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A Multi-Disciplinary Approach to the Removal of Emerging Contaminants in Municipal Wastewater Treatment Plants in New York State (2003-2004)

by P.J. Phillips, B. Stinson, S.D. Zaugg, E.T. Furlong, D.W. Kolpin, K.M. Esposito, B. Bodniewicz, R. Pape and J. Anderson

Authors' Note: ***The authors recognize the complex nature of the chemicals classified as emerging contaminants and that in many cases the parent compound may not be removed but may simply be altered or degraded during treatment, taking on another chemical form. Some of the EC degredants may not specifically be tested for within this study but may still contribute to environmental impacts. While the terms removal and reduction are used with regard to the concentration of specific compounds or groups thereof within this text, the authors are cognizant that insufficient information is available at this time to suggest that the overall concentration of trace chemicals or the associated environmental impacts are subsequently reduced or eliminated.***

Across the United States, there is a rapidly growing awareness of the occurrence and the toxicological impacts of natural and synthetic trace compounds in the environment. These trace compounds, referred to as emerging contaminants (ECs), are reported to cause a range of negative impacts in the environment, such as adverse effects on biota in receiving streams and interference with the normal functions of the endocrine system, which controls growth and development in living organisms.

Wastewater treatment plants (WWTPs) have been identified as a key collection point for ECs in the water cycle and potentially an ideal location at which to treat to remove them, thereby mitigating their release into the environment ***(Figure 1)***. This presents wastewater industry professionals with both a significant opportunity and a tremendous challenge: to identify cost effective treatment processes that can remove or reduce these contaminants before they are released into the environment.

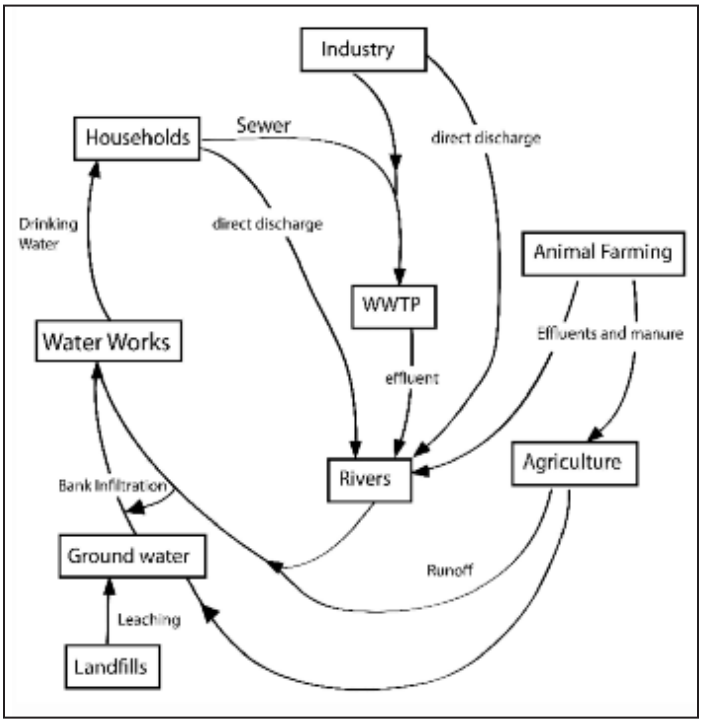

Figure 1: The Water Cycle

Although WWTPs have been identified as strategic focal points and potential treatment locations for the removal of ECs from the environment, little is known about the nature, variability, transport and fate of this class of compounds in typical wastewaters and treatment facilities in the United States. Furthermore few studies have been performed to monitor or understand the capability of conventional or innovative wastewater treatment processes to remove or reduce the concentrations of a wide variety of ECs at wastewater facilities.

This study was designed to provide baseline information on this topic. While other studies have examined the occurrence of a limited number of representative contaminants in the environment (generally five to 10 compounds), this study is unique in that it provides information on a comprehensive list of ECs (63 ECs in total, Contaminant List in Appendix A, not included here) in the wastewater collection and treatment systems for four diverse communities over a two-year period. (It should be noted that the study is ongoing and additional data are pending but only 18 months of data are presented in this paper).

The study was conducted in two phases. Phase 1 was designed to provide information concerning the general character and concentration of ECs commonly detected in wastewaters, the variability over a prolonged period of time, the transport and fate of ECs through typical wastewater treatment plants operating with a range of conventional technologies and the impact of WWTP discharges on receiving streams. It also provided guidance in understanding the capability of distinct wastewater treatment processes or technologies to reduce or remove ECs.

The second phase of the study focused on one of the most common wastewater treatment processes operated in the United States, the Activated Sludge process. Using four controlled parallel activated sludge pilots, a more detailed assessment of the impact of Sludge Retention Time (SRT) on the reduction or removal of ECs was performed.

MATERIALS AND METHODS

Plant Selection

Four full scale WWTPs were assessed during Phase 1 of this study. Phase 1 studies were design to provide a general assessment of the range and concentration of EC typically detected in wastewaters and also to provide some guidance toward understanding the removal capabilities of conventional full-scale wastewater treatment processes.

The four plants selected for this study employed a range of treatment processes. A general description of the processes operating at the plants A-D is provided in ***Table 1***.

