Hazen









Impact of Quaternary Ammonium Compounds on Wastewater Treatment

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Agenda



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Toxicity (Nitrification Inhibition and Effluent Toxicity)



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Introduction

What are Quaternary Ammonium Compounds (QACs)?

- Quaternary ammonium compounds (**QACs, or Quats**) are a **class of chemical compounds** used extensively for their disinfection properties
  - Very effective disinfectant
- **Kills bacteria and viruses** by disrupting the cell membrane and causing the cell or virus to burst
- Applications include:
  - Industrial cleaning products for surfaces
  - Cosmetic products
  - Commercial sanitizers
  - Hand soaps
  - Herbicides and pesticides
  - Fabric softeners









QACs Not a New Topic

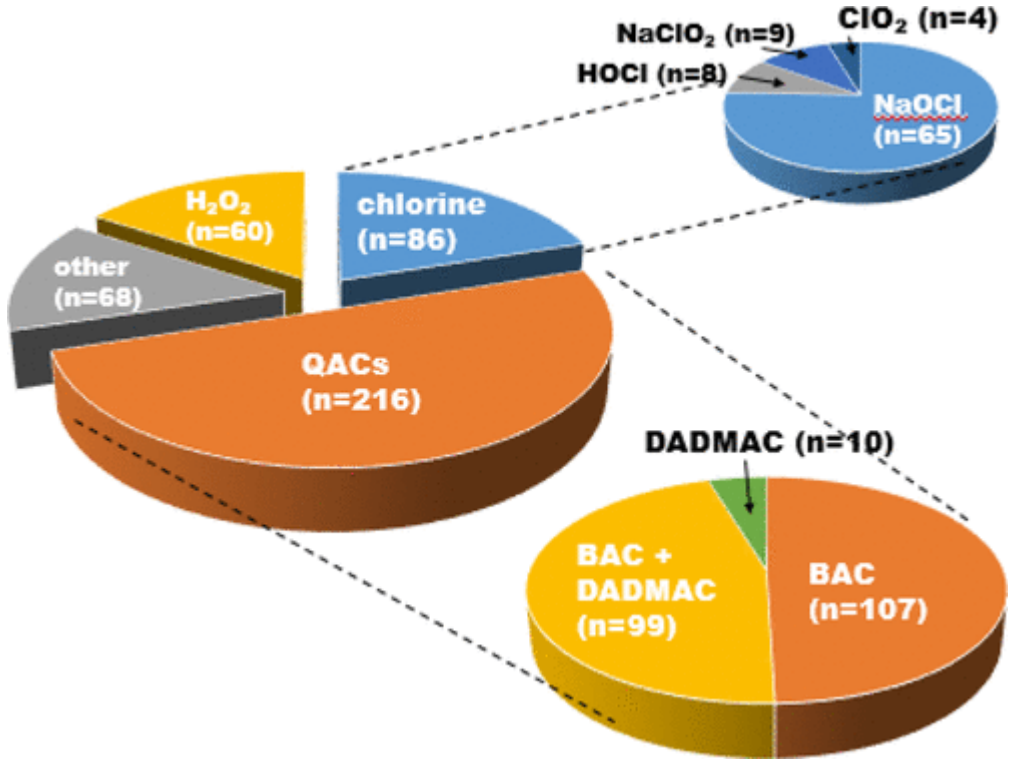
- QACs have been in use a long time
  - Several very good papers from the early 2000s discussing impacts of QACs on wastewater treatment
  - EPA has ECOTOX data available
- Hazen has seen a rise in WWTP upsets associated with QAC products and other biocides
- QAC products can be more cost effective than chlorine
- Attractive due to scarcity of bleach in Covid era
- QAC disinfectants are less corrosive on stainless steel parts than chlorine

Result

- May utilities are not connecting QACs as a probable cause of process upsets

Prevalence of QACs

- 3 major types of QACs
  - **BACs** – benzalkonium compounds
  - **ATMACs** – alkyltrimethylammonium compounds
  - **DADMACs** – dialkyldimethylammonium compounds
- Designated as high production volume chemicals by the EPA
  - **> 1 million pounds/year** manufactured in or imported into the U.S.
- Common active ingredient in disinfection products (cleaners, soaps, sanitizers)

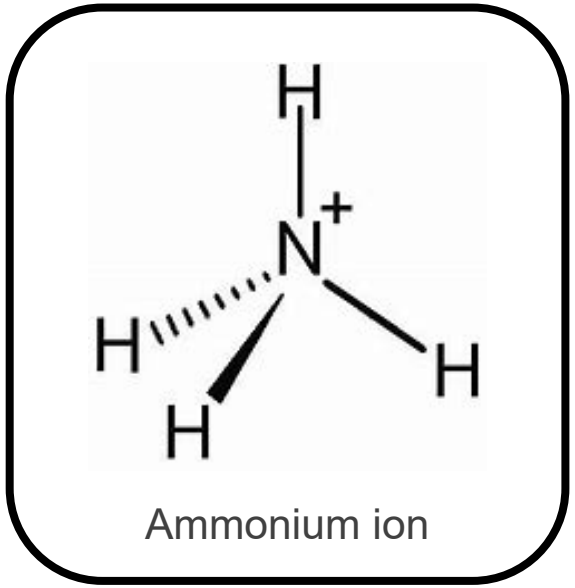


Hora et al. 2020

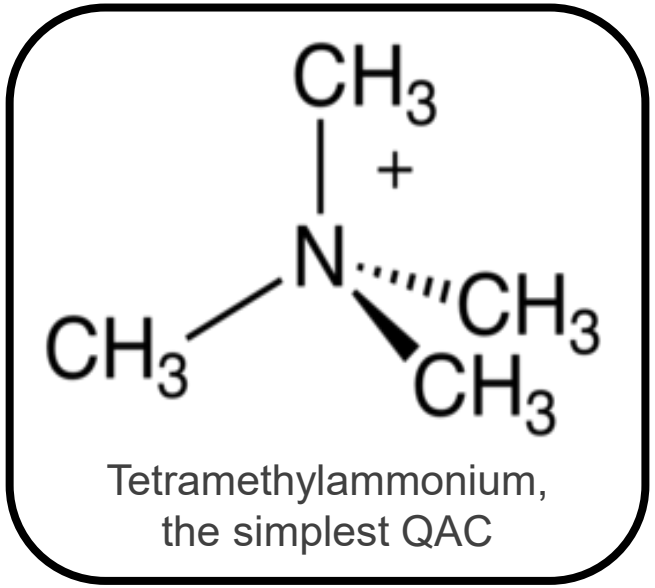
Active ingredients in products on the EPA *List N: Disinfectants for Use against SARS-CoV-2.*

