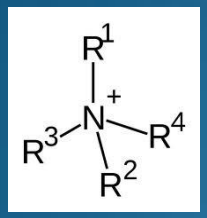
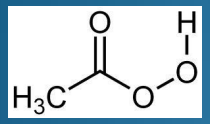
Chemicals of Concern in Wastewater Treatment





USPE Environmental Conference

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Chemicals of Concern

- **Traditional Chemicals**
  - Total Dissolved Solids, Chlorides, Sulfates
  - Nutrients (Nitrogen and Phosphorus)
- **Inhibitory/Toxic Chemicals**
  - Quaternary Ammonium Compounds (QAC)
  - Peracetic Acid Compounds (PPA)
  - Chlorine Compounds

Traditional Chemicals

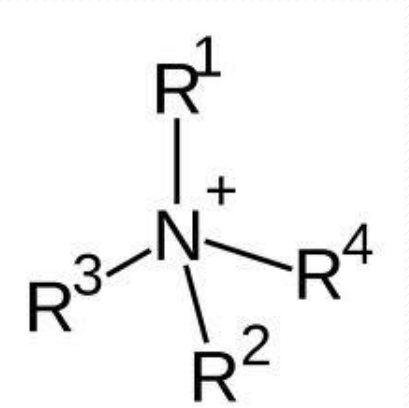
- **Total Dissolved Solids, Chlorides, and Sulfates**
  - TDS – 500 mg/l (+/-)
    - Texas Poultry Plant – Actual 1,200 mg/l; Proposed Limit 698 mg/l
  - Chlorides – 100 mg/l (+/-)
    - Texas Poultry Plant – Actual 167 mg/l; Proposed Limit 140 mg/l
  - Sulfates – 100 mg/l (+/-)
    - Texas Poultry Plant - Actual 331 mg/l; Proposed Limit 140 mg/l
- **Nutrients – Nitrogen and Phosphorus**
  - Chesapeake Bay – 3 mg/l TN; 0.3 mg/l TP
  - Missouri Poultry Plant TMDL – 0.007 mg/l TN; 0.289 mg/l TP

Inhibitory/Toxic Chemicals

- **Quaternary Ammonium Compounds**
  - Plant sanitation
- **Peracetic Acid**
  - Plant sanitation
  - Product antimicrobial

- Why These Chemicals Can Cause Concern
  - Overuse – "More is Better"
  - Shock use on weekends during low flow conditions
  - Spills or dumping

Quaternary Ammonium Compounds



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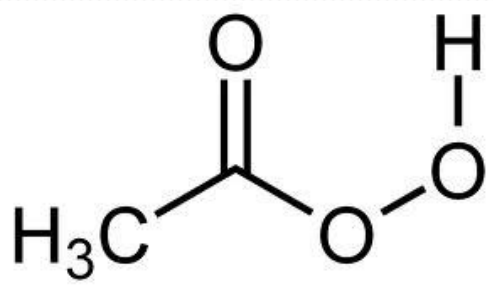
Quaternary Ammonium Compounds

- **Characteristics**
  - Strongly cationic – attaches to organic and inorganic surfaces
  - Stable and hard to break – long lasting biocidal effect
  - Attracts anionic constituents
  - Strong positive charge attaches to negatively charged bacteria – causes membrane leakage and bacteria death
  - Removal occurs through some biodegradability and through attaching to sludge and other biosolids
  - Accumulation of QAC's in undisturbed biosolids can be source of upset conditions if solids are disturbed
- **Pretreatment**
  - Anionic polymer use can be impacted at dosages of 100 mg/l/day or higher
  - Degrades SPN quality and potentially increases free fatty acids

Quaternary Ammonium Compounds

- **Anaerobic Treatment**
  - Inhibition with soluble COD increases and methane gas reduction at dosages as low as 0.5 mg/l/day with resultant increase in volatile acids in anaerobic lagoon effluent – increases odor potential and oxygen demand on aerobic system
  - Toxicity at cumulative level of 25 mg/l (impact same at cumulative level as one time dose at 25 mg/l)
  - Anaerobic organisms do not tend to acclimate even at low doses
- **Aerobic Treatment**
  - Dosage rates as low as 2 mg/l/day show inhibition of nitrification with inhibition increasing significantly as dosage rate increases to 5 mg/l/day and nitrification ceases at an accumulative dose of 15 mg/l
  - Nitrification inhibition due to QAC's increases as temperature decreases
  - Inhibition is manifested by increasing nitrite nitrogen accumulation, increased effluent ammonia nitrogen levels, or both
  - Build-up of nitrites due to QAC nitrification inhibition contributes to other issues such as an increase in chlorine demand for disinfection
  - Dosage rates up to 20 mg/l/day show no toxic impact on aerobic COD removal; COD removal efficiency declines as dosage rate approaches 40 mg/l

Peracetic Acid



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Peracetic Acid

- **Anaerobic Treatment**
  - Inhibition with soluble COD increases and methane gas production decreases at dosages as low as 0.5 mg/l/day when cumulative level of 25 mg/l reached
  - Anaerobic organisms do not tend to acclimate even at low doses
- **Aerobic Treatment**
  - Toxic impacts can be seen at dose rates as low as 5 mg/l/day; toxicity occurs at accumulative dose of 25 mg/l
  - May acclimate to dose rate of 5 mg/l/day or less within 10 days; no recovery seen at 10 mg/l/day or higher dosages
  - Dose rates of 5 mg/l/day toxic to nitrification after 10 days
  - Hydrogen peroxide used in PAA formulations has no adverse impacts
  - Severe foaming occurs in aerobic reactors at onset of PAA toxicity