The influent and effluent flows at each plant were sampled 10 to 12 times over an 18-month test period, April 2003 to August 2004. Plants A-D treat between 0.35 to 1.5 million gallons of wastewater per day (mgd) and employ a range of conventional and advanced treatment technologies including: activated sludge, trickling filters, RBCs (rotating biological contactors), microfiltration, deep bed filters, and ultraviolet and chlorine disinfection processes. The analytical methods used in this study required filtered samples. As a result, raw

Table 1: Characteristics of the Four Wastewater Treatment Plants Included in the Long-Term Sampling Network

Plant	Plant Capacity (million gal.) per day	Secondary Biological Treatment	Tertiary Treatment	Disinfection
A	0.75	Extended Aeration Activated Sludge	Sand/Anthracite Microfiltration	Ultraviolet
B	1.175	Extended Aeration Activated Sludge	Sand Filtration	Chlorination/ Dechlorination
C	1.1	Two Stage Activated Sludge	Sand Filtration	Chlorination/ Dechlorination
D	1.5	Trickling Filter	Sand Filtration	Chlorination/ Dechlorination

Table 2: Characteristics of Plant F and Two of the Four Pilot Processes Evaluated

Plant	Plant Capacity (gpd)	Nominal Hydraulic Retention Time (Hrs)	Secondary Biological Treatment	Sludge Retention Time (SRT) (Days)
F	75 mgd	≈ 4	BNR Activated Sludge	< 5 days
Pilot 1	26,000 gpd	≈ 4	BNR Activated Sludge	≈ 10 days
Pilot 2	26,000 gpd	≈ 4	BNR Activated Sludge	≈ 20 days (suspended solids only) ≈ 26 days (estimate of IFAS & MLSS biosolids included)

influent wastewater samples were not processed, rather the effluent from the primary treatment stage, including processes such as screening and primary clarification, was used to indicate the soluble EC characteristics of the influent wastewater. This allowed for removal of much of the solids material in the primary clarifiers and facilitated more efficient processing of samples without sacrificing data quality. This sample is assumed to be representative of the influent wastewater in this text.

Within each WWTP, all samples were lagged by the hydraulic residence time within the plant in order to follow a slug of water through the plant as accurately as possible.

Composite samples were also collected over a 24-hour period at key locations through Plants A-D to determine the effect of treatment processes on EC removals. In general, samples were collected after the primary, secondary, tertiary and disinfection stages at each plant.

For activated sludge Plant A, 24-hour composite samples were collected from primary and secondary clarifier effluents, after both the sand and microfiltration processes and after chlorination and dechlorination.

For activated sludge Plant B, 24-hour composite samples were collected after the screening process, from the secondary clarifiers effluent after the biological process, after deep-bed sand filtration process and from the final effluent following chlorination and dechlorination.

At Plant C, 24-hour composite samples were collected from the primary effluent, from the clarified effluent of the first stage BOD activated sludge process and from the clarified effluent of the second-stage nitrification activated sludge process. At Plant C, chlorination was performed just after sand filtration such that non-chlorinated samples could not be collected after filtration. The post-filtration samples from Plant C are the only samples that did not receive dechlorination before they were collected, but ascorbic acid was added to these samples in order to prevent chlorination from affecting EC concentrations. A grab sample was also collected from the mixed liquor after the nitrification activated sludge process, prior to alum chemical addition. This sample was filtered and processed immediately in order to preserve the chemical characteristics of the sample.

At Plant D, the trickling filter plant, samples were collected after the primary treatment stage, from the clarifier after the trickling filter process, after the sand filtration stage and from the final effluent after chlorination and dechlorination.

During Phase 2 of the study, a more detailed assessment of the impact of solids retention time (SRT) on EC reductions in the activated sludge process was performed. Four activated sludge pilots were operated in parallel to a full-scale 75 mgd wastewater treatment plant. The full-scale plant and the pilots received the same primary effluent stream but were operated at slightly different SRTs in the range of five to 20 days. All operated with similar hydraulic residence times in the order of four hours. The four pilot plants were specifically designed and operated to perform biological nutrient removal evaluations and operate with flows ranging from 26,000 gallons per day (gpd) to 105,000 gpd. In general, the pilots operated at an SRT of eight to 12 days, but one pilot, pilot 2, operated with integrated fixed film activated sludge (IFAS) media in place, raising the estimated sludge age in that pilot to over 20 days.

For this report, the discussion of results is limited to those from Plant F, Pilot 1 and Pilot 2, as these are representative of the range of SRTs in the activated sludge treatment processes used throughout the pilots.

Removals calculated at different stages in the wastewater treatment processes are based on sequential reductions in concentrations of

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$$\left(\frac{\text{Concentration of EC Before Treatment Process} - \text{Concentration of EC Before Treatment Process}}{\text{Concentration of EC Before Treatment Process}} \right) \times 100 = \text{Percent (\%) Removal}$$

Equation 1 – Calculation of Percent Removal in Wastewater Treatment Processes

analytes from before and after the treatment processes such as the biological treatment process, filtration, chlorination, etc.

Percent removal for the first step in the wastewater treatment plant process is calculated as the decrease in concentration, expressed as percent, from the primary effluent to the secondary effluent, which in all plants involved treatment using a biological treatment process (i.e., the removals that occurred between sample 1 and 2). (See ***Equation 1*** above.) With the exception of Plant C, filtration is the second step in the treatment process; the percent removal for the second step is calculated by comparing the concentration after the second step in the wastewater treatment process to the concentration after the first step in the process, and expressing the result as a percent decrease. This approach is carried through for all successive steps in the wastewater process.

In the case of the pilot plant studies, the only process samples collected were from before and after the biological activated sludge process, thus the only calculations performed were in reference to the removal through the activated sludge treatment process. Percent removals were calculated as the percent difference between influent and effluent concentrations; negative removal percentages thus indicate higher effluent concentrations than influent concentrations.

Sample Processing and Analytical Methods

Samples were collected using standard US Geological Survey (USGS) trace-organic protocols (Shelton, 1995). Most grab samples were collected using Teflon-lined bottles, and bottles were rinsed three times with native-water before the sample was collected. WWTP influent samples were collected using 1 liter baked glass amber bottles, which were not rinsed before sample collection. Composite samples were collected using autosamplers using glass bottles cleaned according to USGS trace-organic protocols. With the exception of a short section of pump head tubing (less than 0.3 m) and a short section of distributor arm tubing (less than 0.3 m length), all the tubing was Teflon-lined. All the equipment used to collect and process samples was cleaned according to USGS trace-organic protocols (Wilde et al., 1999, 2004 and 2004). The non-Teflon lined tubing was cleaned before use, with the final cleaning step including rinsing with organic-free water.