QAC Chemistry

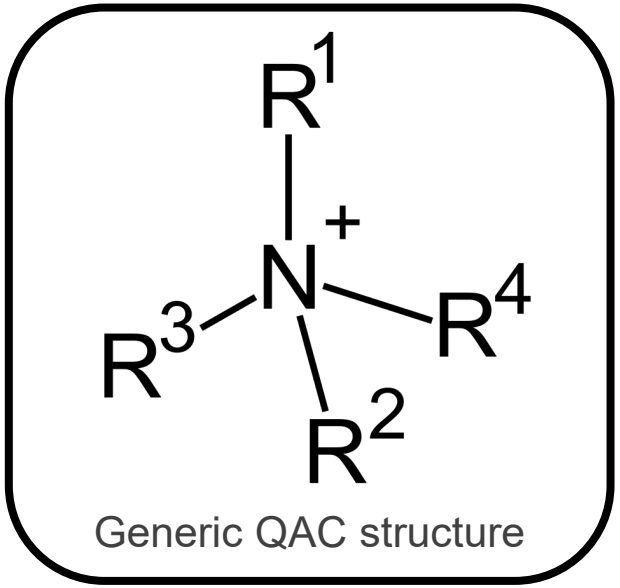
- QACs are a class of chemical compounds that are cationic surfactants
- Derived from ammonium by replacing the H atoms with organic groups (e.g., methyl groups)
  - Organic groups can contain long carbon chains and aromatic rings
- QACs remain positively charged regardless of pH



Ammonium ion



Tetramethylammonium,
the simplest QAC



Generic QAC structure

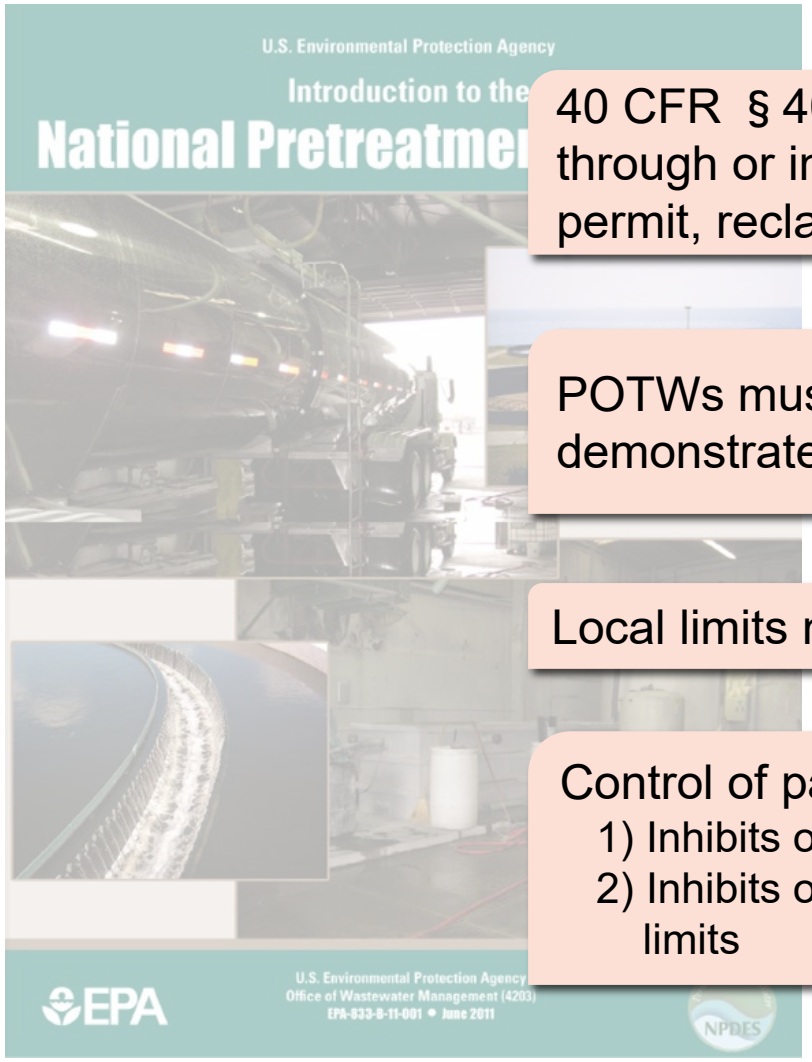
Analytical Methods to Measure QACs

- Colorimetric and chromatography methods exist for measuring QACs
- Chromatography methods (e.g., GC-MS or LC/MS-MS) are better at distinguishing individual QAC compounds at low concentrations
- Colorimetric methods can suffice for higher concentrations of total QACs

Method	Benefits	Limitations
Spectrophotometric methods (e.g., Hach QAC kits)	Quick and easy; Spectrophotometer readily available	Cannot distinguish individual QAC compounds; Susceptible to interference; Limited range of 0.2 to 5 mg/L
Gas Chromatography/Mass Spectrometry (GC/MS)	May have shorter run times and lower detection limits (ng/L range)	Requires extensive sample preparation
Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS-MS)	Less sample preparation, sufficient detection limits for many applications (ng/L range)	May have longer run times and higher detection limits

Pretreatment Regulations

National Pretreatment Regulations



40 CFR § 403 gives POTW legal authority to control discharges to prevent pass through or interference with collection system, treatment processes, discharge permit, reclaimed water permit, biosolids

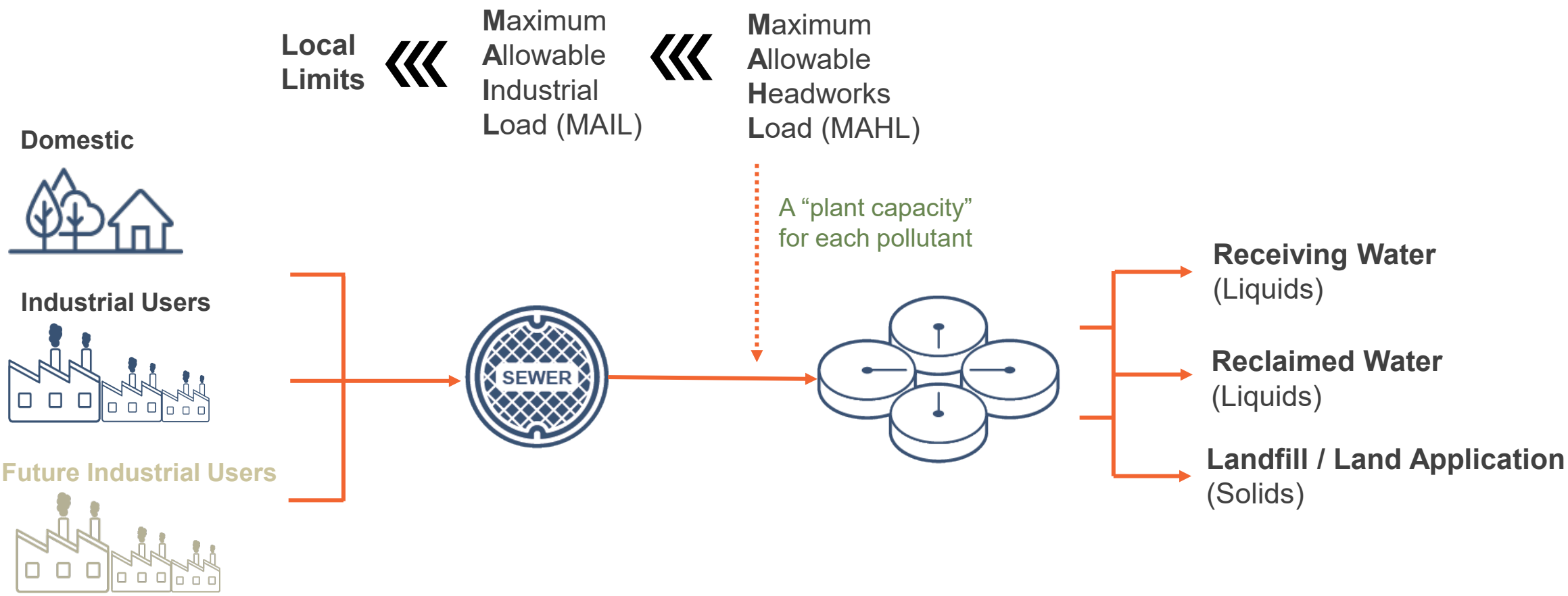
POTWs must develop and enforce specific limits on prohibited discharges or demonstrate that limits are not necessary per 40 CFR 403.5(c)(1)

