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## PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN MUNICIPAL WASTEWATER

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### INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) are considered an emerging issue in municipal wastewater treatment in both Europe and North America (Ternes 2004; Daughton 2004). Pharmaceuticals such as analgesics, blood lipid regulators, antidepressants, and antiepileptics are designed to have specific biological effects on humans and animals at certain doses; antibiotics are used to combat a wide variety of bacterial infections. Their main route to wastewater is through use in private households, followed by excretion or disposal (Daughton and Ternes, 1999). Personal care products containing fragrances, antimicrobials, and many other ingredients are used to enhance personal and household appearance and odour; they are not intended to cause any biochemical effects (Reiner and Kannan 2006). Personal care products enter wastewater after personal and household washing (Salvito et al 2004).

Once in wastewater PPCPs may be removed during the treatment process, remain unchanged in the effluent, or partition to the solids (sludge). Their principal route into the environment is through effluent discharges and the land application of biosolids (Eschke 2004; Xia et al 2005). PPCPs have been recognized as a potential problem in the environment for several years, but until recently the problem could not be quantified due to lack of analytical methods. In the last ten years there has been a great deal of activity in this area and methods have been reported for a wide variety of PPCPs (Miao et al 2004; Hao et al 2006; Lee et al 2003a,b). To date, there has been no coordinated effort in the analytical chemistry community to standardize these methods, nor is there regulatory pressure to monitor for PPCPs in wastewater effluents or biosolids.

Some PPCPs are ubiquitous and persistent in the environment. Others may be considered "pseudopersistent": they dissipate readily, but since they are

continually discharged the receiving environment is continually exposed to them (Daughton and Ternes 1999). There is a growing body of literature examining the effects of various PPCPs on aquatic biota. Results to date indicate that some compounds may have detrimental effects on some organisms, such as endocrine disruption or inhibition of the organism's ability to excrete xenobiotics (Servos et al 2005; Luckenbach and Epel 2005; Veldhoen et al 2006). One recurring concern with antibiotics in the environment is the potential for development of bacterial resistance to antibiotics, thus jeopardizing their effectiveness for therapeutic use (Balakrishnan et al 2006).

In 2002 Environment Canada, the Ontario Ministry of Environment (MOE), and the City of Toronto embarked on a large-scale collaborative wastewater research study to generate information for development of risk management strategies to control the release of PPCPs into the Canadian environment. This study included several facets: development of analytical methods to detect PPCPs in wastewater and sludge; surveys of PPCPs in treatment plant influents, effluents, and sludges; comparison of conventional activated sludge (CAS) and innovative wastewater treatment processes for PPCP removal from wastewater; and controlled bench-scale studies. As of 2006 experimental work has been completed and data analysis is in progress. This paper is intended to provide an overview of the scope and results of each facet in this collaborative research study to municipal wastewater managers, consultants, and other members of the wastewater industry. Details of each portion of the study have been reported previously (Lishman et al 2006; Smyth et al 2007a-d). The bibliography includes Canadian research activity on methods for PPCP analysis, measurement of PPCPs in wastewater and surface water, effects of selected PPCPs on aquatic organisms, and knowledge to date on treatment plant characteristics as they relate to PPCP removal.

## **ANALYTICAL METHOD DEVELOPMENT**

Robust, reproducible analytical methods are a necessary prerequisite for quantification of PPCPs in environment samples, and assessment of the effectiveness of alternative removal technologies. Sewage, sludge, and biosolids have proven to be very challenging matrices for detection of PPCPs due to the many types and quantities of other components, some of which interfere with detection of the analyte of interest. Liquid samples are extracted using solid phase extraction cartridges or classic liquid-liquid techniques. Sludge samples are extracted using accelerated solvent extraction (ASE), microwave-assisted extraction (MAE), or classic Soxhlet techniques. Extracts always need a clean-up step to remove unwanted compounds. Instrumental analysis can be by gas chromatography/mass spectrometry (GC-MS) or liquid chromatography/tandem mass spectrometry (LC-MS/MS) depending on the analyte characteristics and the preference of the laboratory. Confirmation of the analytical procedure is done by spiking a "surrogate" compound into the sample before extraction: the surrogate

is chosen to have very similar molecular characteristics to the analyte of interest. Ideally the surrogate is a radio-labeled version of the analyte: the same molecule with either a deuterium atom in place of a hydrogen atom or a carbon-13 isotope in place of the normal carbon-12. When this project commenced there were very few labeled surrogates available in the analytical market; however a wider variety of surrogates are now available which will aid analytical chemists in confirming their methods.

