### Fate & Removal of PPCPs within WWTFs discharging upstream from the Great Bay Estuary

#### **NEWEA 2020 Annual Conference & Exhibit**

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University of New Hampshire







#### 1. PPCP Background & Knowledge Gaps

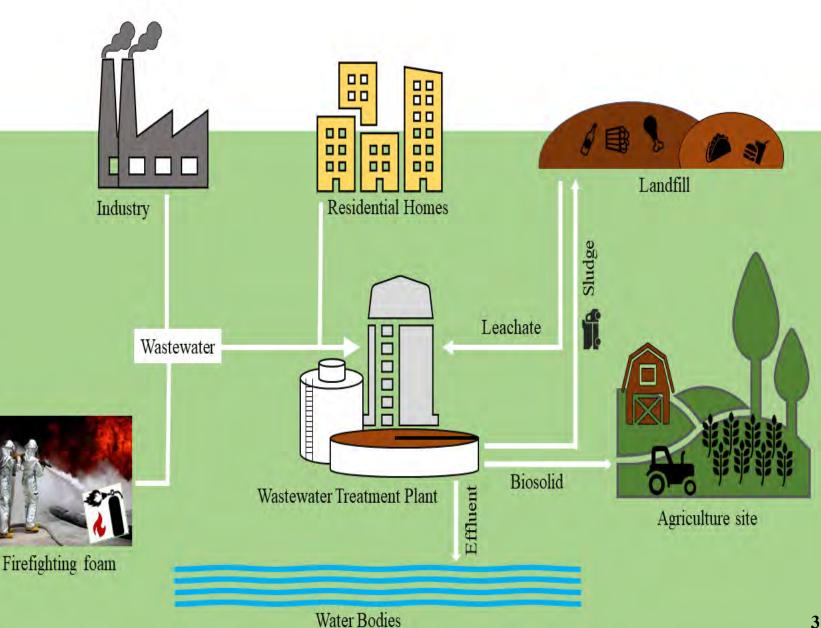
- 2. Research Goals
- 3. Methods & Sampling Plan
- 4. PPCP Results & Preliminary Conclusions
- 5. Next Steps
- 6. References



#### **PPCP Background**

#### Simplified Definition Contaminants of Emerging Concern

- 1) Chemical and non-chemical materials that have a possible pathway into the environment.
- 2) Present potential unacceptable human health and environmental risk.
- 3) Not federally regulated or regulations are currently being developed.





### **PPCP Background**

#### <u>10,000+ PPCPs Constituents</u>

- **15** Pharmaceuticals
- 6 Personal care products









#### risk. 3) Not federally regulated or

Simplified Definition

regulations are currently being developed.

**Contaminants** 

of Emerging Concern

Chemical and non-chemical

2) Present potential unacceptable

materials that have a possible

pathway into the environment.

human health and environmental

Source: Integral Corp.

### **CEC Background: 21 PPCP Analytes**

#### **15 Pharmaceuticals**

#### **6** Personal Care Products

ANAI	LYTES
Analgesic	<b>B-blocker</b>
Acetaminophen \star	Atenolol *
Antibiotic	Narcotic
Amoxicillin	Methadone
Azithromycin	Sedative
Ciprofloxacin *	Diazepam *
Sulfamethoxazole 🔸	Meprobamate
Trimethoprim *	SSRI
Anti-convulsant	Fluoxetine <b>*</b>
Carbamazepine *	Statin
Phenytoin	Atorvastatin
Primidone	

ANA	LYTES
	retardants
ТСЕР	*
ТСРР	*
TDCPP	
Inse	ecticide
DEET	*
Stin	nulant
Caffeine	*
Tobacco m	etabolite
Cotinine	*
	<b>*</b> Frequently

\* Frequently Detected in the environment

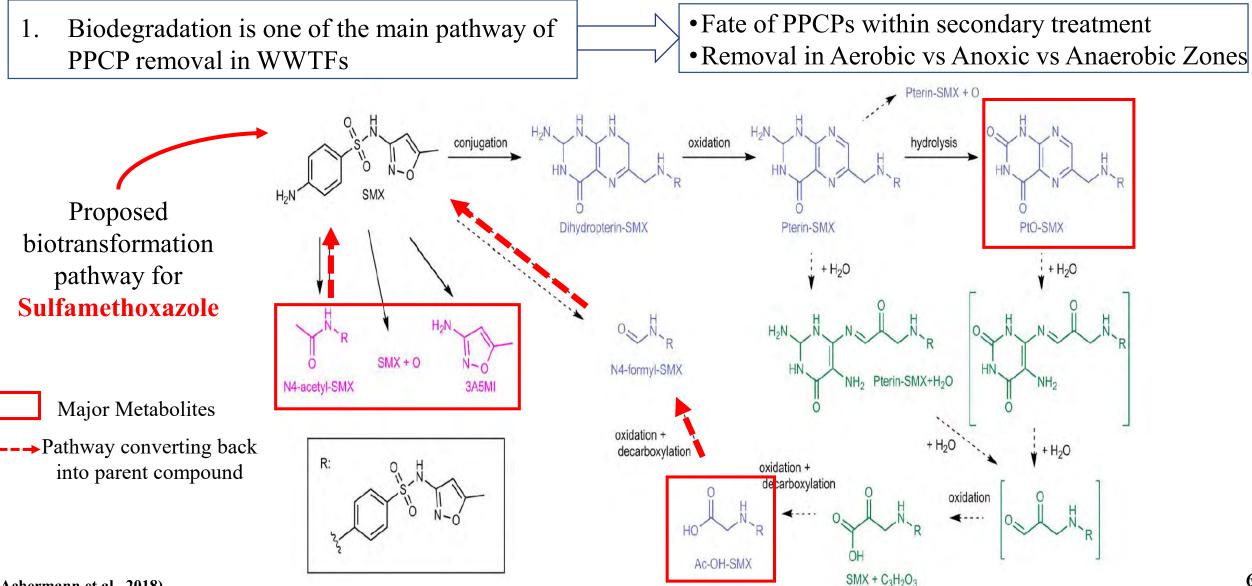


# **PPCP Knowledge and Gaps**

#### What We 'Know'

#### **Current Gaps**

6



(Achermann et al., 2018)



