Characterizing the Passage of Personal Care Products Through Wastewater Treatment Processes

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ABSTRACT: Wastewater treatment facilities use secondary treatment to stabilize the effect of discharged effluent on receiving waters by oxidizing biodegradable organic matter and reducing suspended solids and nutrients. The process was never specifically intended to remove trace quantities of xenobiotics, such as endocrine-disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs). Nevertheless, European studies performed at bench-scale or at small facilities have demonstrated that a critical minimum solids retention time (SRT) can achieve good reduction of many EDCs and pharmaceuticals. The objective of this study was to expand these findings to the removal performance for 20 PPCPs commonly found in the influent to full-scale facilities operating in the United States. The participating plants use SRT conditions ranging from 0.5 to 30 days and include facility capacities ranging from 19 000 m^3/d (5 mgd) to greater than 1 136 000 m^3/d (300 mgd). Two pilot membrane bioreactors were also included in the study.

The 20 PPCPs were categorized into nine bin combinations of occurrence frequency and treatment reduction performance. While most compounds were well removed, galaxolide (a musk fragrance) occurred frequently and was resistant to removal. A minimum critical SRT, defined as the minimum SRT, needed to consistently demonstrate greater than 80% removal (SRT_{80}), was compound-dependent, with most compounds removed at 5 to 15 days and a small group requiring longer SRTs. From limited data, no additional removal could be attributed to the use of membrane bioreactors, media filters, or longer hydraulic retention times. Reverse osmosis was effective in removing any remaining compounds. *Water Environ. Res.,* **79,** 2564 (2007).

KEYWORDS: personal care products, secondary treatment, solids retention time, full-scale treatment plants.

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Introduction

Municipal wastewater treatment facilities in the United States must comply with discharge limits for biochemical oxygen demand, total suspended solids (TSS), and other conventional pollutants. The core treatment used at these facilities is biological secondary treatment, with most metropolitan facilities using an activated sludge process. Supplemental or enhanced treatment is practiced at facilities subject to more stringent discharge requirements or those that produce effluent for reuse applications. It is anticipated that regulations promulgated in the future may add new compounds of concern to the regulatory list, based on the availability of sufficient evidence (i.e., occurrence and toxicological studies) to justify their inclusion (Halling-Sørenson et al., 1998).

Among the compounds that may become regulated in the future, natural and synthetic chemicals, collectively known as endocrine-disrupting compound (EDCs) and pharmaceutical and personal care products (PPCPs), are potential candidates. Studies supporting the theory that some of these chemicals can mimic the activity of natural endocrine hormones have existed for more than 70 years,and target these compounds as suspected causative agents of reported episodes of disruption in wildlife reproductive health (Snyder et al., 2003). Although contamination from these chemicals may originate from nonpoint sources, a significant fraction comes from municipal wastewater treatment plants (WWTPs) (Daughton and Ternes, 1999). Municipal WWTPs act as persistent point sources of EDCs and PPCPs, and trace concentrations of these chemicals have been observed in conventional secondary and tertiary wastewater discharges in the United States and abroad (Clara et al., 2005; Eriksson et al., 2003; Joss et al., 2004; Snyder et al., 2001).

The EDCs and PPCPs have not been subject to scrutiny in the past, mostly because of analytical limitations that prevented accurate detection and quantification of trace concentrations of these compounds (Ollers et al., 2001; Osemwengie and Steinberg, 2001). The advancement of analytical techniques, such as gas chromatography and liquid chromatography with tandem mass spectroscopy, now allow identification and quantification of these compounds at micrograms per liter (parts per billion) or nanograms per liter (parts per trillion) concentrations (Sedlak et al., 2000).

The presence of EDCs and PPCPs in the environment may pose a complex problem for two main reasons—(1) their effects are likely to occur at trace concentrations, and (2) their presence in effluent from municipal WWTPs is mostly the result of unregulated activities of individuals rather than regulated industrial discharges (Daughton and Ternes, 1999; Snyder et al., 2001). Consequently, understanding the ability of conventional wastewater treatment plants to prevent the passage of these compounds into the environment has become a critical concern (Clara et al., 2004).

Extensive research has been conducted to evaluate the occurrence and fate of hormonal EDCs in the environment. Estrogenic hormones (i.e., estradiol, estrone, and ethinyl estradiol), in particular, have been the focus of multiple studies, as they have been related to ubiquitous episodes of intersex in male fish in multiple locations in the United States and Europe (Irwin, 1998; Snyder et al., 2004; Ternes et al., 1999). Synthetic PPCPs remain a category considerably less studied, and comprehensive information on manufacturing, use, and disposal of these chemicals into the environment is less readily available. The findings of a United States Geological Survey (Reston, Virginia) reconnaissance survey of United States urban area streams (Kolpin et al., 2002) and other studies (Eriksson et al., 2003) have recently demonstrated the

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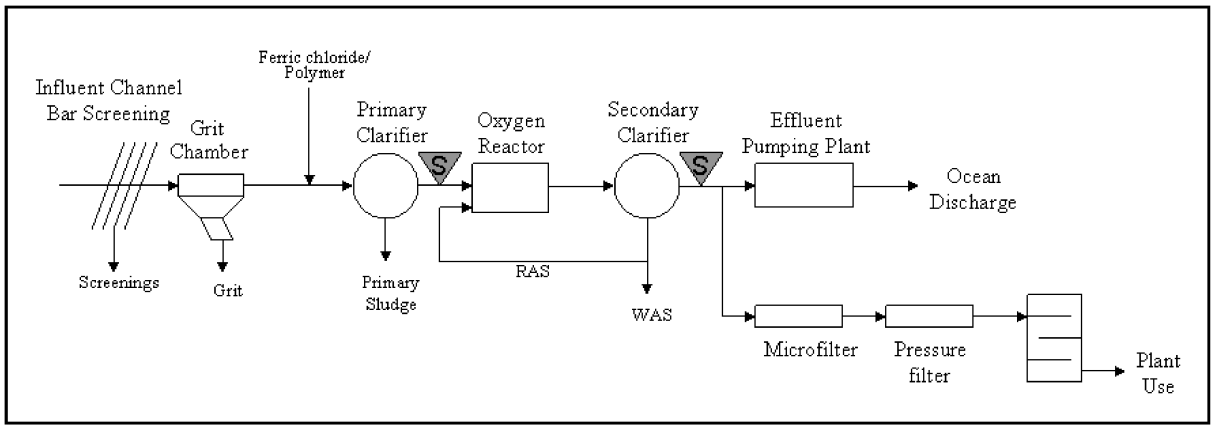
Table 1—Description of participating treatment facilities.

Facility	Wastewater type	Primary treatment	Secondary treatment	Secondary aeration	MLSS (mg/L)	SRT[b] (days)	Filters	Disinfection	Nitrification/ denitrification performance
A	Municipal from major metropolitan area	Polymer ferric	High-purity-oxygen activated sludge	Pure oxygen	1300 to 2600	0.5 to 1.5	None	None	Almost no nitrification[h] Almost no denitrification[i]
B	Municipal with light industrial component	No chemicals	MLE[a] nitrification/ denitrification	Diffused air	1800 to 2000	3 to 5	Deep bed[c]	Chlorine	Partial nitrification[j] Partial denitrification[k]
C	Municipal with light industrial component	No chemicals	Activated sludge	Diffused air	2000 to 3000	4 to 6	Deep bed[c]	UV	Partial nitrification Partial denitrification
D	Municipal with significant industrial component	No chemicals	Nitrification/ denitrification	Diffused air	2500 to 3000	7 to 20	Granular MF/RO	Chlorine	Full nitrification[l] Partial denitrification
E	Municipal with light industrial component	None	Nitrification/ denitrification	Diffused air	2100	11 to 16	None	UV	Full nitrification Partial denitrification
F	Municipal with light industrial component	None	Extended aeration nitrification/ denitrification	Surface air	4000	20 to 30	Deep bed[c]	UV	Full nitrification Full denitrification[m]
MBR #01[d,e]	Municipal with light industrial component	Not applicable	Nitrification/ denitrification	Not applicable	14 000	14	Not applicable	Not applicable	Full nitrification Almost no denitrification
MBR #02[f,g]	Municipal with light industrial component	Not applicable	Not applicable	Not applicable	11 500	15	Not applicable	Not applicable	1st sampling: Partial nitrification Partial denitrification. 2nd sampling: Almost no nitrification Almost no denitrification.