Local limits must be defensible and technically based

Control of pass through and/or interference:

1) Inhibits or disrupts treatment and/or operation of wastewater treatment
2) Inhibits or disrupts sludge disposal or ability for reclaimed water to meet regulatory limits

Headworks Analysis Mass Balance



MAHL is a fixed value per pollutant based on *average day WRF flow*

MAIL = MAHL – Domestic Load

Establishing a Maximum Allowable Headworks Load (MAHL)



EPA and State Adopted Water Quality Criteria



Inhibition Thresholds → EPA Publications, Literature, Site-specific studies



Biosolids Disposal → EPA Part 503 or RCRA



Receiving Stream → Whole Effluent Toxicity



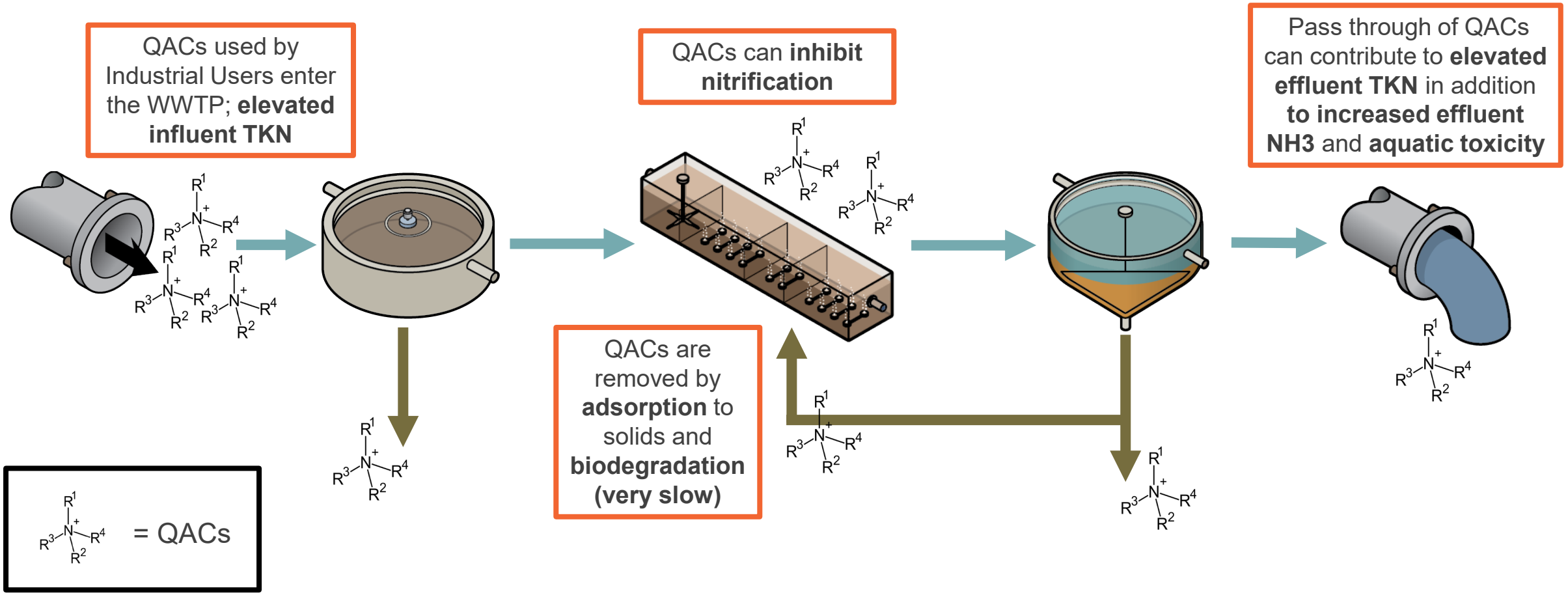
Discharge Permit Requirements

How to establish a MAHL for pollutants not regulated, but are expected to cause pass-through and/or interference?

Toxicity (Nitrification Inhibition and Effluent Toxicity)

Nitrification Inhibition

- Literature studies suggest QACs may **inhibit nitrification at concentrations < 2 mg/L**
- **Biodegradation** is typically **very slow**