# **PPCP Knowledge and Gaps**

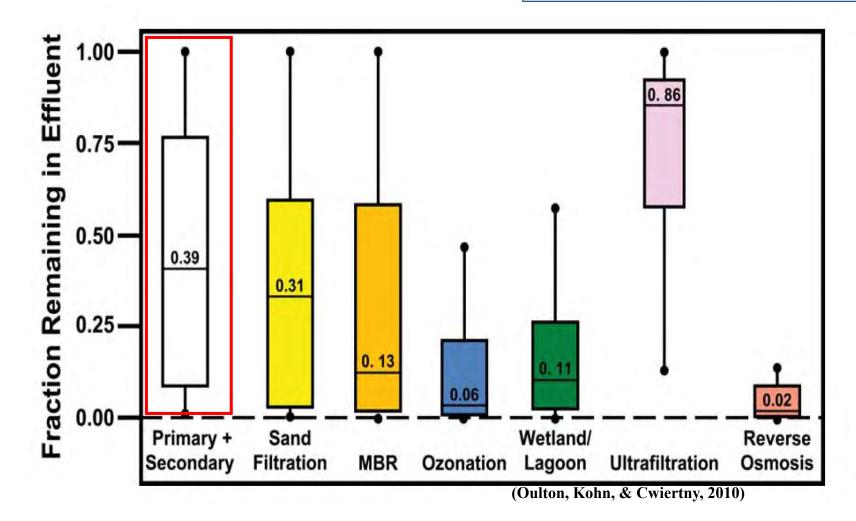
#### What We 'Know'

2. PPCPs are <u>NOT</u> completely removed in conventional WWTFs

**Current Gaps** 

• What is the Best Available Technology (BAT)?

•Future regulations??

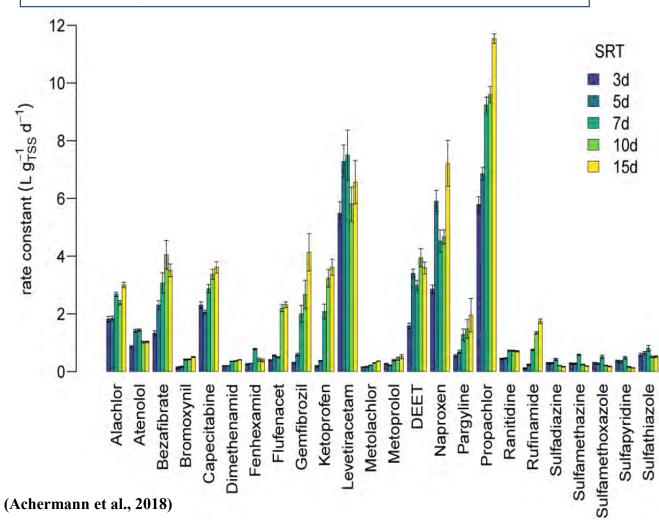




## **PPCP Knowledge and Gaps**

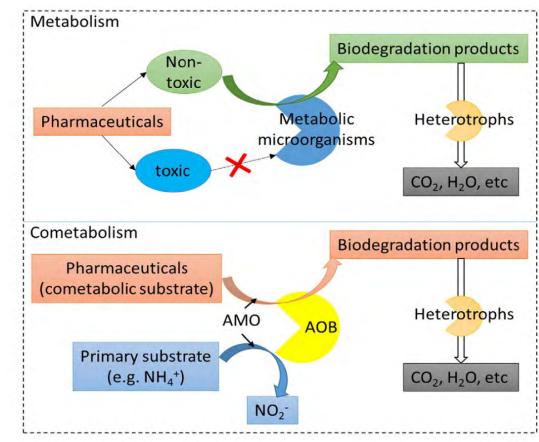
#### What We 'Know'

3. PPCP removal is correlated to sludge retention time (SRT) & nutrient removal



#### **Current Gaps**

- Is there a 'Sweet Spot'?
- What microbes are responsible for PPCP degradation?



(Xu, Yuan, & Ni, 2016)



#### Outline

- 1. PPCP Background & Knowledge Gaps
- 2. Research Goals
- 3. Methods & Sampling Plan
- 4. PPCP Results & Preliminary Conclusions
- 5. Next Steps
- 6. Acknowledgments
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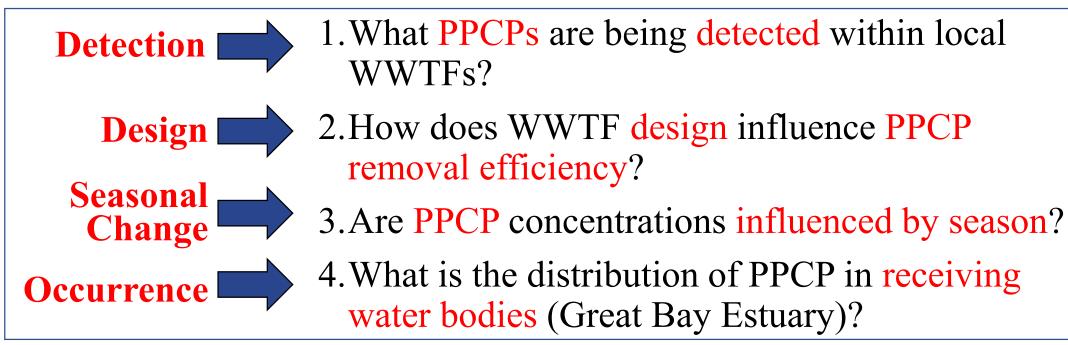


### **Research Goals**

Aim Investigate removal of 21 PPCPs from six WWTFs discharging into
Aim the Great Bay in NH based on (a) treatment process design and
(b) solids retention time (SRT).

HypothesisThere will be a positive correlation between the increase in overallHypothesisPPCP removal with WWTF's that have (a) alternating biologicaltreatment zones (aerobic, anoxic, anaerobic) and (b) longer SRTs.