Controls

Best Management Practices

- Control Usage at the Source
- Have an Action Plan in place in case a QAC and/or PAA issue occurs
- For new facilities design wastewater treatment systems with maximum flexibility and capacity to handle chemicals of concern to the extent practical

Control Usage at the Source

- Implement chemical screening and approval program for any new chemicals to be used at a facility
- Screen QAC and PAA products and use products that offer desired food safety benefits at least environmental risk
- Track QAC and PAA usage
- Test frequently for QAC and PAA levels
  - QAC's
    - Test Strips (typically increments of 50 to 100 ppm – very hard to read)
      - Hydrion
      - LaMotte
      - EM Quant
    - Hach Colorimetric Test Kit
    - ASTM Method D5806-95 for Quats used as disinfectants (potentiometric titration – most accurate)
  - PAA
    - Titration (7191-01-FMC dropper bottle titration kit is one method)
    - Test Strips (FMC Insta-Test 3000 test strip is one method)
- Manage dumps and control spills
- Operations, sanitation, and wastewater department must work closely together to achieve food safety goals while assuring compliance with wastewater effluent requirements

QAC & PAA Usage vs Wastewater Concentration in 1 mgd

	Peracetic Acid						Quaternary Ammonia Compounds					
% by Weight	**3**	**7**	**10**	**15**	**25**	**35**	**3**	**7**	**10**	**15**	**25**	**35**
lbs Chemical/gallon	**0.2707**	**0.6317**	**0.9024**	**1.3536**	**2.2560**	**3.1584**	**0.2527**	**0.5896**	**0.8423**	**1.2635**	**2.1059**	**2.9482**
Gallons used to result in given concentration in 1 mgd wastewater:												
0.5 mg/l	15.4	6.6	4.6	3.1	1.8	1.3	16.5	7.1	5.0	3.3	2.0	1.4
1.0 mg/l	30.8	13.2	9.2	6.2	3.7	2.6	33.0	14.1	9.9	6.6	4.0	2.8
2.0 mg/l	61.6	26.4	18.5	12.3	7.4	5.3	66.0	28.3	19.8	13.2	7.9	5.7
5.0 mg/l	154.0	66.0	46.2	30.8	18.5	13.2	165.0	70.7	49.5	33.0	19.8	14.1
10.0 mg/l	308.1	132.0	92.4	61.6	37.0	26.4	330.0	141.4	99.0	66.0	39.6	28.3
15.0 mg/l	462.1	198.0	138.6	92.4	55.5	39.6	495.0	212.2	148.5	99.0	59.4	42.4
20.0 mg/l	616.1	264.1	184.8	123.2	73.9	52.8	660.1	282.9	198.0	132.0	79.2	56.6
25.0 mg/l	770.2	330.1	231.1	154.0	92.4	66.0	825.1	353.6	247.5	165.0	99.0	70.7

Have Action Plan in Place

- Reduce hydraulic loading on treatment system
- Reduce QAC and/or PAA usage
- Change QAC and/or PAA product used
- Feed products that can adsorb QAC's
- Feed sodium metabisulfite to neutralize PAA
- Feed nitrifiers (only after other actions are taken and QAC and/PAA issue is believed to be under control – no need to throw good money after bad by dumping good nitrifiers into an inhibitory or toxic environment)

Sodium Metabisulfite Neutralization of PAA

1) Product is 15% PAA, 22% H_2O_2.
2) Weight Ratio H_2O_2: PAA is 1.47:1; Each ppm PAA is accompanied by 1.47 ppm H_2O_2.
3) 1 ppm PAA requires 1.25 ppm sodium metabisulfite.
4) 1 ppm H_2O_2 requires 2.79 ppm sodium metabisulfite. Therefore the amount of sodium metabisulfite due to H_2O_2 is 2.79 X 1.47 = 4.1 ppm per ppm PAA.
5) Total amount of sodium metabisulfite due to both PAA and H_2O_2 is 1.25 + 4.1 = 5.35 ppm sodium metabisulfite per ppm PAA

Design New Wastewater Treatment Facilities w/Maximum Flexibility and Capacity to Handle Chemicals of Concern

- Provide aerated equalization following primary/secondary screening before anaerobic lagoon and/or aerobic treatment system
- Provide reactor basins in series versus single reactor basin
- Do not scrimp on size of initial aeration basin
- Provide dedicated nitrification basin after aeration basin

References

- “Impact of Quaternary Ammonia Compounds on Food Industry Wastewater Treatment Plants”; Kim Dirks, Tyson Foods, Inc.
- “Toxic Impact of Commercial Biocides on Industrial Wastewater Treatment Systems”; Durham and Young, WEFTEC 2009.
- “Effect of Alkyl Benzyl Dimethyl Ammonium Chloride and Temperature on Nitrification”; Yang, Li, Tezel, Pierson, Pavlostathis, WEFTEC 2008
- “Nitrification Inhibition by Quaternary Ammonium Compounds in Wastewater From Small Communities and Schools”; Carter, WEFTEC 2008.

