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Environmental Fate and Transport of Microconstituents

San Jose, Calif., takes a preliminary look at how well conventional wastewater treatment removes emerging contaminants

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Recently, there has been significant media attention on the environmental fate, transport, and effects of a broad class of compounds referred to as "microconstituents" or "emerging contaminants." These compounds include personal care products, pharmaceuticals, steroids, hormones, and trace organics, such as polybrominated diphenyl ethers (PBDEs). Much of the media focus has been on the presence of these compounds in drinking water. However, as a water utility, wastewater treatment plants (WWTPs) receive a mass of some of these anthropogenic compounds. Amid increasing public concern, wastewater managers and professionals will need quantitative information to answer questions from the public and media regarding the magnitude of such loads and potential treatment efficiencies. Quantitative information also can be used to determine how best to focus future pollution prevention and source control actions.

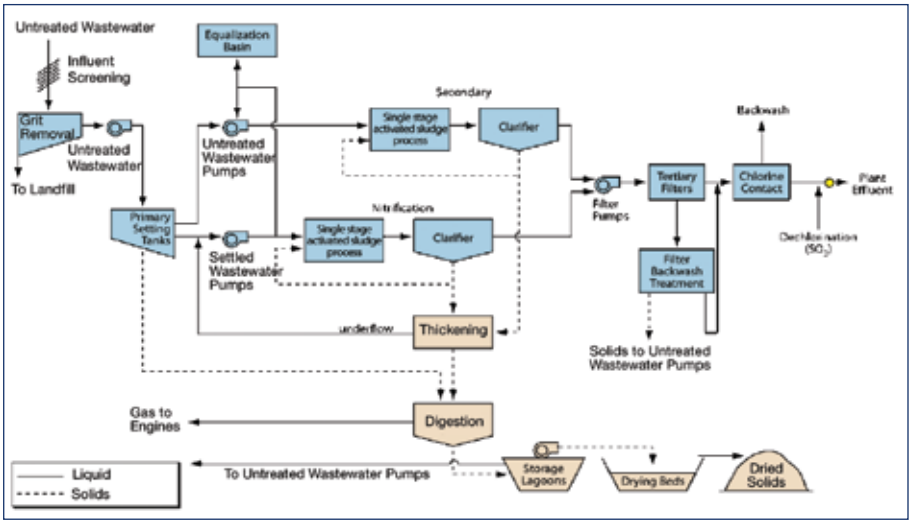
The pathways, loadings, effects, and persistence of these compounds in the environment are poorly understood. A critical first step to understanding the potential for environmental impacts of these compounds is to characterize and begin to quantify potential sources and pathways. One pathway some of these compounds travel into environmental media is through WWTPs. While surveys for some of these compounds have been conducted at WWTPs, facility design, capacity, treatment technology, treatment level, and influent concentration could result in significant variation of environmental loadings. Understanding what happens to emerging contaminants as they pass through or are broken down in WWTPs will help us understand how they may be treated in the future.

One Plant's Findings

The San Jose/Santa Clara (Calif.) Water Pollution Control Plant is a large-capacity advanced wastewater treatment plant that discharges tertiary treated fresh water to south San Francisco Bay. The plant has a capacity of 632,000 m^3/d (167 mgd) and an average dry weather effluent flow of 379,000 m^3/d (100 mgd). The plant may receive large quantities of microconstituents due to its size, with more than 1.4 million residential and commercial customers in a heavily urbanized service area, and average dry season influent flow of 424,000 m^3/d (112 mgd). However, the plant may also remove large quantities of some particle-bound compounds through its high level of treatment. Previous studies on the fate of other compounds, such as various species of mercury, at the plant indicate that particle-bound pollutants are reduced by up to 99%, and dissolved fractions are reduced as much as 50%.