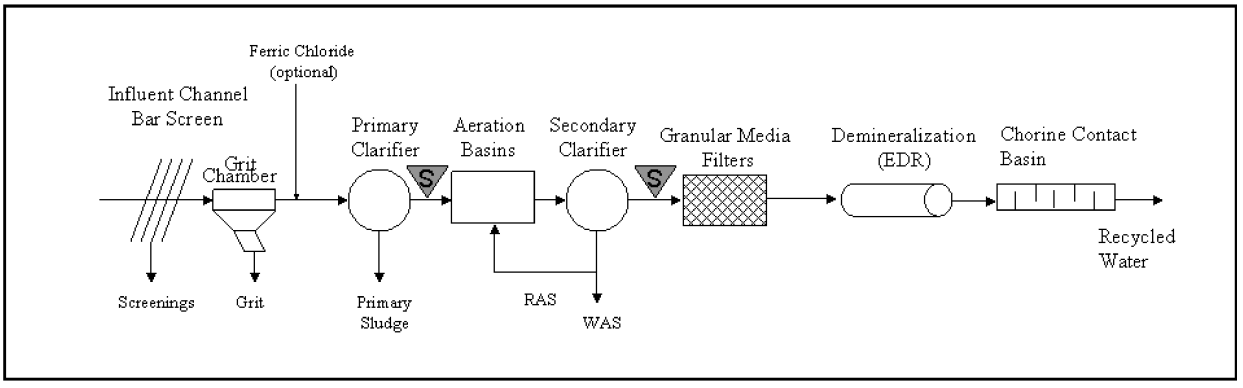
[a] MLE (Modified Ludzack Ettinger Process),
[b] Reported SRT corresponding to total from combined aerobic/anoxic facilities (in plants with nitrification/denitrification),
[c] Granular media,
[d] Uses flat sheet membranes,
[e] Located at plant E,
[f] Uses free-end hollow fiber membranes,
[g] Located at a facility not listed above,
[h] Almost no nitrification = <15% ammonia removal,
[i] Almost no denitrification = <15% total inorganic nitrogen removal,
[j] Partial nitrification = 15 to 90% ammonia removal,
[k] Partial denitrification = 15 to 90% total inorganic nitrogen removal, and
[l] Full nitrification = >90% total ammonia removal.
[m] Full nitrification = >90% total inorganic nitrogen removal.

widespread environmental occurrence of PPCP compounds. These findings have generated public concern about the presence of trace concentrations of these chemicals in the environment (Daughton and Ternes, 1999; Wilson et al., 2003). Some subset of these compounds may ultimately classify as EDCs.

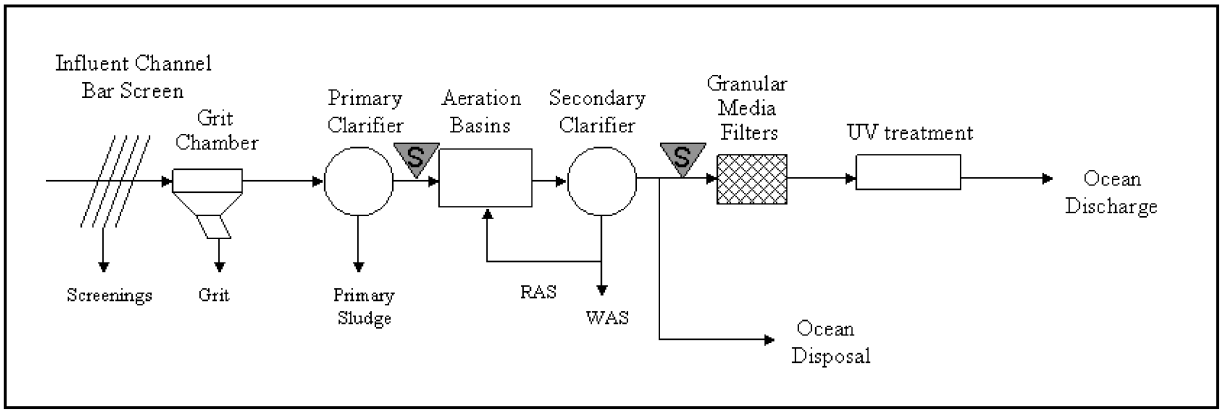
This study surveyed a target list of PPCP compounds, representing a range of chemical characteristics that have routinely been detected in wastewater influent, and assessed the removal of these parent compounds from the aqueous phase of the secondary effluent of the conventional secondary treatment facilities. The data were then evaluated to determine if the removals of these compounds are influenced by the solids retention time (SRT), which is a major variable in the design and operation of activated sludge secondary treatment. In addition, PPCP removal through subsequent tertiary media



Plant A (SRT ~ 0.5 to 1.5 days)



Plant B (SRT ~ 3 to 5 days)

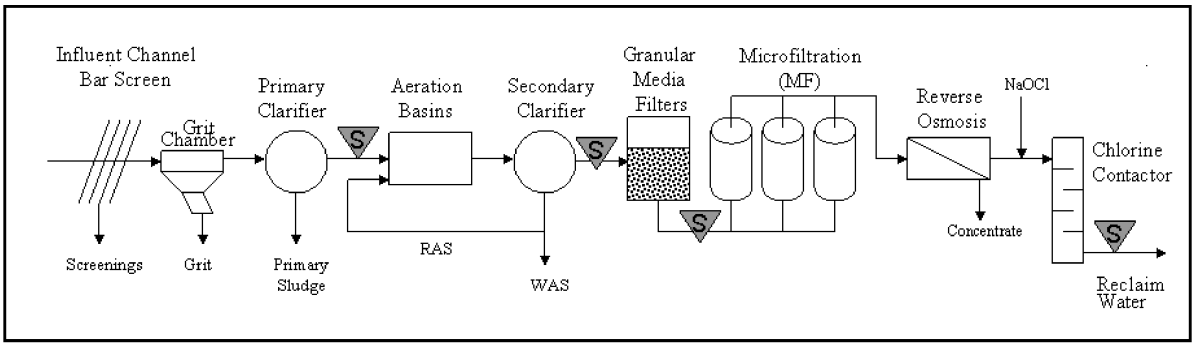


Plant C (SRT ~ 5 to 6 days)

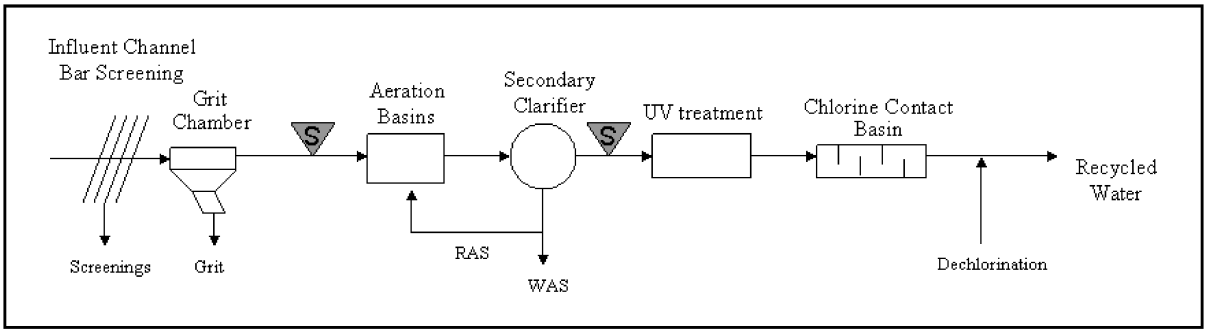
Figure 1—Schematics of participating full-scale facilities (RAS = return activated sludge, WAS = waste activated sludge, and EDR = electrodialysis reversal).

filtration and disinfection and newer hybrid treatment processes, such as membrane bioreactors (MBRs), were also evaluated.

