Benchmarking Trace Organic Contaminant Biotransformation During Biological Nutrient Removal

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dc water is life

WERF
Water Environment Research Foundation
Collaboration. Innovation. Results.

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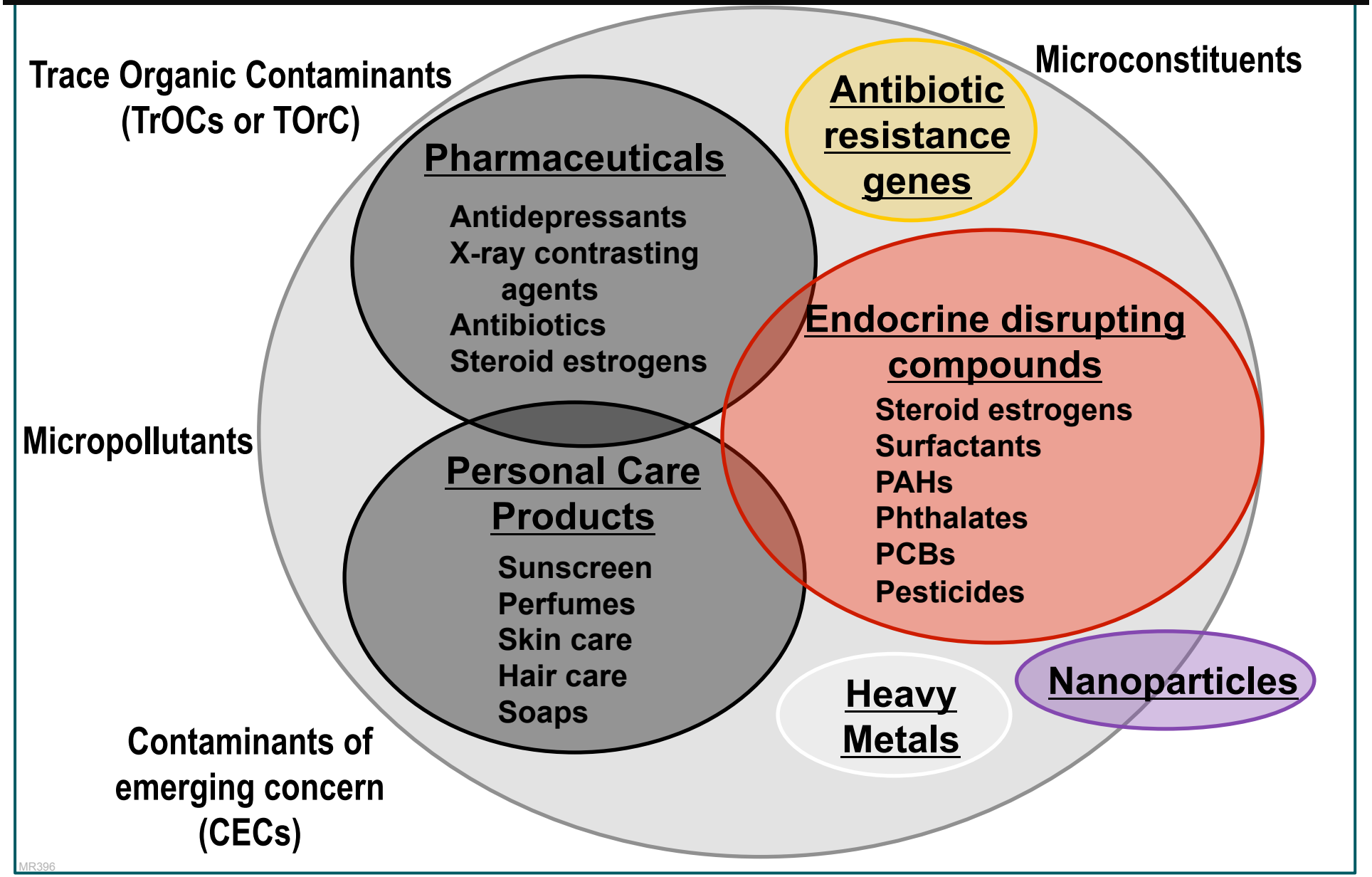
TOrC are compounds that are present in the environment at μg/L to ng/L levels

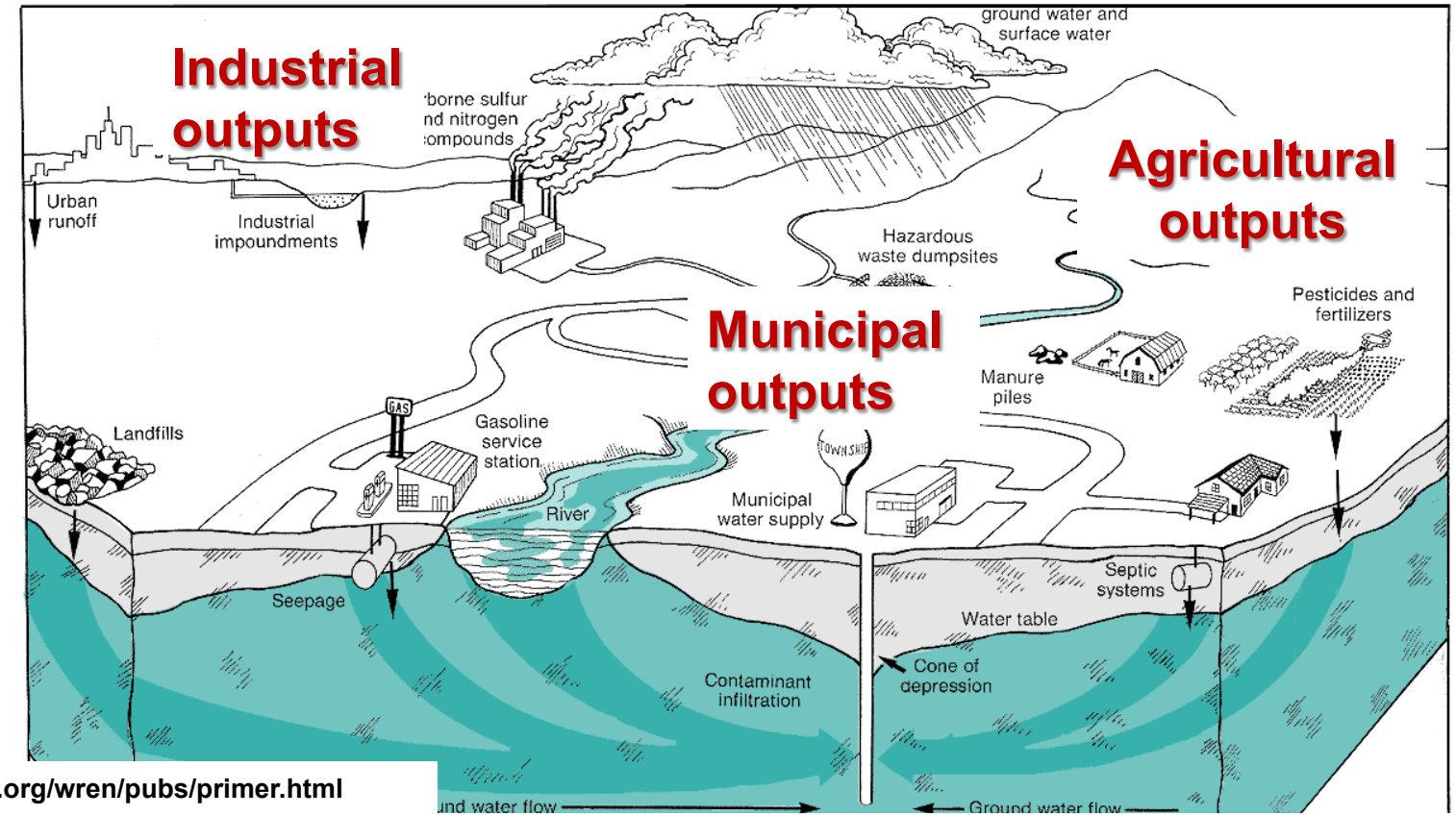


Where have TOrC been found and where do they come from?

TOrC are found throughout the engineered and natural water cycle.

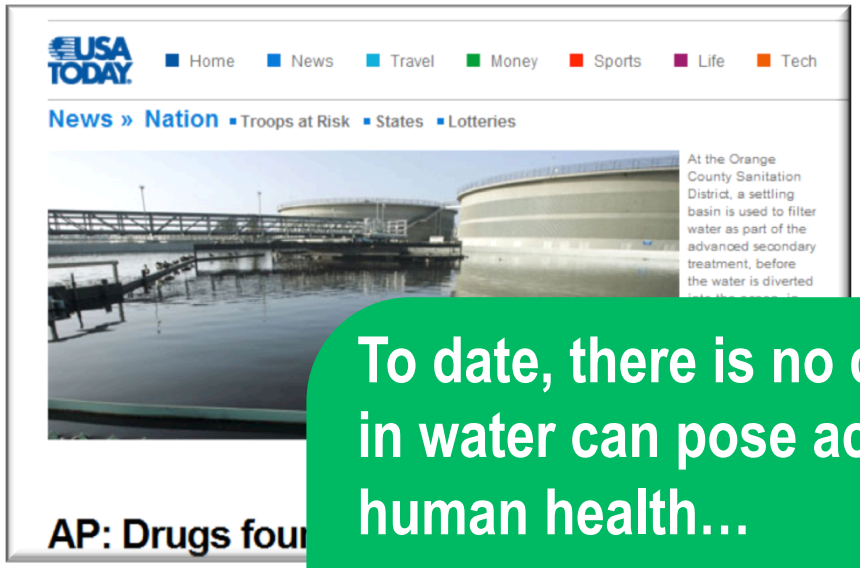
Some are naturally occurring.

Some are the product of human activity.



http://palwv.org/wren/pubs/primer.html

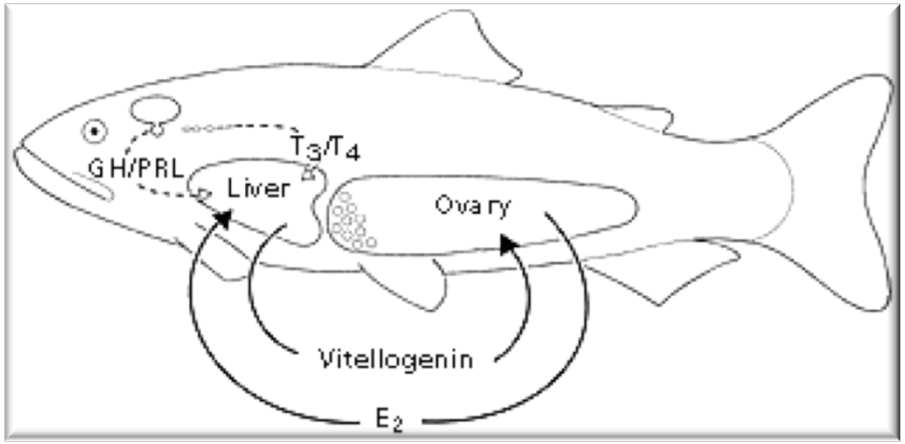
Should we be concerned?



To date, there is no direct evidence that TOrC in water can pose acute toxic effects on human health…

however, future work must be done to study chronic exposure

Should we be concerned?



