Report for 2002MT3B: Pharmaceuticals in Septic System Effluent and a Preliminary Evaluation of Environmental Fate

- Conference Proceedings:
  - Godfrey, Emily and William W. Woessner. 2004. Screening level study of pharmaceuticals in septic tank effluent and a wastewater treatment plant waste stream. Proceedings of the 4th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, held October 13-15, 2004, in Minneapolis, Minnesota (copyright 2004 by the National Ground Water Association, ISBN 1-56034-114-9): 296-308.
- Other Publications:
  - As the 2005 Birdsall Dreiss Distinguished Lecturer for the Geological Society of America, PI William Woessner has incorporated study results in one of the two talks he is invited to present around the country (~15 universities as of May, 2005). Talk Title is: Occurrence, Transport and Fate of Viruses and Pharmaceuticals in Groundwater Impacted by Septic System Effluent: The Hydrogeologists and Human Health.
- Dissertations:
  - Godfrey, Emily. 2004. Screening Level Study of Pharmaceuticals in Septic Tanks, Ground Water and Surface Water in Missoula, Montana. Unpublished Master of Science Thesis, Dept. of Geology, University of Montana.

Report Follows

Screening Level Study of Pharmaceuticals in Septic Tank Effluent and a Wastewater Treatment Plant Waste Stream

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Abstract

Evaluating how pharmaceuticals are entering the environment has been the focus of recent research. Two principal pathways requiring investigation are wastewater treatment plants and septic systems. This study attempts to examine the occurrence and estimate the concentrations of selected pharmaceuticals in these waste systems. Thirty-two single family and ten multiple family septic tanks, as well as the influent and effluent wastewater from the community wastewater treatment plant (WWTP) in Missoula, Montana, were sampled. Samples were analyzed by Time-of-Flight High Performance Liquid Chromatography/ Mass Spectrometry for 19 drug residues and three drug metabolites of both prescription and non-prescription drugs. Only 18 of the 22 pharmaceuticals were present in the septic tanks, 12 were detected in the WWTP influent, and nine were detected in the WWTP effluent. The most frequently detected (>50%) non-prescription drugs were, acetaminophen, caffeine, and nicotine, as well as metabolites of caffeine (paraxanthine) and nicotine (cotinine). Median concentrations of these compounds were 219-ug/L, 80-ug/L, 8.7-ug/L, 175-ug/L, and 4.7-ug/L, respectfully. Prescription drugs were detected less than 30% of the time, with the exception of warfarin, which was detected in approximately 77% of the samples. Prescription drugs found most frequently were codeine, trimethoprim and carbamazepine. This work suggests that concentrations of pharmaceuticals, originating from both septic effluent and wastewater treatment plant effluent could be leaving these treatment systems and entering the associated surface water or ground water resources in Missoula.

INTRODUCTION

During the last three decades, an increased focus on water pollution from organic chemicals such as toxic/carcinogenic pesticides and industrial byproducts has emerged (Christensen 1998). In recent years, pharmaceuticals and personal care products (PPCP's) and their metabolites have been detected in the environment (Raloff 1998; Buser et al. 1999; Hartig et al.1999; Seiler et al. 1999; Heberer 2002a and 2002b; Holm et al. 1995; Kolpin et al. 2002; Scheytt et al. 1998; Eckel et al. 1998; McQuillan et al. 2000, Buerge et al. 2003; Clara et al. 2004; Petrovic et al. 2003). To date, efforts have focused principally on the detection and fate of PPCP's in surface water. Only a few studies (Holm et al. 1995, Umari et al. 1995, Eckel et al. 1998, Seiler et al. 1999, Heberer 2002, Drewes et al. 2003, Verstraeten et al. Draft, Benotti et al. 2003, Cordy et al. 2004) have examined the concentration of pharmaceuticals in raw sewage. As of this writing, no published research has examined pharmaceutical concentrations from individual septic systems. In the US, approximately 25-30% of households use septic systems for wastewater disposal (Verstraeten et al. Draft). This raises concerns that trace pharmaceuticals could enter the ground water underlying these systems.