ASSESSING QUATERNARY AMMONIUM COMPOUND TOXICITY IN THE WASTEWATER LABORATORY

Randy Drake
River Bend Laboratories

Laboratory Testing Methods to Evaluate Quaternary Ammonium Compound Toxicity

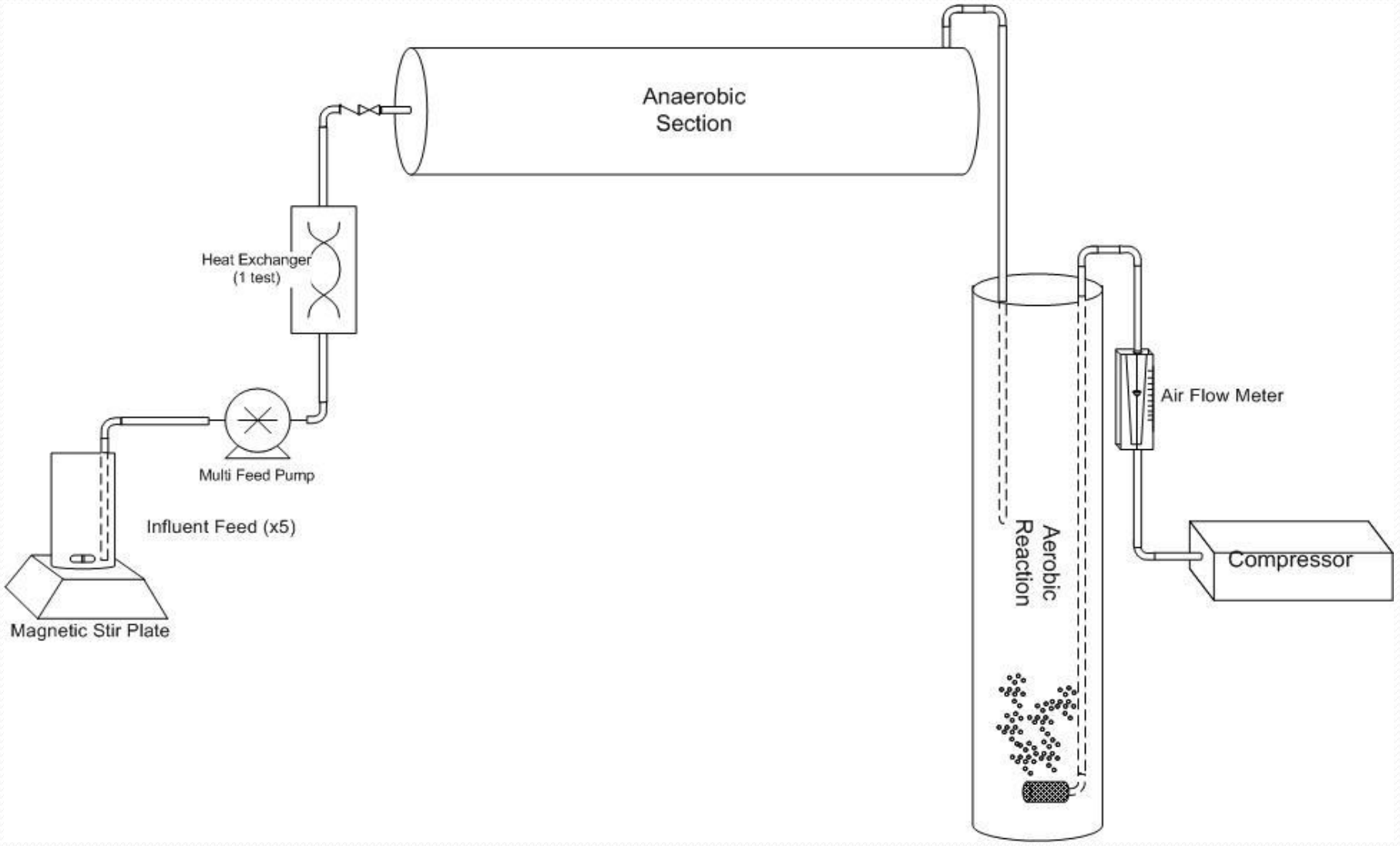
- Bench-Scale Study To Determine The Toxicity Of An Influent Waste Stream & Effluent Waste Stream
- Nitrascreen: Nitrification Inhibition/Toxicity Screening Test
- Delta Tox Toxicity Testing

Bench-Scale Study To Determine The Toxicity Of An Influent Waste Stream & Effluent Waste Stream - Poultry Processing Plant