Specific Questions



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#### Outline

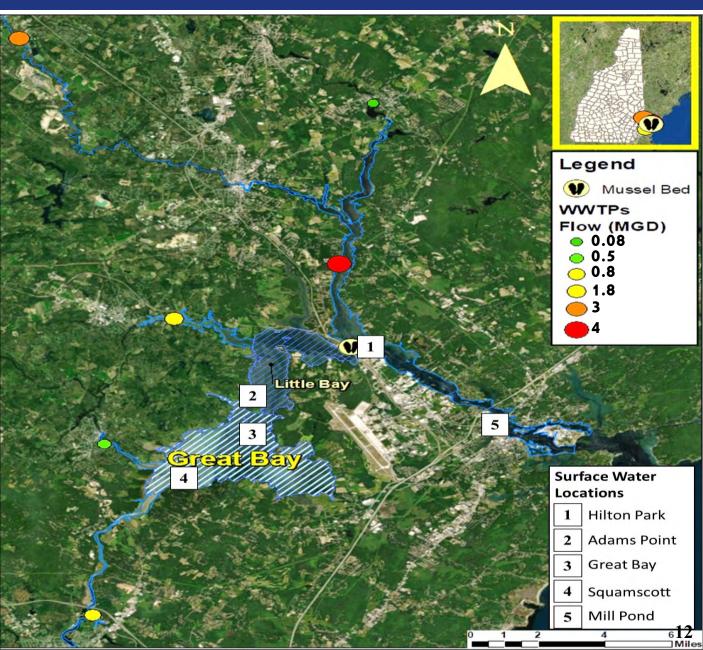
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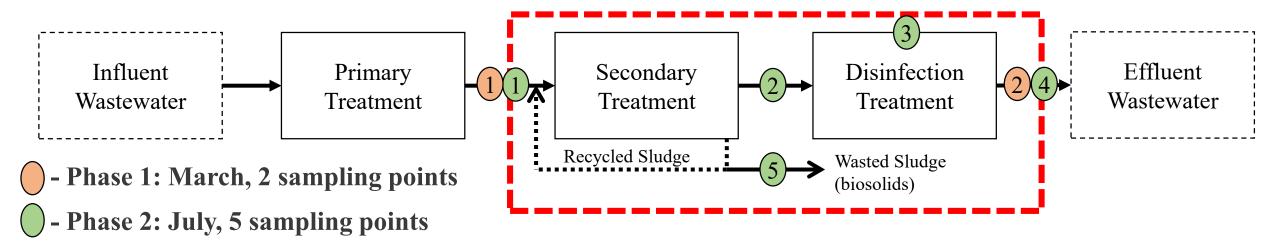
- WWTF approximate locations and flows
- Surface water locations

Phase 1: March
6 WWTF & one surface water

Phase 2: July
4 WWTF & five surface waters

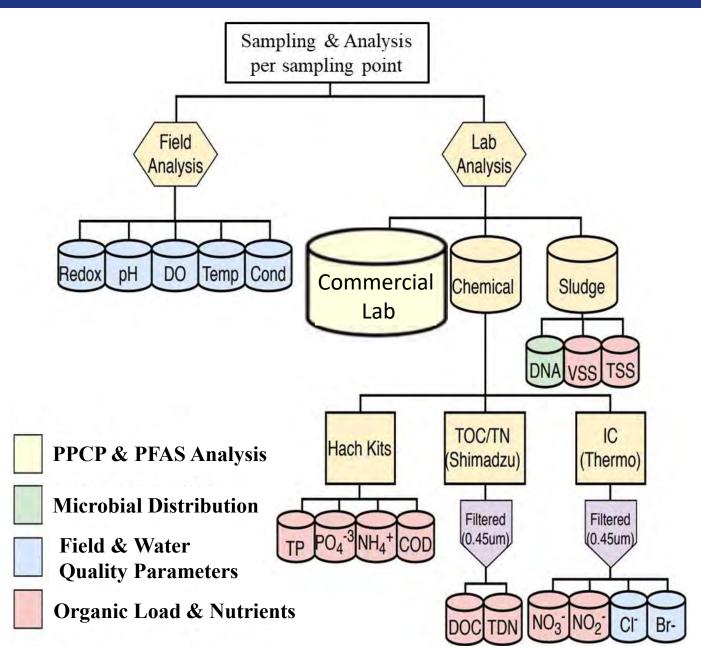








- Field and Laboratory Analyses Performed
- Commercial Lab used for PPCP analysis: Weck Laboratories, Inc.



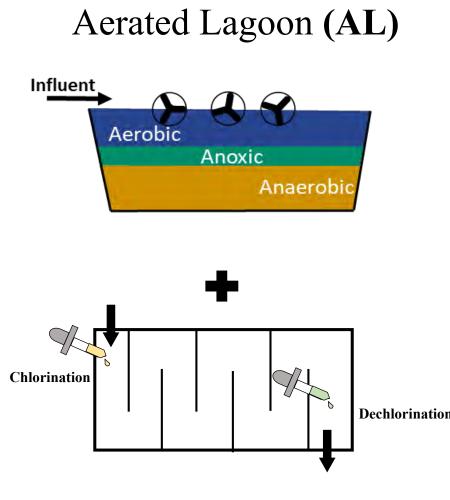
14



- Acronyms for each WWTF that will be used for the rest of the presentation.
- WWTFs chosen for each season; March vs July.
- Phase 2 WWTFs were chosen based on having the same disinfection method (acts as a control).

Phase 1 – March	Phase 2 – July
WWTF # 1 $\rightarrow$ AL + CD	WWTF # 1 $\rightarrow$ Bar4 + CD (1)
WWTF # 2 $\rightarrow$ Bar4 + CD (2)	WWTF # 2 $\rightarrow$ Bar4 + CD (2)
WWTF # 3 $\rightarrow$ Bar4 + CD (3)	WWTF # 3 $\rightarrow$ Bar4 + CD (3)
WWTF # 4 $\rightarrow$ AS + UV (1)	
WWTF # 5 $\rightarrow$ OD + CD	WWTF # 5 $\rightarrow$ OD + CD
WWTF # 6 $\rightarrow$ AS + UV (2)	





	Phase 1 – March	Phase 2 – July
	WWTF # 1 $\rightarrow$ AL + CD	WWTF # 1 $\rightarrow$ Bar4 + CD (1)
	WWTF # 2 $\rightarrow$ Bar4 + CD (2)	WWTF # 2 $\rightarrow$ Bar4 + CD (2)
	WWTF # 3 $\rightarrow$ Bar4 + CD (3)	WWTF # 3 $\rightarrow$ Bar4 + CD (3)
	WWTF # 4 $\rightarrow$ AS + UV (1)	
	WWTF # 5 $\rightarrow$ OD + CD	WWTF # 5 $\rightarrow$ OD + CD
n	WWTF # 6 $\rightarrow$ AS + UV (2)	
	Worst Removal Assum	Best Removal
In	fluent	