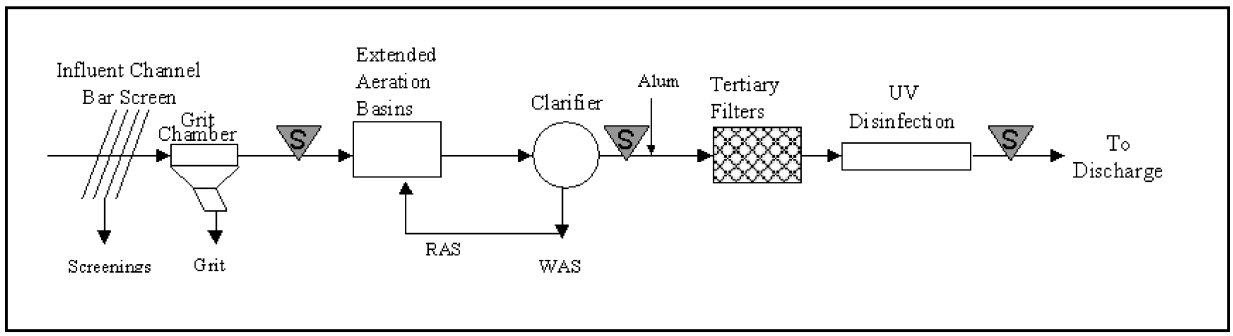
Extended SRTs promote the growth of a more diverse biological community that is able to degrade xenobiotic compounds more efficiently because of co-metabolic effects (Grady et al., 1980). It has been reported that increasing SRT has a beneficial effect on the removal of xenobiotic compounds (Clara et al., 2005; Joss et al., 2004; Kanda et al., 2003; Kreuzinger et al., 2004; Ternes et al., 1999). These data also suggest the existence of a critical SRT value, after which, the removal of these compounds is not improved (Clara



Plant D (SRT ~ 7 to 20 days)



Plant E (SRT ~ 11 to 16 days)



Plant F (SRT ~ 25 to 30 days)

Figure 1—(Continued)

et al., 2005; Joss et al., 2004). These conclusions have been derived from studies conducted at small-scale WWTPs and bench/pilot studies performed under controlled conditions. Many of these studies were conducted in Europe and have been more focused on estrogens and prescription pharmaceuticals than personal care products (Andersen et al., 2003; Kreuzinger et al., 2004; Ternes et al, 1999). For this reason, one of the main objectives of this research is to validate these conclusions using data from a group of large-scale WWTPs located in the United States, which includes facilities with capacities as high as 1 325 000 m^3/d (350 mgd). This study provides a systematic analysis of the effect of SRT on PPCP removal, by analyzing data from six full-scale WWTPs and two pilot-scale MBRs operating over a wide range of SRT values. Development of this information may prove valuable in defining optimum operational parameters for existing WWTPs and the design of future installations, from the perspective of PPCP removal. This study will help utilities to better address growing public concerns about PPCPs (Joss et al., 2004), by identifying those compounds resistant to removal and define critical SRT values where good removal is achieved.

Table 2—General characteristics of the analytical methods used in this study.

Compound	Retention time (minutes)	Major ion (m/z)	Segment	Spiked concentration (μg/L)	Baseline concentration* (μg/L)	MDL (μg/L)	Ratio of MDL to initial concentration
Methyl 3-phenyl propionate	12.2	164	1	0.05	BDL	0.043	0.86
3-phenyl propionate	13.2	150	1	0.50	2.43	10.7	3.64
Ethyl 3-phenyl propionate	13.2	178	1	0.05	BDL	0.012	0.25
Chloroxylenol	13.7	156	1	0.05	BDL	0.015	0.29
Methyl paraben	14.7	152	2	0.5	BDL	0.30	0.61
Butylated hydroxyanisole	14.9	165	2	0.05	BDL	0.011	0.23
DEET	16.1	190	2	0.05	0.189	0.086	0.36
Ibuprofen	16.5	163	2	1.0	BDL	1.44	1.44
Benzophenone	16.8	182	2	0.05	0.112	0.043	0.27
Dibromooctafluorebiphenyl—internal standard	17.3		TIC				
Tri(2-chloroethyl)phosphate	18.1	249	3	0.05	0.302	0.179	0.51
4-octyl phenol	18.2	206	3	0.01	BDL	0.004	0.31
Caffeine	19.1	194	3	0.05	0.019	0.053	1.06
Galaxolide	19.2	243	3	0.01	1.58	0.61	0.39
Benzyl salicylate	19.4	228	3	0.05	BDL	0.022	0.45
Musk ketone	20.4	279	4	0.01	0.065	0.034	0.45
Oxybenzone	20.9	227	4	0.01	0.083	0.06	0.65
Triclosan	21.7	290	4	0.05	0.19	0.35	1.44
Octyl methoxycinnamate	22.1	178	4	0.01	0.074	0.11	1.28
Butyl benzyl phthalate	23.7	206	5	0.01	0.142	0.13	0.88
Triphenyl phosphate	24.3	326	5	0.5	BDL	0.62	1.24
2,4-dichlorophenol-d_3—surrogate	10.7	165	TIC				
Caffeine-$^{13}C_3$ – surrogate	19.1	197	3				
3,3-dichlorobenzidine-d6—surrogate	25.2	258	TIC				
Di(ethylhexyl) phthalate-d_4—surrogate	26.1	283	TIC				

* BDL = below detection limit.

Methodology

Participating Facilities and Sampling Protocols. Unit process descriptions, secondary operating characteristics, wastewater type, and performance of nitrification/denitrification processes corresponding to the six participating full-scale facilities and two pilot MBRs are provided in Table 1. Process schematics of the full-scale facilities, indicating specific sampling locations, are presented in Figure 1.

Table 3—Compound occurrence bin assignment and 50th percentile concentration.

Occurrence bin name	Bin assignment criteria	Compounds	50th percentile value (ng/L)
Infrequent	Detected in <25% of the observations	TCEP	Not detected
		Octylphenol	Not detected
		Methyl-3-phenylpropionate	Not detected
		Triphenylphosphate	Not detected
Variable	Detected between 40 and 70% of the observations	DEET	120
		Ethyl-3-phenylpropionate	26
		BHA	Not detected
		Musk ketone	70
Frequent	Detected in >75% of the observations	Chloroxylenol	520
		Benzyl salicylate	450
		Galaxolide	1850
		Triclosan	5200
		Benzophenone	940
		Octylmethoxycinnamate	1400
		Oxybenzone	1870
		Butylbenzylphthalate	2000
		Caffeine	1900
		Methylparaben	2950
		3-Phenylpropionate	205 000
		Ibuprofen	6300

Table 4—Compound removal bin assignment.

Removal bin name	Bin assignment criteria (X = median percent removal value)	Compounds
Excellent removal	X > 80%	Methyl-3-phenylpropionate*
		Caffeine
		Ibuprofen
		Oxybenzone
		Chloroxylenol
		Methylparaben
		Benzyl salicylate
		3-Phenylpropionate
		Butylbenzyl phthalate
		Octylmethoxycinnamate
		Benzophenone
Moderate removal	50% < X < 80%	Octylphenol*
		Ethyl-3-phenylpropionate
		Triclosan
Poor removal	X < 50%	TCEP*
		Triphenylphosphate*
		BHA
		DEET
		Musk ketone
		Galaxolide

* Treatment classification of compounds from the infrequent occurrence bin is limited by insufficient data, as they were seldom detected in the influent.

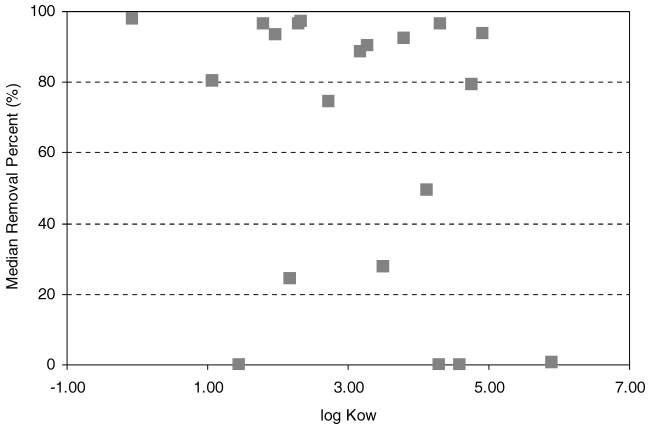


Figure 2—Median removal percentage of PPCP compounds in relation to the octanol-water partition coefficients.