The plant uses several treatment steps to remove particles and pollutants. The plant's treatment process initially consists of screening, grit removal, and primary sedimentation. The secondary treatment step consists of a single-stage activated sludge process that performs carbonaceous removal, nitrification, and denitrification. This is then followed by secondary clarification, filtration, disinfection, and dechlorination. The overall process includes feedback loops and diversions, resulting in a homogenized product as the treatment process progresses (see figure, p. 44). As a result, grab samples taken at various process points generally have no temporal correspondence. In addition, the plant diverts approximately 10% of its influent flow for water

Simplified Diagram of the San Jose/Santa Clara Treatment Plant Process



recycling and reuse, resulting in a lower volume of effluent discharged to San Francisco Bay than influent.

Methodology

City of San Jose staff collected grab samples for untreated wastewater influent, final effluent, and digested solids using the clean hands/dirty hands sampling protocol. Aqueous samples were collected into precleaned 1-L amber glass bottles, while solids samples were collected into either precleaned 250-mL amber glass jars or precleaned 1-L amber glass bottles. The analytical laboratory cleaned and supplied all sample bottles and jars. Sampling occurred on four separate days between 9 a.m. and 11:30 a.m., which is 1 to 3.5 hours prior to typical daily peak influent flow. Within 15 minutes of collecting the final sample for each event, all samples, shipping containers, and packing materials were transferred to a 4°C walk-in refrigerator. All samples were placed in a water bath inside the refrigerator to accelerate cooling. After approximately 24 hours inside the refrigerator, all samples were packed securely into hard-sided plastic coolers with frozen blue ice. Samples and all appropriate customs documents, chains of custody, and other documentation were shipped via FedEx priority delivery to the laboratory.

Samples were analyzed by the laboratory for PBDEs, pharmaceuticals and personal care products, steroids and hormones, multiresidual pesticides, and PCBs. U.S. Environmental Protection Agency (EPA) analytical methods were used to achieve trace-level quantification. Results for PCBs and PBDEs were reported as individual congener concentrations. All 209 congeners were reported for PCBs, and 46 congeners were reported for PBDEs. A sum of 54 PCBs congeners was used to calculate a mass balance for total PCBs in this study. The sum of all 46 reported PBDE congeners was used for PBDE mass balance calculations.

For compounds with a sufficient number of quantified concentrations at more than one sampling point, staff calculated a preliminary removal efficiency and mass balance estimate. Nondetected compounds and estimated (J-flagged) data were not used in these calculations. Mass estimates are based on average daily dry weather influent (424,000 m^3/d [112 mgd]) and effluent (379,000 m^3/d [100 mgd]) flows and average daily flow from the biosolids digesters (3330 m^3/d [0.88 mgd]). The mass balance calculations assume 2% solids for digested solids, which is the average at the plant.

Quality assurance and control. Staff collected field blanks and field duplicates that were analyzed blind by the laboratory to determine the level of sampling contamination and reproducibility of analytical results. All data presented in this report had field blank concentrations that were less than a third of the calculated mean concentration of the compound in aqueous matrices. Duplicate samples for solids had greater variability than aqueous duplicates. This is indicative of the variability and general heterogeneity of biosolids grab samples and matrix interferences often encountered when performing chemical analyses on this matrix. All reported data passed through a rigorous quality check by the laboratory. Data not meeting their nonqualified acceptance criteria

Further Reading

City of San Jose (Calif.) Environmental Services Department (2009). *Clean Bay Strategy Report: 2008 Annual Pollution Prevention Report*.

Downing, James, Eric Dunlavey, Noel Enoki, Peter Schafer, and David Tucker (2008). "Fate and Transport of Mercury in a Large Advanced Wastewater Treatment Plant," *Proceedings* of the 81st Water Environment Federation Technical Exhibition and Conference (October), pp. 339–358. Alexandria, Va.: Water Environment Federation.

Stephenson, Roger, and Joan Oppenheimer (2007). *Fate of Pharmaceuticals and Personal Care Products Through Municipal Wastewater Treatment Processes*. Alexandria, Va.: Water Environment Research Foundation.