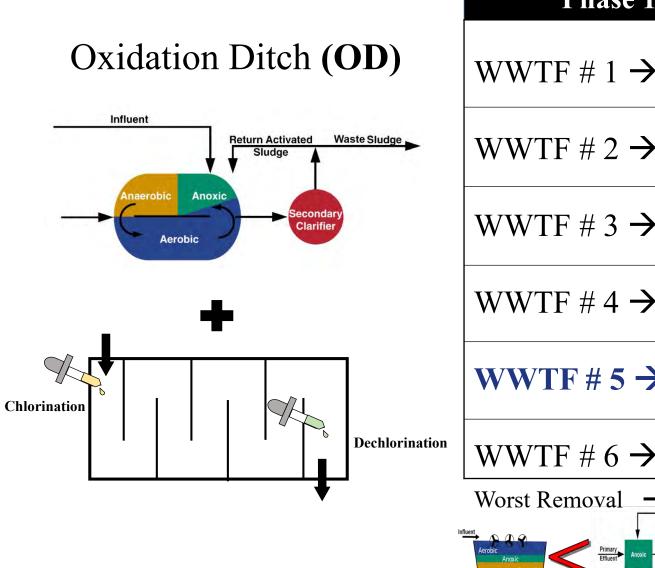


	Phase 1 – March	Phase 2 – July
Activated Sludge (AS)	WWTF # 1 $\rightarrow$ AL + CD	WWTF # 1 $\rightarrow$ Bar4 + CD (1)
Primary Anoxic Aerobic Secondary	WWTF # 2 $\rightarrow$ Bar4 + CD (2)	WWTF # 2 $\rightarrow$ Bar4 + CD (2)
Return Activated Sludge	WWTF # 3 $\rightarrow$ Bar4 + CD (3)	WWTF # 3 $\rightarrow$ Bar4 + CD (3)
Waste Sludge	WWTF # 4 $\rightarrow$ AS + UV (1)	
	WWTF # 5 $\rightarrow$ OD + CD	WWTF # 5 $\rightarrow$ OD + CD
Ultraviolet light	WwTF # 6 $\rightarrow$ AS + UV (2) We set D an a set 1	Intion
	Worst Removal	Best Removal
M	Aerobic Anacrobic Anaerobic Anaerobic	
	Return Activated Studge Waste	17



	Phase 1 – March	Phase 2 – July
4-Stage Bardenpho (Bar4)	WWTF # 1 $\rightarrow$ AL + CD	WWTF # 1 $\rightarrow$ Bar4 + CD (1)
Influent Anoxic Aerobic Aerobic Aerobic Secondary Clarifier	WWTF # 2 $\rightarrow$ Bar4 + CD (2)	WWTF # 2 $\rightarrow$ Bar4 + CD (2)
Return Activated Sludge Waste Sludge	WWTF # 3 $\rightarrow$ Bar4 + CD (3)	WWTF # 3 $\rightarrow$ Bar4 + CD (3)
	WWTF # 4 $\rightarrow$ AS + UV (1)	
Chlorination	WWTF # 5 $\rightarrow$ OD + CD	WWTF # 5 $\rightarrow$ OD + CD
Dechlorination	WWTF # 6 $\rightarrow$ AS + UV (2)	
	Worst Removal Assum	Best Removal
In	Aerobic Anaxic Anaxic Anaxic Anaxic	
	Return Activated Sludge Waste	Return Activated Studge 18





	Phase 1 – March	Phase 2 – July
	WWTF # 1 $\rightarrow$ AL + CD	WWTF # 1 $\rightarrow$ Bar4 + CD (1)
	WWTF # 2 $\rightarrow$ Bar4 + CD (2)	WWTF # 2 $\rightarrow$ Bar4 + CD (2)
	WWTF # 3 $\rightarrow$ Bar4 + CD (3)	WWTF # 3 $\rightarrow$ Bar4 + CD (3)
	WWTF # 4 $\rightarrow$ AS + UV (1)	
	WWTF # 5 $\rightarrow$ OD + CD	WWTF # 5 $\rightarrow$ OD + CD
	WWTF # 6 $\rightarrow$ AS + UV (2)	
	Worst Removal Assum	Best Removal
Inf	Aerobic Anaxic Anaerobic Anaerobic	erobic
	Return Activated Sludge Waste	Return Activated Sludge 19



	Phase 1 – March	Phase 2 – July
Oxidation Ditch (OD)	WWTF # 1 $\rightarrow$ AL + CD	WWTF # 1 $\rightarrow$ Bar4 + CD (1)
Return Activated Waste	WWTF # 2 $\rightarrow$ Bar4 + CD (2)	WWTF # 2 $\rightarrow$ Bar4 + CD (2)
Aerobic	WWTF # 3 $\rightarrow$ Bar4 + CD (3)	WWTF # 3 $\rightarrow$ Bar4 + CD (3)
	WWTF # 4 $\rightarrow$ AS + UV (1)	
Chlorination	WWTF # 5 $\rightarrow$ OD + CD	WWTF # 5 $\rightarrow$ OD + CD
Dechlorination	WWTF # 6 $\rightarrow$ AS + UV (2)	
	Worst Removal <u>Assum</u>	eption → Best Removal
	Aerobic Anaxic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic Anaerobic	rrolic ++ Arosic ++ Secondary Return Activated Studge Weste Weste Weste



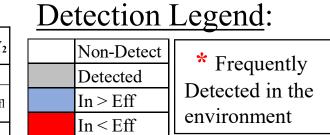
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#### **PPCP** Detection

		General	D 1			: Maı CD <sub>1</sub> : J		F	Bar-4	+CD <sub>2</sub>		E	Bar-4	+CD <sub>3</sub>		AS +	UV <sub>1</sub>		OD	+ CD		AS +	UV <sub>2</sub>
	Compound Class	Name	Removal Trends	Influ	ent	Efflu	ent	Influ	ent	Efflu	ent	Influ	ent	Efflu	ent	Ma	rch	Influ	ient	Efflu	lent	Mar	ch
	Clubb	i (unite	Trenus	March	July	March	July	March	July	March	July	March	July	March	July	Infl	Effl	March	July	March	July	Infl	Effl
Γ	Analgesic	Acetaminophen*	High																				
		Amoxicillin	Med.																				
		Azithromycin	Low																				
	Antibiotic	Ciprofloxacin*	High																				
		Sulfamethoxazole*	High																				
s		Trimethoprim*	Med.																				
Pharmaceuticals		Carbamazepine*	Low																				
lacel	Anti- convulsant	Phenytoin	Low																				
harn	convulsant	Primidone	Low																				
	B-blocker	Atenolol*	Med.																				
	Narcotic	Methadone	Low																				
	Sedative	Diazepam*	Low																				
	Sedative	Meprobamate	Low																				
	SSRI	Fluoxetine*	Med.																				
	Statin	Atorvastatin	Med.																				
		TCEP*	High																				
ducts	Flame retardants	TCPP*	Low																				
Pro	Tetardants	TDCPP	Low																				
Care	Insecticide	DEET*	High																				
Personal Care Products	Stimulant	Caffeine*	High																				
Pers	Tobacco metabolite	Cotinine*	High																				