This study evaluates contaminant removal through secondary treatment. Water quality information for the influent to secondary treatment was obtained from primary effluent or from raw influent, depending if the plant has primary treatment or not. One of the tested MBRs was equipped with submerged flat sheet membranes arranged in cassettes (Kubota Submerged Membrane Unit, Kubota Corporation, Osaka, Japan), and the other consisted of submerged free-end hollow fiber membranes (Koch/Puron, Koch Membrane Systems, Wilmington, Massachusetts). Both were operated in accordance with vendor specified conditions for at least two SRTs before sample collection. Samples were collected from the majority of these facilities during three discrete sampling events.

Secondary influent (i.e., primary effluent) and secondary effluent samples were collected as 24-hour time-weighted composites during typical facility operations using three project-dedicated temperature controlled Glacier composite samplers (Teledyne ISCO, Lincoln, Nebraska). Granular media filtration effluent samples were also collected at facilities D and F, and microfiltration/reverse osmosis effluent samples were also collected at facility F. Samples were collected following the application of any chemical disinfectant applied at the sampling location. The Glacier sampling chest and all associated sampling materials were subject to three rounds of chemical cleaning with acetone and hexane before initiating the sampling process. Handling of all equipment was performed only while wearing powder-free nitrile gloves that were replaced with new gloves at the start of each sampling event.

Each composite sample had a total volume of approximately 10 L, from which, 2 L were transferred to amber glass sample bottles with Teflon-lined caps and shipped overnight on ice to the analytical laboratory for PPCP analysis. The remaining sample volume was sent to a certified laboratory (Applied Physics and Chemistry Laboratory, Chino, California), for analysis of conventional constituents (TSS, volatile suspended solids, total Kjeldahl nitrogen, nitrate-nitrogen, nitrite-nitrogen, and ammonia-nitrogen). These data were only used when on-site plant data for these parameters were not available. At each sampling event, one blank and one duplicate split sample were collected and shipped for analysis. The blank consisted of running sufficient laboratory-grade distilled water through one of the sampling devices before sample collection at each sampling event. This water was then transferred to a separate amber glass bottle and shipped with the rest of the samples for analysis. The duplicate split sample location was randomly rotated during sampling events at each facility. No corrections were made to the sample data based on the results obtained for the blank and split samples.

Target Compounds and Analytical Methods. Samples were analyzed for PPCPs using solid-phase extraction (SPE) followed by analysis with a Perkin Elmer Clarus 500 gas chromatography/mass spectrometer (Perkin-Elmer, Waltham, Massachusetts) operated simultaneously in total ion count (TIC) and selective ion monitoring mode. Samples were initially refrigerated upon receipt and extracted, in most cases, within 24 hours. Samples were prefiltered through precleaned glass fiber filters (Fisher brand G8, 2.5-mm particle retention, and Fisher brand TCLP filter, 0.7-mm pore size; Fisher Scientific, Tustin, California). The filtrate was acidified with concentrated sulfuric acid to pH <2.0. After acidification, aqueous samples were extracted using sulfonated polystyrene divinylbenzene SPE disks (3M Empore SDB-RPS; 3M, Minneapolis, Minnesota). The disks were precleaned with ethyl acetate and then conditioned per manufacturer's recommendation. The flowrate through the disk was maintained at less than 50 mL/min. The SPE disks were then eluted with acetone (3 mL) and a triple aliquot of ethyl acetate (5 mL). The eluate was dried over sodium sulfate, and the volume reduced to 0.5 mL. The concentrate was transferred to a 2-mL gas chromatography vial sealed with screw caps, with polytetrafluoroethylene-coated rubber septa. 4,4-Dibromooctafluorobipheyl (Supelco, Bellefonte, Pennsylvania) was added before analysis as an internal standard.

The gas chromatography method was as follows: 2.0 μL injection, splitless, injector temperature 175°C, 40°C for 2 minutes, then 10°C/min ramp to 250°C, hold for 14 minutes, ramp to 290°C at a rate of 25°C/min, and hold for 2 minutes. The column was a RTX-MS5 3 m × 0.25 m internal diameter, 0.25-μm film

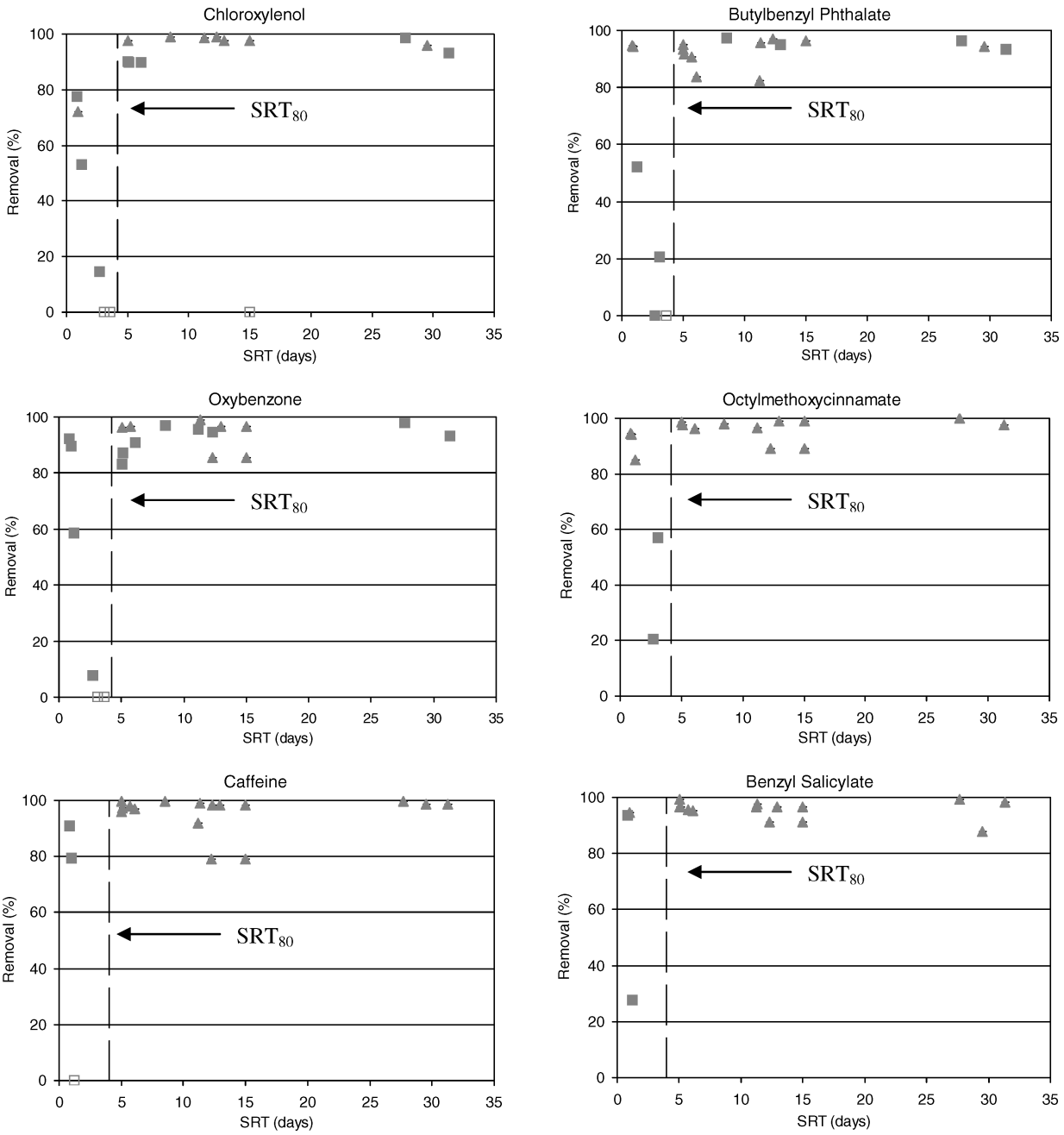


Figure 3—Percent removal in relation to SRT for excellent removal bin compounds (■ = actual removal, ▲ = removal greater than the percentage value presented, and □ = effluent concentration greater than influent concentration).

thickness (Restek Corporation, Bellefonte, Pennsylvania). The TIC masses were scanned from 70 to 350 m/z from 6 to 37 minutes. There were 5 selective ion response (SIR) segments, as follows:

(1) SIR 1 scans 150, 156, 164, and 178 m/z from 12.1 to 14.0 minutes;
(2) SIR 2 scans, 152, 163, 165, 182, and 190 m/z from 14.0 to 17.2 minutes;
(3) SIR 3 scans 194, 197, 206, 228, 243, and 249 m/z from 17.5 to 20.0 minutes;
(4) SIR 4 scans 178, 227, 279, and 290 m/z from 20.0 to 23.0 minutes; and
(5) SIR 5 scans 149, 206, and 326 m/z from 23.0 to 26.5 minutes.