Table 1 lists the PPCP analytes for which methods were developed during this study. Methods for the anti-epileptic Carbamazepine, cholesterol-lowering statin drugs, and additional antibiotics have been developed by Dr. Chris Metcalfe's group at Trent University.

TABLE 1: PHARMACEUTICAL AND PERSONAL CARE PRODUCT ANALYTES IN EC/MOE STUDY

Acidic and Neutral Drugs in Wastewater (Lee et al, 2003b, Hao et al, 2006)	Antibiotics in Wastewater (Hao et al, 2006)	Musk Fragrances in Wastewater and Sludge (Lee et al, 2003a, Svoboda et al, 2007, Smyth et al, 2007a)	
Acetaminophen	Carbadox	Cashmeran	Polycyclic
Bezafibrate	Chloramphenicol	Celestolide	
Carbamazepine	Chlortetracycline	Phantolide	
Clofibric Acid	Doxycycline	Traseolide	
Diclofenac	Erythromycin	Galaxolide	
Fenofibrate	Lincomycin	Tonalide	Nitro
Fenoprofen	Meclocycline	Musk Ambrette	
Gemfibrozil	Monensin	Musk Xylene	
Ibuprofen	Oxytetracycline	Musk Moskene	
Indomethacin	Roxithromycin	Musk Tibetene	
Ketoprofen	Sulfachloropyridazine	Musk Ketone	
Naproxen	Sulfadimethoxine		
Salicylic Acid	Sulfamerazine		
	Sulfamethazine		
	Sulfathiazole		
Antimicrobial in Wastewater (Lee et al, 2003b)	Tetracycline		
	Trimethoprim		
	Tylosin		
Triclosan	Virginiamycin		

## FIELD SAMPLING METHODS

All samples for the field studies were collected in the same manner. Bulk composite sewage samples were collected into stainless steel 20L cans which had been cleaned with Contrad 70 detergent (Decon Laboratories Inc., Bryn Mawr,

PA), followed by multiple rinses with tap water, then 3 rinses with deionized water and 3 rinses with methanol (Caledon Laboratories, Georgetown, ON). Sample collection tubing was lined with Teflon, with the exception of about 1 m of silicone pump tubing. The intake strainers were stainless steel. The Sigma 900 refrigerated autosamplers (American Sigma, Loveland, CO) maintained the sample temperature at approximately 4°C over the 24-hour sampling period; actual sample temperatures were measured and recorded at the end of each sampling period. The autosamplers were programmed to collect 350 mL of sample every 30 minutes over the 24-hour period, with one rinse of the intake tubing before sample collection. Each sampling event consisted of three 24-hour composite wastewater samples. The process temperature of the wastewater at each sampling point was recorded each sampling day.

Grab samples of sludge and biosolids were collected into stainless steel 20 L cans which had been cleaned as described above. The sludge pumping lines were flushed for varying periods of time, depending on how recently the operators had used the pumps, before samples were collected.

All samples were transported on ice. Wastewater samples were subdivided the same day and delivered to the laboratory. Sludge samples were stored at 4°C overnight while the total solids determination was completed, then subdivided and delivered. Precleaned amber glass jars with Teflon-lined lids were purchased from Systems Plus, Baden, ON. Wastewater samples were analyzed for conventional parameters including pH, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total Suspended Solids (TSS), alkalinity, Total Kjeldahl Nitrogen (TKN), ammonia, and nitrate to provide a context for observations on PPCP concentrations.

## THAMES RIVER SURVEY

The goals of this survey were to expand the Canadian database of municipal wastewater influent and effluent concentrations for selected PPCPs, and to determine if three treatment configurations (lagoons, CAS, and CAS plus filtration) affected the concentrations of PPCPs during the wastewater treatment process. Selected PPCPs included ten acidic pharmaceuticals, triclosan, and six polycyclic musks.

The influent and effluent at 12 wastewater treatment plants (WWTPs) discharging into the Thames River were sampled for 3 consecutive days in the fall of 2002. The organic strength and nitrogen content of the influents were weak to medium strength, except for one lagoon and one CAS+filtration plant which received higher strength influent. All plants produced effluent that met or exceeded the Typical Performance Criteria of 25 mg/L BOD and 25 mg/L TSS for mechanical plants and 30 mg/L BOD and 40 mg/L TSS for lagoons. No process upsets were noted during the sampling periods.