- March: On average detected 19 PPCPs in Influent and Effluent
- July: On average detected 18 PPCPs in Influent and 16 in Effluent
- 15 PPCPs increased from Influent to Effluent at least once



#### **PPCP Detection**

-											<b></b>			·1	<u>D</u>	etection I	<u>_egend</u> :
	h avec	Com	1	Demovol	Bar-4 +0	: March	Bar-4	4 +CD <sub>2</sub>	Bar-4	4 +CD <sub>3</sub>	$AS + UV_1$	OD +	⊦ CD	$AS + UV_2$		Non-Detect	* Frequently
	ompound Class	Gene		Removal Trends	Influent	Effluent	Influent	Effluent	Influent	Effluent	March	Influent	Effluent	March		Detected	
	Clubb				March July	March July	March July	March July	March July	March July	Infl Effl	March July	March July	Infl Effl		In > Eff	Detected in the
[ ]	Analgesic	Acetami	ophan*	High	40.											In < Eff	
		Amox		<b>ive</b> a	IIS:												
		Azithro		Low											•	March: (	On average
	Antibiotic	Ciproflo Sulfameth		High High										4		detected	19 PPCPs in
	ļ f	Trimeth		Sam	pung	, meu	noa (ş	grad s	sampi	les not	t very	repr	esent	ative)		Tefluont	I Effluent
ticals		Carbama	1	Low												Influent a	nd Effluent
laceu	Anti- convulsant	Phen Primi		Low		1.		1 1.	1.	• 0							
harn		Primi	l <b>Æ</b> o	Ana	lytica	I ISSU	ies (a	etecti	on lin	iits &	labo	rator	y diai	nk con	itan	nination)	average
["	B-blocker	Aten		Med.												detected	18 <b>PPCPs</b> in
1  '	Narcotic	Metha		Low				••••••			-	CCI					
1   '	Sedative	Diaze		-	rix is	sue (	dirty	mili	ient o	k 'clea	aner	efflue	ent)			Influent	an <mark>d 16</mark> 1n
	SSRI	Meprol Fluoxe		Low Med.												Effluent	
'	Statin	Atorva	astatın	Med.													
		TCE	EP*	High											•	<b>15 PPCP</b>	's increased
oduct	Flame retardants	ТСР	P*	Low													
e Pro		TDC	CPP       Low       Image: Comparison of the second						from Infl	uent to							
l Car	Insecticide	DEE		High												Effluent a	at least once
rsona	Stimulant	Caffe	ine*	High													
Pe	Tobacco metabolite	Cotin	ine*	High													

-

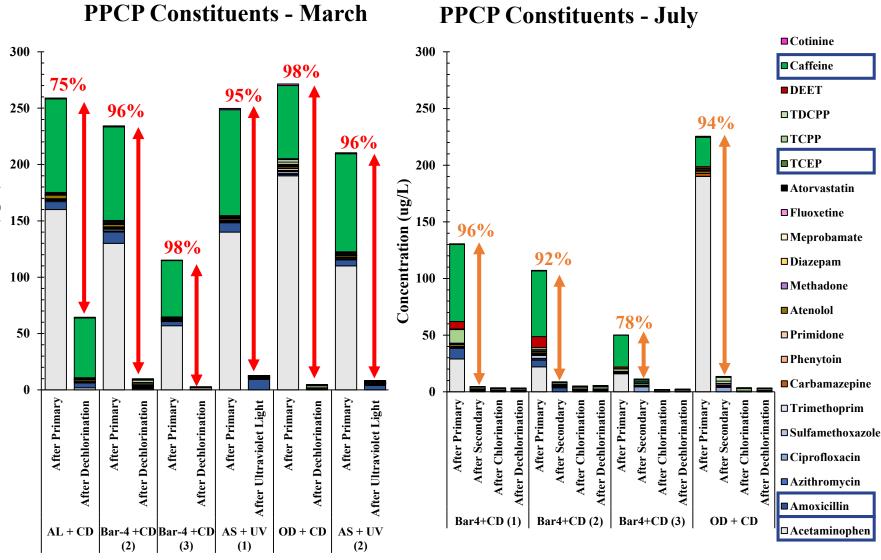


#### **PPCP Detection**

	Compound	General	Removal			: Ma CD <sub>1</sub> : .		1	Bar-4	+CD2	2	-	Bar-4	4 +CD3	;	AS +	UV <sub>1</sub>	OD	+ CD	AS +	UV <sub>2</sub>		Surfa	ice W	ater S	ample	ès	]
	Class	Name	Trends	Influ	ient	Efflu	lent	Influ	lent	Efflu	lent	Influ	uent	Efflu	ıent	Ma	rch	Influent	Effluent	Mar	ch					Great	Squam-	
				March	July	March	July	March	July	March	July	March	n July	March	July	Infl	Effl	March July	March July	Infl	Effl	Park (Mar.)		Pond (Aug.)		Bay (Aug.)	scott (Aug.)	
	Analgesic	Acetaminophen*	High																									_
		Amoxicillin	Med.																								L	14
		Azithromycin	Low																									
	Antibiotic	Ciprofloxacin*	High																									<b>PPCPs</b>
		Sulfamethoxazole*	High																								L	Detected
ls		Trimethoprim*	Med.																									Delected
utica	Anti	Carbamazepine*	Low																									In
nace	Anti- convulsant	Phenytoin	Low																								L	
harr		Primidone	Low																									Great
	B-blocker	Atenolol*	Med.																			Χ					Dou	
	Narcotic	Methadone	Low																								L	Bay
	Sedative	Diazepam*	Low																								L	_
		Meprobamate	Low																								L	_
	SSRI	Fluoxetine*	Med.																								L	_
	Statin	Atorvastatin	Med.																									
s		TCEP*	High																				X					
duct	Flame retardants	TCPP*	Low																				X					
Pro		TDCPP	Low																									
Care	Insecticide	DEET*	High																									
onal	Stimulant	Caffeine*	High																									
Pers	Tobacco metabolite	Cotinine*	High																				X			X	X	



- An Analgesic, Antibiotic, Stimulant and Fire retardant were dominant constituents in Influent for both seasons. Conentration (ug/L)
- Overall, good removal across all WWTFs.
- PPCP concentrations decreased after secondary treatment indicating biodegradation as a primary mechanism for removal.

