# The Fate and Removal of Pharmaceuticals and Personal Care Products within Wastewater Treatment Facilities discharging upstream from the Great Bay Estuary

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## Abstract

Pharmaceuticals and personal care products (PPCPs) are contaminants of emerging concern that derive primarily from combined sewer overflows and discharges from industrial and municipal wastewater treatment facilities (WWTFs). Some PPCPs may exhibit a wide range of health or behavioral effects in aquatic life (e.g., neural, instinct response, reproductive) at part per billion levels while others may bioaccumulate, amplifying effects up the food chain. **In collaboration with six local WWTFs, we have: (1) investigated concentrations for 21 PPCPs occurring in WWTFs discharging into the Great Bay National Estuarine Research Reserve and (2) examined differences in WWTF design influencing removal of select PPCPs**. The six WWTFs highlight different secondary treatment designs and disinfection methods to better understand the treatment mechanisms associated with PPCP removal. Samples were taken at influent and effluent locations as well as intermediate steps to not only estimate the percent removal per compound but to also document the change in PPCP concentrations along the treatment train. This provided insight to elucidate the most effective treatment method for reducing PPCPs in effluent. The preliminary results from two phases of sampling (March; n = 12 & July; n = 20) indicate that all 21 PPCPs were detected either in the influent, effluent, or both at each WWTF. Also, WWTFs with an enhanced biological treatment and longer sludge retention times (SRTs) resulted in higher overall PPCP removal. Due to the widespread use of PPCPs and their incomplete removal from WWTFs, the literature lists 13 of the 21 PPCPs as 'most frequently detected' in surface waters. In total, six surface water samples were collected across the Great Bay estuary resulting in 9 of the 13 frequently detected PPCPs being present, confirming previously reported observations, and 14 PPCPs being detected overall. Understanding the fate of PPCPs in conventional WWTFs is important to protecting coastal ecosystems and supporting long-term stewardship of our marine resources.

## Project Aims and Hypotheses

**Aims:**

1. Document the detection of 21 target PPCP analytes within six local WWTFs and across the Great Bay estuary.
2. Investigate the removal efficiency for all 21 PPCPs based on (a) treatment process design and (b) operational conditions, specifically solids retention time (SRT)
3. Assess the microbial diversity and abundance for each WWTF while identifying commonalties and/or unique variations.

**Hypothesis:**

There will be a positive correlation between the increase in overall PPCP removal with WWTF's that have **(a)** alternating biological treatment zones (aerobic, anoxic, anaerobic) and **(b)** longer SRTs.

**Rationale (a):** Biological treatment with alternating treatment zones provide changes in conditions (oxygen abundant to oxygen limiting) it also inherently changes the microbial community within each zone allowing for more diverse co-metabolic reactions to occur throughout the treatment tank furthering the system's ability to remove various PPCPs

**Rationale (b):** SRT is one of many deterministic factors that influence the microbial composition including important nitrifiers such as ammonia-oxidizing bacteria (AOB) utilizing ammonia monooxygenase (AMO) enzymes that have been seen to catalyze biotransformation. The idea here is that longer SRTs gives the opportunity for slower growing microbes, like AOBs, to become more abundant by establishing a stable population providing the microbes with more contact time to break down PPCPs.

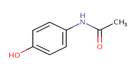
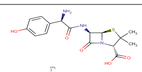
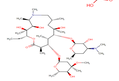
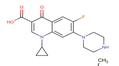
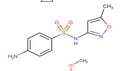
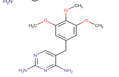
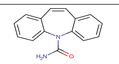
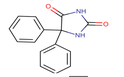
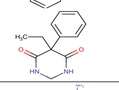
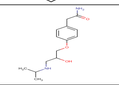
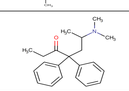
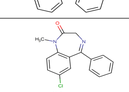
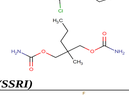
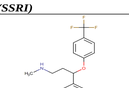
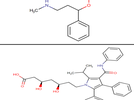
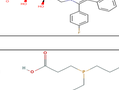
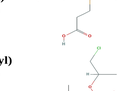
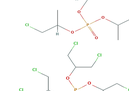
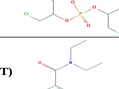
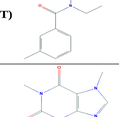
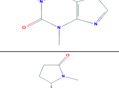
## Background

The Great Bay National Estuarine Research Reserve in New Hampshire supports 169 bird, fish, and plant species. Unfortunately, there have been signs indicating that the Great Bay estuary's ecosystem is failing due to the continuous input of pollution from human activity; therefore, understanding the sources and fate of PPCPs in its contributing tributaries is essential to protecting its delicate ecosystem.