Proceedings of the National Academy of Sciences of the United States of America

Collapse of a fish population after exposure to a synthetic estrogen

Karen A. Kidd[*,†], Paul J. Blanchfield[*], Kenneth H. Mills[*], Vince P. Palace[*], Robert E. Evans[*], James M. Lazorchak[‡], and Robert W. Flick[‡]

No laughing matter

Discovery of intersex fish p
for Chesapeake Bay

Monday, January 29, 2007

Pharmaceuticals in Our
Mutations to Wildlife

By Greg Peterson, E Magazine
Posted on August 9, 2007,

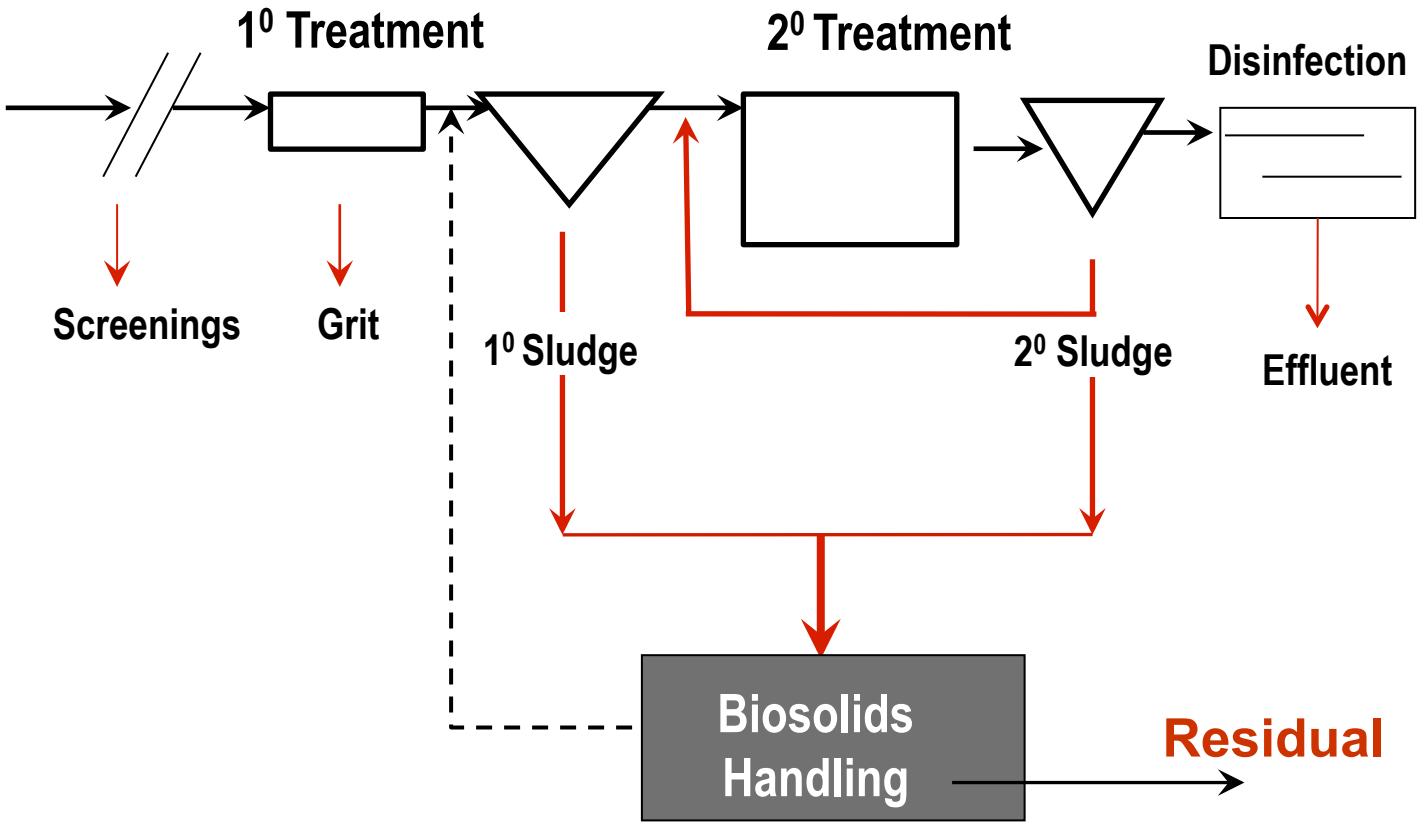
Data suggest that accumulation of certain TOrC could detrimentally impact wildlife

High Prevalence of Vancomycin-Resistant Enterococci in Swedish Sewage

Aina Iversen,[1]* Inger Kühn,[1] Anders Franklin,[2] and Roland Möllby[1]

Microbiology and Tumor Biology Center, Karolinska Institutet, SE-171 77 Stockholm,[1] and Department of Antibiotics, National Veterinary Institute, SE-751 89 Uppsala,[2] Sweden

WRRFs act as a line of defense against direct output of TOrC to the environment



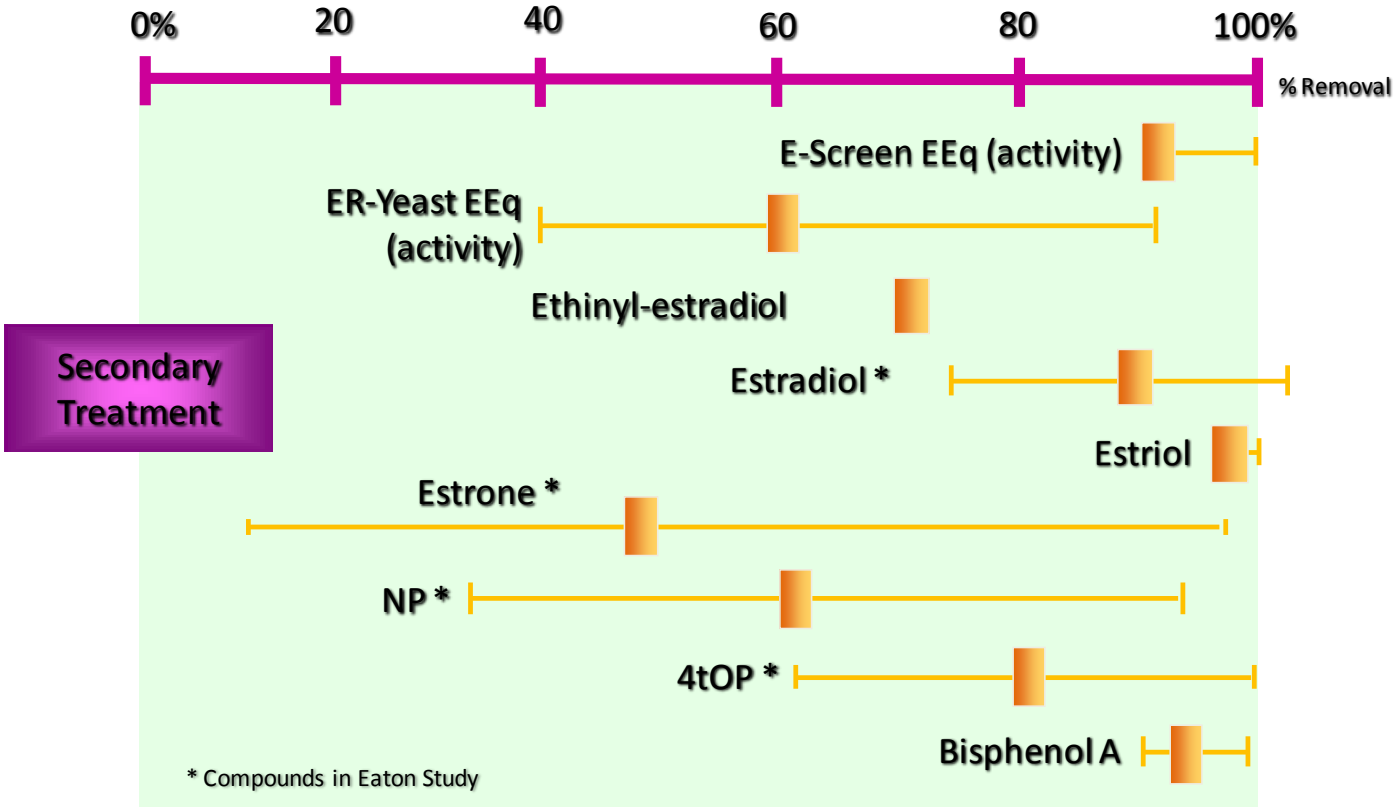
WRRFs designed for bulk carbon and pathogen reduction

More recently, there has been a focus on biological nutrient removal

> 84% of WRRFs facilities in USA have some form of biological treatment

How well does the existing biological treatment infrastructure deal with TOrC?

Using endocrine disrupting chemicals as case study



WERF 2006, Removal of Endocrine Disrupting Compounds in Water Reclamation Processes

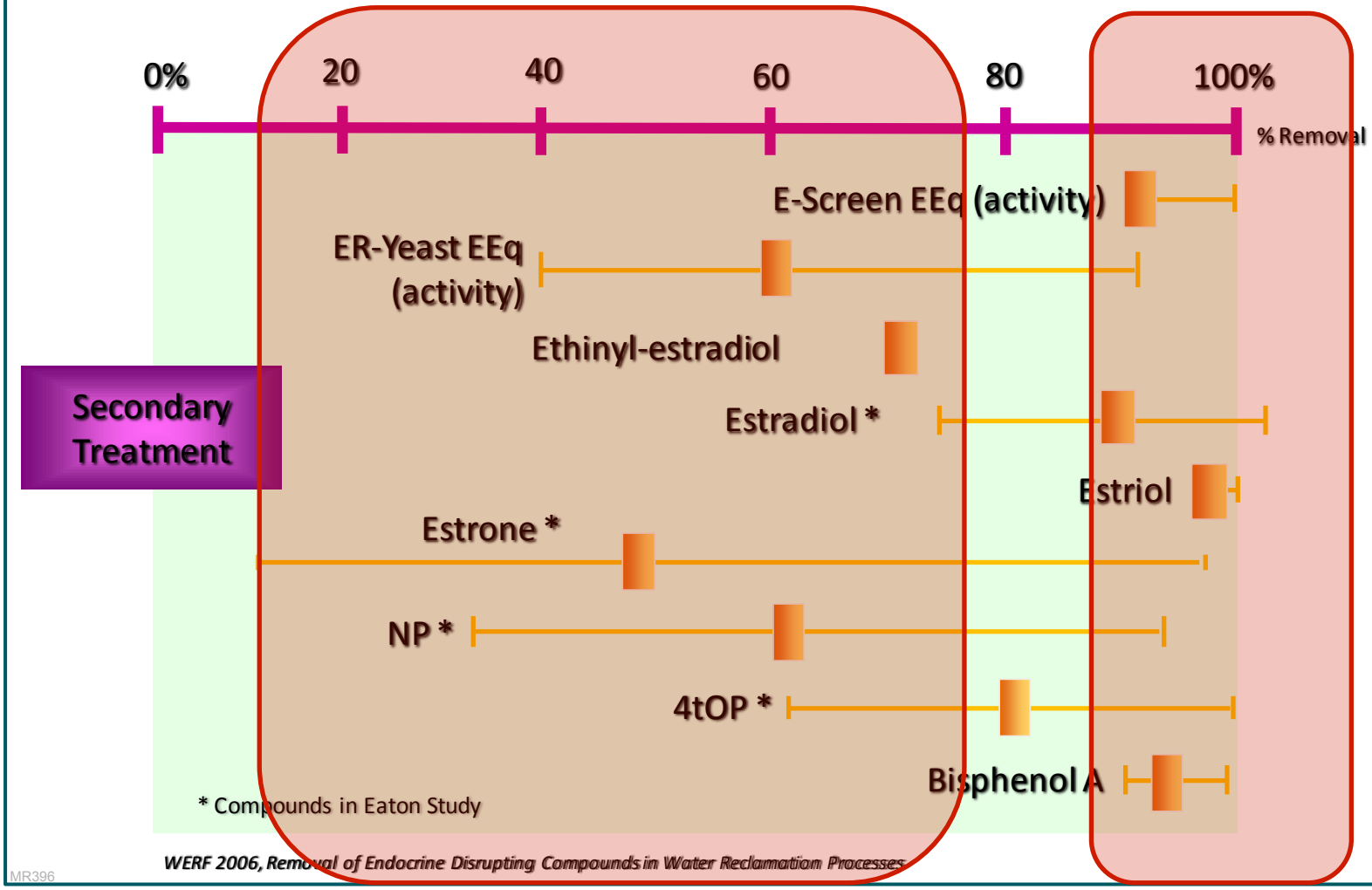
Removal ranges from 20 – 100% for some EDCs
Cannot use this information to accurately predict removal

Variability in TOrC removal results can be magnified if consistent test procedures are not followed

Is this variability due to differences in technology?