The most frequently detected acidic pharmaceuticals in the influents were ibuprofen, gemfibrozil, naproxen, and diclofenac, with median concentrations of 13 700 ng/L, 450 ng/L, 5600 ng/L, and 200 ng/L respectively. Clofibric acid, fenoprofen, and fenofibrate were not detected in any influent samples. Reduction of ibuprofen and naproxen from influent to effluent was consistently high (89 to 99%), while reduction of ketoprofen, diclofenac, and indomethacin was lower and highly variable. Lagoon systems showed the best reduction performance. Triclosan was detected in all influent samples with a median concentration of 1900 ng/L. Reduction from influent to effluent ranged from 74 to 95%; lagoon effluents did not contain any detectable triclosan. The polycyclic musks Galaxolide and Tonalide were detected in all influents, with median concentrations of 5200 ng/L and 2000 ng/L respectively. Reduction from influent to effluent ranged from 0 to 70% for CAS and CAS+filtration WWTPS, while reduction in lagoons was consistently above 90%.

These data demonstrated that there are detectable levels of PPCPs entering Canadian receiving waters in WWTP effluents, and that only some of these compounds are reduced during the wastewater treatment process. Complete results are reported in Lishman et al (2006).

## INTERSTAGE STUDY

The purpose of the interstage study was to investigate the occurrence and fate of eleven (six polycyclic and five nitro) synthetic musk fragrances in raw influent, primary effluent, primary sludge, secondary effluent, and waste activated sludge (WAS) in a CAS plant. Eight sampling events were completed between August 2003 and April 2005. Raw influent, primary effluent, secondary effluent, primary sludge, and waste activated sludge (WAS) concentrations were correlated to seasonal process temperatures. The treatment schematic and sampling points are illustrated in Figure 1. Complete results are reported in Smyth et al (2007d).

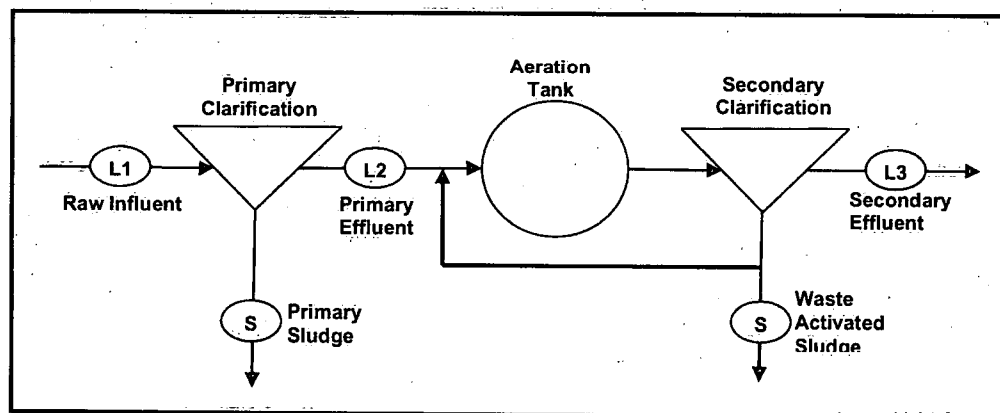


FIGURE 1: PROCESS DIAGRAM AND SAMPLING POINTS FOR THE INTERSTAGE STUDY ON THE OCCURRENCE AND REMOVAL OF SYNTHETIC MUSKS IN WASTEWATER TREATMENT

The plant was receiving medium to high strength wastewater with about 60% residential and 40% industrial/commercial/institutional content. The treatment process was achieving typical removals of COD (90%), BOD (95%) and TSS (91%), and achieving some nitrification. Process temperatures were divided into two ranges for data analysis: Warm (mean 22°C) and Cold (mean 15°C). Concentrations of conventional parameters and removals of COD, BOD, and TSS were generally the same during the warm and cold sampling periods. Some exceptions were noted: raw influent TSS and BOD concentrations were somewhat higher and TSS removal during primary clarification was higher in the warm sampling periods than in the cold sampling periods, and the percentage of nitrified effluent was slightly higher in the cold sampling periods than in the warm sampling periods. Median values for mixed liquor suspended solids (MLSS) were 1900 mg/L in the warm sampling periods and 2020 mg/L in the cold sampling periods. Median hydraulic retention time (HRT) in the aeration tank was 9 hours at both temperature ranges. Solids retention time (SRT) for each sampling event was estimated using measured values for COD removal, mixed liquor volatile suspended solids, and aeration tank HRT, and tabulated values of 0.45 g VSS/g COD and 0.05 d<sup>-1</sup> for the yield and decay coefficients respectively. This estimation exercise showed that the median SRT in the aeration tank was 7.5 days at both temperature ranges.