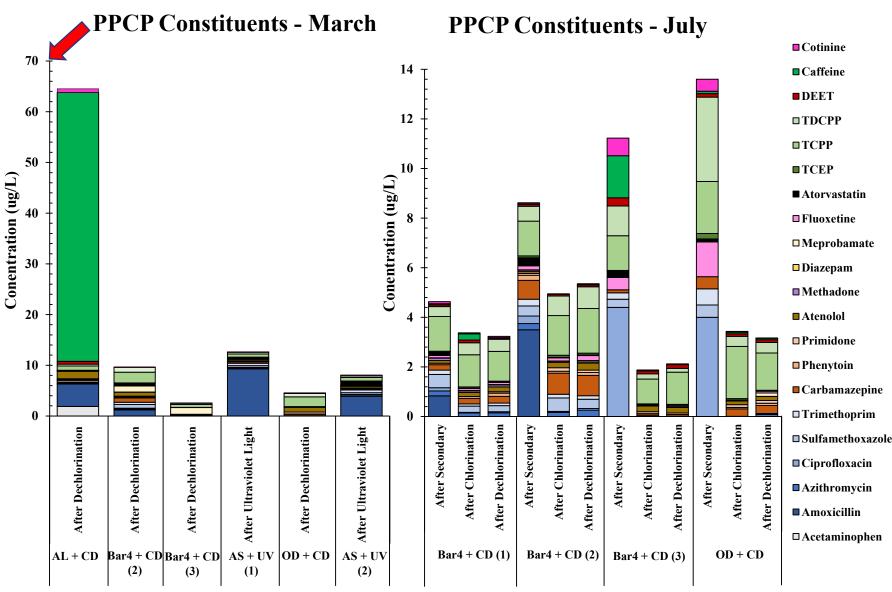




# • Caffeine was not well

Excluding 'After Primary'

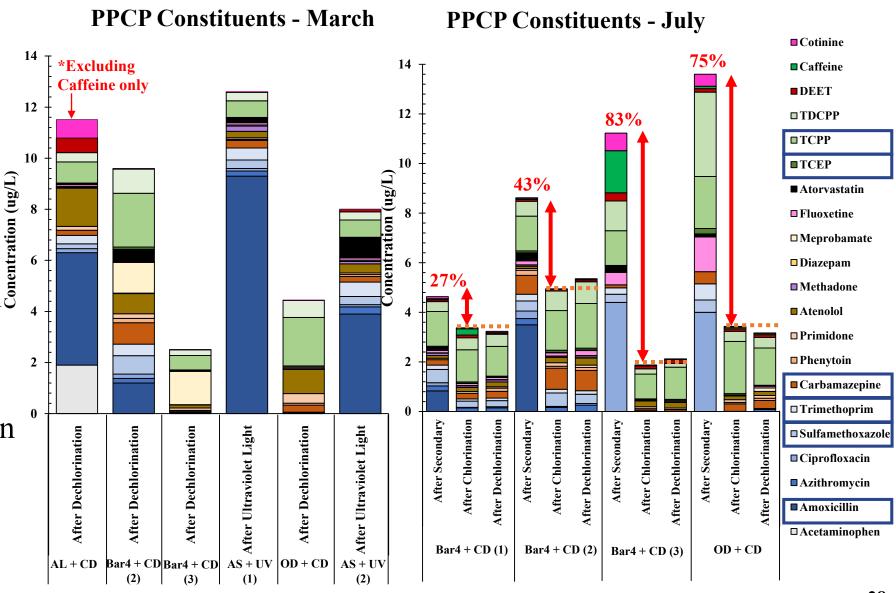
- removed from AL which results in a higher y-axis
- Exclude value to visualize bars better.





#### Excluding 'After Primary'

- Antibiotics, Anticonvulsant and Fire retardants were dominant constituents in Effluent for both seasons.
- PPCP concentrations decreased after chlorination indicating further oxidation.
- Little to no change from chlorination to dechlorination
- In general, July's **concentrations** were less than March, but it was not **significantly different.**





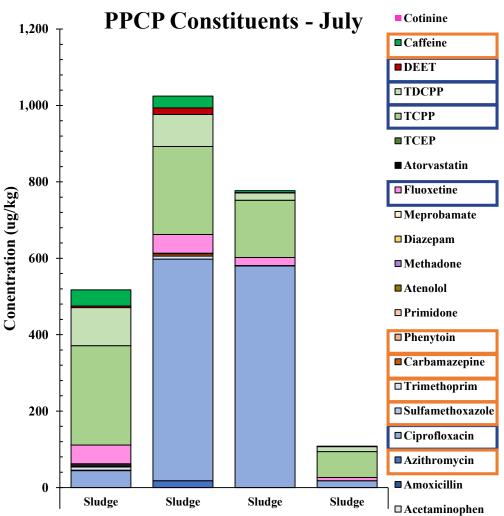
#### **Sludge Concentrations:**

- An Antibiotic, Insecticide, SSRI and Fire retardants were detected within sludge across all 4 WWTFs.
- In general, less PPCP detection within sludge (11of 21)

#### **Detection at each sampling point:**

<b>March Sampling</b>	AL + CD	Bar-4 +CD (2)	Bar-4 +CD (3)	AS + UV (1)	OD + CD	AS + UV (2)
After Primary	19	20	17	19	17	19
After Dechlorination	18	20	18	19	18	20
July Sampling	<b>Bar4+CD (1)</b>	<b>Bar4+CD (2)</b>	<b>Bar4+CD (3)</b>		OD + CD	
After Primary	19	20	20		12	
After Secondary	19	19	11		12	
After Chlorination	17	17	17		15	
After Dechlorination	18	18	13		16	
Sludge	11	10	7		5	

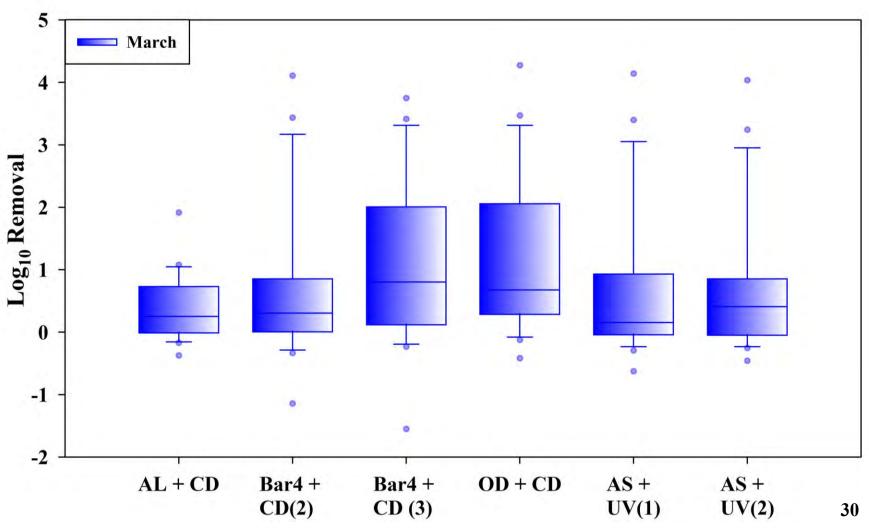
• No clear increasing or decreasing trend for PPCPs detected within each stage of the treatment train.