Table 1. Influent (RS) and Effluent (FE) Concentrations, Removal Efficiency, and Mass Balance Estimate for Constituents Removed With Solids

Constituent	RS (ng/L)	RS mass (kg/d)	Solids mass (kg/d)	FE conc. (ng/L)	FE mass (kg/d)	% to solids	% reduced in FE
Total PBDE	354	0.15	0.17	15.2	0.006	115%	96%
Triclosan	2210	0.94	0.95	83.5	0.03	101%	97%
Total PCBs	8.9	0.004	0.006	0.19	0.00007	158%	98%
beta-Stigmastanol	22,450	9.5	11.91	73.2	0.03	125%	99%
Cholestanol	36,800	15.6	43.9	484	0.18	281%	99%
4,4'-DDE	2.8	0.001	0.002	0.16	0.00006	152%	95%
Epicoprostanol	14,300	6.06	57.6	88	0.03	951%	99%
Ciproflaxin	652	0.28	0.91	95	0.036	331%	87%
Chlordane, gamma (trans)	3.05	0.0013	0.0028	0.36	0.0001	216%	90%

PBDE = polybrominated diphenyl ether.

were either reported as not quantified or flagged as estimates with appropriate qualifiers.

Results

In all, 166 constituents were measured in this study using the five separate analytical methods. Of these constituents, 71 were not detected in any samples, and 95 were detected in at least some samples. Only 53 of the 95 detected compounds were measured at quantifiable levels in enough samples to allow for removal efficiency and overall mass balance estimations. The remaining 42 detected compounds were not quantified in the majority of the samples. Very few compounds had quantified concentrations in all samples of all process points, adding uncertainty to any mass balance calculations. However, there were sufficient quantifications in untreated wastewater influent samples to begin to characterize influent loads and possible removal efficiencies even if samples from farther down the treatment chain were nondetectable or not quantified. This is true for the majority of the 53 quantified constituents.

Removal with solids. The most common pathway of pollutant reduction in conventional wastewater treatment is through solids removal. Compounds that have a high affinity to particles are removed with solids. These can then be broken down further through additional treatment in digesters or degrade during dewatering. While many of these compounds appear to be efficiently removed via solids separation, the mass balance can be grossly inaccurate, with the estimated mass in solids greatly exceeding that estimated in influent. Some of the extreme examples of this are epicoprostanol, cholestanol, and ciproflaxin (see Table 1, above). Similar solids-related removal efficiencies were measured for tetracycline; desmosterol; nonachlor, cis-; nonachlor, trans-; and chlordane, alpha (cis).

Removal through other treatment or degradation. In addition to pollutant removal with solids, the plant employs biological and chemical treatments that may degrade, transform, or remove constituents. Based on these data, these are the compounds that show reductions from influent to

Table 2. Influent (RS) and Effluent (FE) Concentrations, Removal Efficiency, and Mass Balance Estimate for Constituents Reduced Through Treatment or Degradation

Constituent	RS (ng/L)	RS mass (kg/d)	Solids mass (kg/d)	FE (ng/L)	FE Mass (kg/d)	% to solids	% reduced in FE
Ibuprofen	14,533	6.2	0.16	19.4	0.007	2.6%	99%
Gemfibrozil	3517	1.5	0.04	65.1	0.02	2.4%	98%
Naproxen	10,617	4.5	0.006	41.4	0.02	0.1%	99%
Caffeine	59,867	25.4	0.02	27.1	0.01	0.1%	99%
Cholesterol	1,315,000	557	82	1286	0.49	15%	99%
Estrone	89	0.04	0.009	12.2	0.005	23%	88%
Campestorol	73,750	31.3	16.4	307	0.12	52%	99%
Clarithromycin	373	0.16	0.002	34.4	0.01	1.2%	92%
Ranitidine	1136	0.48	0.001	39.2	0.01	0.22%	97%
Permethrin	175	0.07	0.026	1.2	0.0005	35%	99%
Cypermethrin	19	0.008	0.003	ND	ND	42%	100%

ND = nondetectable.