GOALS AND OBJECTIVES

This study characterizes the occurrence and estimates the concentration of a selected group of pharmaceuticals in septic system effluent and wastewater inflows and outflows from a municipal sewage treatment plant. The specific study objectives were to: (1) identify target compounds; (2) develop sampling and analyses procedures; (3) characterize individual and community septic tank effluent, and compare these results to the character of municipal sewage wastewater.

METHODS

Identify target compounds of concern

Pharmaceuticals selected for this study were based on the following criteria: 1) they are commonly used drugs; 2) compounds found in the environment reported by other studies; 3) they ionize well under positive electron spray mode (analytical consideration). Certain compounds, like ibuprofen, that fit criteria one and two, were not included as they cannot be easily detected using the chosen analytical technique. Target compounds including 19 pharmaceuticals, both prescription and non-prescription drugs, and three metabolites were selected for evaluation (Table 1).

Table 1. Pharmaceuticals selected for analyses. The last two columns report the maximum recommended dose for an adult and maximum urinary excretion percentage

Compound	Type	Use	Maximum Recommended Dose for adults	Maximum Urinary Excretion (%) (Goodman and Gilman, 1990)
Acetaminophen	Non-prescription drug	Antipyretic	1000mg, 4-6hrs***	3 +/- 1
Antipyrine (Phenazone)	Prescription	Analgesic	54mg, 3 times/day**	ND*
Caffeine	Non-prescription drug	Stimulant	210-440mg coffee (Buerge et al. 2003), 200mg, 3-4 hrs pill***	1.1 +/- 0.5
Carbamazepine	Prescription drug	Anticonvulsant, antineuralgic, antimanic, antidepressant, antipsychotic	75-300mg/day**	<1, 3**
Cimetidine	Non-Prescription drug	Antiasthmatic	200mg, 12hrs**	62 +/- 20
Codeine	Prescription drug	Analgesic (anti-cough)	10-60mg, 1-4 times/day**	Negligible
Cotinine	Metabolite	Nicotine metabolite	Metabolite	ND*
Diltiazem	Prescription drug	Antihypertensive	480 mg/day**	<4
Erythromycin-18	Metabolite of Prescription drug	Antibiotic	Metabolite	12 +/- 7
Fenofibrate	Prescription	Lipid Metabolism Regulator	201 daily**	ND
Fluoxetine	Prescription drug	Antidepressant, antiobsessional, and antibulimic	80mg/day**	<2.5
Hydrocodone	Prescription drug	Analgesic (anti-cough) and antitussive	7.5/day**	ND*
Ketoprofen	Non-Prescription	Anti-inflammatory	12.5mg, 4-6hrs***	<1
Metformin	Prescription drug	Antihyperglycemic	2550mg/day**	ND*
Nicotine	Non prescription drug	Stimulant	21mg/hr patch***	16.7 +/- 8.6
Nifedipine	Prescription drug	Antianginal (blood pressure control)	120mg/day**	~0
Paraxanthine (1,7-dimethylanthine)	Metabolite	Caffeine metabolite	Metabolite	ND*
Ranitidine	Non- Prescription drug	Histamine	75mg, 12hr***	69 +/- 6
Salbutamol	Prescription drug	Relax restricted airways	5mg/day**	ND*
Sulfamethoxazole	Prescription drug	Antibiotic	80mg, 3-4hrs**	14 +/-2
Trimethoprim	Prescription Drug	Antibiotic	20mg, 3-4 times/day**	69 +/- 17
Warfarin	Prescription drug	Anticoagulant	10mg/day**	<2

ND*= no data, **= Physicians desk reference 1999, ***=Physicians desk reference 2001

Field Sampling and Site Description

Two types of wastewater were sampled for pharmaceuticals: 1) individual and community septic systems and 2) the city wastewater treatment plant. Thirty-two single-family and ten community septic tanks were sampled in the City of Missoula (Figure 1).