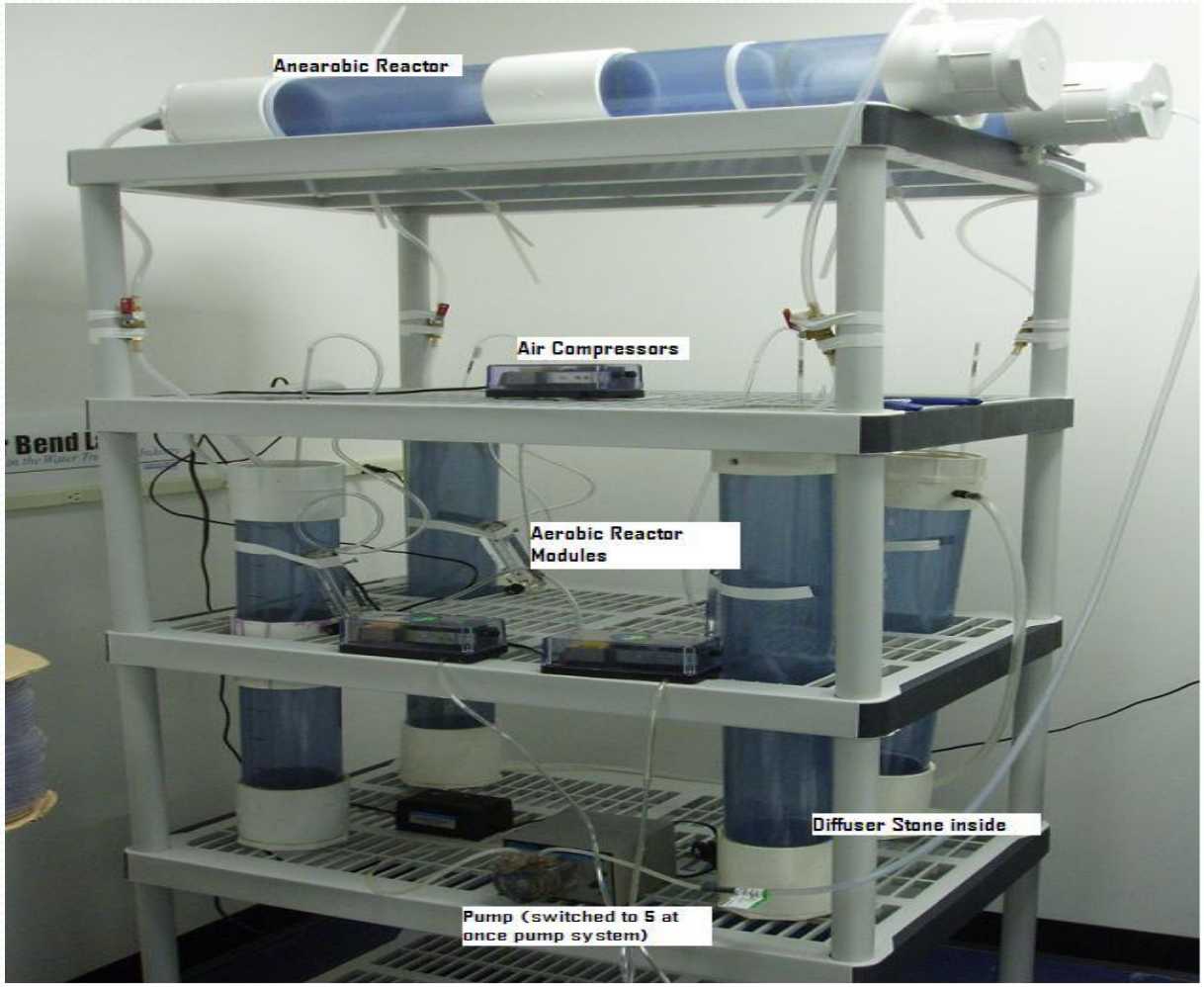
Scope of Bench-Scale Study

- A Bench-Scale Treatability Study was performed on the effluent of the poultry process plant wastewater from the Tyson Fresh Meats processing plant discharging to a municipal system. The study was performed to better understand the impact of two quaternary ammonium compounds on the final effluent emanating from the city's wastewater treatment facility. At the time of the study the effluent from the city owned wastewater treatment plant was failing the 48-hour Ceriodaphnia dubia acute toxicity test

BENCH-SCALE WASTEWATER SETUP



BENCH-SCALE WASTEWATER SETUP



Bench-Scale Study WWT Microcosm Setup

- **TEST 1 Control Reactor – Ana 4-Day HRT – SBR 2.67 day HRT - Temp main. 75^0–80^0 F – CONTROL**
- **TEST 2 Same as Control With Addition of Increasing Amounts of # 134 FS Quaternary Ammonia - INCREASED FS**
- **TEST 3 Same as Control With Addition of increasing amounts of #239 DQS Quaternary Ammonia - INCREASED DQS**
- **TEST 4 Same as Control With Addition of Activated Carbon to Remove Quaternary Ammonia - Quaternary Ammonia Removal**
- **TEST 5 Control Reactor – Ana 6-Day HRT – SBR 1.67 day HRT - Temp main. 45^0–50^0 F - LOW TEMP**

Bench-Scale Study Operational Notes

- After a two-week bacterial seed development period, the treatability study incorporated a sampling schedule to coincide with periodic sampling events performed to gather information on TSS, VSS, pH, NH_3-N and COD.
- At the conclusion of the study a 2-liter effluent sample was collected from each test reactor and shipped to American Aquatic Testing Inc. for toxicity testing of acute mortality (48-hour) on Ceriodaphnia dubia.
- The test period of the study was 10 weeks.
- The influent flow was 1 liter per day for the seed development period and then 1.5 liters per day for the duration of the study