Samples were filtered using glass-fiber filters (0.7 um pore diameter) using ceramic-head pumps, stainless steel filter units, and Teflon-lined tubing. Samples were kept chilled (to 4° C or less) between collection and filtration. Once filtered, samples were shipped overnight to the USGS National Water Quality Laboratory in Denver, Colorado for extraction and analysis.

Samples were analyzed using a GCMS (gas chromatography/mass spectrometry) method, which included analysis of 63 ECs (as described by Zaugg et al., 2001). This method includes extraction of filtered samples using disposable, polypropylene solid phase cartridges, and compound concentrations were determined by capillary-column gas chromatography/mass spectrometry.

For the purposes of this report, only results from seven compounds (*para*-nonylphenol, triclosan, caffeine, HHCB, cholesterol, TBEP and DEET) are discussed; these compounds were among the most frequently detected compounds in a study of streams across the United States study (Kolpin et al., 2002).

A number of detections discussed in this report for the GCMS method include concentrations reported below the reporting levels. Because the GCMS method identifies compounds by mass spectrometry, results are not censored at the minimum reporting levels (Zaugg et al., 2001); calibration standards for the GCMS method points are included at concentrations well below the minimum reporting level (usually 0.08 µg/L; Zaugg et al., 2001) in order to accurately quantify concentrations below the method reporting level. Replicate data collected as part of this study (discussed in subsequent sections) indicated good reproducibility (within 8 percent) for data reported below the minimum reporting level, and indicated the method was able to consistently provide results below the minimum reporting level for a variety of compounds.

Statistical Methods

Non-parametric statistical comparisons are used in this study. Non-parametric comparisons are especially appropriate for non-normally distributed data as well as data that are censored (Helsel and Hirsch, 1992). Kruskal-Wallis and Tukey tests are used to compare differing concentrations, percent differences among different types of replicates, or percent removals. A p-value of 0.05 is used to determine statistical differences.

Quality Assurance Samples

Field quality assurance samples included blanks and sample replicates. Because many of the compounds included in the GCMS method are commonly used, at least one blank sample was collected for each week of sampling. Laboratory grade organic-free water was used to prepare blanks, and these blanks were processed in an identical fashion to the environmental samples. Blank samples included equipment blanks, field blanks, and source water blanks. Autosamplers were also sampled for blanks by running blank water through tubing or by analyzing blank water poured into glass sample jars from the automatic samplers.

Blanks

Concentrations in environmental samples were compared with 27 blanks that were collected as part of the study; 23 compounds were detected in one or more blanks, and with few exceptions, blank concentrations were less than 0.1 µg/L. Over half (13) of the 23 compounds were only detected in one blank. Three compounds (phenol, triphenyl phosphate, and DEET) were detected in more than seven blanks. Six compounds (caffeine, benzophenone, HHCB, methyl salicylate, and *para*-cresol) were detected in between three and six blanks; with the exception of *para*-cresol, (which was detected in one blank at 0.23 µg/L), these six compounds were never detected at a concentration above 0.09 µg/L. Environmental concentrations within four times the concentrations reported in corresponding field blanks were censored to less than the reporting level.

Replicates

Differences in individually paired replicate samples will be evaluated by the relative percent difference method (RPD). RPD is defined as:

[RDP = [(C1-C2) x 100]/[(C1+C2)/2]]

Equation 2 – Calculating Differences in Replicate Samples

C1 equals the larger of the two concentrations, and C2 equals the smaller of the two concentrations.

A total of 18 replicate samples suitable for comparison of EC variability were collected as part of this study. These 18 replicate samples yielded 286 instances where at least one concentration was reported in either the environmental sample or the replicate; 255 of these comparisons had a reported concentration in both the environmental sample and in the replicate sample, leaving 31 instances where a reported concentration was matched with a non-detect (referred to as unmatched comparisons), or a rate of 11 percent unmatched comparisons. For the 255 comparisons, median difference was 7.14 percent, with 80 percent of the replicate pairs having a difference of 20 percent or less. Analysis of replicate data indicated that RPDs for some compounds with low or inconsistent recoveries exceeded 10 percent and that RPDs for sterol and stanols (including cholesterol) were as much as 40 percent. These data indicate that data reported below the method reporting levels have similar precision to data reported above the reporting levels.

Results and Discussion

Although the overall research included data for over 60 compounds, this paper will focus on seven of those compounds which will give an overall indication of the fate and transport of these compounds through wastewater treatment plants. Seven of the 63 compounds analyzed by the method ***(Table 3)*** described in Zaugg et al. (2001) are discussed in this paper in detail: HHCB, caffeine, cholesterol, DEET, *para*-nonylphenol, TBEP, and triclosan – which are representative of the range of EC concentrations observed at the WWTPs. Each of these seven compounds is also a member of a different general use category ***(Table 3)***. Overall, each of these compounds was detected in over 95 percent of the influent samples collected at each plant.

Table 3: List of selected analytes, including reporting level (RL), compound use or category, and CAS number

Compound	RL (µg/L)	Compound Use/ Category	CAS Number
HHCB[1]	0.5	Fragrance	21145-77-7
Caffeine	0.5	Non-prescription drug	58-08-2
Cholesterol	2.0	Sterol/Stanol	57-88-5
DEET[2]	0.5	Insect Repellent	134-62-3
para-Nonylphenol	5.0	Detergent Degradant	84852-15-3
TBEP[3]	0.5	Flame Retardant	78-51-3
Triclosan	1.0	Disinfectant	3380-34-5

[1]HHCB = Galaxolide
[2]DEET = N, N-diethyl-meta-toluamide
[3]TBEP = Tri (2-butoxyethyl) phosphate)

Concentration of ECs in WWTP EC Influent and Effluent Flows

In general, it appears that the concentrations of organic compounds in WWTP effluents and receiving streams vary in

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response to the technology and operation of the WWTP, and chemical characteristics of raw sewage influents.