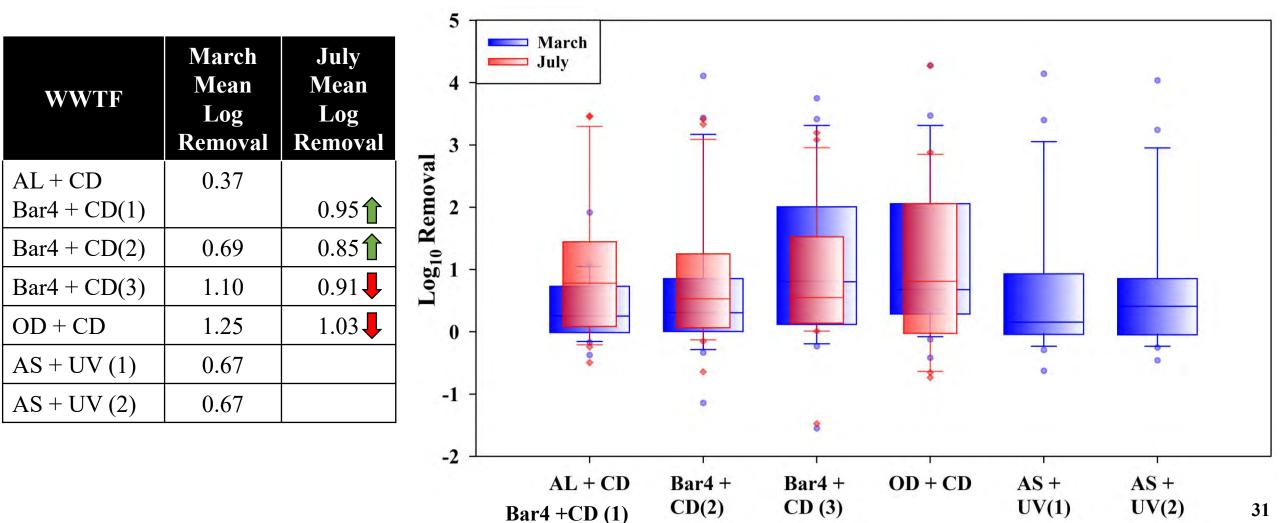
- In general, there is **NO significant difference** in **Log Removal** comparing all the WWTFs.
- Individually, there IS a significantly difference when comparing AL to Bar4 (3) & OD.

WWTF	March Mean Log Removal			
AL + CD	0.37			
Bar4 + CD(2)	0.69			
Bar4 + CD(3)	1.10			
OD + CD	1.25			
AS + UV(1)	0.67			
AS + UV(2)	0.67			

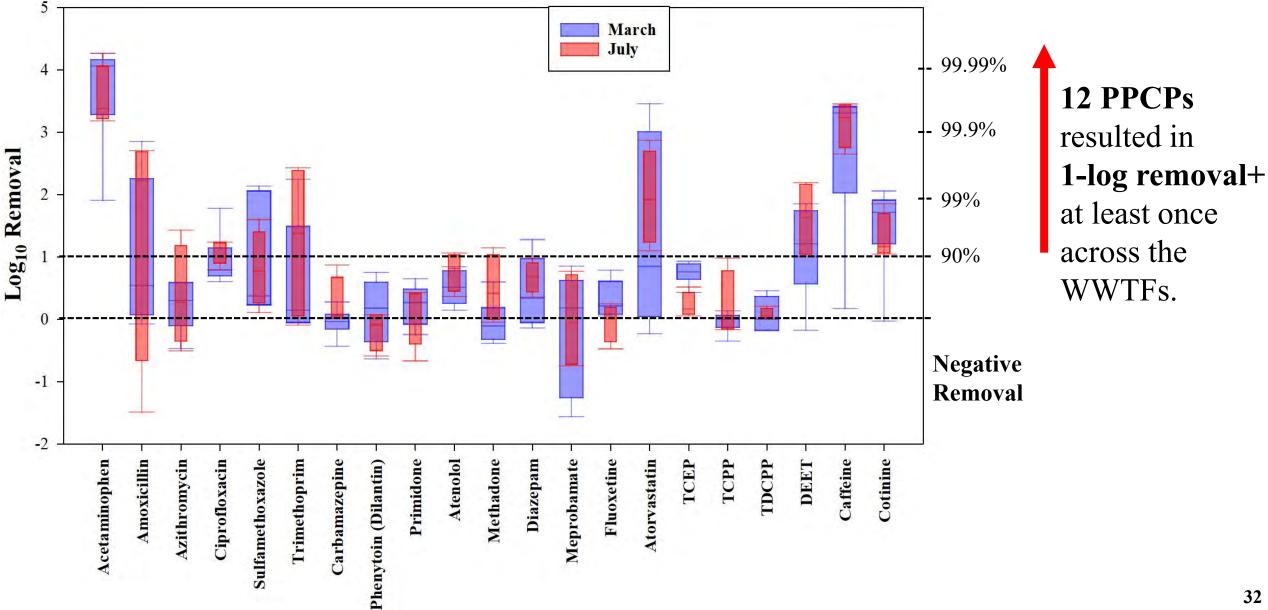




- In general, there is **NO significant difference** in **Log Removal** comparing all the WWTFs.
- However, there IS a significantly difference when comparing the upgrade from AL to Bar (1).