Retention times and monitored ions for the target compounds are listed in Table 2.

The materials used to prepare the standards were obtained from the following suppliers. The phthalate standards were prepared using EPA 525 Update Phthalate Ester Mix obtained from Supelco (50 µg/mL). The internal standard 4,4-dibromooctafluorobiphenyl was obtained from Supelco also. Ethyl 3-phenylproprionate (98%),

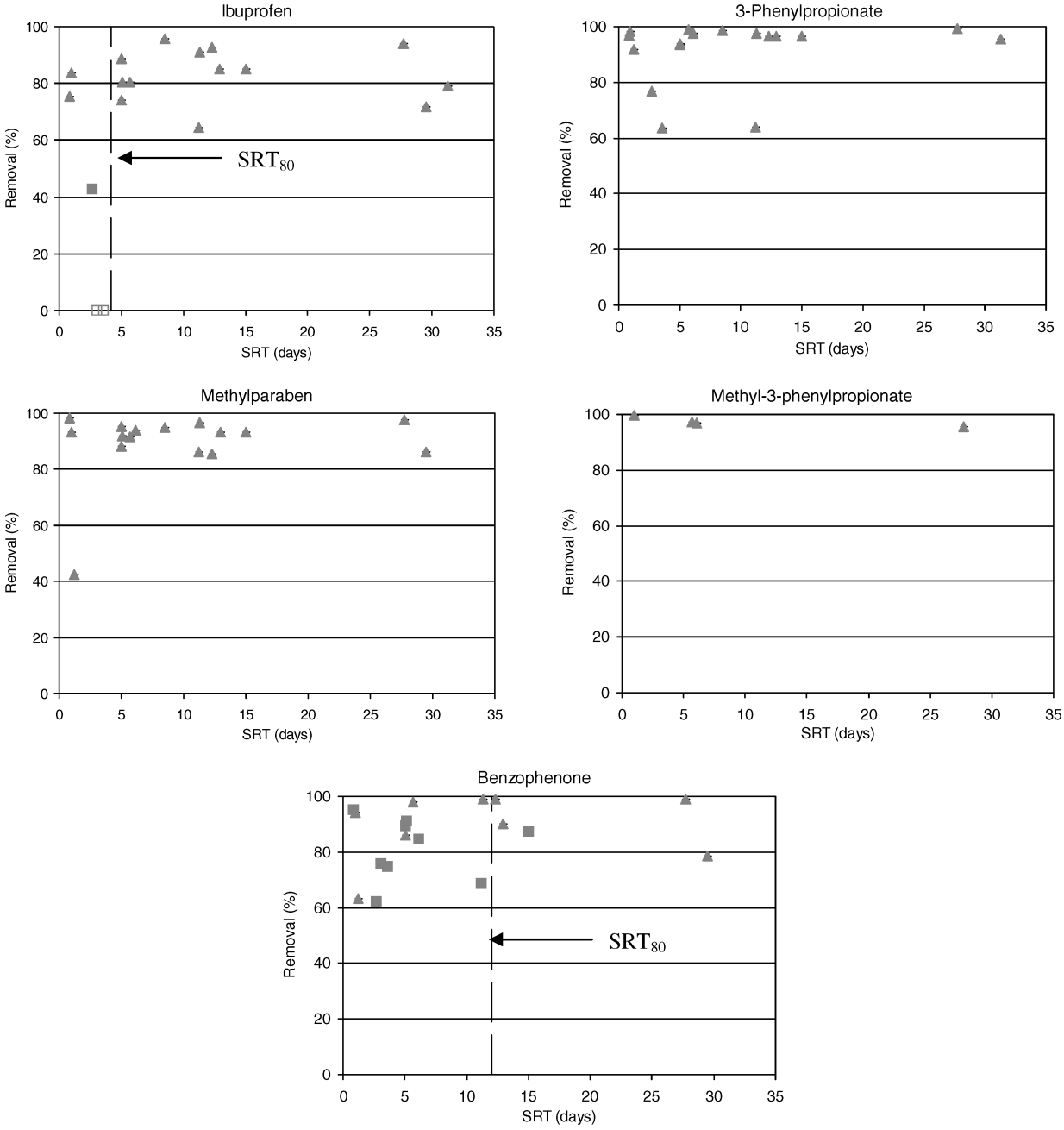


Figure 3—(Continued)

benzophenone (99%), caffeine (98.5%), benzyl salicylate (98%), tris (2-chloroethyl) phosphate (97%), butylated hydroxyanisole (96%), 3-phenylpropionate (99%), oxybenzone (98%), and octyl methoxy cinnamate (98%) were obtained from Acros (Allentown, Pennsylvania). Galaxolide (50% in diethyl phthalate), 4-octyl phenol (99%), musk ketone (98%), methylparaben (National Formulary/Food Chemicals Codes), and chloroxylenol (99%) were obtained from Sigma-Aldrich (St. Louis, Missouri). Methyl 3-phenylpropionate (98%) was obtained from Alfa Aesar (Wardhill, Massachusetts). Triclosan (irgasan 97%; Fluka, Ronkonkoma, New York), triphenyl phosphate (500 µg/mL; Protocol, Acros Organics, Morris Plains, New Jersey), ibuprofen (98%, Sigma-Aldrich, St. Louis, Missouri), and DEET (100 µg/mL; Ultrascientific, North Kingstown, Rhode Island) were also used. Radio-labeled surrogates; 2,4-dichlorophenol-ring D_3 (98%); bis(2-ethylhexyl)phthalate-ring-D_4 (98%); 3,3'-dichlorobenzidine-diphenyl-D_6 (98%); and caffeine-trimethyl-13C3, 99%) were obtained from Cambridge Isotope Laboratories (Andover, Massachusetts).

Calibration curves were prepared using four concentration levels spanning at least one order of magnitude. All calibration curves had a root mean square of at least 0.95. The calibration standards were prepared to cover the range of expected concentrations after extraction and concentration from 2000 mL to 0.5 mL. U.S. Environmental Protection Agency (Washington, D.C.) guidelines (U.S. EPA, 1993) were followed to obtain instrument detection limits (IDLs) and method detection limits (MDLs). The IDLs were