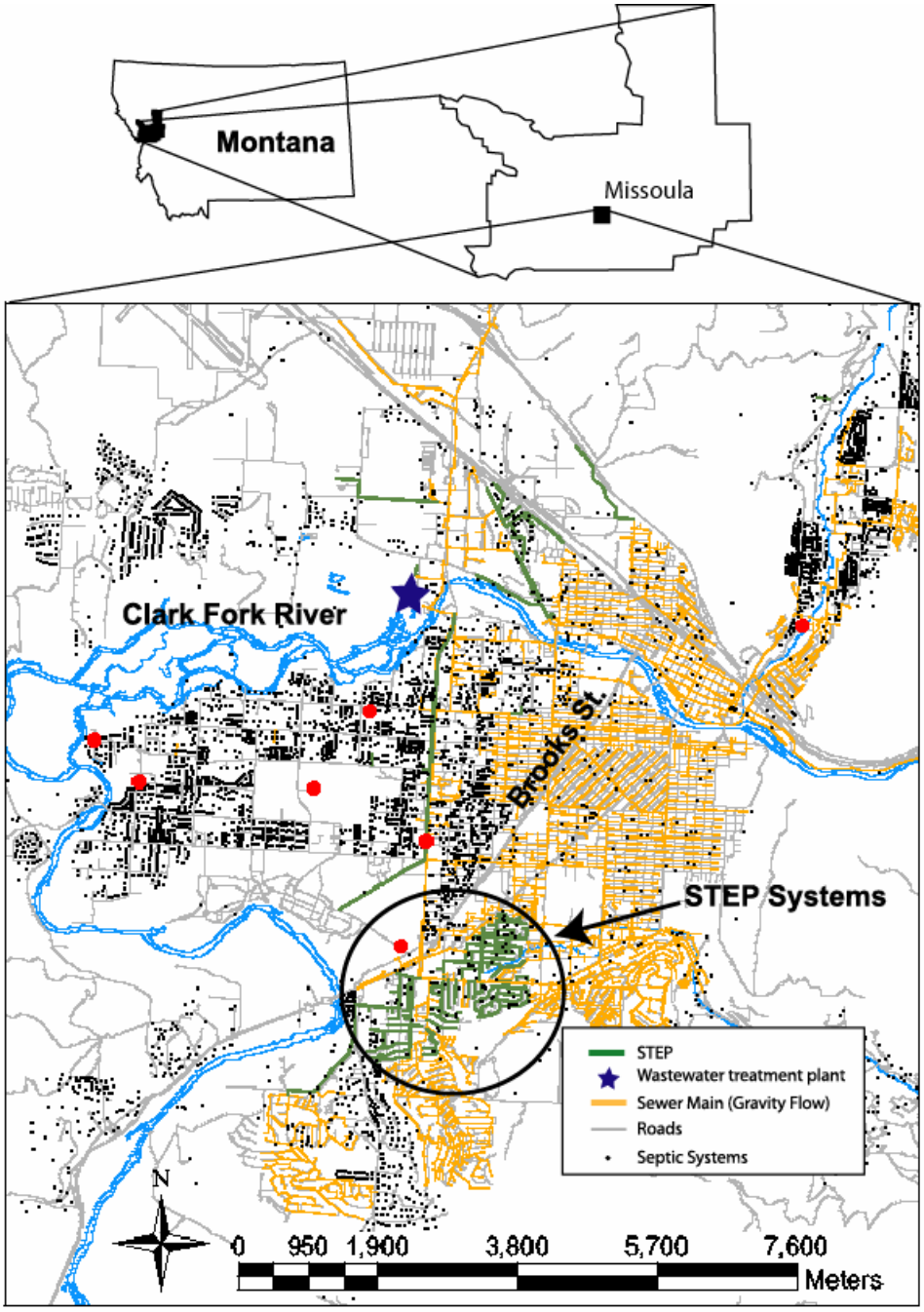

Figure 1. Location map of the City of Missoula. Shown are sewer systems (gravity flow and STEP), unsewered areas and the wastewater treatment plant in the city of Missoula, Montana (Map source: Department of Water Quality Missoula, Montana)

tank's liquid effluent reaches a volume of 2,600-L, it is pumped from the septic tank to the city sewer line. Solids that settle to the bottom of the tank are pumped out as needed (Figure 2). Community STEP tanks function the similar to single-family STEP systems except community tanks hold 11,300 to 30,300-liters of effluent.