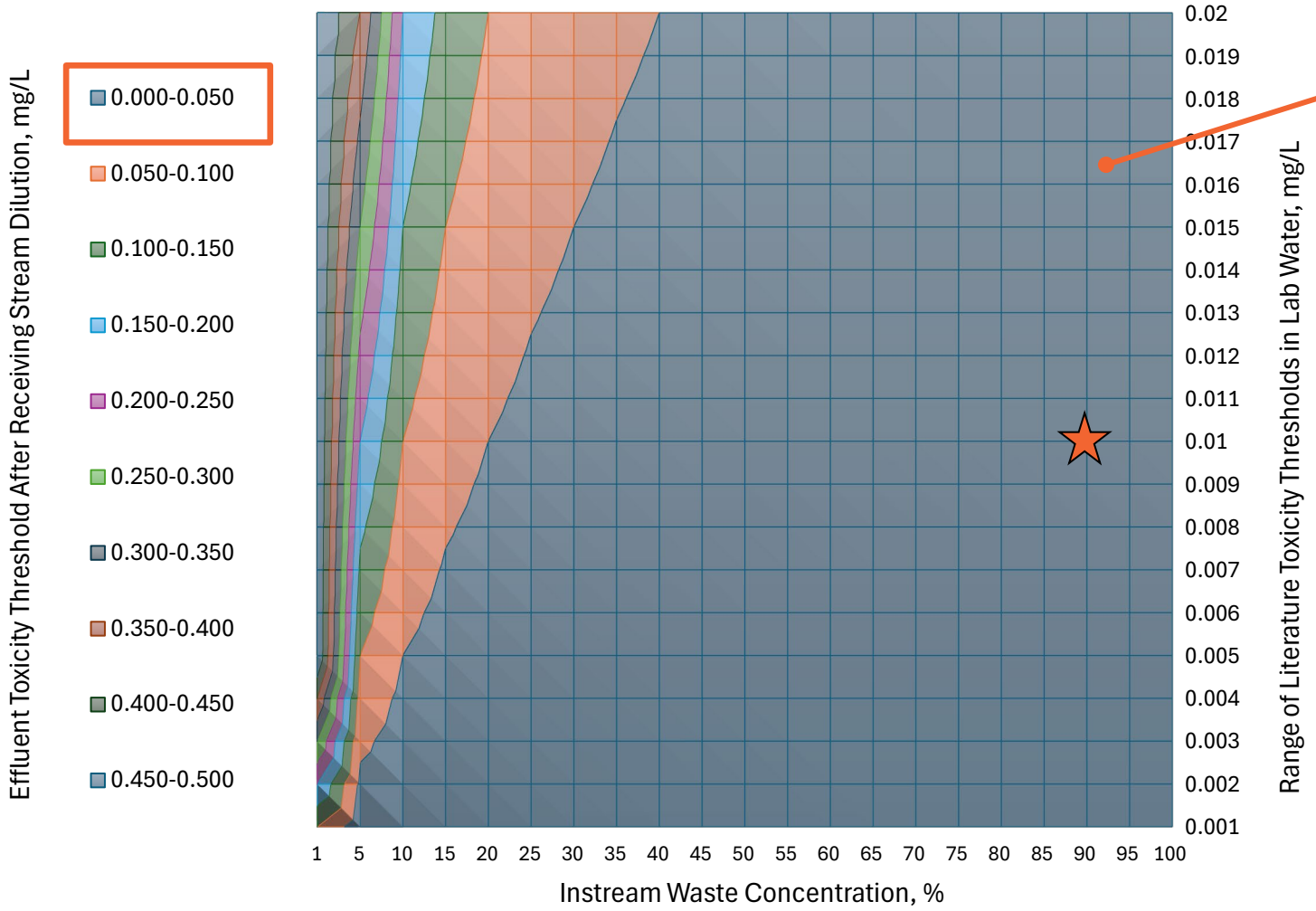
Effluent Toxicity

Summary of U.S. and European Toxicity Data for Quaternary Ammonium Compounds

Species Group	Exposure	Endpoint	Concentration	Reference	Chemical Tested
Algae	Chronic	EC50	0.113 mg/L	European Chemicals Agency	Tricetylmethyl ammonium chloride
	Chronic	NOEC	0.068 mg/L	European Chemicals Agency	Tricetylmethyl ammonium chloride
Crustaceans	Chronic	EC50	0.18 mg/L to > 10 mg/L	EPA ECOTOX	Di-C12-20-alkyldimethyl, chlorides
	Acute	LC50	0.49 mg/L to > 10 mg/L	EPA ECOTOX	Di-C12-20-alkyldimethyl, chlorides
Invertebrate	Chronic	NOEC	0.00415 mg/L	European Chemicals Agency	(C16-18 and C18unsatd. alkyl) trimethyl, chlorides
	Acute	EC50	0.012 mg/L	European Chemicals Agency	(C16-18 and C18unsatd. alkyl) trimethyl, chlorides
Fish	Chronic	NOEC	0.0322 mg/L	European Chemicals Agency	(C16-18 and C18unsatd. alkyl) trimethyl, chlorides
	Acute	LC50	0.150 mg/L	European Chemicals Agency	(C16-18 and C18unsatd. alkyl) trimethyl, chlorides

Impact of Dilution on Effluent Toxicity of One QAC Compound

Specific Chemical Analysis on a QAC Compound in a Disinfection Product



Area shaded in blue represents effluent toxicity concentration between 0.0 and 0.05 mg/L of one QAC compound

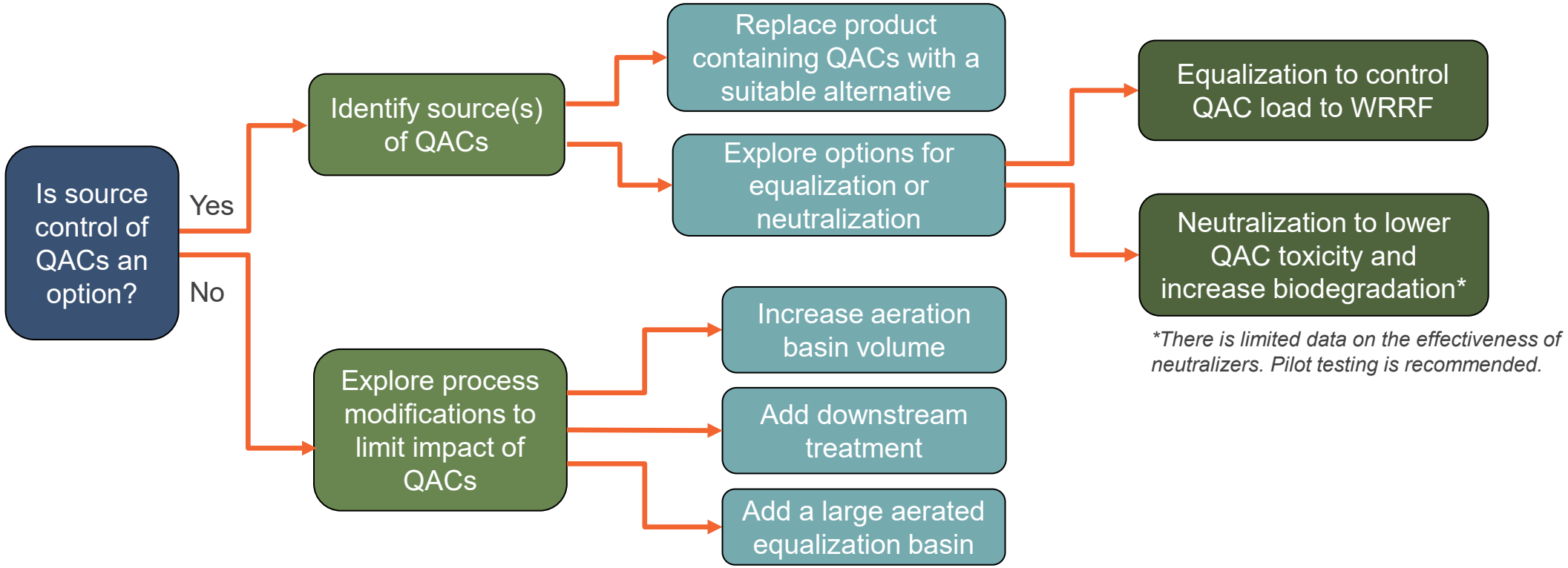
Example:
90% IWC at *C. daphnia* toxicity threshold of 0.01 mg/L = MAHL of 0.011 mg/L

Effluent toxicity thresholds are at least an order of magnitude less than nitrification inhibition

Mitigation

WWTP Mitigation Options

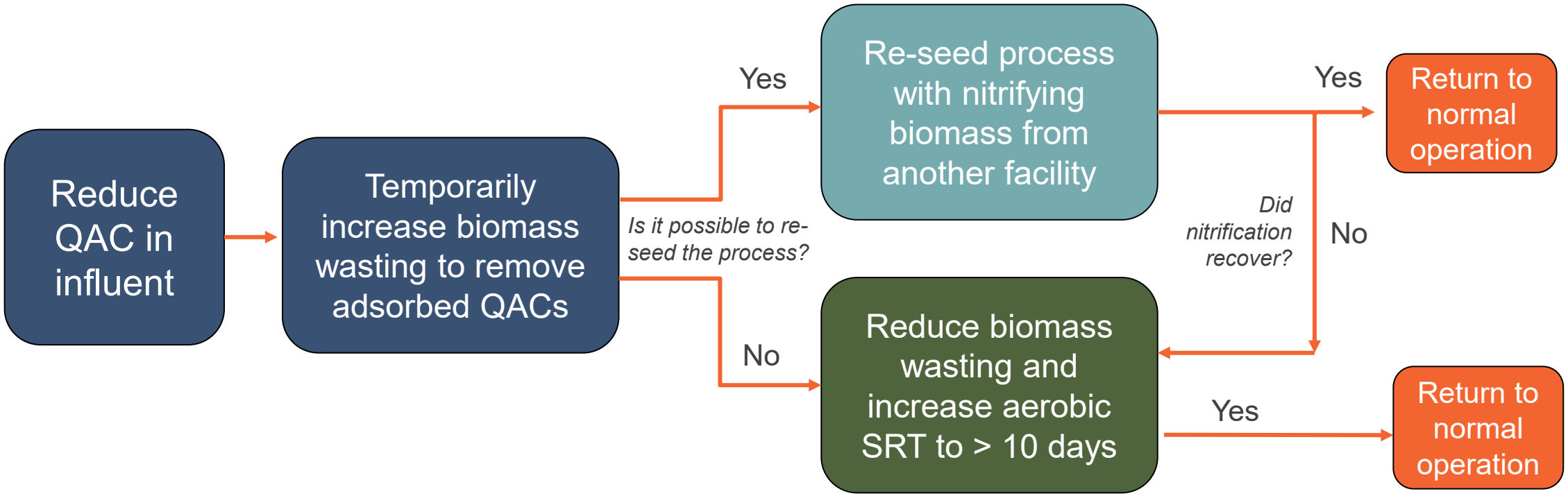
- Limiting influent QAC when possible is important to mitigate nitrification inhibition
- Process or configuration changes may be necessary if QACs are not controlled at the source
- Process modifications can include equalizing influent and/or increasing aerobic hydraulic retention time to improve QAC biodegradation and allow more time for nitrification