OR

Is this variability a reflection of multiple testing conditions?



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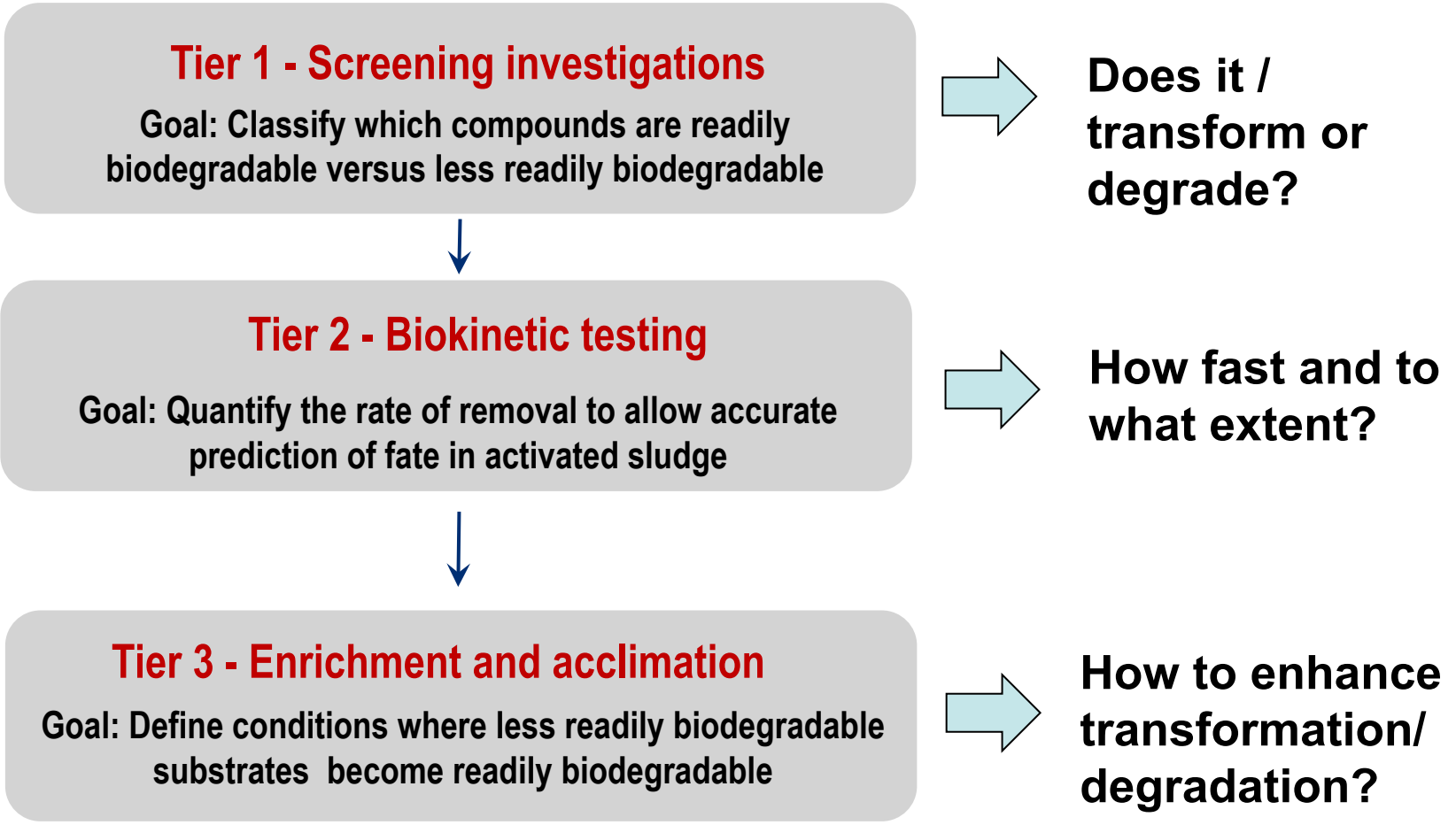
Our objective was to promote a method that would allow researchers to answer fundamental questions about TOrC fate



Adapted from Grady Jr., 1984 Biotechnology and Bioengineering, Vol 27, pp 660-674

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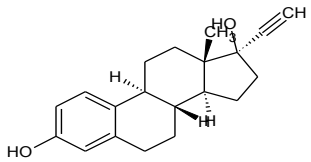
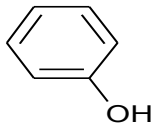
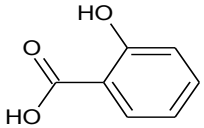
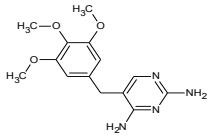
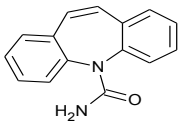
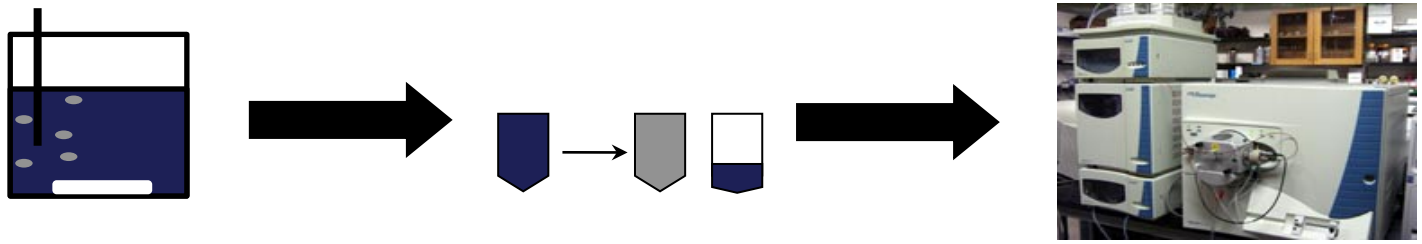
We used 5 well characterized TOrC in these investigations

Chemical	Structure	Use
17α-ethinylestradiol (EE2) $C_{20}H_{24}O_2$		Synthetic estrogen
Nonylphenol (NP) $C_{15}H_{24}O$		Surfactant
Salicylic Acid (SA) $C_7H_6O_3$		Analgesic and Antimicrobial
Trimethoprim (TMP) $C_{14}H_{18}N_4O_3$		Antibiotic
Carbamazepine (CBZ) $C_{15}H_{12}N_2O$		Antiepileptic

These TOrC were selected based on prior fate studies and collaborator interest

We used a consistent method for probing biotransformation at lab and full-scale

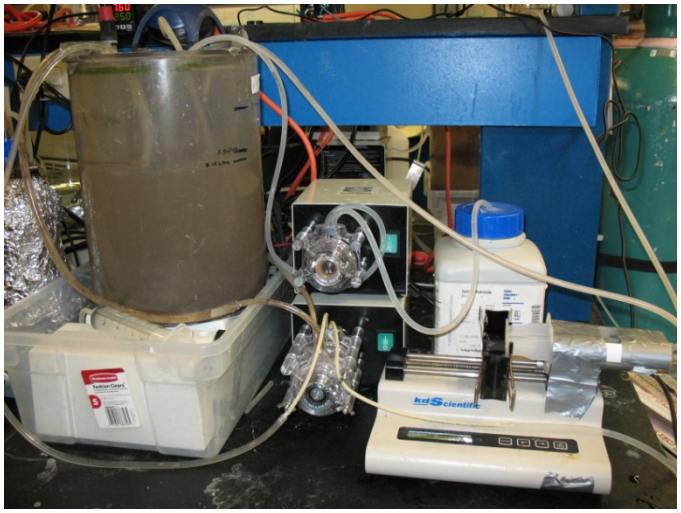


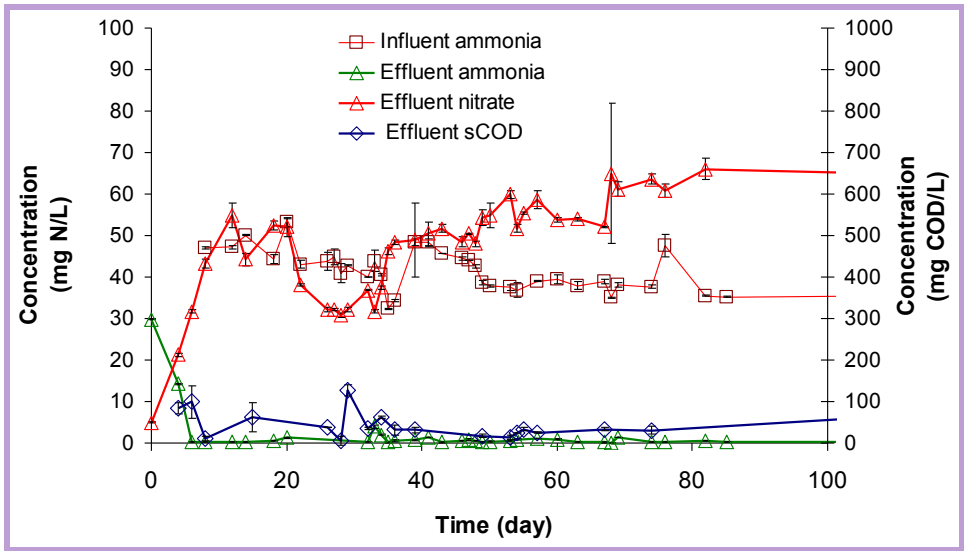
Consistent conditions for biology	Consistent sampling methods	Consistent analytical methods
Short-term experiments	Solid phase extraction with deuterated standards using HLB cartridges	Single injection method with deuterated standard

Results from Lab-Scale Experiments

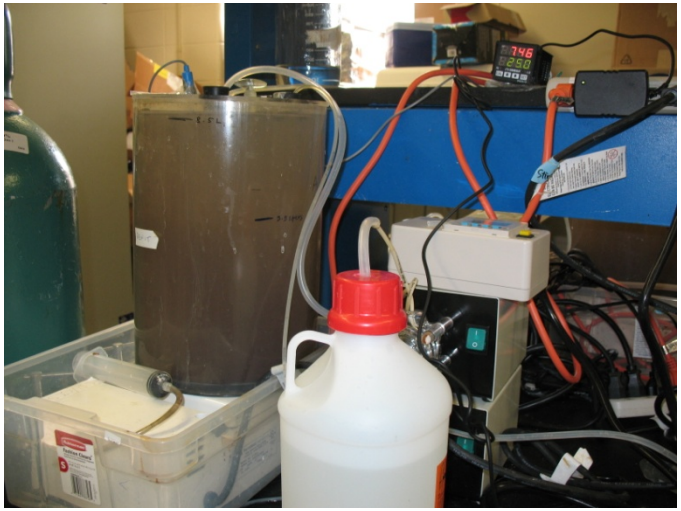
We performing experiments with aerobic and anoxic mixed cultures