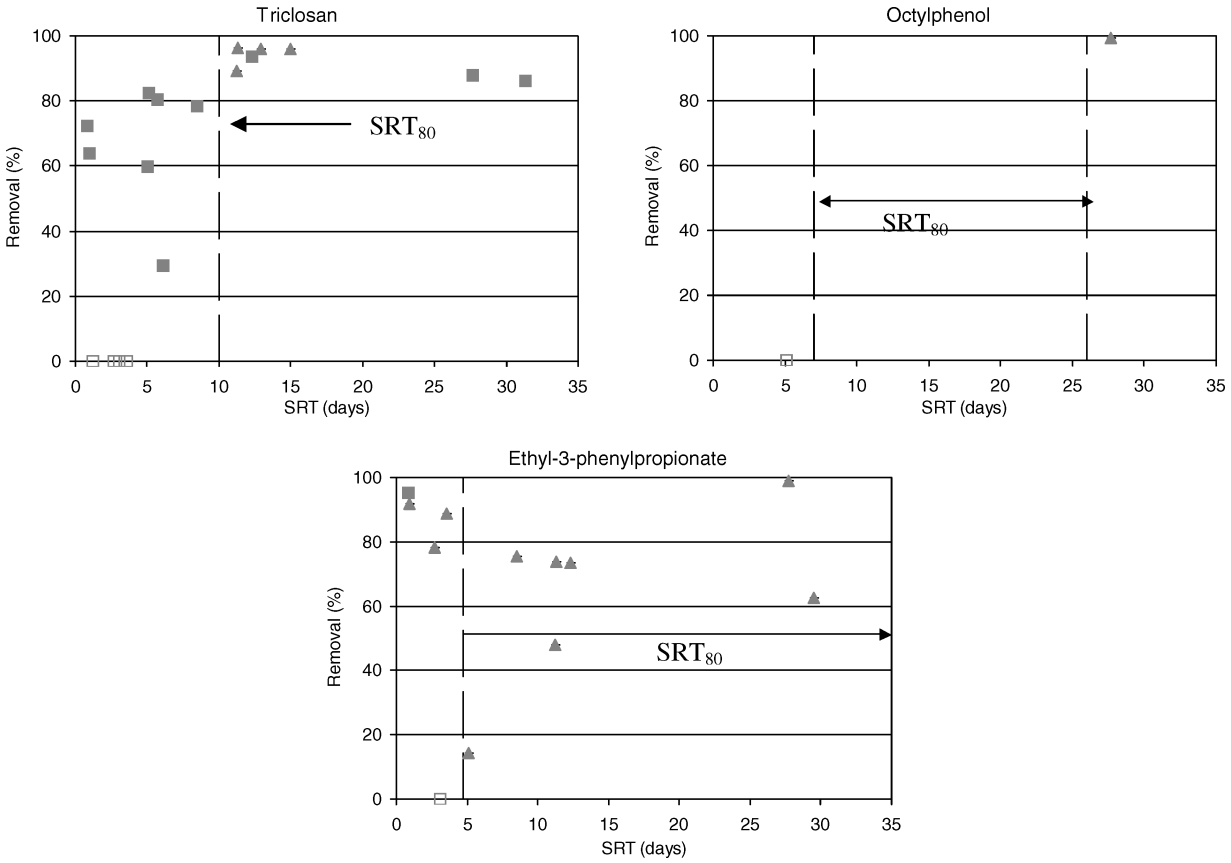


Figure 4—Percent removal in relation to SRT for moderate removal bin compounds (■ = actual removal, ▲ = removal greater than the percentage value presented, and □ = effluent concentration greater than influent concentration).

determined for pure compounds spiked in ethyl acetate. The MDLs were determined by spiking a stock solution containing the surrogates and a mixture of the analytes into aliquots of dual glass-fiber-filtered secondary effluent obtained from a U.S. East Coast treatment facility. A baseline aliquot, extracted and analyzed without the addition of the analytes, provided background concentrations of the target analytes. Table 2 also provides the spiked concentrations, baseline concentrations, calculated MDLs, and ratio of MDL to the initial concentrations. The initial concentrations consisted of the spiked concentration or the spiked concentration plus the baseline concentration whenever the baseline concentration was 20% or greater than its spiked concentration. Di(ethylhexyl)phthalate was dropped from the study because of high blank contamination from the SPE disks (Loraine and Pettigrove, 2002).

Results and Discussion

Occurrence Data and Secondary Treatment Performance. Cumulative probability plots of each target PPCP compound for the secondary influent samples were used to classify the compounds into three occurrence bins. Bin definitions, compound assignments, and 50th percentile values are provided in Table 3. Sixty percent of the compounds occurred frequently, 20% occurred sporadically, and the remaining 20% occurred infrequently. There was no correlation between frequency of occurrence and compound octanol-water partition coefficient (K_{ow}), an empirical measurement of organic chemical hydrophobicity.

On a few occasions, the effluent concentration was greater than the influent concentration, and this difference sometimes exceeded the relative percentage difference observed for the split samples. The reason this occurs is unknown, but may be the result of such factors as (1) the difference in analytical capabilities for the different matrices, or (2) desorption from the bioreactor solids. When this occurred, the percentage removal was considered to be zero. The definition of treatment performance classifications and assignment of compounds into bins on the basis of observed percentage removals are provided in Table 4. Fifty-five percent of the compounds were well removed, 15% were moderately removed, and 30% were poorly removed through secondary treatment. Treatment classification of compounds from the infrequent occurrence bin is limited by insufficient data, as they were seldom detected in the influent. Changes in the influent concentration of the investigated PPCPs with respect to influent flowrates were monitored, but did not seem to affect their removal performance. Also, as shown in Figure 2, no consistent correlation was observed between removal performance and K_{ow} values of the investigated compounds, which suggests that biodegradation was effective in reducing some low K_{ow} compounds not amenable to adsorption and that solids adsorption was not sufficient in completely removing some compounds with high K_{ow} values.

Critical Solids Retention Time Values. Full-scale activated sludge processes are inherently dynamic, because they experience variable conditions of loading and operation. As a result, the true SRT of such systems can be difficult to determine at a given time.

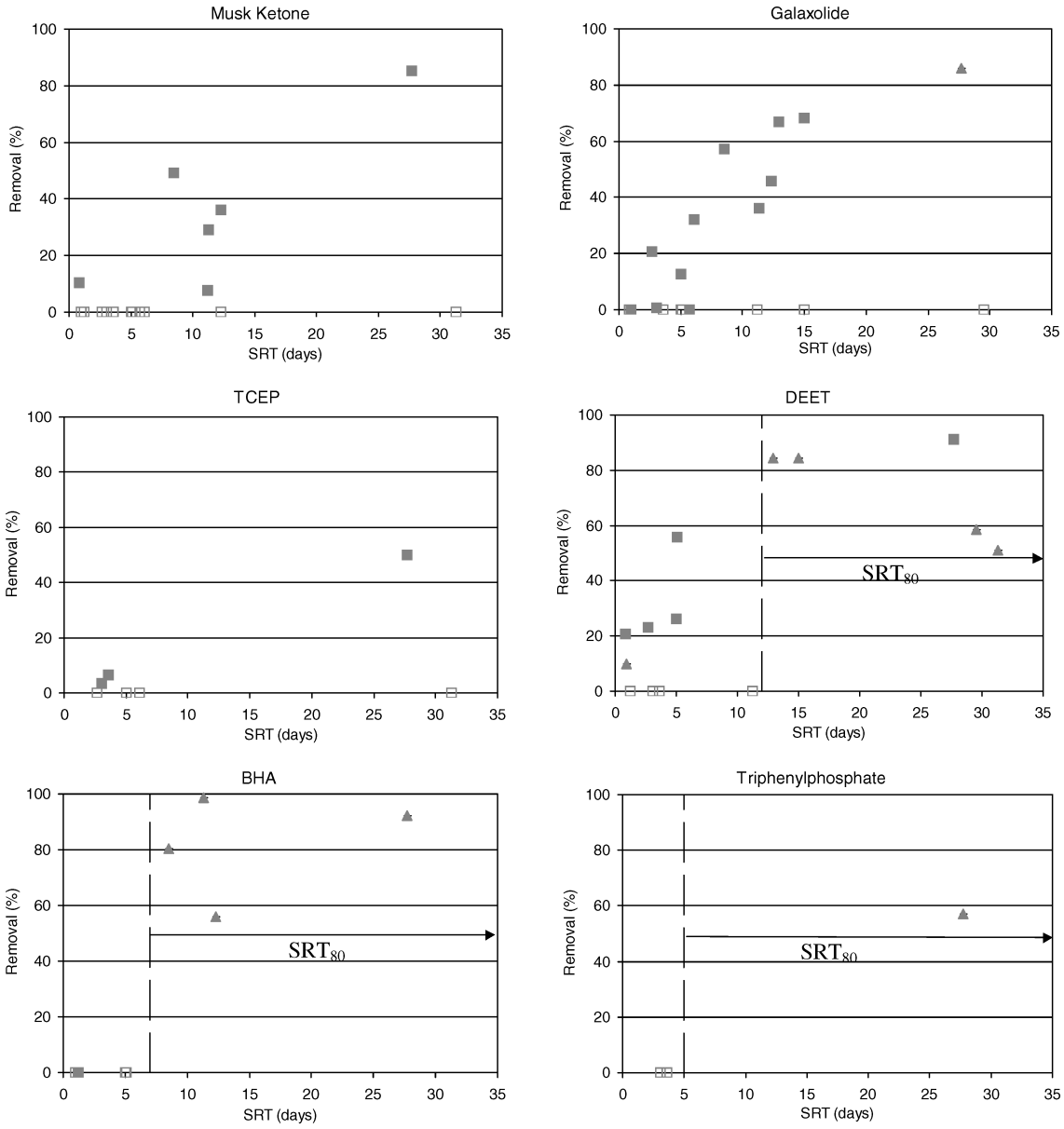


Figure 5—Percent removal in relation to SRT for poor removal bin compounds (■ = actual removal, ▲ = removal greater than the percentage value presented, and □ = effluent concentration greater than influent concentration).