Maximum influent concentrations of polycyclic and nitro musks were 7030 ± 2120 ng/L for Galaxolide and 158 ± 89 ng/L for Musk Ketone. Influent musk concentrations were not correlated with temperature. Maximum secondary effluent concentrations were 2000 ± 686 ng/L for Galaxolide and 51 ± 14 ng/L for Musk Ketone. Temperature appeared to influence the degree of removal of musks from wastewater during primary treatment: a median musk removal of 40% was observed at warm temperatures, while a median removal of only 9% was observed at cold temperatures. This temperature influence extended to overall treatment: a median musk removal of 82% at warm temperatures and 74% at cold temperatures. The removal of musks during secondary treatment did not appear to be influenced by process temperature: median removal was 71% at warm temperatures and 70% at cold temperatures. These results indicate that WWTPs who employ only primary treatment may be achieving minimal removal of musks at colder temperatures. Primary treatment plants which use chemical addition to enhance solids removal may achieve better musk removal than the primary treatment stage of this CAS plant; further study may be warranted.

Polycyclic musks were found in primary sludge at concentrations up to 35000 ng/g dry weight (dw) for Galaxolide and nitro musks up to 490 ng/g dw for Musk Ketone, and in waste activated sludge at concentrations up to 52 000 ng/g dw for Galaxolide, and up to 1100 ng/g dw for Musk Ketone. Keeping in mind the augmentation of musk concentrations in WAS due to sludge recycling, the longer HRT and higher suspended solids in the aeration tank appeared to be correlated with a higher degree of partitioning of musks to sludge. The results of this study corroborate earlier work in Europe, which indicated that volatilization

and biodegradation of musks is minimal in wastewater treatment; musks are removed from the liquid phase by partitioning to the solids phase of wastewater (Artola-Garicano et al, 2003). Therefore optimization of solids separation may be one strategy for minimizing discharges of musks to the environment in wastewater effluents.

## GRAND RIVER SURVEY

The Grand River survey measured eleven (six polycyclic and five nitro) synthetic musk fragrance compounds in influent, effluent, raw sludge, and biosolids, from six WWTPs over four seasons from Fall 2003 to Summer 2004. Plant types included lagoon, oxidation ditch (OD), extended aeration (EA), and CAS. The wastewater results and sludge results have been submitted separately for publication (Smyth et al 2007b, 2007c).

The wastewater results from the Grand River survey investigated seasonal fluctuations in influent concentrations and loadings of six polycyclic and five nitro musks, seasonal variations in effectiveness of their removal from wastewater, and removal of musks by four different types of WWTPs. A summary of WWTP conventional performance provides the context for observations of musk removals. Influent strength for the lagoon, OD, EA, and CAS plant 2 was generally low to medium, while influent strength for CAS plants 1 and 3 was medium to high. Water temperatures ranged from 2°C in February to 22°C in July with the lagoon and oxidation ditch showing the widest variations. Removal of cBOD<sub>5</sub> and TSS was generally better than 90%, while removal of COD was better than 80%. Both the OD and EA plants were operated to nitrify: the OD plant produced fully nitrified effluent in all seasons while the EA plant did not achieve nitrification in the Winter or Spring, and only partially nitrified in the Fall. The CAS plants were not operated to nitrify, however CAS 1 achieved partial nitrification in the Summer and CAS 3 achieved partial nitrification in all seasons. The HRT of the WWTPs ranged from weeks for the lagoon to days for the OD plant, to hours for the EA and CAS plants. SRTs for each plant were estimated in the same manner as described for the Interstage Study, resulting in SRTs ranging from weeks for the OD plant, 7 to 25 days for the EA plant, and 1 to 4 days for each of the CAS plants.