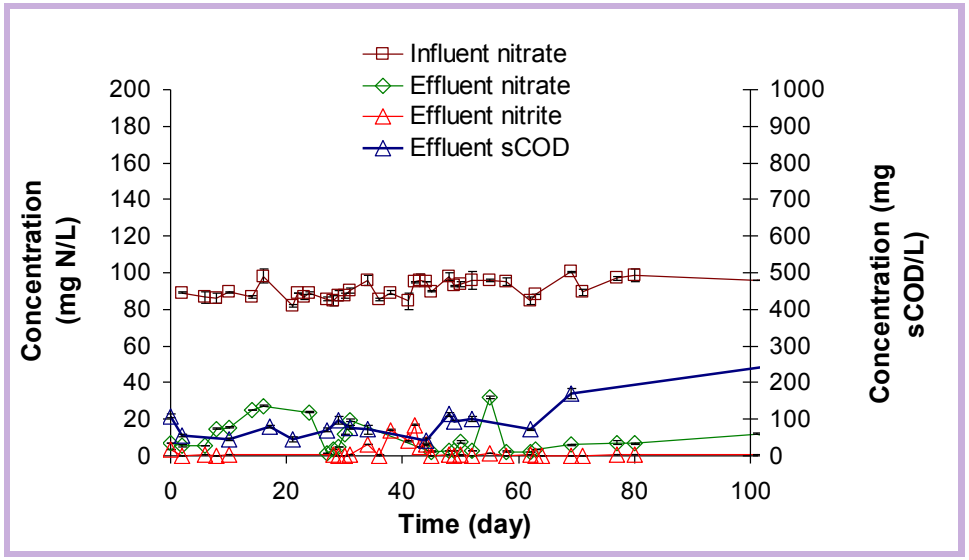
Nitrifying activated sludge (NIT)





Denitrifying activated sludge (DNIT)





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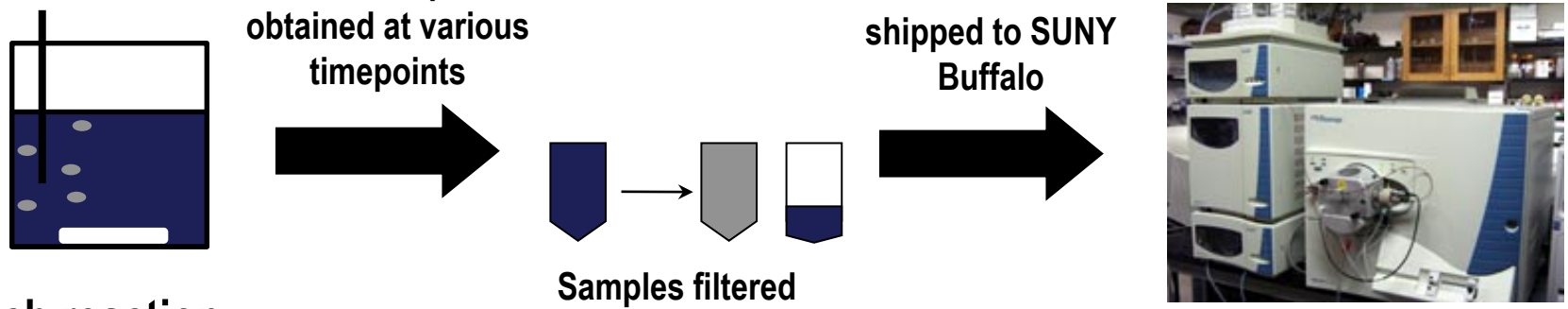
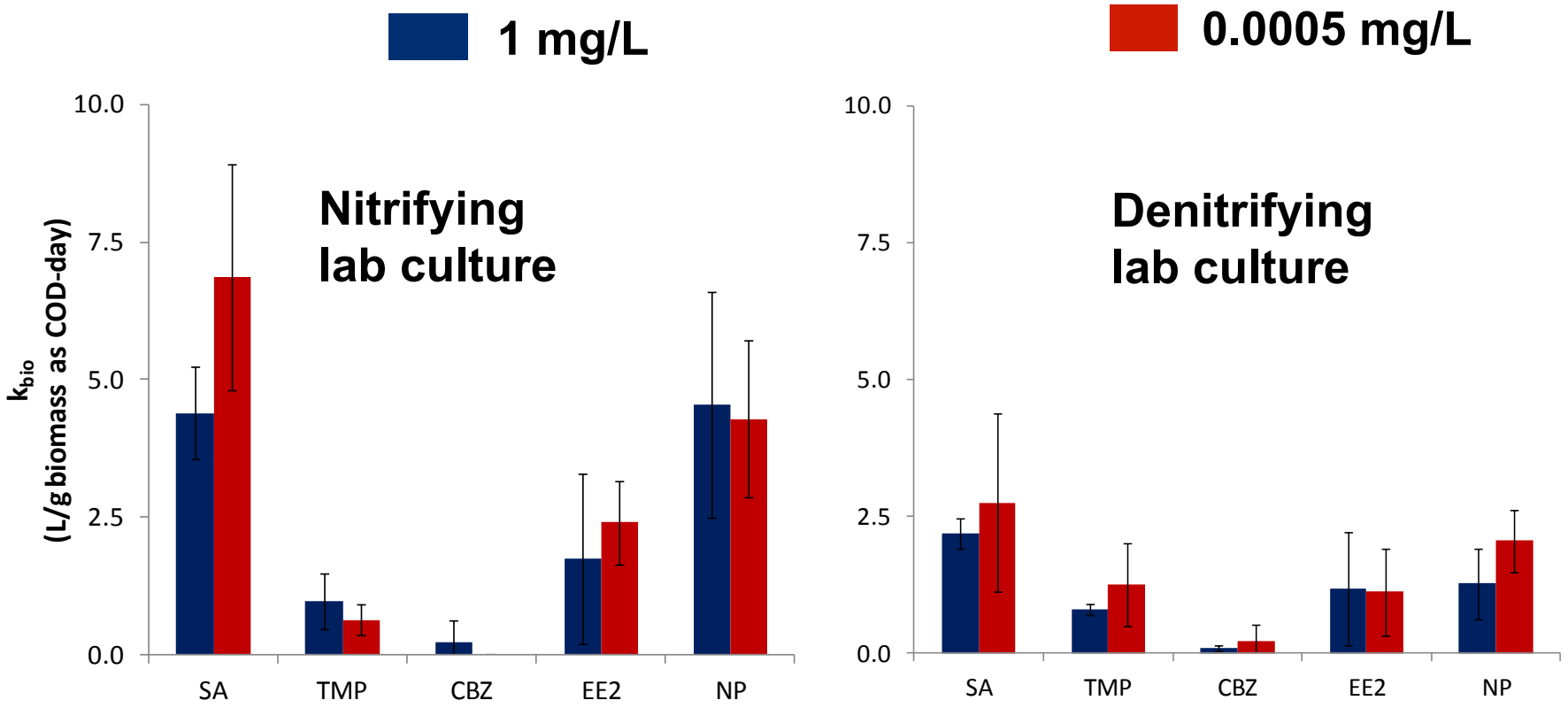
Experiments were performed to answer two fundamental questions

- **Does the initial TOrC concentration to biomass ratio (S_0/X_0) have an impact on the estimated pseudo-first order kinetic parameters?**
- **Does the presence of readily biodegradable substrate (rbCOD) impact the estimated pseudo-first order kinetic parameters**



Su, Khunjar and Aga 2014, Rapid Communications in Mass Spectrometry, 28 (11)
Su et al., 2014, Journal of Hazardous Materials (In press)

No statistical difference existed in estimated parameters between tests at 1 mg/L and 0.0005 mg/L

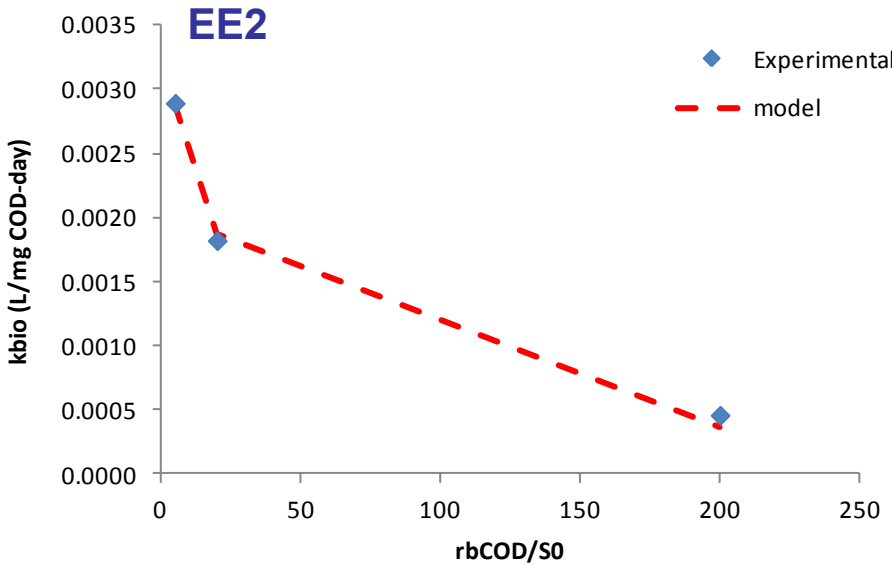


- SA, EE2 and NP more readily bio-transformed under aerobic conditions

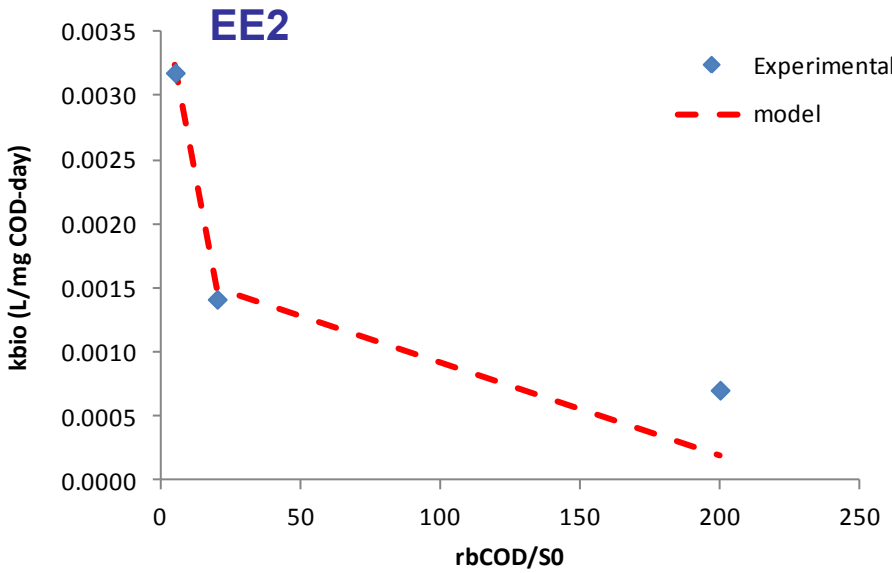
Su et al., 2014, Journal of Hazardous Materials (In press)