There is limited data on the effectiveness of neutralizers. Pilot testing is recommended.

Nitrification Recovery

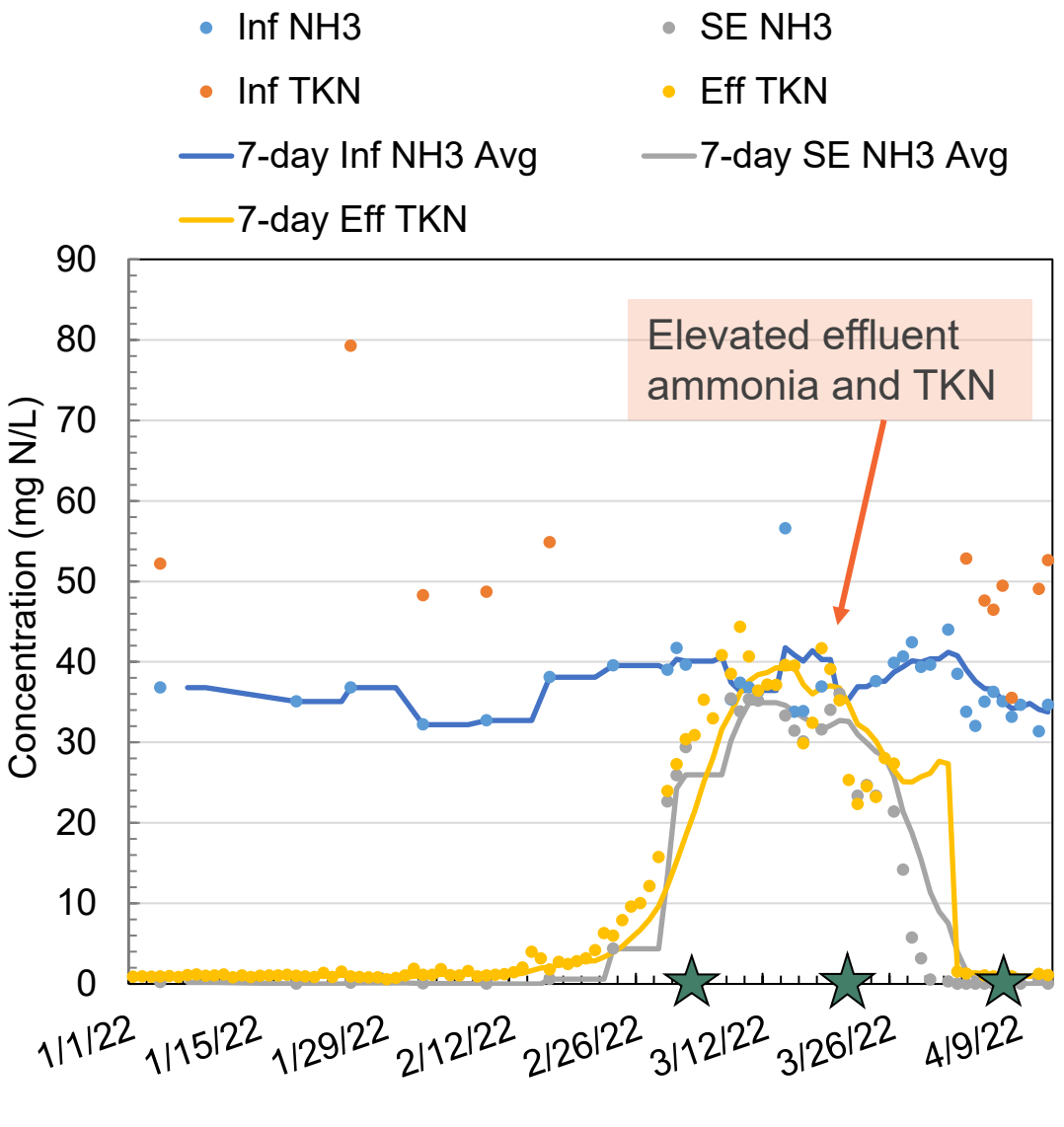
- Options for nitrification recovery include:
  - Increase biomass wasting to remove QAC adsorbed to solids
  - Re-seed to increase nitrifier population



Case Studies

Case Study A

- WWTP experienced a **sudden increase in effluent NH3 and TKN**
- Special sampling performed to identify possible causes
- Most toxicants tested were non-detects
- **QACs were detected**
  - Industrial User 1 (carwash, measured at source) at 1.9 mg/L
  - Industrial User 2 (data center, measured at source) at 0.9 mg/L
  - Primary effluent – 0.9 mg/L
  - Secondary effluent – 3.9 mg/L
  - Final effluent – 0.6 mg/L



★ *Bench tests*

Case Study A

- Batch tests performed to evaluate nitrification activity and to monitor the recovery process

Early in process upset, batch tests indicated **presence of toxicant(s)** and reduced nitrification activity

During process recovery, batch tests suggested toxicant no longer present, but **nitrification not yet fully recovered**

After the process recovered, batch tests confirmed a return to **normal nitrification activity**