Influent musk concentrations were affected by seasonal flow fluctuations, while loadings were generally consistent across seasons. These observations corresponded with the expectation that usage of personal care products containing musks would be generally consistent across the seasons, while influent musk concentrations would fluctuate due to seasonal flow variations. Lagoon treatment produced the highest percent removal and the lowest effluent concentrations of musks. The lagoon and oxidation ditch showed the most extreme ranges of process temperature, ranging from 2°C to 22°C, and musk removal was better at the higher temperatures. The extended aeration and



CAS plants showed somewhat less of a temperature range (7°C to 20°C), and there was no correlation between musk removal and process temperature. HRT and SRT in mechanical treatment plants were not correlated with musk removal; results indicated that the nature of the plant inputs and operation may have a greater influence on musk removal than simple retention time. For example CAS plant 3 consistently showed better removals than the extended aeration plant. It was also observed that CAS 3 consistently achieved more complete nitrification than the extended aeration plant during all seasons. In contrast the oxidation ditch plant achieved complete nitrification in all seasons, and had a SRT of weeks, but did not show consistently better removal performance than CAS 3. Table 2 shows all six plants ranked by median removal performance ((influent concentration minus effluent concentration)/influent concentration) for each season.

TABLE 2: RANKING OF GRAND RIVER WWTPS BY MEDIAN MUSK REMOVAL PERFORMANCE

Summer		Fall		Winter		Spring	
WWTP	% Removal	WWTP	% Removal	WWTP	% Removal	WWTP	% Removal
Lagoon	97	Lagoon	95	Lagoon	95	Lagoon	93
CAS 3	90	CAS 1	85	CAS 3	95	CAS 3	77
Oxidation Ditch	78	Oxidation Ditch	82	CAS 1	89	Extended Aeration	69
Extended Aeration	75	CAS 3	78	Oxidation Ditch	72	CAS 1	56
CAS 1	72	CAS 2	62	Extended Aeration	63	Oxidation Ditch	55
CAS 2	71	Extended Aeration	57	CAS 2	62	CAS 2	50

These results indicate that CAS plants are capable of high removals of musks from wastewater, and that process temperature is not necessarily a limitation to removal. Our results, along with those reported by several other researchers, do not show a consistent correlation between HRT or SRT and removal. If effects and risk assessment research indicate that it is necessary to remove PPCPs from municipal wastewater effluents (MWW) to protect aquatic ecosystems, optimization of removal may need to be done on a plant-by-plant basis.

Polycyclic and nitro musks tend to partition to solids during wastewater treatment. If musk discharges in MWW can be minimized through optimal solids separation, then the musk content of land-applied biosolids may be an important source of these compounds to the environment. Therefore understanding the fate of musks during sludge handling, treatment, and utilization is essential to reducing their presence in the environment.

The sludge and biosolids aspect of the Grand River survey investigated concentrations of 6 polycyclic and 5 nitro musks in raw sludge and digested biosolids, and compared musk removal during aerobic and anaerobic digestion processes at the five mechanical WWTPs. The oxidation ditch and extended aeration plants used aerobic digestion and the three CAS plants used anaerobic digestion. Polycyclic musks were present in raw sludge at concentrations up to 47000 ng/g dw (Galaxolide), while nitro musks were present at concentrations up to 600 ng/g dw (Musk Ketone). Higher raw sludge concentrations corresponded with higher removals of musks from the wastewater. Polycyclic musks were present in digested biosolids at concentrations up to 68000 ng/g dw (Galaxolide), while nitro musks were present at concentrations up to 300 ng/g dw (Musk Ketone and Musk Xylene). Concentrations of musks in aerobically digested biosolids decreased proportionally with destruction of volatile solids, indicating that musks are removed under aerobic conditions. Concentrations of polycyclic musks in anaerobically digested biosolids increased proportionally with destruction of volatile solids, indicating that polycyclic musks are not removed under anaerobic conditions. Concentrations of nitro musks decreased with destruction of volatile solids however the correlation was not statistically significant; nitro musks may be removed during anaerobic digestion but more study is needed. This study showed that the fate of musks during sludge digestion is dependent on both the musk type and the digestion process.

## MEDIA TECHNOLOGY

The AnoxKaldnes Moving Bed<sup>TM</sup> Biofilm Reactor (MBBR) process is a continuously operating, non-clogging biofilm reactor with low headloss and high specific biofilm surface area. It can be operated as a flow-through process without return sludge flows for some applications. The MBBR process is achieved by having biomass grow on small carrier elements within a reactor. The movement of carriers and wastewater within the reactor is produced by coarse-bubble aeration. The MBBR flow-through process may be retrofitted into existing tankage to increase SRT and thus provide more extensive removal of carbon and nitrogen compounds without increasing the plant footprint. The flow-through process underwent an extensive testing program at the Highland Creek Treatment Plant in Toronto (Johnson et al, 2003), and the scope of the project was extended to include removal of PPCPs.