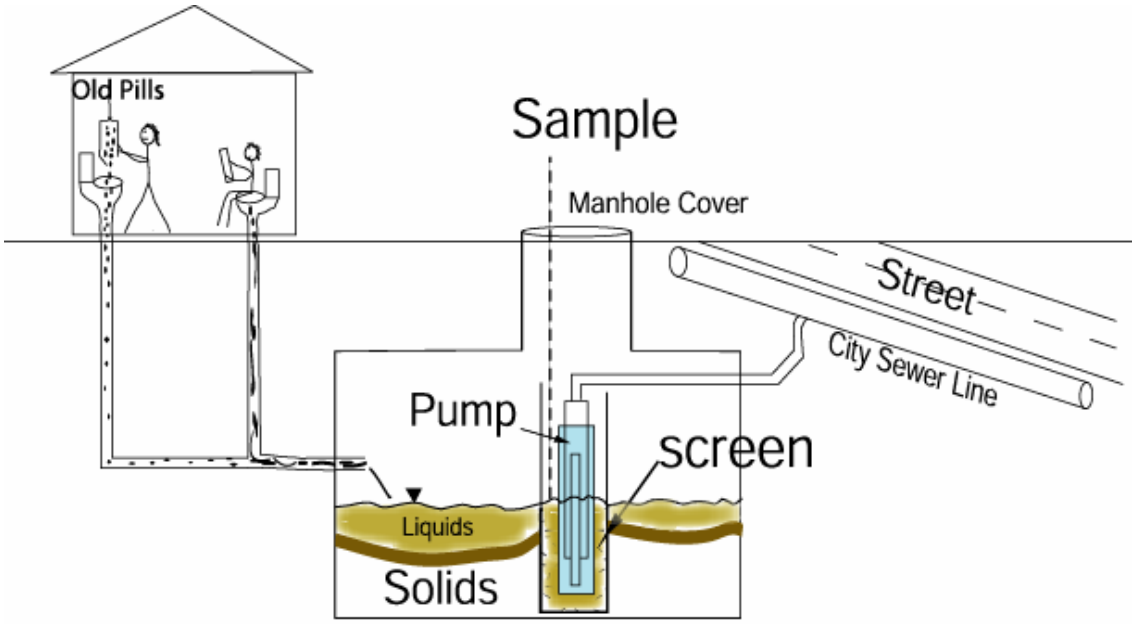

Figure 2. Schematic diagram of STEP (Septic Tank Effluent Pumping) system for a single-family residence

Each septic tank effluent sample was collected from STEP systems using a parastolic pump equipped with new 30-cm length of silicon tubing and 1.5 to 7.6-m new 0.6-cm diameter polyethylene tubing. Samples pumped from the tanks were collected in a 2.5-L glass bottle. All bottles were pre-washed with methanol and Milli-Q water and dried overnight. All sampling tubing was discarded after sample collection.

The municipal wastewater treatment plant (WWTP) in Missoula, Montana is connected to about 57,000-population equivalents. The WWTP utilizes commonly used treatment steps, preliminary sedimentation followed by activated sludge treatment and final clarification by chlorination. After primary sedimentation, three influent samples were obtained at the WWTP by submersing a 2.5-L glass bottle into the liquid flowing into the secondary treatment basin. As an advanced wastewater treatment, Missoula WWTP uses ultraviolet treatment during the summer months to further treat photoreactive compounds. Two effluent samples were taken before and after ultraviolet treatment. Effluent from the WWTP is then discharged into the Clark Fork River.