Preliminary data from the National Oceanic and Atmospheric Administration's (NOAA) Mussel Watch Program 2016 survey identified 9 PPCPs in mussels collected in the Great Bay which included DEET, atenolol, and fluoxetine. The detection of these compounds in mussel tissue suggests PPCPs are prevalent along New Hampshire coastlines and that WWTFs discharging to Great Bay estuary are ineffective at removing some PPCPs.

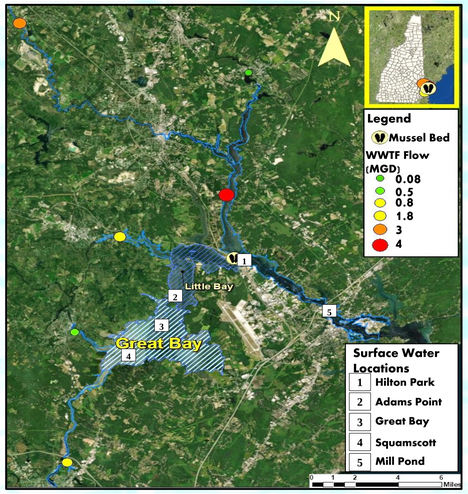
Conventional WWTFs have four stages of treatment (preliminary, primary, secondary, disinfection), but most PPCP removal occurs during secondary treatment through biodegradation by a diverse aerobic microbial community. Recent studies have shown secondary treatment designed to achieve low effluent nutrient levels (nitrogen and phosphorous) have a positive relationship on PPCP removal. The selected WWTFs represent a range of different secondary treatment designs (i.e., conventional activated sludge, 4-stage Bardenpho, aerated lagoons, and oxidation ditch) and disinfection methods (i.e., chlorination/dechlorination and ultraviolet (UV) light disinfection).