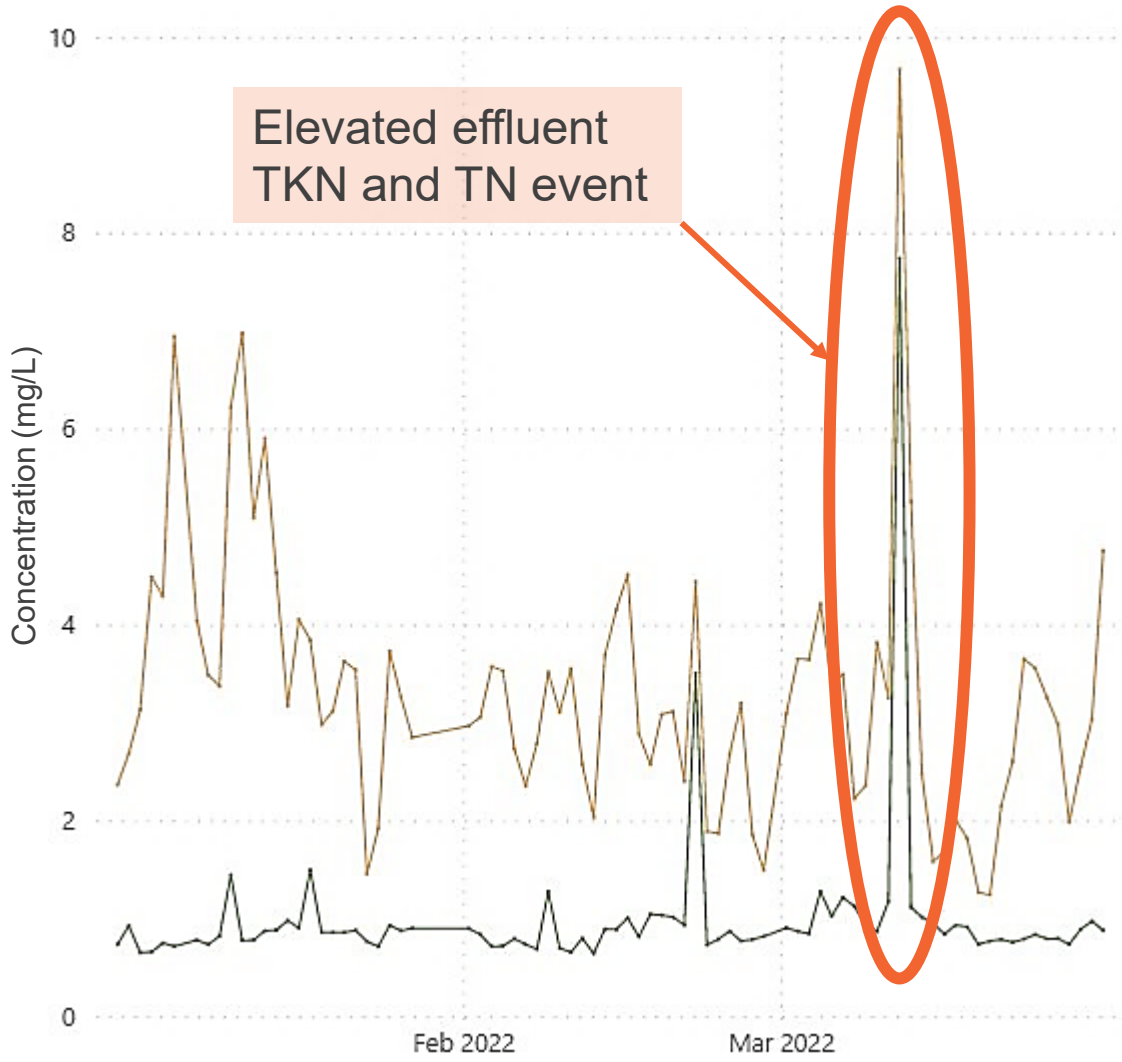
Process recovered by **increasing biomass wasting temporarily** to remove inhibitory compounds and **re-seeding** with biomass from a nitrifying WWTP.

Case Study B

- **Nitrification inhibition** event at a WWTP
- Potential contributing industrial discharger identified
- Actions taken:
  - Reviewed industry's cleaning agent composition
  - Characterized industrial discharge
  - Nitrifier activity testing
- Cleaning agent contained **QACs and triazole**, which can also inhibit nitrification

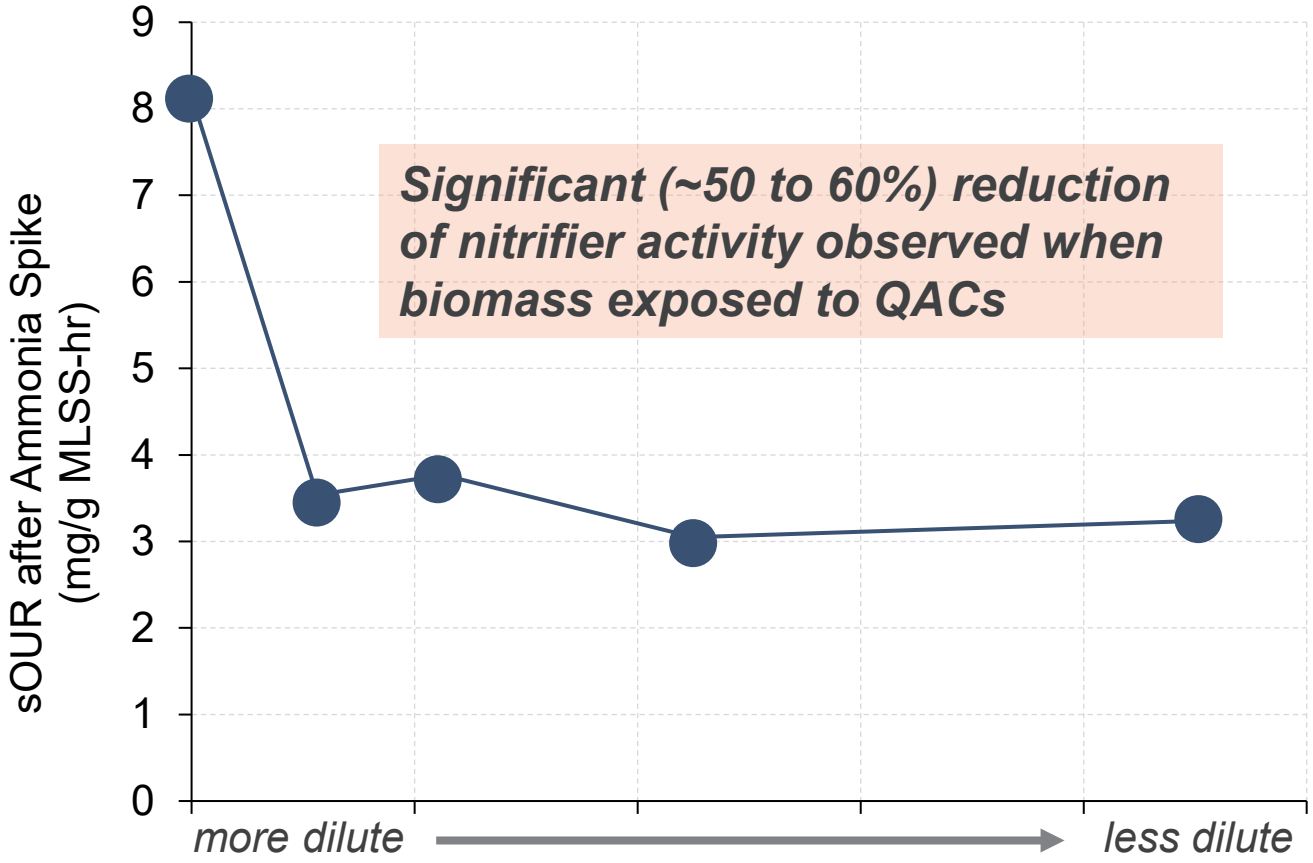
Cleaning agent used by industrial discharger

Parameter	Unit	Cleaning Product Concentration
tCOD	mg/L	250,000
sCOD	mg/L	190,000
NH3-N	mg-N/L	2,320
QAC	mg/L	375



Case Study B

- Bench tests exposed biomass to various dilutions of industrial discharge and measured nitrification activity
- Dilutions mimicked % industrial discharge in WWTP's typical influent flow
- Dilutions equivalent to industrial discharge comprising as little as 1.5% of the WWTP's influent flow inhibited nitrification activity
- Inhibition likely a **combined effect** of multiple products used