Readily biodegradable substrates can "suppress" TOrC biotransformation

Nitrifying lab culture



Denitrifying lab culture

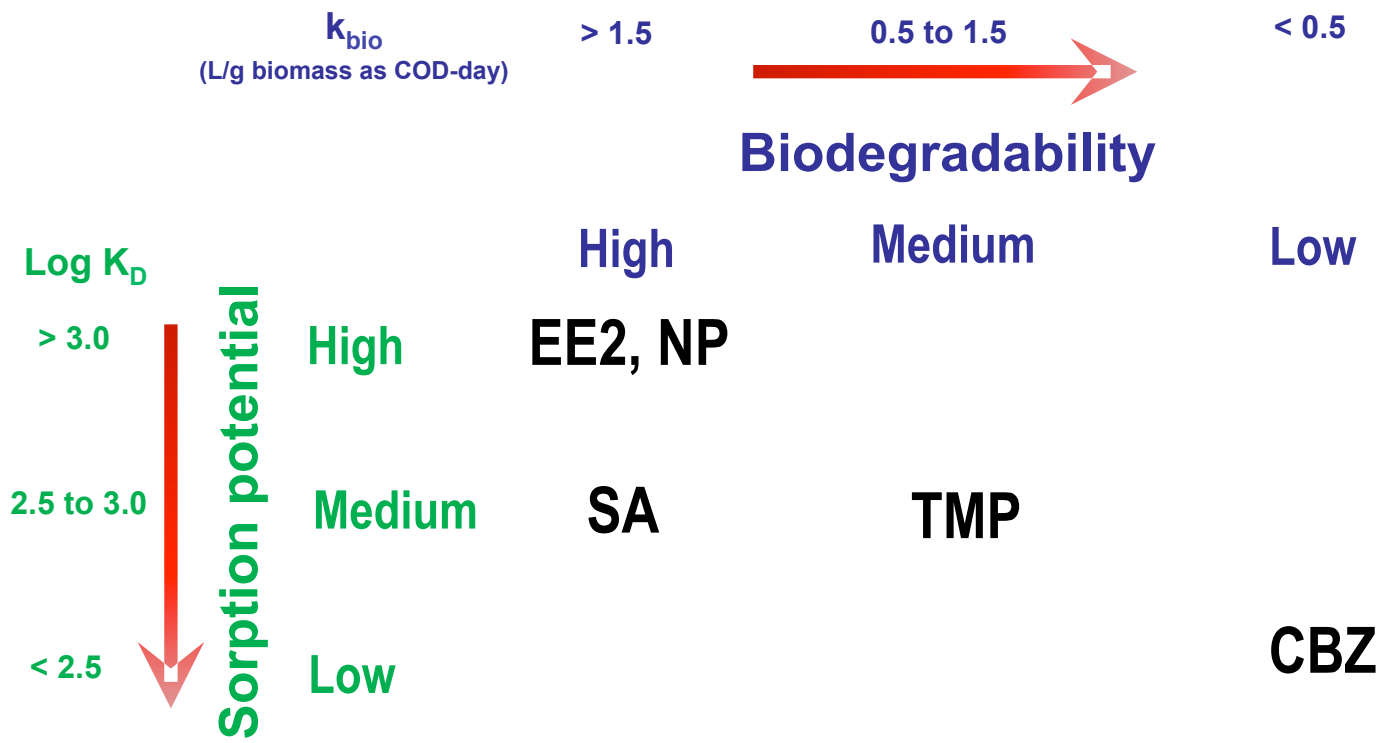


$$kb_{io,TOrC} = k_{bio,TOrC_{max}} \left(1 - \left[\frac{\left(\frac{rbCOD}{S}\right)}{\left(\left(\frac{rbCOD}{S}\right) + K_{TOrC}\right)} \right] \right)$$

Unique parameters that need to be estimated

Su et al., 2014, Journal of Hazardous Materials (In press)

Findings from lab-scale results suggests that biotransformation of TOrC is linked to sorption



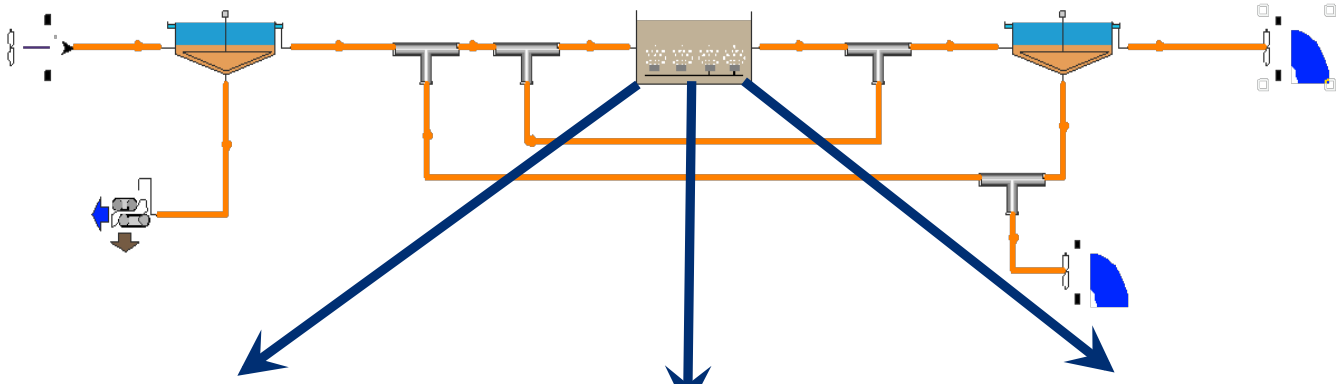
"readily"
biotransformable TOrC

Sorption of carbamazepine, 17α-ethinylestradiol, iopromide and trimethoprim to biomass involves interactions with exocellular polymeric substances

Wendell O. Khunjar [a,1], Nancy G. Love [b,*]

2011 Chemosphere, 82 (6)

We modified an existing process model to include TOrC sorption and biotransformation



Organic carbon removal

Nitrification
Denitrification
Bio-P removal

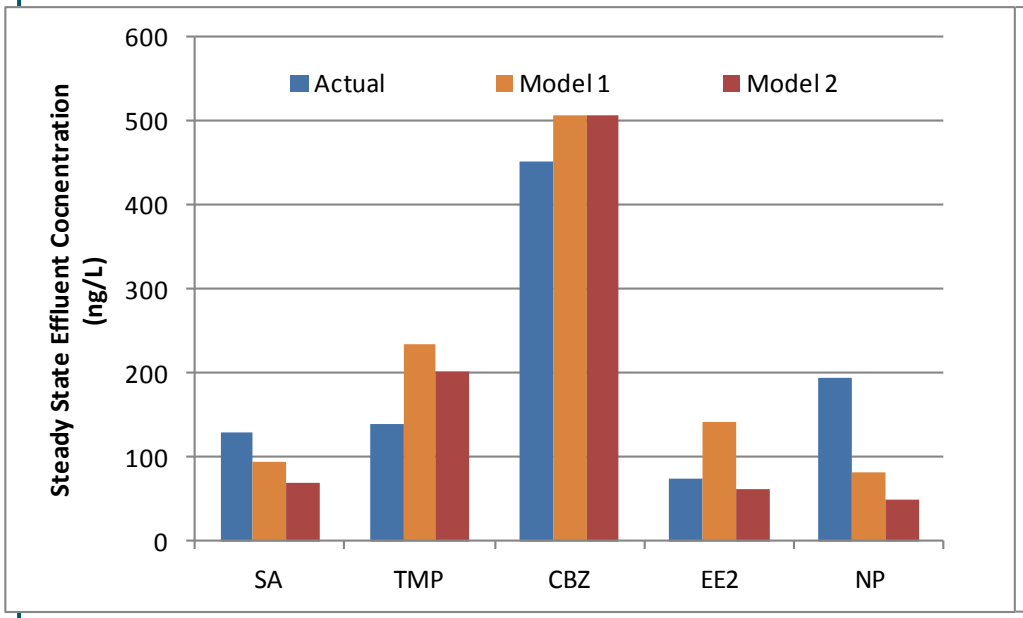
TOrC removal
•Sorption
•Biotransformation

Model 1 – does not account for impact of rbCOD

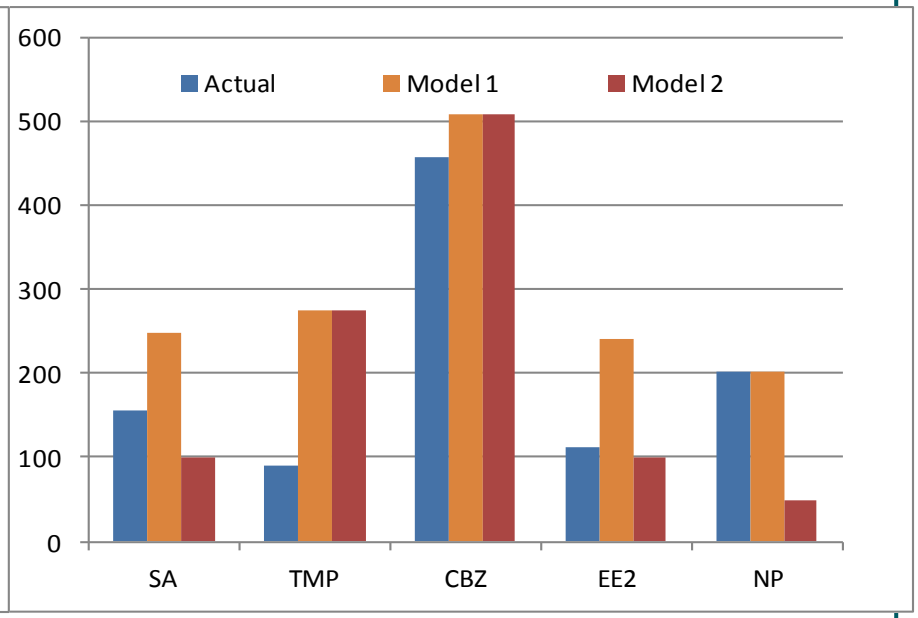
Model 2 – accounts for impact of rbCOD

Utilizing these results, we simulated TOrC biodegradation using a modified Biowin™ model

Nitrifiying Chemostat



Denitrifiying Chemostat



Extended models predict steady state effluent concentrations for CBZ, SA and EE2 (within 20% variance)

Less accuracy associated with TMP and NP

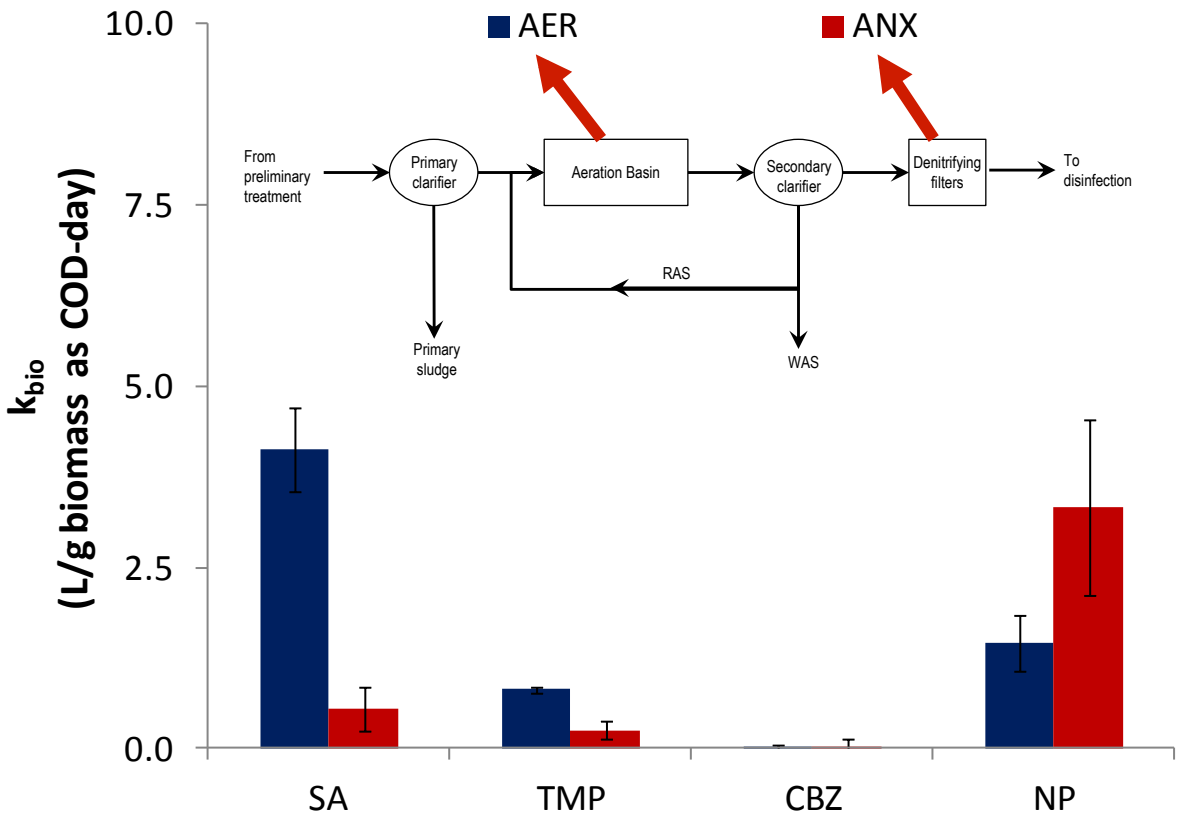
Lab-scale results indicate…

- Biotransformation rates were similar at high (1 mg/L) and low (0.0005 mg/L) TOrC concentrations
  - Feasible to operate experiments at higher concentrations to aid with costs, analyses requirements
- Presence of rbCOD can impact TOrC biotransformation rate
- Extended process model shows promise for describing C, N, P and TOrC fate

Are results conserved in full-scale applications?