## Table 1: PPCP Analytes

| Therapeutic Class | PPCP Name<br>Chemical Formula<br>(CAS#) | Structure | Common Brand Names | Associated Conditions |
|---|---|---|---|---|
| *Analgesic* | | | | |
| Pharmaceuticals | **Acetaminophen**<br>$C_8H_9NO_2$<br>(103-90-2) |  | Tylenol, Mapap, Ofirmev | Fever, Severe to Moderate Pain, Minor aches |
| *Antibiotic* | | | | |
| | **Amoxicillin**<br>$C_{16}H_{19}N_3O_5S$<br>(26787-78-0) |  | Moxatag, Dispermox, Amoxil, Trimox, Wymox | Bacterial infections |
| | **Azithromycin**<br>$C_{38}H_{72}N_2O_{12}$<br>(83905-01-5) |  | Zithromax, Zmax, | Bacterial infection |
| | **Ciprofloxacin**<br>$C_{17}H_{18}FN_3O_3$<br>(85721-33-1) |  | Cipro, Proquin | Bacterial infections |
| | **Sulfamethoxazole**<br>$C_{10}H_{11}N_3O_3S$<br>(723-46-6) |  | Sulfatrim, Bactrim | Bacterial infections |
| | **Trimethoprim**<br>$C_{14}H_{18}N_4O_3$<br>(738-70-5) |  | Primsol | Bacterial infections |
| *Anti-convulsant* | | | | |
| | **Carbamazepine**<br>$C_{15}H_{12}N_2O$<br>(298-46-4) |  | Carbatrol, Epitol, Equetro, Tegretol | Epilepsy, Seizures, Nerve pain, Bipolar |
| | **Phenytoin**<br>$C_{15}H_{12}N_2O_2$<br>(57-41-0) |  | Phenytek, Dilantin | Epilepsy, Seizures |
| | **Primidone**<br>$C_{12}H_{14}N_2O_2$<br>(125-33-7) |  | Mysoline, Primaclone, Desoxyphen-obarbital | Epilepsy, Seizures |
| *Beta blocker* | | | | |
| | **Atenolol**<br>$C_{14}H_{22}N_2O_3$<br>(29122-68-7) |  | Tenormin | High blood pressure |
| *Narcotic/Opiate* | | | | |
| | **Methadone**<br>$C_{21}H_{27}NO$<br>(76-99-3) |  | Dolophine, Methadose | Severe pain |
| *Sedative* | | | | |
| | **Diazepam**<br>$C_{16}H_{13}ClN_2O$<br>(439-14-5) |  | Valium | Anxiety, Muscle spasms, Seizures, Agitation |
| | **Meprobamate**<br>$C_9H_{18}N_2O_4$<br>(57-53-4) |  | Equanil (Wyeth), Meprospan, Miltown | Anxiety |
| *Anti-depressant agent (SSRI)* | | | | |
| | **Fluoxetine**<br>$C_{17}H_{18}F_3NO$<br>(54910-89-3) |  | Prozac, Sarafem, Adofen | Depression, Anxiety, Bipolar, Obsessive Compulsive Disorder, Panic |
| *Statin* | | | | |
| | **Atorvastatin**<br>$C_{33}H_{35}FN_2O_5$<br>(134523-00-5) |  | Lipitor | High Cholesterol |
| *Flame retardants* | | | | |
| Personal Care Products | **Tris(2-carboxyethyl) phosphine (TCEP)**<br>$C_9H_{15}O_6P$<br>(5961-85-3) |  | | Prevent Fire |
| | **Tris(1-chloro-2-propyl) phosphate (TCPP)**<br>$C_9H_{18}Cl_3O_4P$<br>(13674-84-5) |  | | Prevent Fire |
| | **Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)**<br>$C_9H_{15}Cl_6O_4P$ |  | | Prevent Fire |
| *Pesticide* | | | | |
| | **N,N-Diethyl-3-methylbenzamide (DEET)**<br>$C_{12}H_{17}NO$<br>(134-62-3) |  | OFF!, CVS Insect Repellent Woodland Trail | Insect repellant |
| *Stimulant* | | | | |
| | **Caffeine**<br>$C_8H_{10}N_4O_2$<br>(58-08-2) |  | Starbucks, Dunkin Donuts, Maxwell House, Folgers | Drowsiness, Headaches |
| *Tobacco metabolite* | | | | |
| | **Cotinine**<br>$C_{10}H_{12}N_2O$<br>(486-56-6) |  | | Depression, PTSD, anxiety, fear-related behavior |

## Site

### Figure 1: Wastewater Treatment Plant Flow




**WWTF Treatment Operations:**

| Secondary Treatment Options: | Disinfection Options: |
|---|---|
| 1. Aerated Lagoons (**AL**) | 1. Chlorination - Dechlorination (**CD**) |
| 2. 4-Stage Bardenpho (**Bar4**) | 2. Ultraviolet Light (**UV**) |
| 3. Activated Sludge (**AS**) | |
| 4. Oxidation Ditch (**OD**) | |

### Table 2: WWTFs per Phase

| Phase 1 – March | Phase 2 – July |
|---|---|
| WWTF # 1 → AL + CD | WWTF # 1 → Bar4 + CD (1) Upgrade* |
| WWTF # 2 → Bar4 + CD (2) | WWTF # 2 → Bar4 + CD (2) |
| WWTF # 3 → Bar4 + CD (3) | WWTF # 3 → Bar4 + CD (3) |
| WWTF # 4 → AS + UV (1) | |
| WWTF # 5 → OD + CD | WWTF # 5 → OD + CD |
| WWTF # 6 → AS + UV (2) | |

**Table 2:** The project was split into two sampling phases; mid-March 2019 (phase-1) and mid-July 2019 (phase-2). Phase-2 focused on four of the six WWTFs utilizing the same disinfection method (CD). Keeping the disinfection method constant allows for better comparison of the secondary treatment methods. Also, one WWTF went through a secondary treatment upgrade between phase to meet nutrient permit.