The trends in influent and effluent EC concentrations for the samples collected from Plants A-C differ for most compounds. This indicates that the effluent concentrations are not simply reflective of the source concentration (i.e., the influent concentration) but that the type and mode of operation of wastewater treatment process has an impact on the removal of the ECs.

As a general observation, effluent concentrations from Plant D were consistently higher than those observed at the other plants.

Four of the seven compounds discussed in this paper had median influent concentrations, greater than 10 µg/L, at Plants A-D: caffeine, cholesterol, *para*-nonylphenol, and TBEP. With the exception of cholesterol (which was not included in the Plant F sampling) and *para*-nonylphenol (8 µg/L), concentrations for these four compounds also exceeded 10 µg /L at Plant F. The other three compounds (DEET, triclosan, and HHCB) had median influent concentrations of between 1 and 4 µg/L for samples collected at Plants A-D, and for the influent sample collected at Plant F. Despite the fact that Plants A-D were located in smaller more rural townships and Plant F is located in a major metropolitan area (New York City) the influent concentration in all seven indicator EC compounds were very similar.

Three compounds (cholesterol, DEET, and triclosan) had no significant difference in influent concentrations among the samples collected from Plants A-D, but had significantly higher concentrations for effluent samples collected from Plant D (the trickling filter plant) for two of these compounds. Median effluent concentrations for these plants ranged from 0.2 µg /L or less for samples collected from Plants A-C, and between 1 and 2 µg /L for samples collected from Plant D ***(Table 4)***. The median concentration for effluent samples collected from Plant D was significantly higher than the medians for samples collected from Plants A-C for both cholesterol and triclosan. This finding indicates that, in general, the plants operating with activated sludge processes were consistently capable of effecting greater EC removals than the plant operating with the trickling filter process.

Plant C had particularly high influent concentrations *para*-nonlyphenol (detergent degradate) and TBEP (flame retardant). This plant received primarily domestic wastewater but also had both a notable flow contribution from a nearby hospital. Median influent concentrations for these two ECs for samples collected from Plant C exceeded 50 µg/L, whereas, median influent concentrations for the samples collected from Plants A, B and D were between 2 to 20 µg /L. By contrast, median effluent concentrations for samples collected from Plant D were significantly higher than those from Plants A-C ***(Table 4)*** for these two compounds, with median concentrations above 10 µg/L at Plant D effluent, but less than 1.5 µg /L for effluent samples collected from the other three plants. The interesting observation here is that, unlike Plant D (trickling filter plant), Plant C (activated sludge plant) was able to achieve significant removals (approximately equal to 98 and 100 percent, respectively) of these compounds through the treatment processes, ***Table 4)***. Plant D (trickling filter) was unable to achieve more than 10 percent reduction of these compounds.

Table 3a: Influent concentrations for seven selected emerging contaminants (ECs). Median concentration for influent samples collected from Plants A-D and influent concentrations for the August 2004 sample at Plant F

Compound	Plant				
	A	B	C	D	Plant F + Pilot 1 & 2
	Concentrations in micrograms per liter (µg /L)				
HHCB[1]	3.95	1.2	3	2.35	1.3
Caffeine	135	43	73	43	19
Cholesterol	10.35	19.5	21	9.5	Na
DEET[2]	0.48	1.26	1.6	1.8	1.6
para-Nonylphenol	14.5	4.65	62	18	8
Triclosan	2.65	2.45	2.3	1.85	1.2
TBEP[3]	14.5	2.55	160	13	32

[1]HHCB = Galaxolide
[2]DEET = N,N-diethyl-meta-toluamide
[3]TBEP = Tri(2-butoxyethyl)phosphate)

Median influent concentrations for HHCB and caffeine were higher for samples collected from Plant A than all other plants, and concentrations for these compounds for influent samples collected at Plant B were lower than at any other plant ***(Table 3a)***. However, as with many other compounds, the median effluent concentration of caffeine from Plant D was significantly higher (greater than 10 µg /L) than the median for concentrations observed at Plants A-C (0.1 µg /L) ***(Table 4)***. By contrast, effluent HHCB concentrations for samples collected from Plants A-D largely mirrored the pattern of influent samples. Effluent HHCB concentrations for Plants A, C, and D did not differ significantly, with medians at all plants between 1.8 and 2.2, whereas the median for effluent samples collected at Plant B was significantly less than the other plants (0.49). Final effluent concentrations for HHCB reported by Simonich and others (2000) for activated sludge and trickling filter plants in the United States ranged from 1.2 to 1.6 µg /L for HHCB, which is similar to the effluent range for Plants A-D, Plant F and the pilot plants.

In general, influent concentrations at Plant F, and the effluent concentrations at Plant F and the four Pilot plants were similar to those measured at Plants A-D ***(Tables 3a and 4)***. With the exception of caffeine, the influent concentration for Plant F was between the low and high median influent concentrations for Plants A-D for the six compounds with available data (HHCB, caffeine, DEET, *para*-nonylphenol, triclosan, and TBEP). Concentrations for samples collected from pilot 1, 2, 3 and 4 were intermediate between the median effluent concentrations for samples collected from Plants A-D ***(Table 4)***. Effluent concentrations for Plants F were also within the range of median concentrations for effluent samples from Plants A-D, except for triclosan and TBEP, which were higher in effluent from the pilots than the medians of samples collected at Plants A-D. For all six of these compounds, effluent concentrations at Plant F were higher than any of the pilot concentrations, and concentrations collected at Pilot 2 were less than those collected at any of the other pilots. It should be noted that Plant F and the pilots all received the same influent wastewater but that Pilot 2 operated at a high SRT than both Plant F and the other pilots. This may have contributed to its ability to reduce the EC concentrations.