Table 3. Removal Efficiency and Mass Balance Estimate for Conservative Constituents

Constituent	RS (ng/L)	RS mass (kg/d)	Solids mass (kg/d)	FE (ng/L)	FE mass (kg/d)	% to solids	% reduced in FE
Simazine	8.5	0.004	0	13	0.005	0%	Increase
Azithromycin	851	0.36	0.07	414	0.16	20%	57%
Carbamezepine	323	0.14	0.011	304	0.12	8.1%	16%
Triclocarban	399	0.17	0.69	145	0.05	409%	68%
Fluoxitine	21.5	0.009	0.032	28	0.01	353%	Increase
Oflaxacin	305	0.13	0.33	109	0.04	254%	68%
Albuterol	14	0.006	0	9	0.003	0%	43%
Erythromycin-H2O	243	0.1	0.002	169	0.06	2.2%	38%
Lincomycin	19.4	0.008	0	15.3	0.006	0%	30%
Thiabendazole	37	0.016	0.006	70	0.026	37%	Increase

RS = influent.
FE = effluent.

effluent, but very little, if any, mass is recovered in the solids (see Table 2, p. 45). Removal efficiencies can be very high (often greater than 90%), but without focused, process-specific sampling, the exact removal mechanism can only be hypothesized.

Apparent removal through treatment other than solids removal was the most common group of quantified constituents. In addition to those presented in Table 2, the other quantified constituents that displayed this removal pattern were coprostanol; cimetidine; beta-sitosterol; codeine; cotinine; diltiazem; diphenhydramine; metformin; sulfadiazine; sulfamethoxazole; trimethoprim; stigmasterol; permethrin, cis-; permethrin, trans-; and perthane.

Conservative constituents. Finally, some compounds show poor (less than 75%) or no reductions when comparing influent and effluent concentrations. These constituents are conservative through the wastewater stream to varying degrees. The pass through the plant neither degraded nor removed them with solids (See Table 3, above).

Plant Performance

Overall, the plant appears to remove most microconstituents measured in this study very well, with 43 of the 53 quantifiable compounds removed at greater than 75% efficiency. Some, such as the pesticides perthane and nonachlor, were not detected in effluent samples at all. It appears that while solids removal does account for efficient removal of some microconstituents, more than 60% of the compounds that are reduced efficiently occur as a result of biological treatment, chemical treatment, or another degradation process.

Only 10 measured compounds were removed at less than 75% efficiency. Of the 10 compounds, three also had very poor mass balance, with a much greater mass measured in biosolids than in plant influent. Triclocarban, fluoxitine, and oflaxacin all showed this unusual trend. Simazine, carbamezapine, erythromycin-H2O, lincomycin, albuterol, and thiabendazole do not appear to be removed efficiently at the plant from a mass balance perspective. However, the concentration and estimated mass of many of these compounds (simazine, albuterol, and lincomycin) in plant effluent is small, and all measurements were near the quantification limit. Finally, although triclocarban, azithromycin, and oflaxacin are removed at less than 75% efficiency when comparing effluent loads to influent loads, they still display reasonable removal (57%–68%). This is especially true considering the anomalously high mass of triclocarban and oflaxacin measured in biosolids.

While a mass balance estimation is presented here, these estimates are preliminary and not based on a large data set needed to accurately calculate mass loadings and mass balance. However, the data are useful for focusing future microconstituent sampling efforts at the San Jose/Santa Clara Water Pollution Control Plant or other similarly designed WWTPs servicing urban areas. These data are a critical first step in understanding and prioritizing compounds for future study. Ambient environmental monitoring and additional sampling of intermediate treatment steps are two areas in which these data could be useful for focusing and economizing future sampling and analysis of microconstituents. Additional plant sampling would be particularly useful for determining which process steps account for concentration reductions that are not due to solids removal. These data also can be used to prioritize pollution prevention and source control efforts in the plant's service area.

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