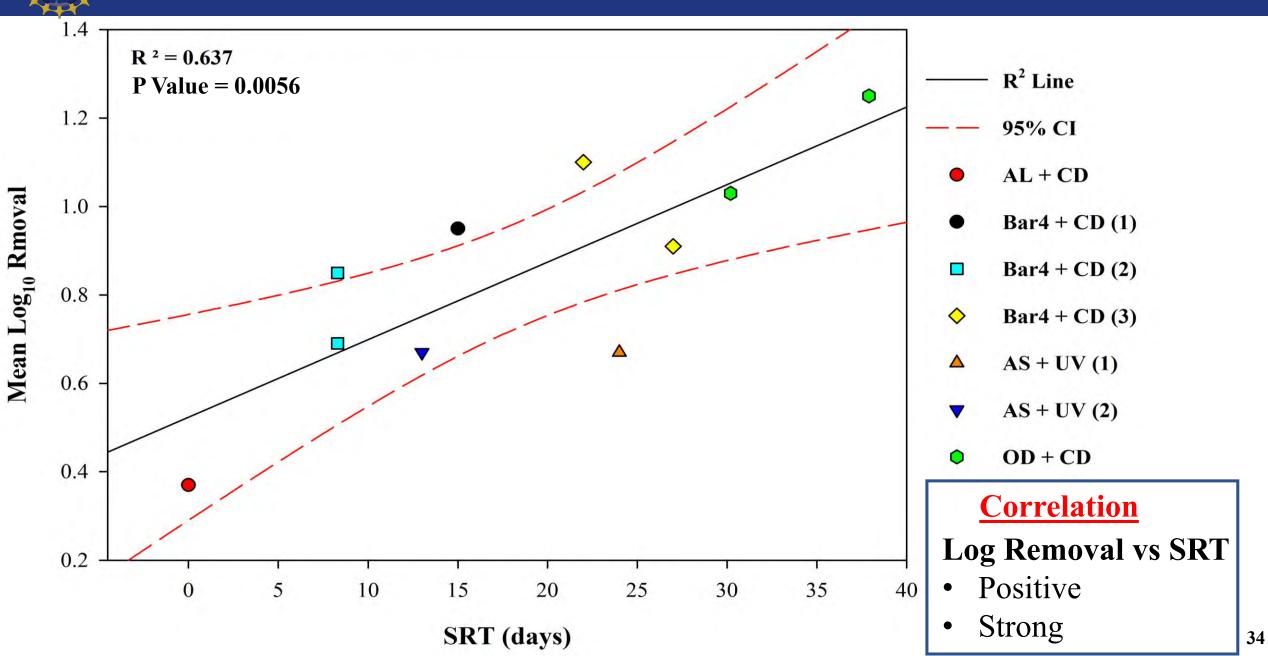






#### **Operational Conditions and Water Quality Parameters**

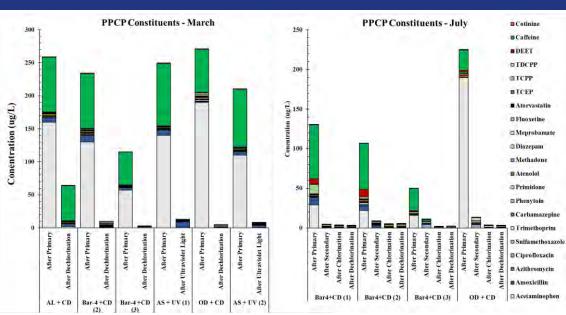
Phase 1: March										
WWTFs	BOD	TSS	TDN	SRT	pН	Cond.	DO	REDOX	Temp	
	Removal	Rmoval	Removal	(days)		(uS/cm)	(mg/L)	(mV)	$(C^{\circ})$	
AL + CD	86.0	81.0	23.3	-	7.4	1,152	8.0	-25.5	7.0	
Bar4 + CD(2)	97.5	98.0	74.7	8.3	7.5	1,509	8.5	-27.6	10.3	
Bar4 + CD $(3)$	95.8	95.8	77.8	22.0	7.2	1,388	6.7	-10.8	10.3	
AS + UV(1)	98.2	99.7	76.8	24.0	7.4	1,130	7.8	-22.5	9.4	
OD + CD	100.0	100.0	95.8	37.9	7.4	1,206	6.4	-26.6	9.7	
AS +UV (2)	98.3	98.1	80.6	13.0	7.0	1,470	4.9	-2.5	10.3	
Phase 2: July										
Bar4 + CD $(1)$	96.9	99.4	87.8	15.0	7.0	795.7	4.0	-4.0	22.3	
Bar4 + CD $(2)$	99.1	99.4	94.5	8.3	7.1	897.8	4.7	-7.0	23.5	
Bar4 + CD $(3)$	93.7	99.7	95.1	27.0	6.8	738.1	3.6	6.5	23.8	
OD + CD	99.0	100.0	75.6	30.2	7.3	798.6	3.3	-16.9	22.0	



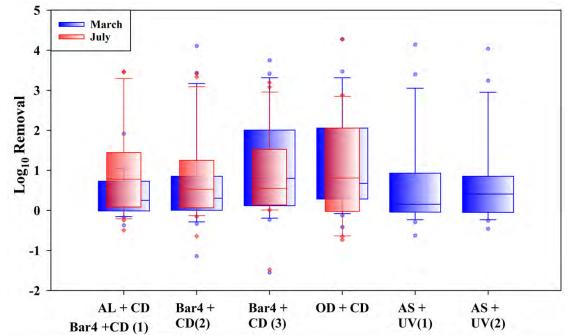


### **PPCP Seasonal Variation**

In general, there is NO
 significant difference in
 for influent and effluent
 Concentrations across
 both seasons.



 In general, there is NO significant difference in overall PPCP Log Removal across both seasons except for WWTF#1 that upgraded from an AL to Bar4 system.





Detection

# **Key Points – PPCP**

- All 21 PPCPs were detected either in the influent, effluent, or both at each WWTF.
- Antibiotics and Fire retardants were dominant in the influent, effluent, and sludge samples.
- Enhanced biological treatment with alternating zones lead to higher PPCP removal.
- In this case, a **longer SRT positively correlated** with **higher PPCP removal**, but with this limited data set it is currently unclear if this relationship is holds true.



Occurrence

Design

- No, influent and effluent concentrations and removal did not change significantly from March to July (except WWTF#1).
- 9 out of 14 PPCPs detected within the Great Bay, were listed as 'most frequently detected' in surface waters.
- All **6 personal care products** (3 fire retardants) and all **5 Antibiotics** were detected which relates to the dominant constituents in the effluent.





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### Next Step

- 1. Determine what parameters could be influence results the most:
  - Operational conditions
  - Water quality parameters
  - PPCP characteristics / properties
  - Analytical / sampling methods
- 2. Work on mass balance calculations and incorporate sludge data:
  - Most recent sludge produced and wasted data. (In = Out)?
- 3. Determine the microbial abundance for each facility:
  - Identify the similarities and differences across all facilities



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#### **Special Thank You**

#### Support

- The WWTFs and their operators
- UNH undergraduates
  - Lucas Theoharidis
  - Catherine Murphy
- UNH graduate students
  - Christian Rodriguez
  - Carmela Antonellis
  - Ellie Tavasoli

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#### Outline

- 1. PPCP Background & Knowledge Gaps
- 2. Research Goals
- 3. Methods & Sampling Plan
- 4. PPCP Results & Preliminary Conclusions
- 5. Next Steps
- 6. Acknowledgments
- 7. References

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