The SRT values reported in this work were provided by the participant facilities and correspond to the daily SRT value calculated by the plant for the date of collection. For this reason, the degree of confidence of the reported SRTs is directly linked to the accuracy of the procedures used by the facilities to generate these values.

Plots of the percentage removal of each target compound versus the SRT of the secondary treatment process were used to define a critical SRT (SRT_{80}). The SRT_{80} represents the minimum SRT value needed to consistently achieve compound removal greater than 80%. For the 11 compounds categorized under the ''excellent removal'' bin classification (Figure 3), the SRT_{80} was <5 days, with the exception of benzophenone, with an SRT_{80} of 13 days. Only one of the three compounds categorized under the ''moderate removal'' bin classification (Figure 4) had sufficient occurrence data to enable determination of SRT_{80} values to be made. Triclosan required an SRT_{80} value of 10 days. The compounds in the ''poor removal'' bin classification (Figure 5) showed the most pronounced dependence on SRT. Musk ketone, galaxolide, and tris(2-chloroethyl)phosphate (TCEP) had SRT_{80} values in excess of 15 days. The wide variation in removal observed for these compounds at an SRT of 30 days could not be attributed to any apparent differences in plant operations. The good removals were all attained during an October 5 sampling event, and the poor removals were all attained during November 12 or January 9 sampling events (Figure 6). The plant daily effluent discharge temperatures for these dates do not support a seasonal influence on removal, because recorded temperatures were 25.8°C on October 5, 24.4°C on November 12, and 18.9°C on January 9. A mass-balance study is needed to assess whether longer SRT values can result in

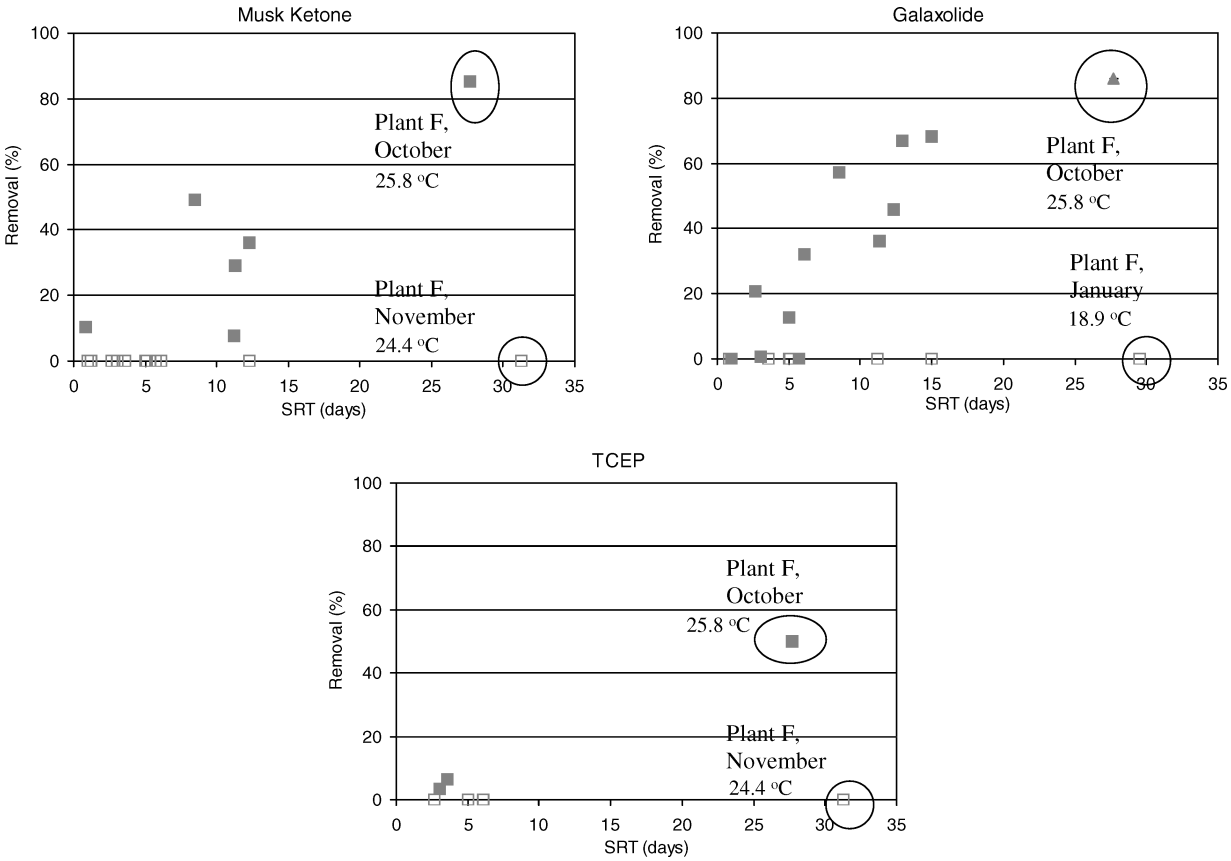


Figure 6—Seasonal variation in the removal of musk ketone, galaxolide, and TCEP in plant F (■ = actual removal, ▲ = removal greater than the percent value presented, and □ = effluent concentration greater than influent concentration).

desorption from the sludge. At the longer SRT values, the poor removals occurred when influent values were less than twice the MDL, and the good removals occurred when influent values were greater than five times the MDL. Desorption, if occurring, would be more noticeable at low influent conditions and would manifest as a lower percentage removal.

Membrane Bioreactors, Media Filtration, and Membrane Performance. The MBR#02 was run in parallel with the plant E activated sludge process using identical influent. Because of the high SRT values of the MBR and the plant (approximately 11 to 15 days), only the compounds with demonstrated SRT_{80} values in excess of 15 days would be expected to have sufficient levels remaining in the secondary effluent to allow a comparison of percentage removals. Of these compounds, only DEET and galaxolide were detected in the influent during one sampling event. Although the data are limited, the results demonstrate the comparability of performance, with 67% removal of galaxolide for plant E and 68% removal for the MBR. The DEET was reduced below the MDL for both plant E and the MBR. This supports the expectation that ultrafiltration MBR membranes cannot provide an additional benefit of removing PPCP compounds by sieving, as the PPCP molecules are more than 100 times smaller than the pore size of the membranes. These results support previous authors (Clara et al., 2005; Joss et al., 2005).

When PPCP compounds were still detected after secondary treatment, further treatment with media filtration was rarely effective in providing additional removal (Table 5).

In most cases, removal was less than 15%, and sometimes filter effluent values were greater than filter influent values. This may have occurred because the daily composite influent and effluent sample collection was not offset by the hydraulic retention time (HRT) of the filters or because of sloughing of the filter surface biofilm. Only 6 out of 30 observations demonstrated positive removals greater than 25%. These occurred as single events for chloroxylenol (>42%), methylparaben (>97%), DEET (26%), musk ketone (>55%), oxybenzone (>68%), and triclosan (67%). Approximately 50% of these positive removals occurred during the second sampling event for plant F, and the other 50% occurred for the first sampling event of plant D. Because the PPCP compounds were only measured in the aqueous phase of the filter influent and filter effluent samples, the demonstration that media filtration contributed little or no removal of these compounds is expected. Reverse osmosis treatment, however, was effective in removing any remaining aqueous phase compounds to less-than-detectable levels. Benzophenone showed low removal after reverse osmosis treatment, but this might be the result of trace contamination in the samples (traces of this compound were present in sampling blank).