Reduction of EC Concentrations

Comparison of influent versus effluent concentrations showed that although EC reductions vary, the greatest reductions were observed at plants that operate the activated sludge process (AS) for biological treatment ***(Figures 4 and 5, Table 5)***. These patterns also indicate that in some cases, effluent concentrations alone are insufficient to indicate percent reductions in organic compounds during the wastewater treatment process.

Over half of the frequently detected ECs were reduced by 95

Table 4: Median effluent concentrations for selected emerging contaminants for samples collected from Plants A-D, Plant F and Pilots 1 and 2. Concentrations are in micrograms per liter (µg/L)

Compound	Plant					Pilot	
	A	B	C	D	F	Pilot 1	Pilot 2
HHCB[1]	2.15	0.495	1.8	1.8	2.2	2.1	1.8
Caffeine	0.061	0.023	0.11	23	7.2	0.35	0
Cholesterol	0	0	0.88	1.7	Na	na	na
DEET[2]	0.096	0.043	0	1.5	1.3	0.38	0.36
para-Nonylphenol	1.2	1.1	1.15	19	2.8	2.5	1.5
Triclosan	0.13	0.14	0.12	1.0	1.7	0.33	0.29
TBEP[3]	0	0.39	0	11	17	9.6	1

[1]HHCB = Galaxolide [2]DEET = N,N-diethyl-meta-toluamide [3]TBEP = Tri(2-butoxyethyl)phosphate)

Table 5: Median concentration reductions for selected emerging contaminants at Plants A-D and concentration reductions at Plant F and Pilots 1 and 2

Compound	Plant					Pilot	
	A	B	C	D	F	Pilot 1	Pilot 2
HHCB[1]	43	52	40	20	-69	-62	-38
Caffeine	100	100	100	40	62	98	100
Cholesterol	100	100	96	70	Na	na	Na
DEET[2]	100	100	100	26	19	76	78
para-Nonylphenol	100	74	98	9	65	69	81
TBEP[3]	99	98	100	10	47	70	97
Triclosan	94	94	93	40	-42	73	76

[1]HHCB = Galaxolide [2]DEET = N,N-diethyl-meta-toluamide [3]TBEP=Tri(2-butoxyethyl)phosphate)

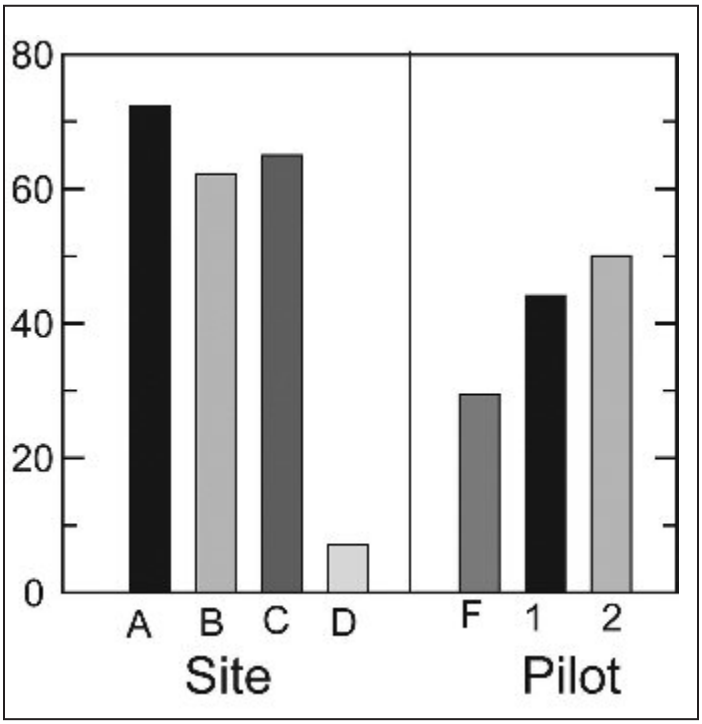

Figure 4: Percentage of compounds reduced in concentration by 95 percent or more: median percent for A, B, C and D, and percentage for August 2004 sample at Plant F and Pilots 1 and 2

percent or more in samples collected at Plants A-C, which operate the activated sludge process ***(Figure 4)***. Less than 10 percent of the ECs were reduced by 95 percent or more at Plant D, which uses a trickling filter treatment process.

Median reduction percentages were significantly lower for samples from Plant D (the plant which operates the trickling filter process) than at for Plants A-C, which operate activated sludge processes, ***(Figure 5)***. For the seven compounds considered in this report, the percentage reduction was consistently greatest and most significant for cholesterol. Cholesterol reductions at Plants A-C were consistently in the order of 100 percent while the reduction at Plant D was 70 percent ***(Figure 5, Table 5)***. Of all seven compounds discussed in this paper, cholesterol was the only one with a median reduction of greater than 50 percent at Plant D.

Three compounds (DEET, caffeine, and TBEP) had median reductions of greater than 95 percent for samples collected from Plants A-C, but median reductions of less than 40 percent for samples collected from Plant D ***(Figure 5, Table 5)***. Although median reductions were higher than 95 percent at Plants A-C, some samples had considerable variability in reduction percentages for DEET and TBEP. Overall reductions for caffeine for Plants A-C did not vary much, with few reductions less than 99 percent; these reductions are similar to those found in samples collected from a Swiss activated sludge WWTP with a sludge age of greater than 5 days (Buerge et al., 2003). The large variability in the percent reductions TBEP for samples collected from Plant B, result in reductions for samples collected at this Plant being significantly less than those collected at Plants A and B. Similarly, samples from Plants A and B have a large variability in the percent reductions for DEET, which result in the percent reductions for samples from these plants being not significantly different from those from Plant D.