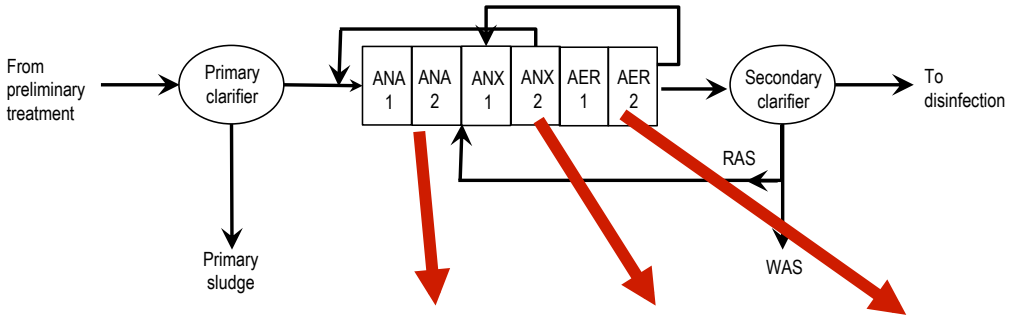
Results from Full-Scale Experiments

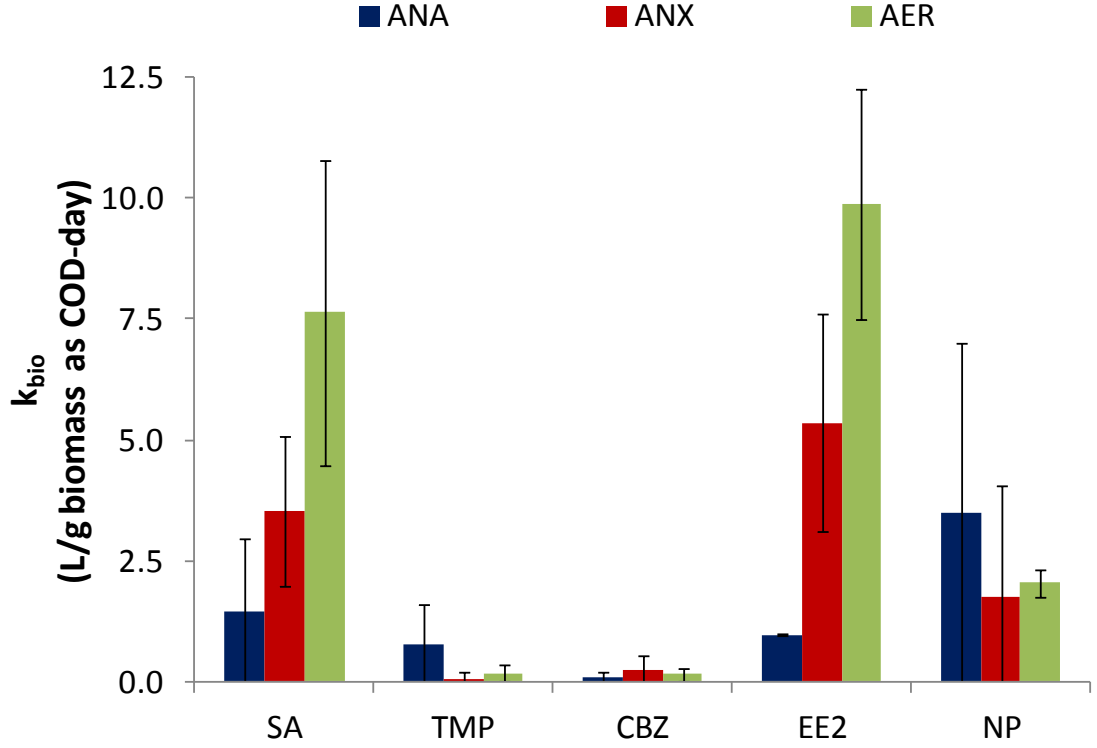
Insights from Plant 1 batch testing



- **SA and TMP more readily biotransformed under aerobic conditions**
- **NP more readily biotransformed under anoxic conditions**

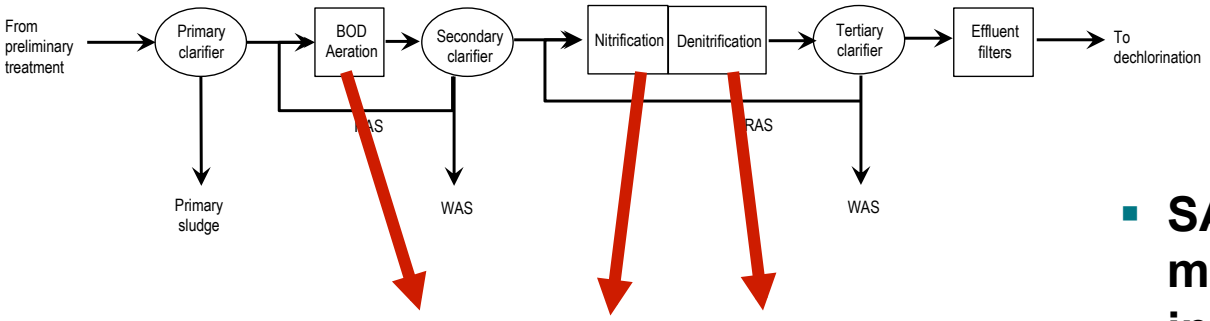
Insights from Plant 2 batch testing

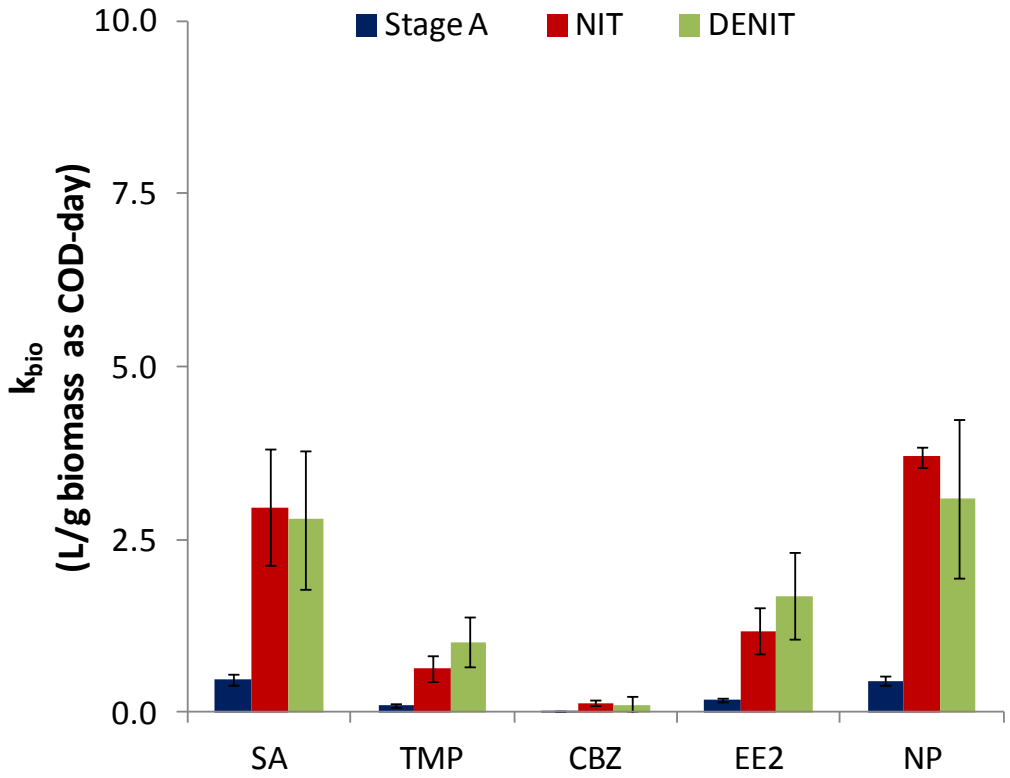




- **SA and EE2 are more readily biotransformed under aerobic conditions**
- **NP more readily biotransformed under anaerobic conditions**

Insights from Plant 3 batch testing





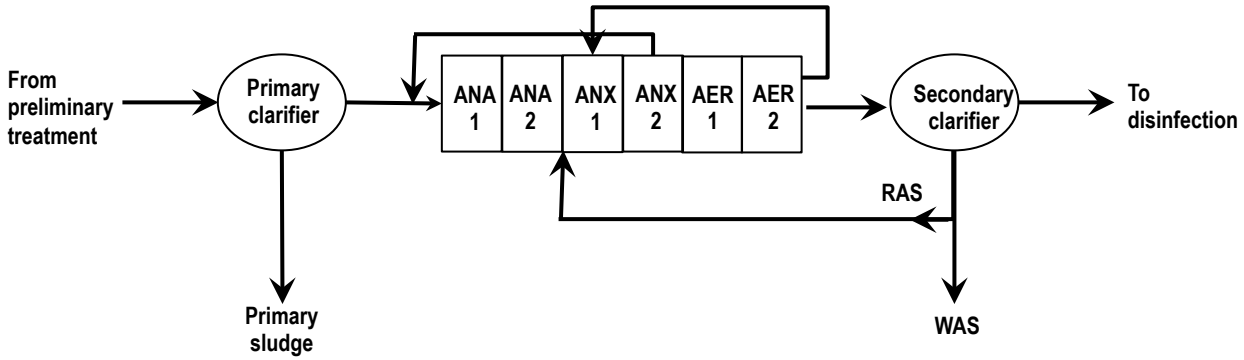
- **SA, TMP, EE2 and NP are more readily transformed in the nitrification/ denitrification stage**
- **Little biotransformation observed in the high rate activated sludge**
  - **Sorption dominates**