Influence of Hydraulic Retention Time. For the majority of participating secondary processes, the HRT correlated well with the SRT (Figure 7). The exceptions occurred for plant E operated below capacity, for one sampling event at plant D during operation at above-average flow, and the two MBR systems. These four systems were operated under similar SRTs (11 to 15 days), but distinct HRTs (5 to 30 hours). Comparison of the two compounds with high

Table 5—Percent removal of PPCPs through tertiary filters and reverse osmosis.[a]

PPCP	Plant F filter (% removal)	Plant D filter (% removal)	Plant D reverse osmosis (% removal)
Chloroxylenol	−27[b]	<−147[c]	>59
	0	>42[d]	
	ND	ND	
Methylparaben	>97	ND	
	ND	ND	
	ND	ND	
DEET	26	−8	>48
	ND	ND	
	ND	ND	
Benzophenone	<−88	−12	41[e]
	ND	−23	>38
	ND	ND	
TCEP	12	ND	
	−17	−100	>65
	ND	ND	
Galaxolide	ND	8	>42
	ND	−37	>46
	−18	−51	>77
Musk ketone	12	−2	>43
	0	>55	
	ND	−20	>68
Oxybenzone	3	ND	
	0	>68	
	ND	ND	
Triclosan	67	ND	
	15	−27	>93
	ND	−74	>79
Butylbenzyl phthalate	−24	ND	
	>4	ND	
	ND	ND	

[a] Table only presents the compounds that were detected in the secondary effluent; ND = not detected, both in influent and effluent.
[b] Negative percent removal indicates that the filter effluent concentration is greater than the filter influent concentration.
[c] "<" indicates that the removal is smaller than the percentage value presented, because the influent concentration is below the MDL.
[d] ">" indicates that the removal is greater than the percentage value presented, because the effluent concentration is below the MDL.
[e] Low apparent removal, probably because of trace contamination in the sample blank.

SRT_{80} values that were detected in these plant influents (i.e., galaxolide and musk ketone) have insufficient data to be conclusive, but demonstrate little apparent effect of HRT alone on compound removal through secondary treatment (Figure 8).

Conclusions

Analysis of influent and effluent samples from six full-scale secondary treatment facilities and two pilot MBR reactors generated a database used to characterize 20 target PPCP compounds into nine categories of occurrence and ease of removal through treatment (Figure 9).

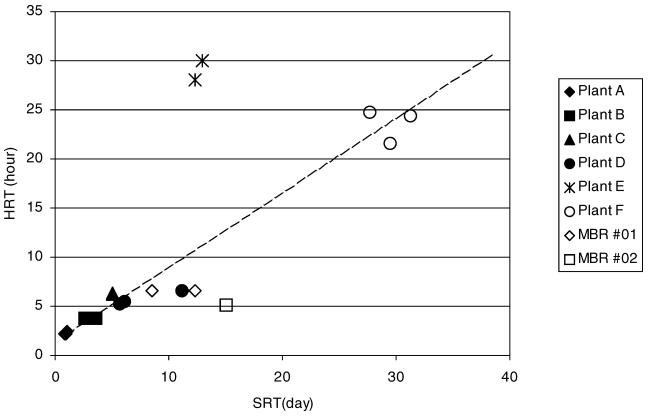


Figure 7—Correlation of HRT and SRT in the sampled secondary treatment systems.

The major conclusions of this study can be summarized as follows:

- 45% of the 20 PPCP target compounds showed frequent occurrence in secondary influent, but were also well removed (>80%) at a critical SRT_{80} of less than 5 days. These compounds were caffeine, ibuprofen, oxybenzone, chloroxylenol, methylparaben, benzyl salicylate, 3-phenylpropionate, butylbenzyl phthalate, and octylmethoxycinnamate.
- The most problematic compounds are those that occurred frequently, but demonstrated low removals, until a much higher critical SRT_{80} value was provided. Compounds that occurred frequently and required a critical SRT_{80} value greater than 15 days were the fragrances musk ketone and galaxolide. Triclosan and benzophenone, while also frequently detected, exhibited a lower critical SRT_{80} value in the vicinity of 10 to 15 days. Insufficient data were available to characterize the critical SRT_{80} for DEET and BHA, but it was in excess of 5 days.
- Better removal was not observed for a pilot MBR operated in parallel with a conventional activated sludge system or for an activated sludge system operated at longer HRTs. While little additional removal of target compounds was evident for media filters, reverse osmosis was effective in reducing any remaining target compounds below detection limits.
- Because there are no definitive action levels for the monitored PPCPs, design recommendations based on the findings of this study are not appropriate, at this point. However, the results suggest the potential benefit derived from designing and operating municipal WWTPs at higher SRTs with respect to the fate of these compounds.

Credits

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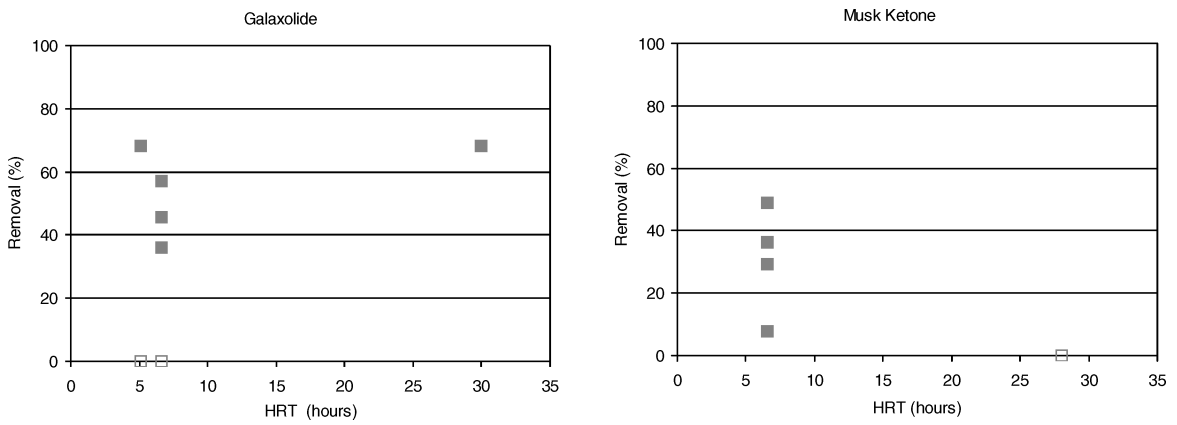

Figure 8—Influence of HRT on percent removal of galaxolide and musk ketone (SRT of 11 to 15 days).

David Sedlak, University of California (Berkeley). Gratitude is also extended to Shane Snyder (Southern Nevada Water Authority) and Rhodes Trussell (Trussell Technologies Inc., Pasadena, California) for their guidance and advice. We also acknowledge the PPCP analytical work provided at the laboratory of Greg Loraine, with Dynaflow Inc. (Jessup, Maryland). We are also indebted to the participating utilities for their support and assistance during this project and to Suvid Surendran of Montgomery Watson Harza (MWH, Pasadena, California) for sample collection.

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Treatment / Occurrence	Bin T1 Excellent removal	Bin T2 Moderate removal	Bin T3 Poor removal
Bin O1[a] Infrequent	Methyl-3-phenylpropionate	Octylphenol	TCEP Triphenylphosphate
Bin O2 Variable		Ethyl-3-phenylpropionate	**BHA** **DEET** **Musk ketone**
Bin O3 Frequent	Caffeine Ibuprofen Oxybenzone Chloroxylenol Methylparaben Benzyl Salicylate 3-Phenylpropionate Butylbenzyl Phthalate Octylmethoxycinnamate	**Triclosan** **Benzophenone[b]**	**Galaxolide**

[a]Treatment classification of compounds in this bin is limited by insufficient data, as they were seldom detected in the influent.
[b]Although benzophenone classified as bin TI based on median removal >80%, it was moved to bin T2, because it required a much higher SRT_{80} than the other bin T1 compounds.

Figure 9—Distribution of target PPCP compounds into occurrence and treatment performance bins.

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