | Unit | Standard |
|------------------|-------------------------------------|--------|--------------------------------|--------------|
| 1 ppm | Gas Production from Fresh Material | 570 | NI biogas/kg (fresh material) | DIN 38414-S8 |
| | Gas Production from Total Solids | 597 | NI biogas/kg (total solids) | DIN 38414-S8 |
| | Gas Production from Volatile Solids | 597 | NI biogas/kg (volatile solids) | DIN 38414-S8 |
| 10 ppm | Gas Production from Fresh Material | 555 | NI biogas/kg (fresh material) | DIN 38414-S8 |
| | Gas Production from Total Solids | 582 | NI biogas/kg (total solids) | DIN 38414-S8 |
| | Gas Production from Volatile Solids | 582 | NI biogas/kg (volatile solids) | DIN 38414-S8 |
| 40 ppm | Gas Production from Fresh Material | 524 | NI biogas/kg (fresh material) | DIN 38414-S8 |
| | Gas Production from Total Solids | 548 | NI biogas/kg (total solids) | DIN 38414-S8 |
| | Gas Production from Volatile Solids | 548 | NI biogas/kg (volatile solids) | DIN 38414-S8 |
| Positive Control | Gas Production from Fresh Material | 528 | NI biogas/kg (fresh material) | DIN 38414-S8 |
| | Gas Production from Total Solids | 552 | NI biogas/kg (total solids) | DIN 38414-S8 |
| | Gas Production from Volatile Solids | 552 | NI biogas/kg (volatile solids) | DIN 38414-S8 |

UW-Oshkosh Study Summary

- It appeared that quats were less toxic in anaerobic systems than aerobic systems.
- At lower dose rates, quats were used as food and actually lead to a slight increase in methane production compared to the control.
- Methane quality began to drop at about 40 ppm of Quat added. This is likely much higher levels than would be typically observed in wastewater systems.



Current and Future Testing

- Currently we're working on determining the effectiveness of Quat binding products in different applications.
- In the future, we will likely perform more in-depth analysis about the effects of Quat on systems with alternative forms of stress
- We would like to analyze the toxicity of different Quat products to understand the variation of toxicity between Quats.

We are intending on developing more effective ways to prevent Quat toxicity and boost recovery time afterwards.

Overcoming Toxicity

Preventing Toxicity

- This is quite difficult in most cases as optimal prevention of toxicity occurs by resolving the issue at its source
- Quat for example can be relatively easily neutralized at the site where it is used
- Best option is simply maintaining a healthy system that can handle toxicity more effectively (still alternative forms of stress may be difficult to prevent as well)
- Aquafix is currently working on a Quat binding solution that can be effectively applied upstream from a wastewater system. We still have a long way to go.

Overcoming Toxicity

Recovering from Toxicity

- Bringing in replacement sludge and sludge hauling is always a good option
- The less stress a plant has to deal with, the less time it will take to recover from toxicity
- Aquafix offers VitaStim Rebuild, and SmartBOD to quickly grow floc forming bacteria after toxicity
- If you can determine the cause of toxicity, more effective recovery methods can be determined

Questions?

Proven Product Leader

AQUAFIX^{Inc.}

Call: 888.757.9577

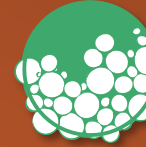
Monday — Friday

7:30 am — 4:00 pm CST

orders@teamaquafix.com



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RED WORMS



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AEROBIC DIGESTION



ANAEROBIC DIGESTION



PH CONTROL