The MBBR process was compared to the CAS process for its ability to remove PPCPs from wastewater. The two systems were fed a common primary effluent, which was sampled along with the secondary effluent and waste activated sludge from each system. Four experimental conditions were examined:

1. MBBR only, regular flow, warm temperature
2. MBBR + CAS, regular flow, warm temperature
3. MBBR only, double flow, cold temperature
4. MBBR + CAS, double flow, cold temperature

In experimental conditions 1 and 3, the HRT in the flow-through MBBR process was 40% of the HRT in the comparison CAS process. Each condition was sampled twice between August 2003 and May 2005. Samples were analyzed for ten acidic drugs and eleven musks. Data analysis is in progress.

## REACTOR STUDIES

The purpose of the controlled reactor study was to determine the effect of temperature and solids retention time (SRT) on the ability of the activated sludge process to remove selected PPCPs from municipal wastewater. The wastewater source was the City of Burlington. Primary clarification of the wastewater was carried out on site, and the primary effluent fed into 20 L glass reactors with water jackets for temperature control. The reactors were run in sequencing batch mode with a cycle time of 6 hours.

The controlled study examined PPCP removal at the following conditions:

- 2 aerobic reactors at nominal SRT of 4 days, one reactor at 10°C and one reactor at 20°C. At this short SRT, nitrification did not occur.
- 2 aerobic reactors at nominal SRT of 10 days, one reactor at 10°C and one reactor at 20°C. Nitrification occurred at 20°C and partial nitrification at 10°C at this longer SRT.

The percent removal of polycyclic musks from the aqueous stream (influent minus effluent concentration) ranged from 60 to 80 % with the higher SRT providing the higher removal rates. The higher removal rates also coincided with partial and fully nitrifying conditions. The polycyclic musks associated with solids ranged from 15000 to 27000 ng/g dw and the lowest concentration was observed at the 10 day SRT and 20 °C which also coincided with nitrifying conditions. A significant concentration difference of polycyclic musk associated with solids was observed between nitrifying and non-nitrifying conditions. Under the controlled operating conditions SRT followed by T and the interaction term TxSRT were found to be the most important operating parameters, in priority sequence, which influenced the partitioning of polycyclic synthetic musks between the solids and aqueous matrix (Pileggi, 2007). Further data analysis from this study is in progress.

## CONCLUSIONS AND FUTURE DIRECTIONS

A strategic research collaboration between Environment Canada and the Ontario MOE has examined the occurrence and fate of PPCPs through the stages of CAS treatment, in various typical Canadian WWTP alternatives, in an innovative treatment alternative, and in controlled reactor studies. This study has greatly increased the Canadian database on the presence of PPCPs in municipal

wastewater and the correlation between treatment stage or type and removal of PPCPs from the liquid treatment train. Lagoons appear to provide the most complete removal of these compounds from MWW. There is no consistent correlation between PPCP removal and HRT or SRT in mechanical treatment plants; however enhanced PPCP removal may be associated with nitrification and solids removal. Some PPCPs partition strongly to sludge and are not removed during the digestion process.

Studies to date have only measured concentrations of parent compounds. It has been previously reported that ingested pharmaceuticals undergo conjugation reactions within the body before excretion and that these reactions can be reversed to release the parent compound during wastewater collection and treatment. Some results have indicated "creation" of an analyte from influent to effluent, suggesting that this deconjugation occurs within the WWTP. Other researchers have cautioned that breakdown metabolites of PPCPs may have more environmental potency than the parent compounds. Analytical methods and standards for conjugated compounds and metabolites are not yet available to confirm these hypotheses.

Government and academic researchers are working on a wide variety of studies to determine the potential for PPCPs to exert adverse effects in the environment. The challenge in effects research is choosing an endpoint to monitor within an organism, and determining how many types of organisms should be studied. According to European and North American research to date, achieving non-detection of PPCPs in wastewater effluents and sludges would require significant upgrades to most WWTPs. Effects researchers are striving to determine if the environmental impacts of PPCPs are serious enough to warrant such a costly undertaking.

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