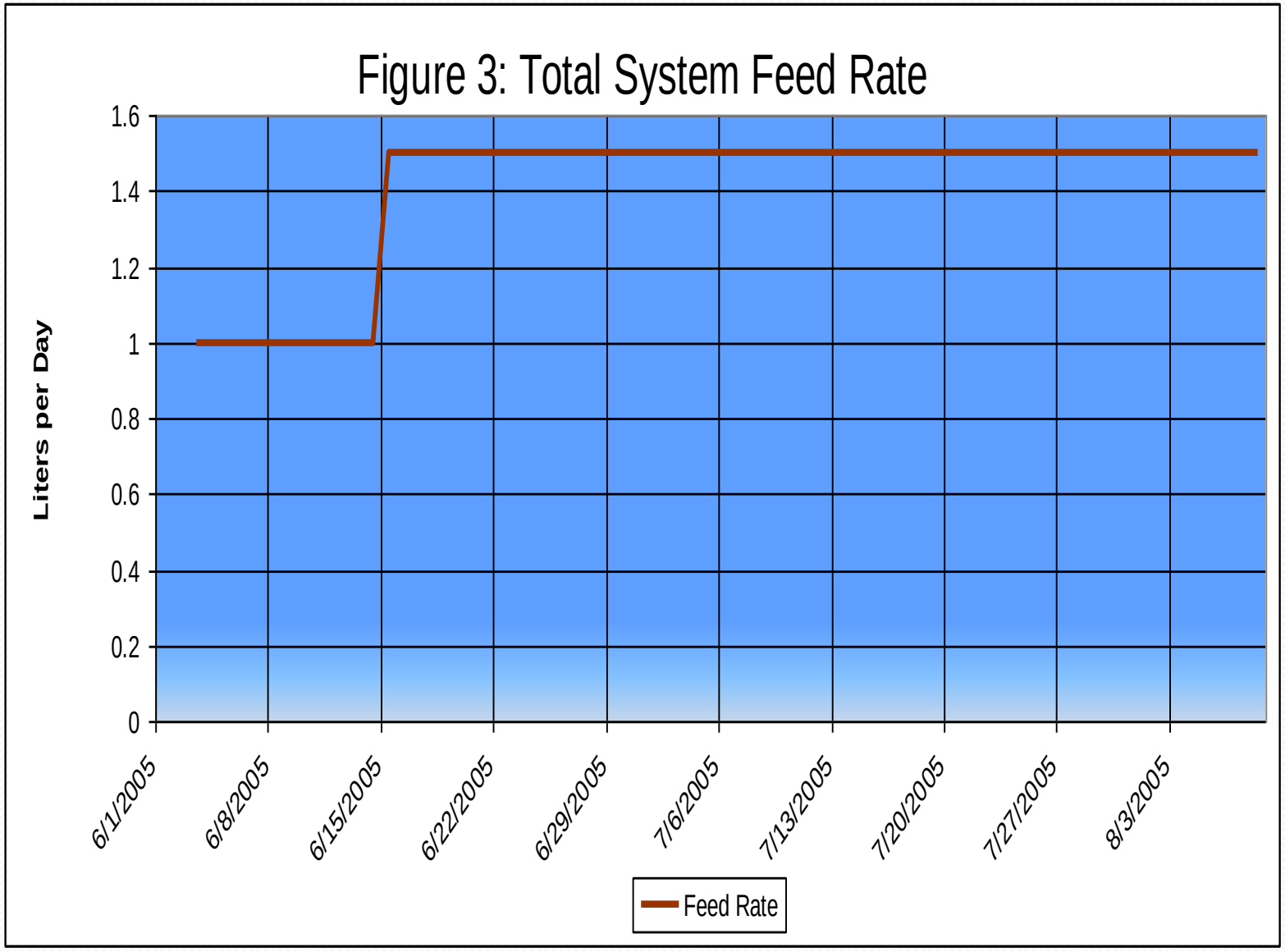


Figure 3: Total System Feed Rate
Liters per Day
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
6/1/2005
6/8/2005
6/15/2005
6/22/2005
6/29/2005
7/6/2005
7/13/2005
7/20/2005
7/27/2005
8/3/2005
Feed Rate

Environmental Factors Examined

- The inclusion of pre-selected quaternary ammonia compounds [the products #134 Floor San FS (a dual-chained quaternary ammonia compound) and #239 DQS (a quaternary ammonia compound containing 4-chains) currently being utilized for sanitizing purposes] at increased waste stream concentrations
- The removal of waste stream quaternary ammonia compounds (via proprietary quaternary ammonia binding materials).
- The effect of temperature (low temperature wastewater system).