Not all ECs are reduced by the same amount at all activated sludge plants. Median reductions for *para*-nonylphenol exceeded 98 percent for samples collected from Plant A and Plant C ***(Table 5)***; by contrast, median reduction in concentration for samples from Plant B were only 74 percent, indicating that this compound is not reduced with the same efficiency at all activated sludge treatment plants. The reason for this difference is not clear, although Plant B, unlike the other activated sludge plants, receives a large amount of sewage from a large dairy processing facility and as a result has a higher than average influent organic load relative to the other wastewater treatment facilities. Furthermore, it operates a high rate activated sludge process. Although para-nonylphenol percent reductions are lower for samples collected from plant B than for the other two activated sludge plants, median effluent concentrations did not differ significantly among Plants A, B, and C, demonstrating effluent concentrations alone are not always indicators of a plant's ability to reduce concentrations of organic compounds. Little to no reduction of *para*-nonylphenol occurred during the wastewater treatment process at Plant D.

The median percent reduction at Plants A-C for triclosan were all greater than 90 percent and were consistent with reductions reported for activated sludge plants in Switzerland (Singer et al., 2002), which were reported at 94 percent. Concentrations for the effluent at these four plants were also similar to those reported in Switzerland, as both generally ranged between .04 and .21 µg/L (Singer et al., 2002).

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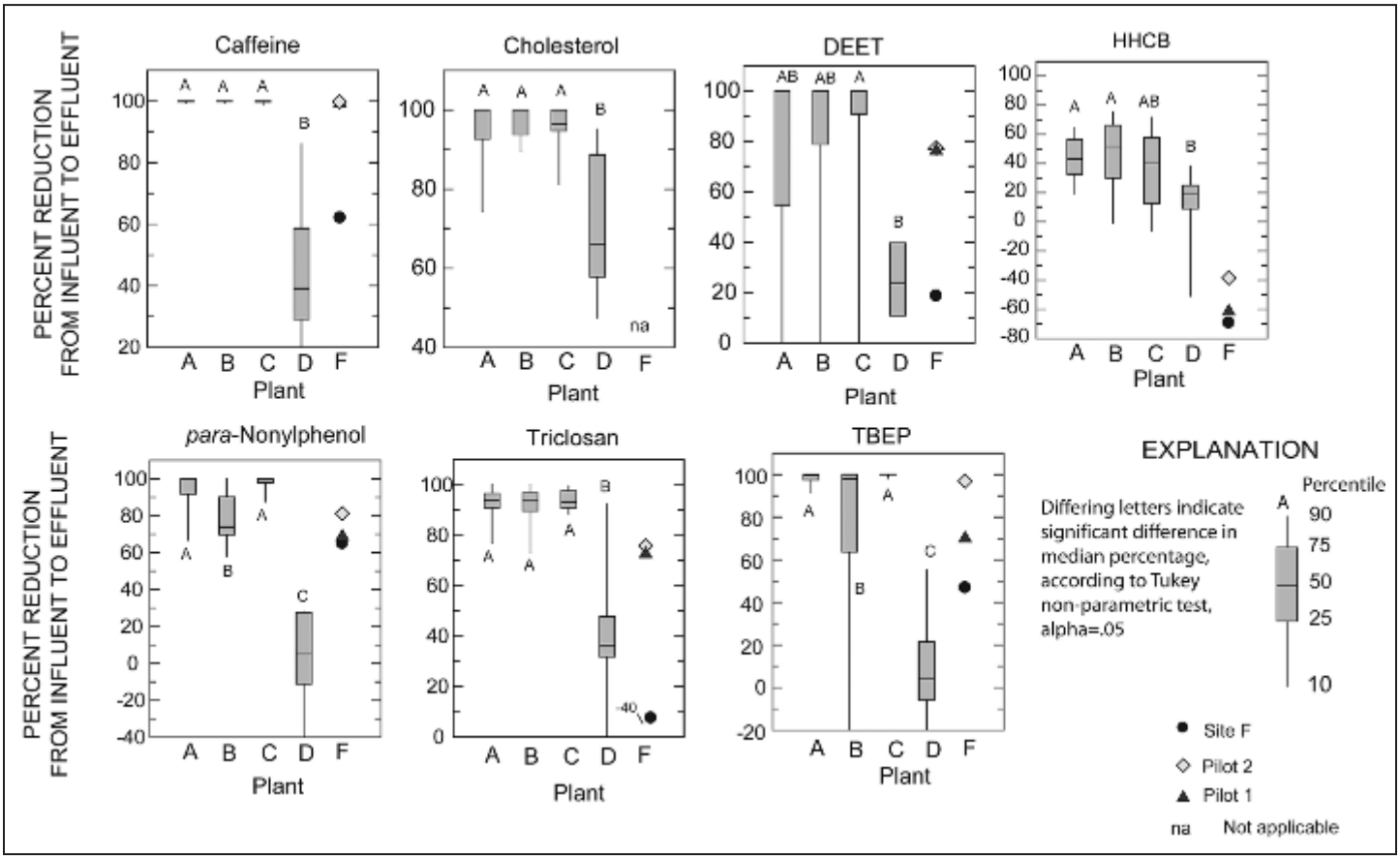
Figure 5: Percent difference between influent and effluent concentrations by plant (statistical comparisons only made between Plants A, B, C, and D due to small number of samples at Plant F and Pilots)



HHCB had the lowest median reduction in concentrations for the seven compounds considered in this paper, with the three activated sludge plants having median reductions ranging from 40 to 52 percent ***(Figure 5)***. Median reductions for samples collected at Plants A and B were significantly higher than that at Plant D, which was only 20 percent. HHCB reductions were less than zero for samples collected from Plant F and the four pilots, suggesting minimal HHCB reduction at these plants. This was not anticipated as the pilot facilities in particular were operating an activated sludge plant at reasonably high SRTs.