## Methods / Analyses

### Figure 2: Sampling Overview

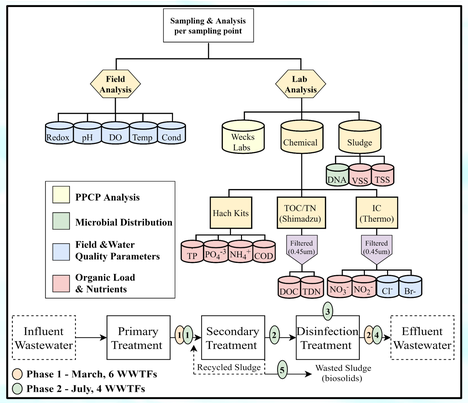



**Figure 2** shows an overview of the sampling locations and the analyses performed for each sample. Field and laboratory analyses performed to better understand the specific conditions and provide context for the functional potential of the microbial community. For example, most microbial gene functions are dependent on pH, temperature, dissolved oxygen, nutrients such as nitrogen and phosphorus, organic load (total carbon), and electron donators/ accepters. This information will provide insight into conditions related to PPCP removal.

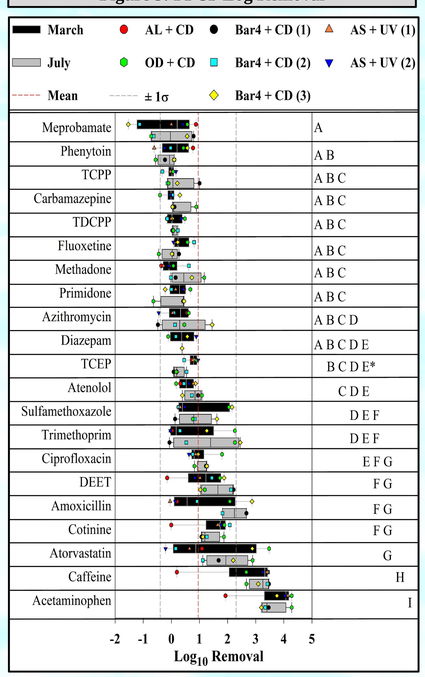
## Preliminary Results and Discussion

### Table 3: Overall Detection

| Compound Class | General Name | Aqueous Phase: AL+CD: March Bar-4 +CD$_1$: July — Influent | Aqueous Phase: AL+CD: March Bar-4 +CD$_1$: July — Effluent | Aqueous Phase: Bar-4 +CD$_2$ — Influent | Aqueous Phase: Bar-4 +CD$_2$ — Effluent | Aqueous Phase: Bar-4 +CD$_3$ — Influent | Aqueous Phase: Bar-4 +CD$_3$ — Effluent | Aqueous Phase: AS + UV$_1$ — Influent | Aqueous Phase: AS + UV$_1$ — Effluent | Aqueous Phase: OD + CD — March | Aqueous Phase: OD + CD — Effluent | Aqueous Phase: AS + UV$_2$ — March | Aqueous Phase: AS + UV$_2$ — Effl | Solid Phase: Bar-4 + CD$_1$ — Sludge | Solid Phase: Bar-4 + CD$_2$ — Sludge | Solid Phase: Bar-4 + CD$_3$ — Sludge | Solid Phase: OD + CD — Sludge | Great Bay Surface Water: Hilton Park | Great Bay Surface Water: Mill Pond | Great Bay Surface Water: Adams Point | Great Bay Surface Water: Great Bay | Great Bay Surface Water: Squam-scott | Commonly Detected Matrixes: Wastewater | Ground Water | Surface Water | Effluent | Biosolids | Marine Sediments | Marine Organisms | Toxicity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Mar. | July | Mar. | July | Mar. | July | Mar. | July | Mar. | July | Mar. | July | Infl | Effl | Mar. | July | Mar. | July | Aug. | Aug. | Aug. | Aug. | | | | | | | |
| Pharmaceuticals | Analgesic | Acetaminophen* | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Antibiotic | Amoxicillin | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | | Azithromycin | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | Ciprofloxacin* | | | | | | | | | | | | | | BL | BL | BL | BL | | | | | | | | | | | T |
| | | Sulfamethoxazole* | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | | Trimethoprim* | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | Anti-convulsant | Carbamazepine* | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | | Phenytoin | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | | Primidone | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | B-blocker | Atenolol* | | | | | | | | | | | | | | | | | BL | | | | | | | | | | | T |
| | Narcotic | Methadone | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Sedative | Diazepam* | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | | Meprobamate | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | SSRI | Fluoxetine* | | | | | | | | | | | | | | | | | | | | | | | | | | | | T |
| | Statin | Atorvastatin | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Personal Care Products | Flame retardants | TCEP* | | | | | | | | | | | | | | | | | BL | | | | | | | | | | | |
| | | TCPP* | | | | | | | | | | | | | | | | | BL | | | | | | | | | | | |
| | | TDCPP | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Insecticide | DEET* | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Stimulant | Caffeine* | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | Tobacco metabolite | Cotinine* | | | | | | | | | | | | | | | | | BL | | | BL | BL | | | | | | | |