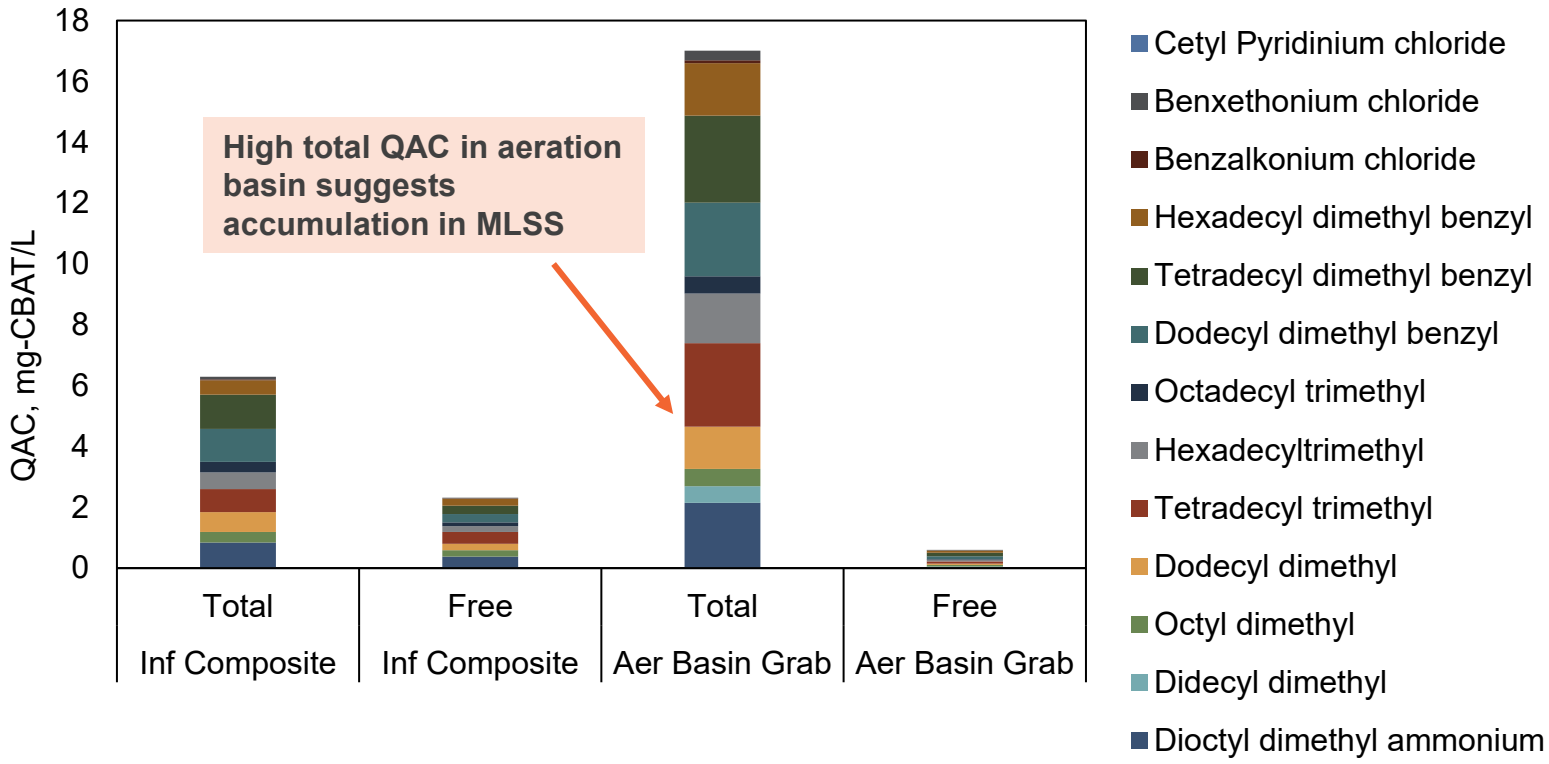


*Recommendation for the industry **to reduce the discharge rate** to prevent slugs at WWTP.*

Case Study C

- WWTP experienced effluent ammonia spikes
- QACs observed across all samples with free QACs reaching 2 mg/L in influent
- Suspected **influent QAC concentrations and QAC adsorption to MLSS** leading to chronic inhibition of nitrifiers
- Free QAC concentrations of 2 mg/L or less can be inhibitory
  - Inhibition threshold of total QAC unknown

Elevated QAC concentrations during spike in effluent ammonia



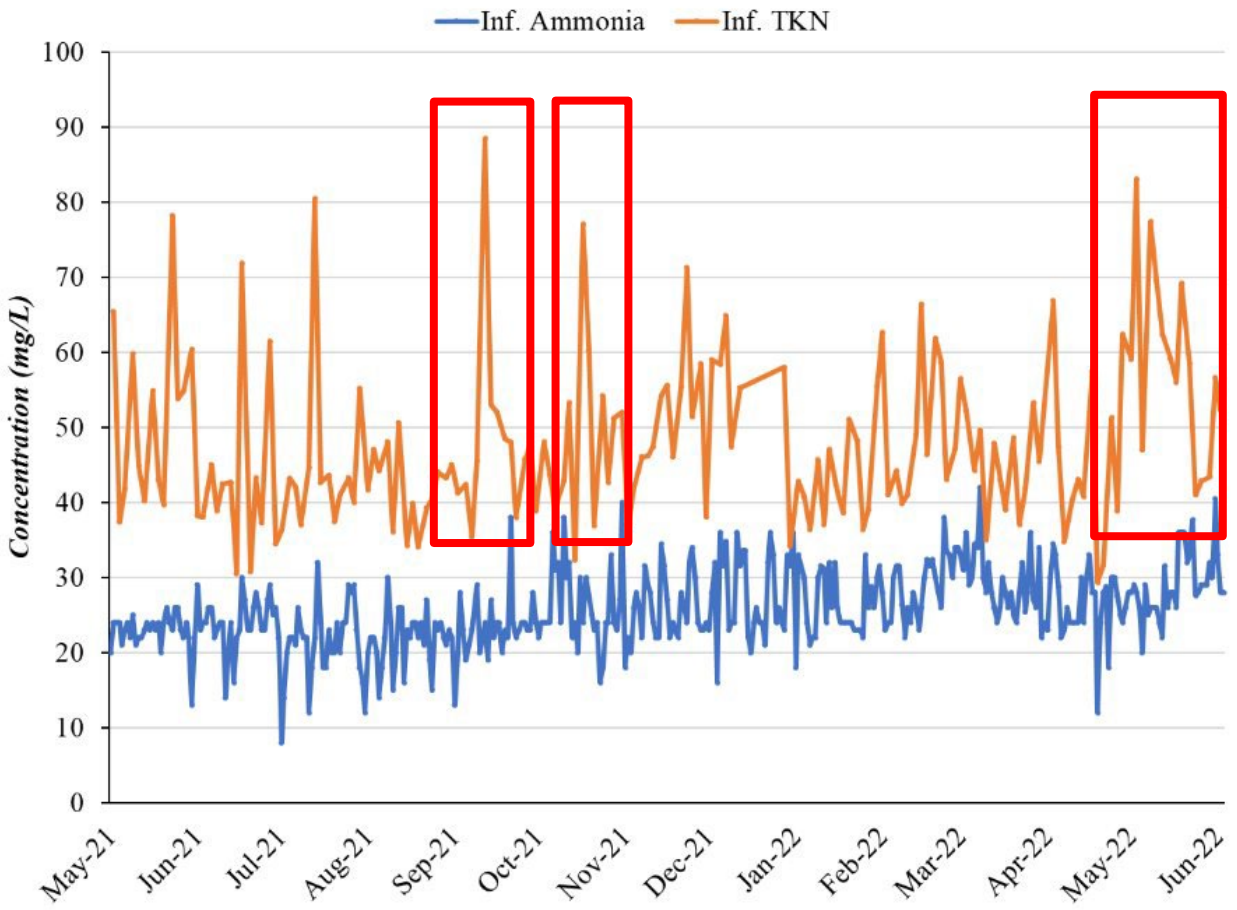
Recommendation to work with industry to consider alternative disinfection products or consider equalization and/or neutralization.