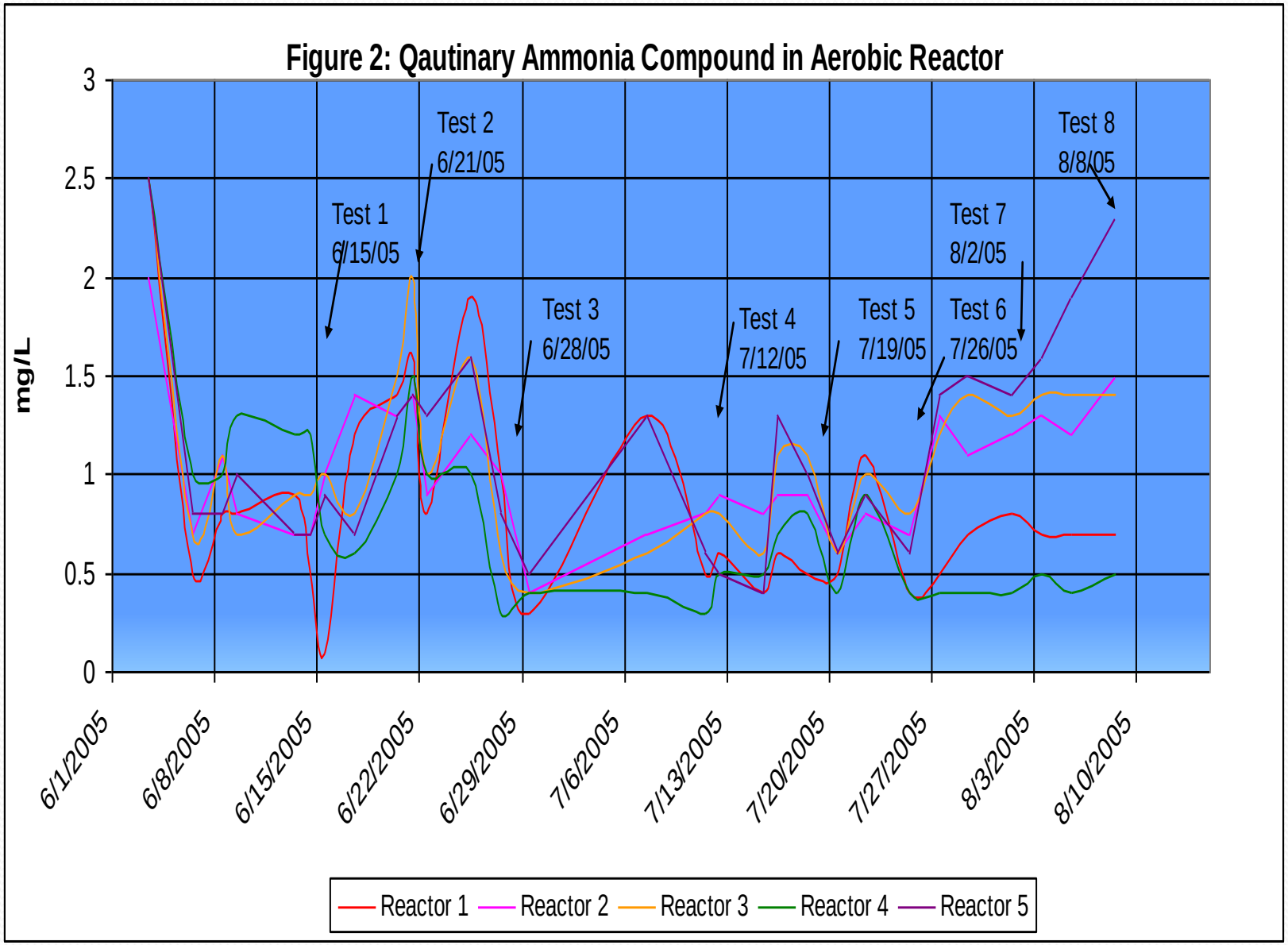


Figure 2: Qautinary Ammonia Compound in Aerobic Reactor
mg/L
3
2.5
2
1.5
1
0.5
0
Test 1
6/15/05
Test 2
6/21/05
Test 3
6/28/05
Test 4
7/12/05
Test 5
7/19/05
Test 6
7/26/05
Test 7
8/2/05
Test 8
8/8/05
6/1/2005
6/8/2005
6/15/2005
6/22/2005
6/29/2005
7/6/2005
7/13/2005
7/20/2005
7/27/2005
8/3/2005
8/10/2005
Reactor 1
Reactor 2
Reactor 3
Reactor 4
Reactor 5

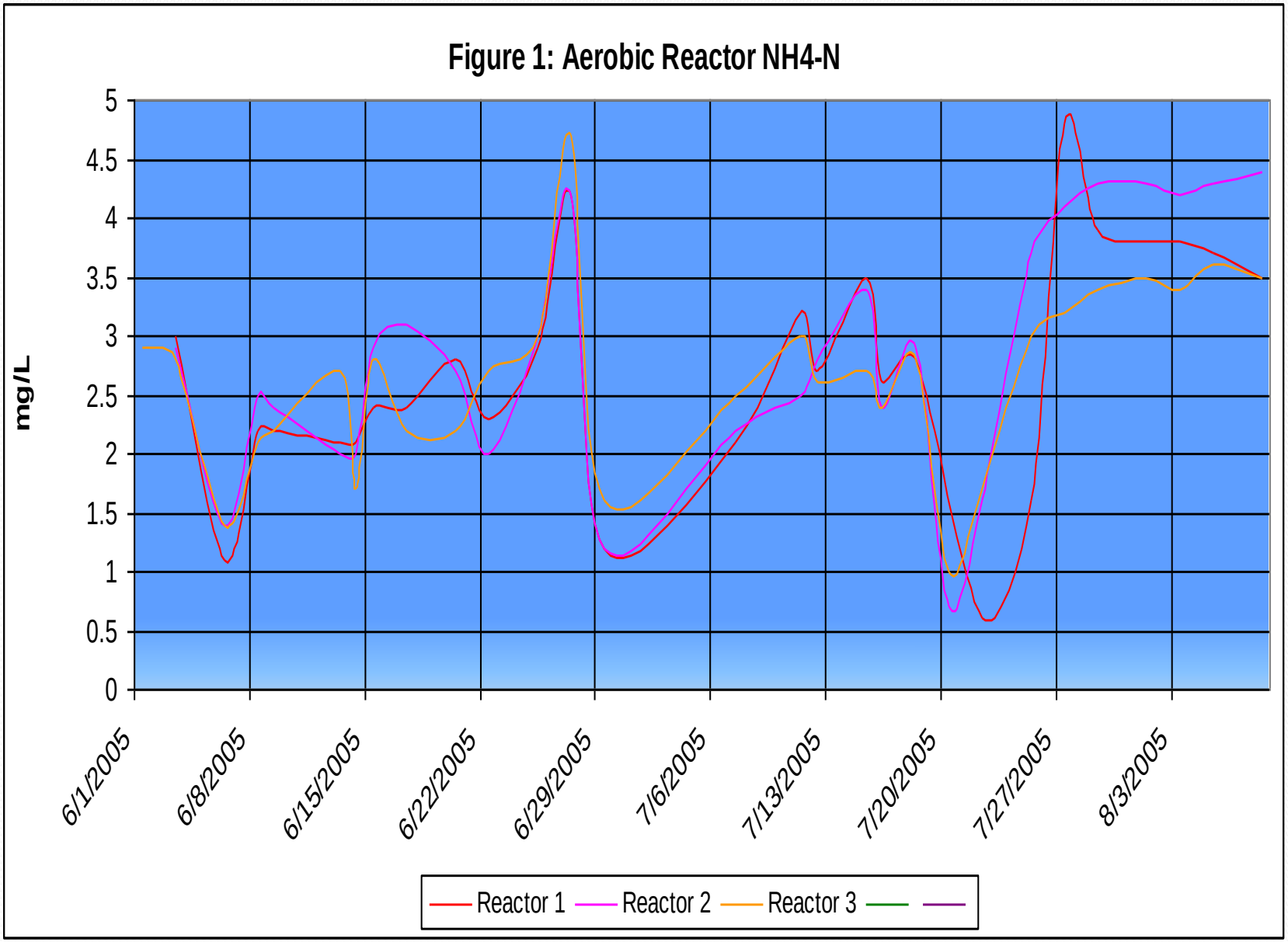


Figure 1: Aerobic Reactor NH4-N
mg/L
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
6/1/2005
6/8/2005
6/15/2005
6/22/2005
6/29/2005
7/6/2005
7/13/2005
7/20/2005
7/27/2005
8/3/2005
Reactor 1
Reactor 2
Reactor 3