**Table 3 - Overall Detection :**The compounds with a red asterisk text are frequently detected within the environment. Color Scheme: Non-Detect = White ; Detect = Gray ; Decreased Concentration = Blue ; Increased Concentration = Red. Abbreviations: Infl = Influent ; Effl = Effluent ; BL = Potential Lab Blank Concentration. Commonly Detected Matrix References: Luo et al., 2014; Lubliner et al., 2010; Arpin-Pont et al., 2016; Hedgespeth et al., 2012; De Voogt et al., 2009.

### Figure 3: PPCP Log Removal




### Figure 4: WWTF Log Removal

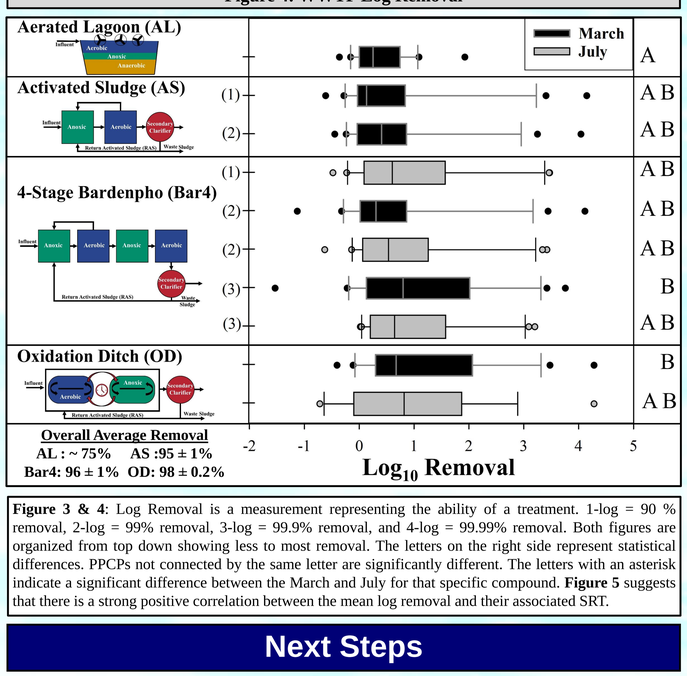
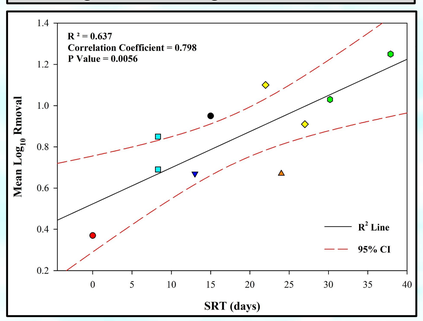
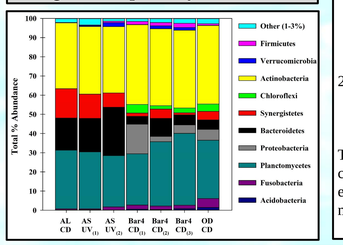



**Figure 3 & 4**: Log Removal is a measurement representing the ability of a treatment. 1-log = 90 % removal, 2-log = 99% removal, 3-log = 99.9% removal, and 4-log = 99.99% removal. Both figures are organized from top down showing less to most removal. The letters on the right side represent statistical differences. PPCPs not connected by the same letter are significantly different. The letters with an asterisk indicate a significant difference between the March and July for that specific compound. **Figure 5** suggests that there is a strong positive correlation between the mean log removal and their associated SRT.

### Figure 5: Mean Log Removal vs. SRT




### Figure 6: Top 10 Phylum Present




## Next Steps

1. Determine what parameters could be influence results the most: Operational conditions, Water quality parameters, PPCP characteristics and /or properties, or analytical / sampling methods.
2. Determine the microbial abundance for each facility and compare similarities and differences. Also, identify potential important players in degradation.

This process will elucidate changes in the microbial communities, degradation pathways, and utilized enzymes to better understand PPCP removal mechanisms during secondary treatment.

### Acknowledgments

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