Simonich et al. (2002) found a total of 89 percent reduction in HHCB concentrations in activated sludge plants, and estimated about 30 percent of reduction from primary treatment. Thus, the reduction during biological treatment reported by Simonich et al. (about equal to 60 percent) is similar to that for the activated sludge Plants A-C evaluated during this study. The reason for the difference in the overall HHCB reductions observed during this study and that conducted by Simonich et al. (2002) can be attributed to differences in how samples were processed after collection. Simonich et al. (2002) used whole water samples, in conjunction with C18 discs with a graded pre-filter; concentrations of influent HHCB were around 10 µg /L for activated sludge plant influent. By contrast, influent concentrations for HHCB were between 1 and 4 µg/L for the plants sampled during this study, where filtered samples were being analyzed. Effluent concentrations were similar between the two studies. The higher influent concentrations, large amount of removal of HHCB during primary treatment, and use of unfiltered samples in the Simonich study probably resulted in higher HHCB concentrations than the present study due to a higher amount of particulate bound HHCB in the former study.

Reduction by Different WWTP Processes

Data on reduction percentages representing different processes within the wastewater treatment plants indicate that biological treatment processes accounted for the most significant reductions in EC concentrations. For all compounds, median percent reductions during the secondary biological treatment processes ranged from 100 percent for samples from Plants A and B to over 80 percent during the first stage bioreactor for Plant C. Reduction during the trickling filter biological treatment stage for Plants D ranged from 20 percent to 60 percent. With the exception of one of the samples from Plant D, the reduction percentages associated with biological treatment were significantly higher than for the filtration or disinfection processes for all EC compounds. The median removals observed through the filtration and disinfection processes were less than 10 percent at all plants, with the exception of Plant D. Most of the reduction in EC concentrations for Plant C took place during the first stage bioreactor; some additional reduction occurred during the nitrification activated sludge process for a few select ECs, but no significant additional reductions occurred after the second stage clarification.

The high amount of variability at Plant D may be related to the biological treatment processes used at this facility. As indicated in previous sections, the trickling filter process demonstrated lower overall EC removals when compared to the activated sludge

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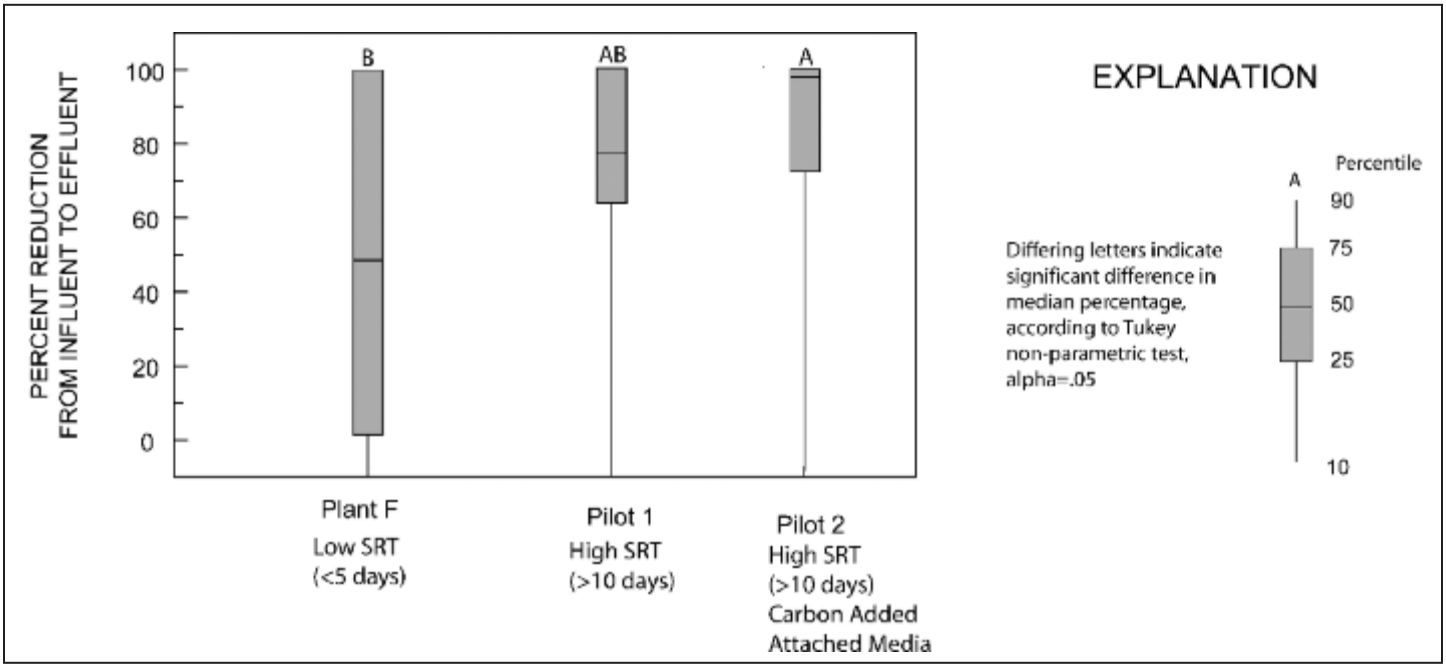
Figure 7: Percent difference in all EC concentrations between influent and effluent, for Plant F and Pilots 1 and 2



processes. The flow to this particular plant, however, was quite variable both on a daily and seasonal basis and, as a result, the trickling filter media may not always have been maintained in a wet and active condition. This most likely contributed to the variability in EC removals. By contrast, samples from Plant A taken on subsequent days demonstrated consistent and reliable EC reductions through the biological treatment stage.