Case Study D

- Suspected issues with QACs discharged to the WWTP
  - Repeated inhibitory issues observed at WWTP
  - Bench testing has confirmed the use of QACs
- POTWs discussions with industries and implementing Best Management Practices (BMPs) has reduced severity of inhibition issues
- Adversarial relationship with several industries that refuse to implement BMPs or product substitution
  - Suspect that several industries have miscategorized type(s) of process (e.g., SIC codes)
  - Suspected use of QACs
- POTW used QACs as pass through and/or interference to classify uncooperating industries as significant industrial users (SIUs)

Case Study E

- WWTP experienced multiple events of **deteriorating nitrification** performance
- Sampled influent and two industrial discharges (school and landfill)
- Performed **batch tests** to evaluate nitrifier activity
- Nitrification activity results indicated **presence of toxicant** in influent
- Influent samples contained low concentration of QACs (< 0.5 to 0.6 mg/L)
- Other contaminants tested (metals, amines, etc.)



Influent TKN spikes without accompanying ammonia spikes suggested QACs may be present in influent.

Case Study E

Actions taken to resolve upset:

1) Optimized aeration by increasing aerobic SRT
2) Added PlantPRO (NH3 Control Nitrifiers) product
3) Identified potential sources of toxicant
4) Investigated QACs being released by industrial users

High concentrations of QACs and zinc in discharge from an upstream high school:

- QACs = 4.5 mg/L
- Zinc = 4.7 mg/L

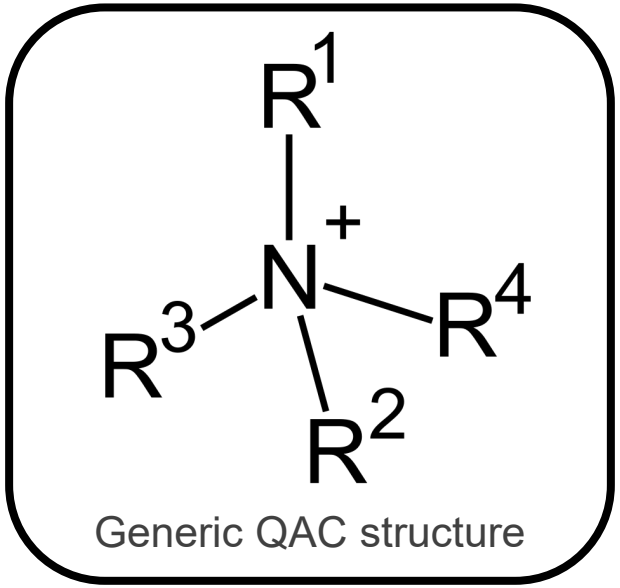
Recommendations:

- *Periodically **quantify QACs** in WWTP influent and at industrial discharges of concern*
- *Identify **strategies for remediation***
- *Continue to **monitor SDS for industrial dischargers***
- ***Plan corrective actions** for process upsets due to changes in influent characteristics*

Final Thoughts

Evolving Understanding of QAC Impact on Wastewater Treatment

- QACs are not a new topic
- Use of QAC-based disinfection products becoming even more frequent in post-Covid world
- QACs are a class of complex compounds
  - Impacts not fully understood (e.g., biodegradation potential, toxicity, etc.)
- Difficult to model QACs in wastewater treatment processes:
  - Lack of kinetic information regarding rate of biodegradation for different types of QACs
  - Lack of information on adsorption / de-sorption reactions
- Tracking QACs through a WWTP is difficult because simpler (e.g., Hach QAC kits) do not measure individual types of QACs
  - Sample pre-processing is necessary for measuring solids adsorbed QACs versus soluble or “free” QACs

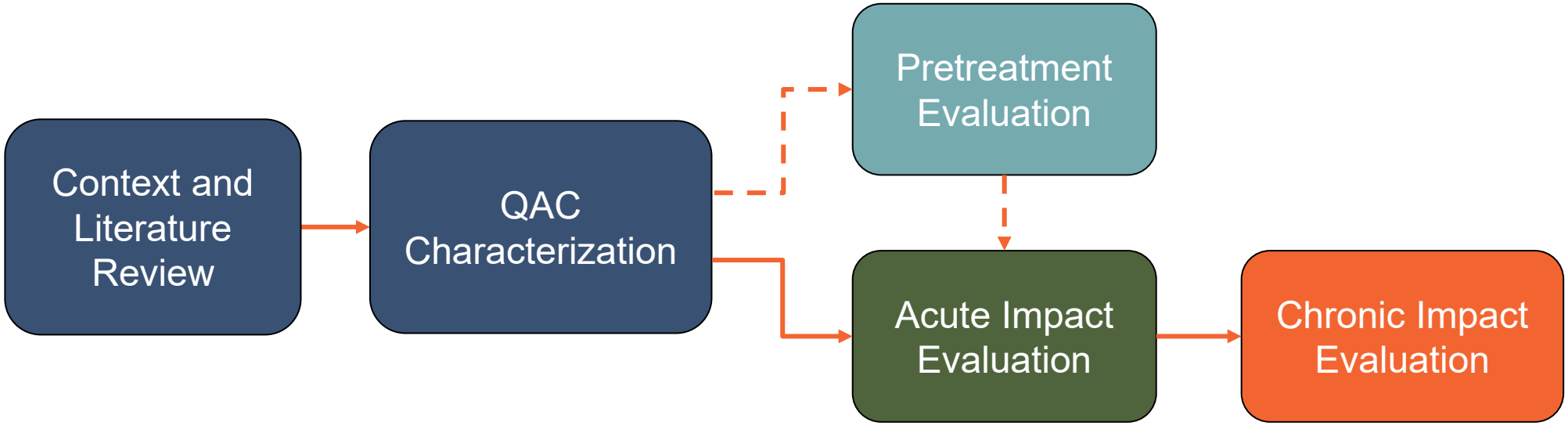


Generic QAC structure

Studying Specific Impacts at a Wastewater Treatment Facility

Multi-Phase Study

- What types of QACs are anticipated to be discharged?
- Dose, frequency, and duration?
- Is pretreatment or additives effective in mitigating impact on treatment and discharge?
- How much QAC can a WWTP accept?
- Acute versus chronic inhibition – Which is limiting?



Mitigation is Key

- **Mitigation strategies** include:
  - Alternative products that do not contain QACs
  - Equalization of industrial discharges containing QACs
  - Neutralization using neutralizer products (must show that product is effective!)
  - WWTP process modifications
- Develop strategies and communicate with Industrial Users and commercial businesses about QAC impact on the WWTP
  - Pretreatment programs are the regulatory mechanism for response and enforcement



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