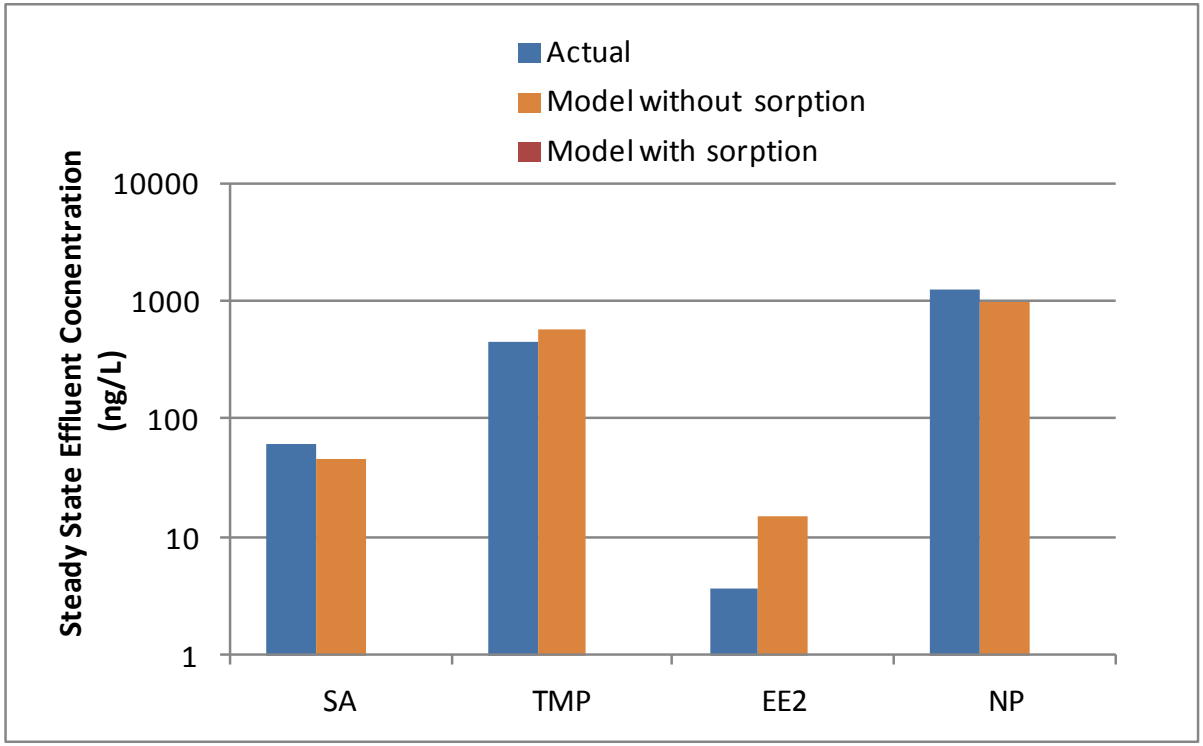
Results from short-term batch experiments provided additional insight into TOrC fate

	Biotransformation potential		
	Anaerobic	Anoxic	Aerobic
EE2	+	++	+++
SA	+	++	+++
NP	++	++	+
CBZ	+	+	+

- Trimethoprim biotransformation rates showed no preference for anaerobic, anoxic or aerobic conditions

Modeling of TOrC fate at Plant 2 suggests that care must be taken in assumptions regarding sorption





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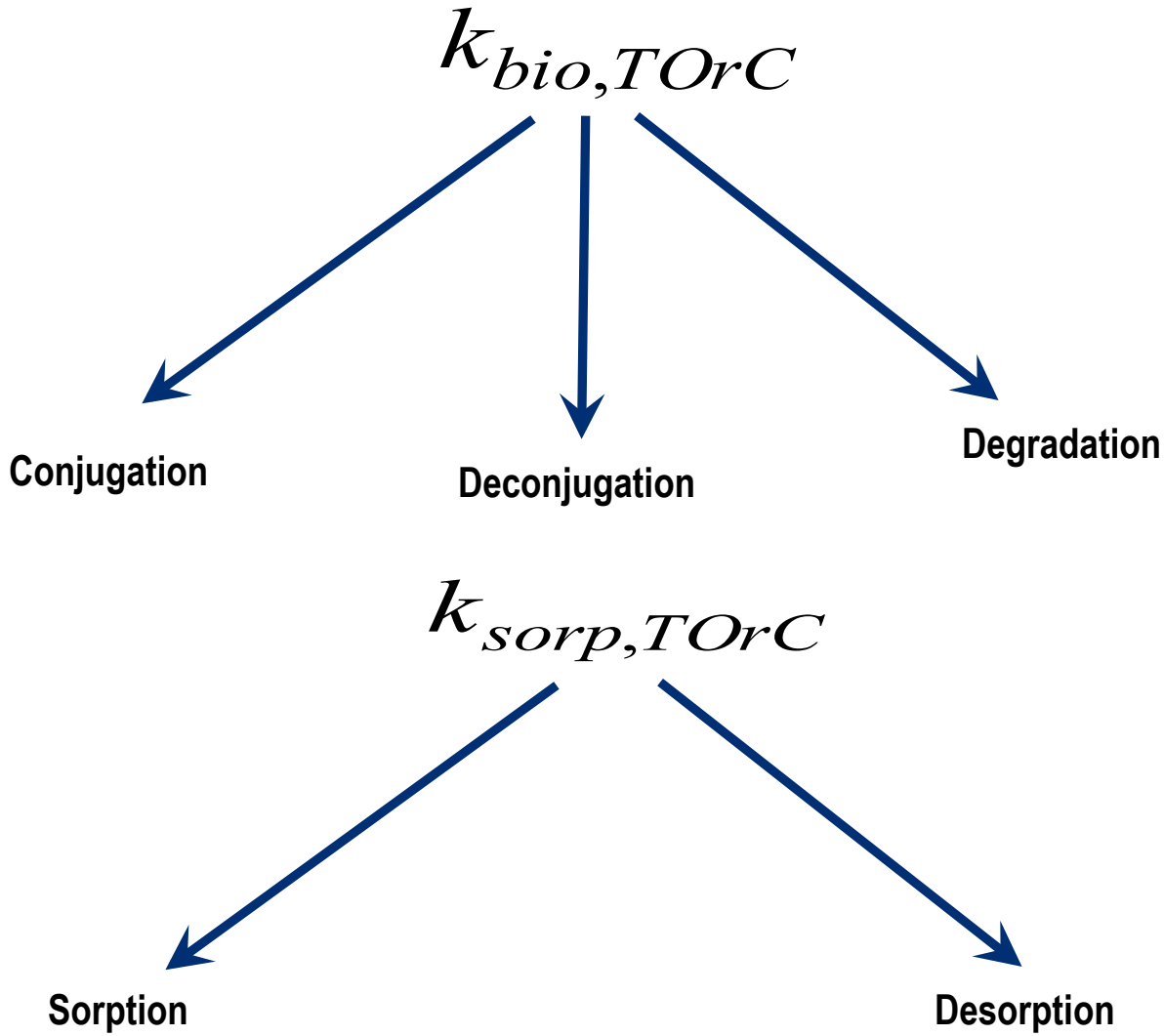
Insights provided by the modeling exercise



What we have learned…

- TOrC removal in biological reactors can be effectively described using short-term batch experiments
- Batch tests should be performed in the presence and at the incident concentration of the *in-situ* rbCOD to gauge accurate TOrC removal kinetics
- Strategies that aim to enhance attenuation of SA and EE2 should focus on maximizing the aerobic reaction time under carbon limited conditions ($HRT_{AER,Climit}$)
- Efforts to maximize NP removal during wastewater treatment may benefit from long anaerobic reaction times under carbon limited conditions

Questions and Contact Information

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(703)-267-2759

Extra Slides

Our standardized protocol exploited existing knowledge on the fate of synthetic compounds

Test conditions mimic redox conditions found in bioreactor
i.e. Aerobic, anoxic or anaerobic conditions

Representative biomass sample from studied system must be used

Test duration must not result in significant change in the condition of the cells (3-6 hrs sufficient)

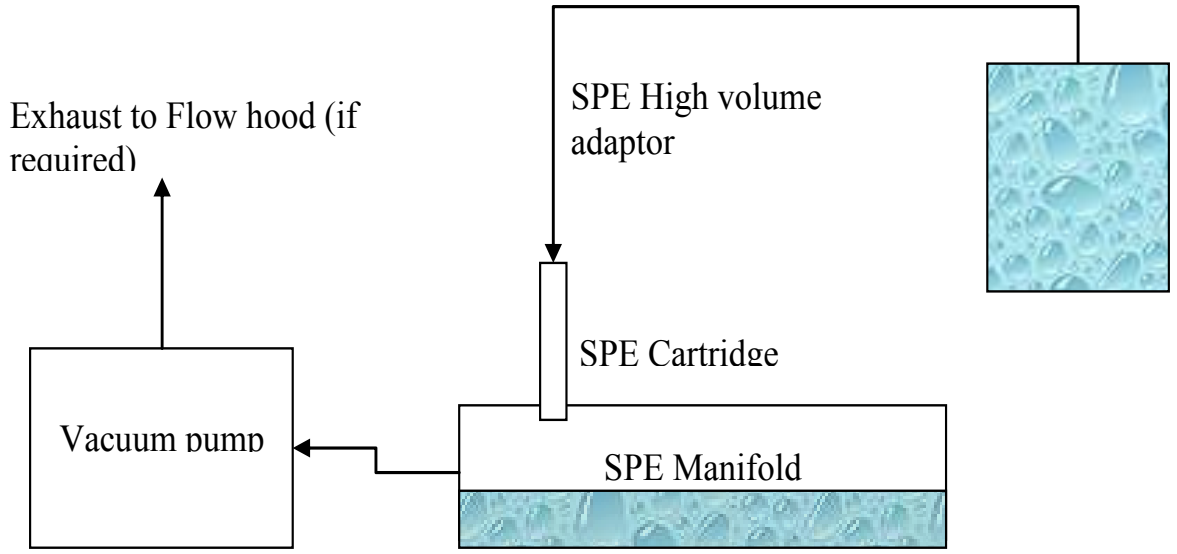
Initial substrate concentrations should not induce inhibition

Test should be fast and allow direct measure of removal

Sample preparation and analyses should be cheap

Ideal test should incorporate all of the above

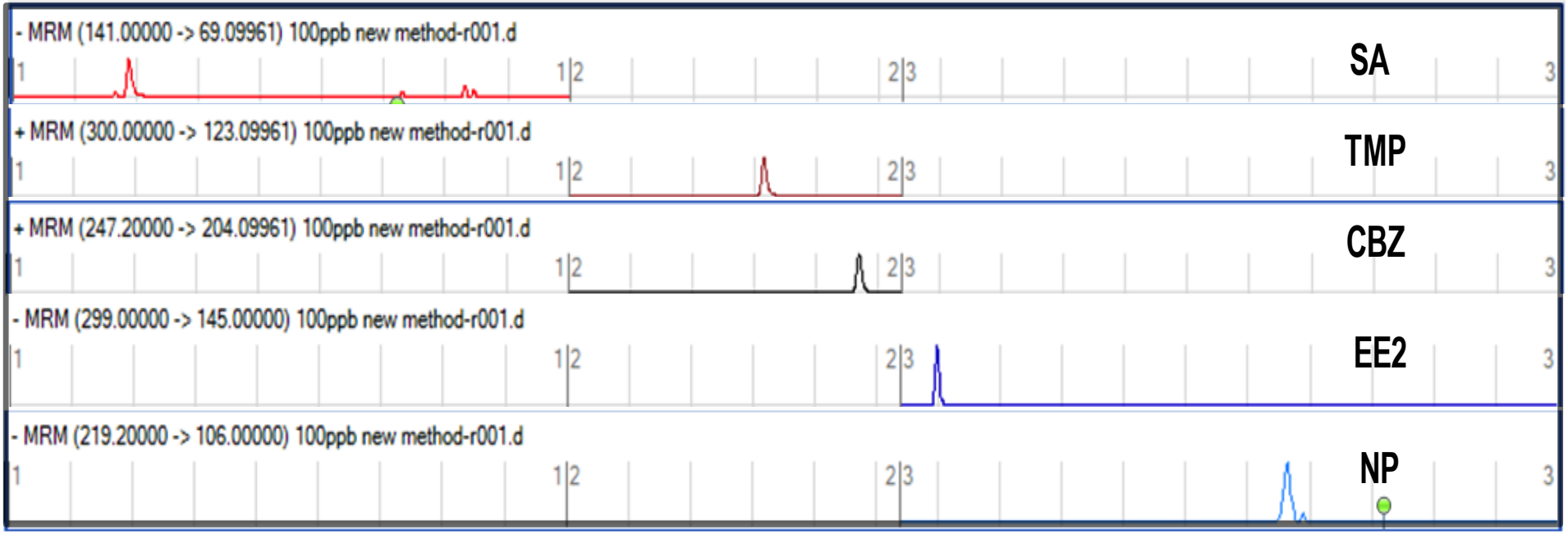
Solid phase extraction method was consistent throughout the study