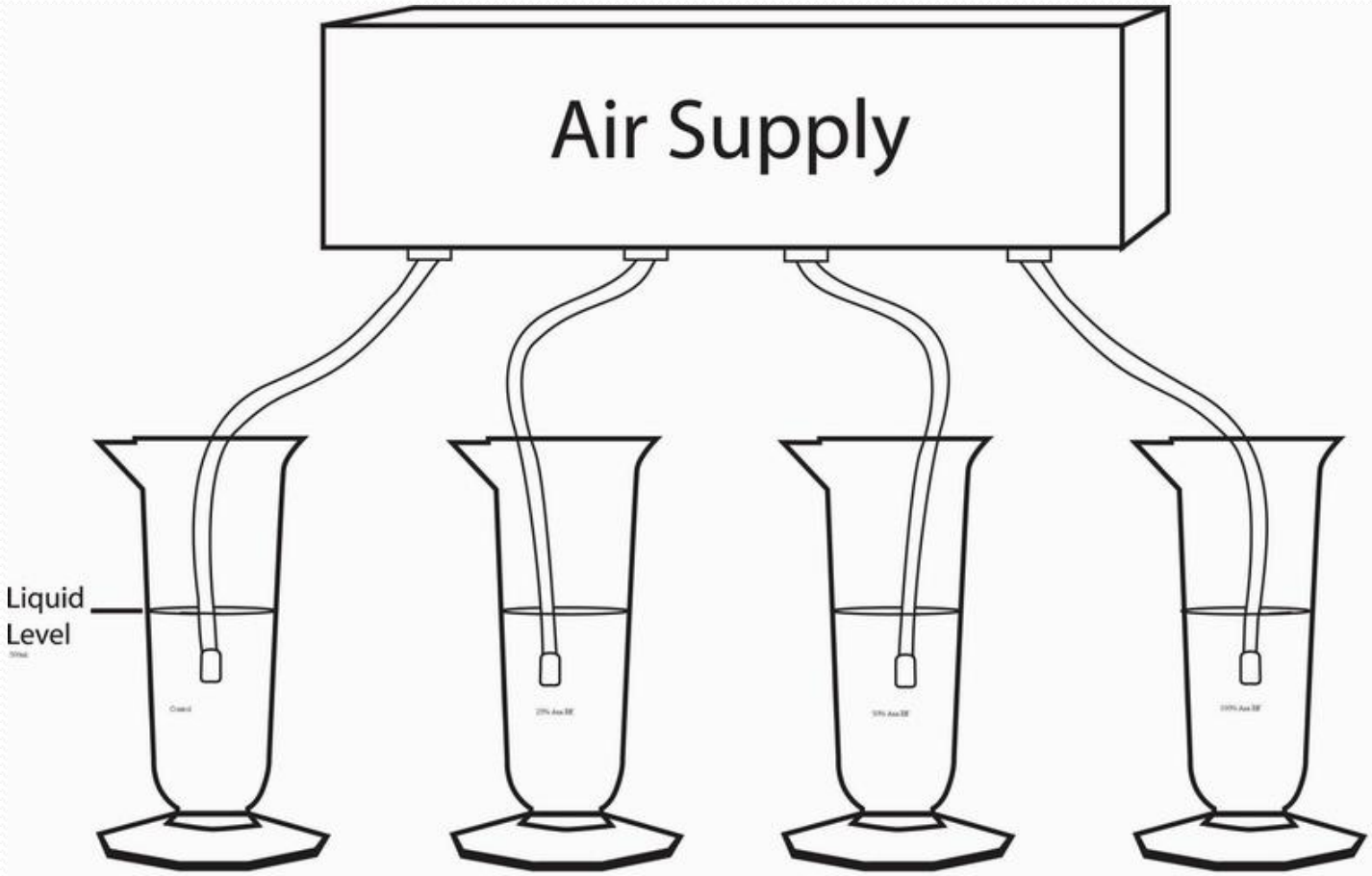
Utilizing Nitrifying Bacteria Cultures to Assess the Inhibition/Toxicity of Quaternary Ammonium Compounds

Nitrascreen:
Nitrification inhibition/toxicity test

NITRA SCREEN (Nitrification Inhibition Study)

Description: The Nitra Screen Test is a twenty-four-hour nitrification inhibition screening that analyzes the nitrification activity of a standardized quantity of concentrated nitrifying bacterial cultures. The nitrifying bacteria utilized in the Nitra Screen test are used to evaluate the toxicity to nitrifying bacteria of specific waste streams versus a "control". The control consists of distilled water, pH buffers, and a source of alkalinity and 10 ml of concentrated nitrifying bacteria. The test samples, consisted of discrete amounts of a quaternary ammonium compound and were to be evaluated against the control utilizes the same volume of material and is equal in volume to the distilled water utilized in the control test. Ammonia-Nitrogen (NH_3-N) and pH are monitored before and after the test.

Nitra Screen Setup



Nitra Screen Setup

NITRA SCREEN (Test Setup)

The control Test was run with 100% distilled water versus Screening Tests run at 5 ppm quaternary ammonium, 10 ppm quaternary ammonium & 25 ppm quaternary ammonium .