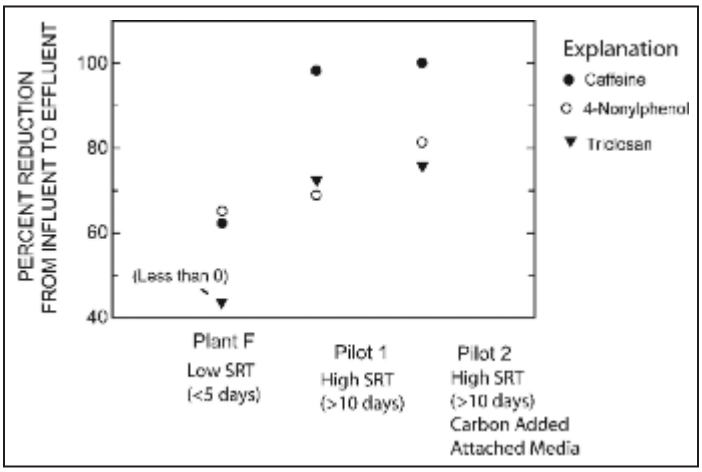
Results from the pilot sampling indicate that increasing the SRT in the activated sludge process can effect better EC removals. Median reductions for all detected compounds ranged from slightly less than 50 percent for Plant F which operated with an SRT of under five days, to over 95 percent for Pilot 1, which operated with an SRT of approximately 10 days ***(Figure 7, Table 6)***. Although median percent reductions were only significantly different between Plant F and Pilot 2, more than 70 percent of the compounds detected at Pilot 1 were reduced by more than 70 percent ***(Figure 7)***. The increase in percent reduction and reliability corresponds to an increase in SRT from Plant F at less than a five-day SRT, to Pilot 1 operating at a 10-day SRT to Pilot 2, which was operating at between a 20 and 26 days SRT, when consideration is given to biomass on the Integrated Fixed Film Activated Sludge (IFAS) media.

Table 6: Percent reductions for selected emerging contaminants at Plant F and Pilots 1 and 2 for the August 2004 sampling event

Compound	Plant F	Pilot 1	Pilot 2
HHCB[1]	-69	-62	-38
Caffeine	62	98	100
Cholesterol	Na	na	Na
DEET[2]	19	76	78
para-Nonylphenol	65	69	81
TBEP[3]	47	70	97
Triclosan	42	73	76

[1]HHCB = Galaxolide
[2]DEET = N,N-diethyl-meta-toluamide
[3]TBEP = Tri (2-butoxyethyl)phosphate)

Figure 8: Percent reduction in caffeine, 4-nonylphenol and triclosan between the influent and effluent at Plant F and Pilots 1 and 2



Differences in percent reduction among Plant F, Pilot 1 and Pilot 2 indicate that biological treatment technologies may vary in their ability to reduce different compounds. Triclosan and caffeine showed improved reduction between Plant F and the pilots, reflecting the increased removals associated with increased SRTs in the activated sludge process ***(Figure 8)***. These findings agree with those of Buerge et al. (2000) who found greater than 99 percent reduction of caffeine in activated sludge plants operating with a sludge age in excess of five days, but between 80 and 99 percent reductions by activated sludge plants with less than five days sludge age.

By contrast, the detergent degradate 4-nonylphenol seemed to be less affected by the increased SRT demonstrating only slight improvement in removals between Plant F and the pilots. Nevertheless, the reduction for 4-nonylphenol in Pilot 2 (>20 day SRT) was almost 20 percent higher than that in plant F (<5 day SRT), supporting the theory that increased SRT may enhance the EC removal capabilities of the activated sludge process.

The most significant impact of SRT appears to occur as the sludge age increases from five to 10 days. The incremental improvement in

removals of all three ECs was less notable once the SRT increased above 10 days.

Conclusions

Wastewaters appear to contain a wide range of ECs. The study monitored for 63 different ECs at five full-scale WWTPs. Over 55 different ECs were detected in the wastewaters examined, 44 of these were detected frequently.

The median cumulative concentrations of EC in the wastewaters ranged from between 120 µg/L to just over 500 µg/L. The influent concentrations of the seven indicator EC compounds were very similar at all the plants evaluated, despite the fact that four of the plants are located in rural areas or small townships while Plant F is located in a large metropolitan area.

The WWTPs examined were effective in removing significant amounts of the ECs using conventional wastewater treatment processes. The median cumulative WWTP effluent EC concentrations ranged from between 10 µg/L to just over 55 µg/L. Results indicated that the type of technology operated and the mode of operation both had an impact on the removal capability of the plants.

Comparison of influent versus effluent EC concentrations showed that while EC reductions vary, the greatest reductions were observed at plants that operate the activated sludge process (AS). Over half of the frequently detected ECs were reduced by 95 percent or more in samples collected at plants which operated an activated sludge process. Less than 10 percent of the ECs were reduced by 95 percent or more at Plant D, which uses a trickling filter treatment process. This is a promising observation for the wastewater industry.

Furthermore, focused pilot studies indicated that increased removals of ECs were closely associated with increased SRTs in the activated sludge process. The most significant impact of SRT appeared to occur as the sludge age increased above five days. While removals continued to improve as the SRT increased above 10 days, the benefits were less marked.

It should be stressed, however, that detection of ECs does not infer toxicity. Extensive toxicology evaluations are required before the relevance of these findings is determined. This study does provide critical information to assist in those evaluations. This study has developed a baseline understanding of the type and concentration of compounds that are representative of both raw and treated wastewaters in the United States. Toxicology and other environmental impact analyses should consider the compound impact of a range of frequently detected ECs. This study provides guidance on that topic.

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