- **Extracted acidified sample onto Oasis HLB 6cc cartridges**
- **Cartridge preconditioned with methanol**
- **Deuterated standards spiked into matrix to account for extraction efficiency**

We developed a novel method to analyze for these 5 TOrC in wastewater matrices

Su et al., 2014 (submitted), Rapid Communications in Mass Spectrometry

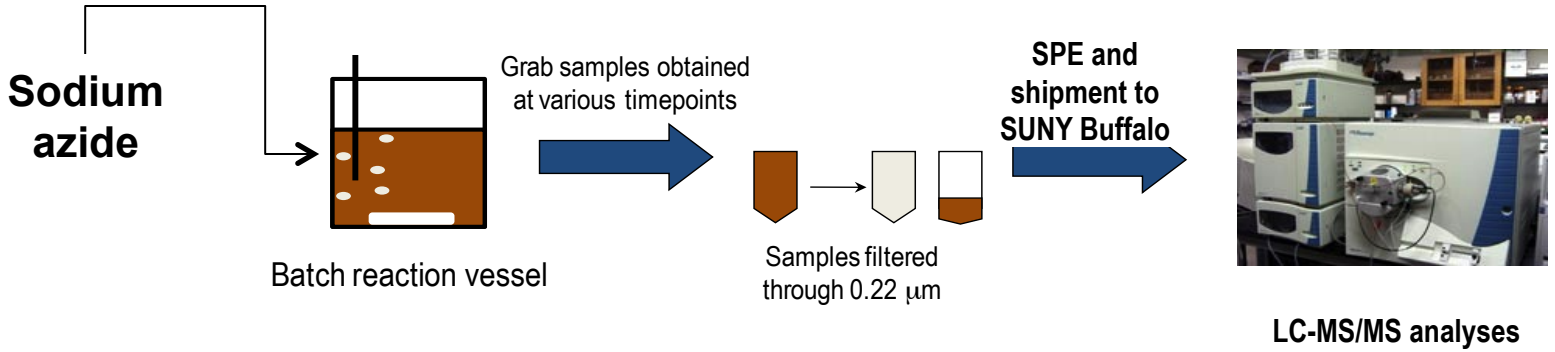


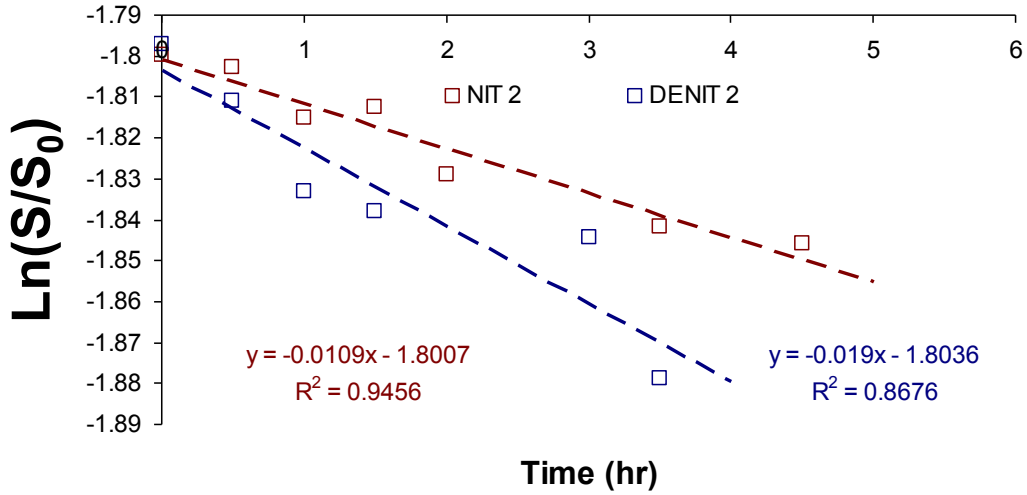
Collaborators at SUNY Buffalo developed a method that allows determination of 5 separate TOrC using single injection

Method allows for rapid quantification of TOrCs in wastewater matrix

Cuts sample requirements and costs associated with method

Inactivated controls were performed to account for sorption





$$\frac{dS}{dt} = \frac{-k_{bio,TOrC}}{1 + K_D X} X S$$

Biotransformation

Sorption control exps.

Full-scale sampling was performed at the three facilities from 2011 to 2012

Composite sampling

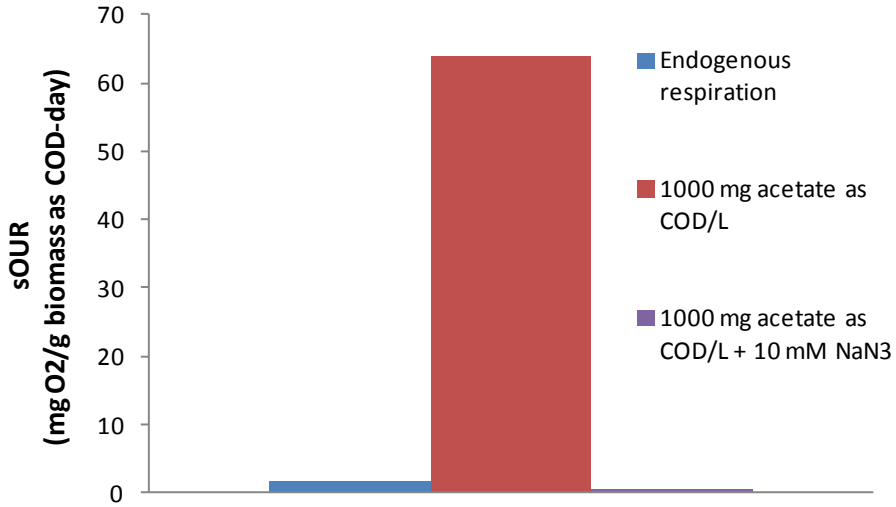
- 24 hr composite samples
- Filtered through 0.22 um filters
- Solid phase extraction
- LC-MS/MS analyses performed

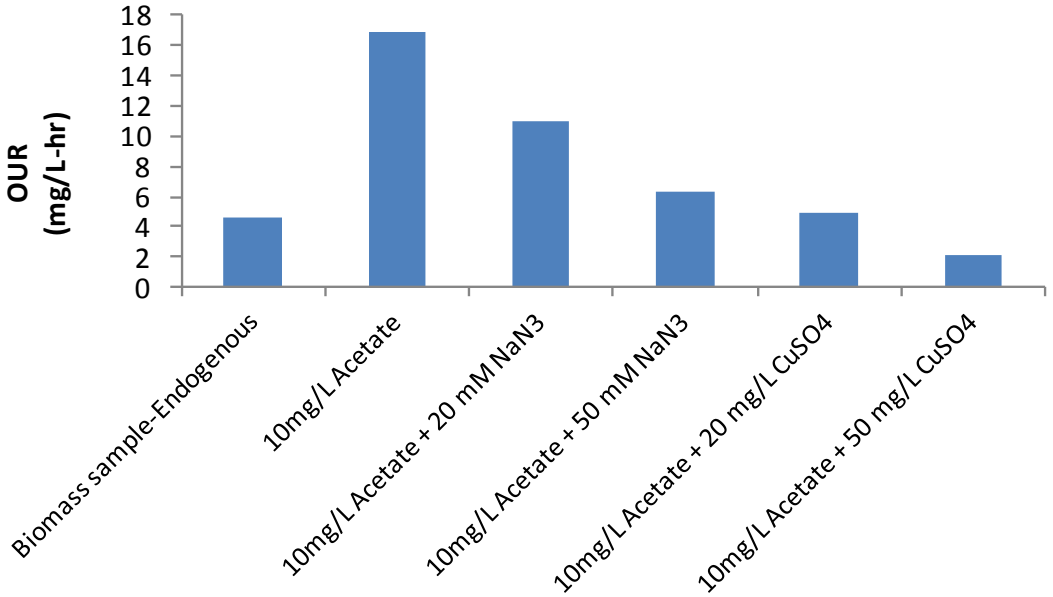
Batch Testing

- Aerobic and Anoxic conditions
- Copper sulfate sorption controls

Our first detour…

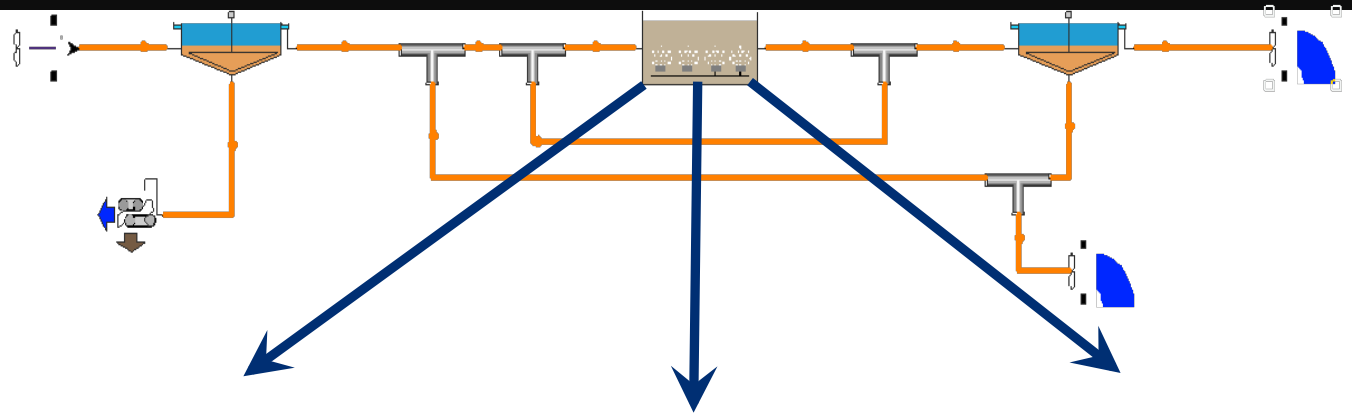
- **Sodium azide was effective inhibitor for lab-scale biomass**





- **Sodium azide was not effective inhibitor for full-scale biomass**

We modified an existing process model to include TOrC sorption and biotransformation



Organic carbon removal

Nitrification
Denitrification
Bio-P removal

TOrC removal
- **Sorption**
- **Biotransformation**

$$r_{sorp} = -k_D S Z_{bh} Q$$

$$r_{AER,TOrC} = -k_{bio,TOrC,AER} S Z_{bh} \frac{DO}{K_{o,bh} + DO}$$

$$r_{ANX,TOrC} = -k_{bio,TOrC,ANX} S Z_{bh} \left(\frac{K_{o,bh}}{K_{o,bh} + DO}\right)\left(\frac{NO3-N}{K_{no3} + NO3-N}\right)$$

$$k_{bio,TOrC} = k_{bio,TOrC\max}\left(1 - \left[\frac{\left(\frac{rbCOD}{S}\right)}{\left(\left(\frac{rbCOD}{S}\right) + K_{TOrC}\right)}\right]\right)$$

$$r_{ANA,TOrC} = -k_{bio,TOrC,ANA} S Z_{bh} \left(\frac{K_{o,bh}}{K_{o,bh} + DO}\right)\left(\frac{K_{no3}}{K_{no3} + NO3-N}\right)$$