NITRA SCREEN RESULTS

	NH3N Time 0	NH3N Time 24 hr	NH3N Change	% Inhibition
Control	127 mg/l	0.4 mg/l	126.6 mg/l	
5 ppm QAC	127 mg/l	0.7 mg/l	126.3 mg/l	< 0%
10 ppm QAC	134 mg/l	1.3 mg/l	132.7 mg/l	< 0%
25 ppm QAC	136 mg/l	2.5 mg/l	133.5 mg/l	< 0%

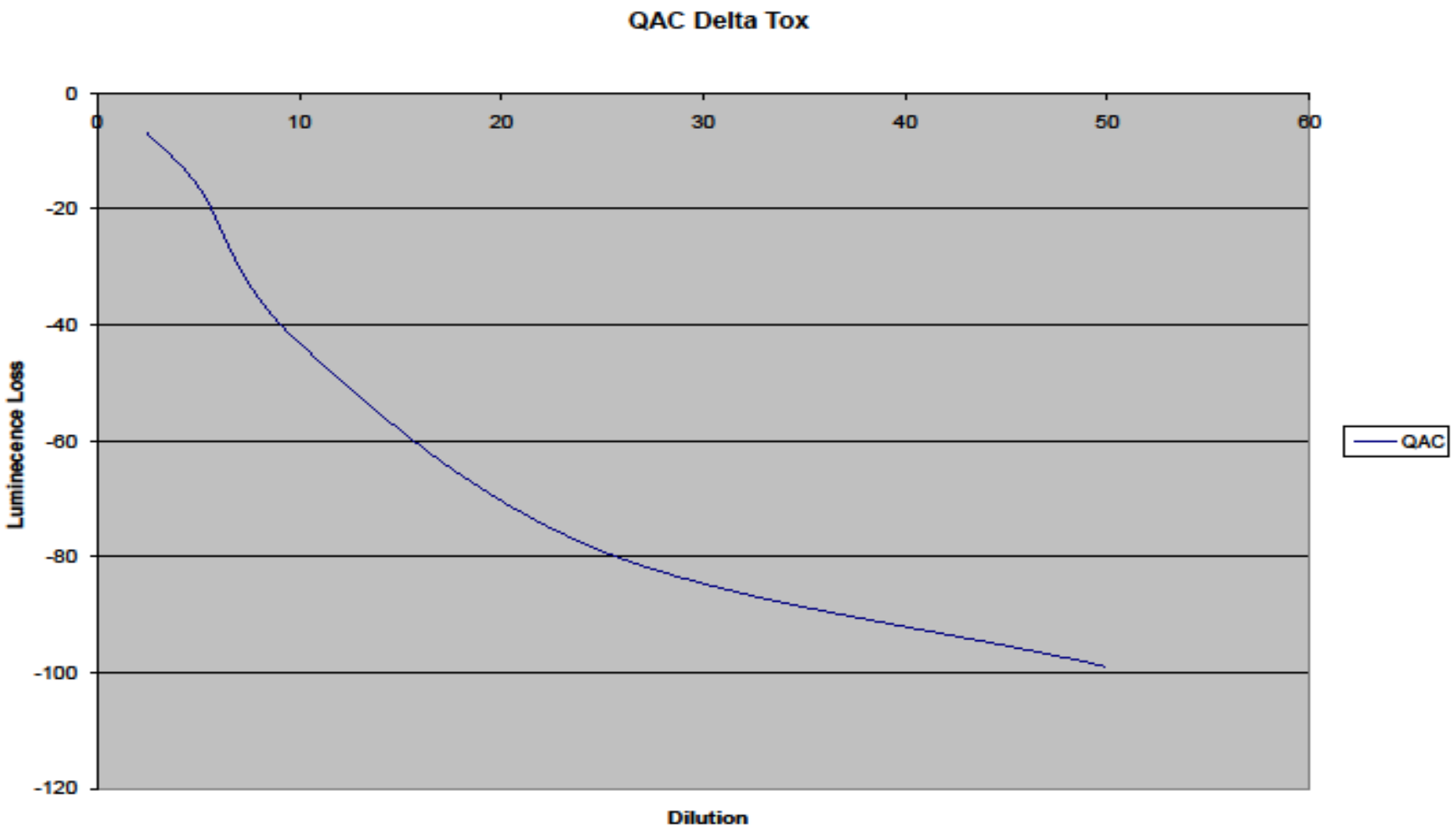
Utilizing the Delta TOX Toxicity Testing System to Assess the Toxicity of a Quaternary Ammonium Compound

Delta TOX Toxicity Testing

DELTA TOX SDIX ANALYZER

Delta Tox Toxicity Testing System

- The Delta Tox Toxicity Test System was utilized to asses the potential toxicity of a quaternary ammonium compound at 2.5 ppm, 5 ppm, 10 ppm, 25 ppm and 50 ppm versus a buffered distilled water control.
- Delta Tox is a recent improvision of the MICROTOX Toxicity Testing System developed by SDIX.
- Like MICROTOX, DELTA TOX utilizes the bacterium Vibrio fisheri, a marine aerobic gram-negative bacterium.
- At high cell densities this bacterium emits light at 490 nm.
- Toxicity manifests itself by a decrease in emitted light.


QAC Delta Tox
0
-20
-40
-60
-80
-100
-120
0
10
20
30
40
50
60
Luminecence Loss
Dilution
QAC

DELTA TOX DATA

QAC in ppm	Decrease in Emitted Light
2.5 ppm	-7
5.0 ppm	-16
10 ppm	-43
25 ppm	-79
50 ppm	-99

Questions?