Sample Preparation

At this time no standardized procedure has been adapted for sample preparation and analysis. Samples were placed on ice in the field and refrigerated at 4ºC in the lab. They were prepared within 1-3 days of collection for analysis using adjusted methods described by Kolpin et al. (2002) (pharmaceutical extraction method 3). This method was designed to target human prescription and non-prescription drugs and their metabolites. In brief, first a pre-filtration step was initiated by passing the sample through a 0.45-um glass fiber filter (Whatman, 47-mm). Then one-liter of sample was processed on a solid phase extraction (SPE) cartridge that contained 6-cc, 500-mg of sorbant Hydrophilic-Lipophilic-Balance (Oasis, HLB) at a flow rate of 15 to 25-mL/min. Next, compounds were extracted from the SPE cartridge using two 3-mL aliquots of methanol (CH_3OH) and two 3-mL aliquots of methanol acidified with trifluoroacetic acid (0.1% trifluoroacetic acid, $C_2HF_3O_2$). Compounds

were slowly reduced to near dryness under N_2 gas and then brought to a 1-mL solution volume with 10-mM ammonium formate/formic acid, (pH=3.7). All effluent samples were filtered with a 0.2-um PTFE (Polytetrafluoroethylene) syringe filter, and then diluted to a 10% solution, prior to analysis. As part of the method development and to maximize the resolution and sensitivity of the HPLC-TOF-MS, three samples were prepared at sample concentrations of 10%, 50% and 100% solution. The 10% diluted sample solution was chosen for its ability to produce chromatograms with the least amount of matrix interference and a discernable internal standard peak. Thus for all samples, prior to HPLC analysis, a 10% diluted sample solution was used.

Compounds were separated and measured by Time-of-Flight, High Performance Liquid Chromatography coupled with Mass Spectrometry (HPLC-TOF-MS, Waters HPLC system) in the Marine Sciences Research Center laboratory at Stony Brook University, the State University of New York, using a polar (neutral silanol) reverse-phase octylsilane (C8) HPLC column (Metasil Basic 3-um, 150*2.0-mm; Metachem Technologies). This preparation procedure was used for all samples (Benotti et al., 2003).

For quality control, one internal standard, $^{13}C_3$ labeled caffeine was used (Cambridge Isotope Laboratories in Cambridge, Ma). Pharmaceutical standards were obtained from Aldrich and prepared by the personnel of the Marine Sciences Research Center laboratory. Analyses were conducted in ESP+ mode with a selected mass range of 100 to 800 Da. A lock mass, leucine enkephalin (Sigma #P9003), was added post-column at a flow rate of 1-uL/min, with a concentration of 5-ng/mL. After analysis, all sample chromatograms were corrected by using a single point correction of the base calibration file with the lock mass (Benotti et al. 2003, Ferrer and Thurman 2003). Quantification of compounds was estimated from the internal standard ($^{13}C_3$ labeled caffeine) injected into the sample prior to analysis.

ANALYTICAL CHALLENGES

As this research effort was a screening level study and minimally funded, the analytical approach involved sample preparation in Missoula and preliminary runs of samples for selected compounds at the University of Montana Liquid Chromatography Lab in the Chemistry department. However, due to an absence of environmental QA/QC protocols and shared use of the instrument, analytical assistance was sought by Professor Bruce Brownawell and Ph.D. student Mark Benotti at the Marine Science Research Center, Stony Brook University in New York. A guest arrangement allowed us to travel to the lab with an HPLC column and operate the equipment under their guidance using a provided 20 compound standard. After analyzing all samples in New York, we returned to the University of Montana to process the results.

The standards examined during sample analysis (11/03) did not produce reliable results, so standards were remade and analyzed on a later date (01/04). The reason for unreliable standards, analyzed on 11/03, is a result of human error during standard preparation. Due to changing the detector voltage prior to analyzing the samples, it is impossible to compare the stability of the machine before and after samples were analyzed. In attempt to demonstrate the stability over a length of time, responses for standards from February 2004 are 109 +/- 12 (n=6) and May 2004 are 108 +/- 20 (n=6). The standard responses compare favorably over a four-month period. Moreover the response for standards, used for sample quantification on January 2004 was 107 +/- 13.

Analytical difficulty also occurred during sample preparation and SPE concentration. Using the stated preparation methodology, target compounds were captured from a one-liter filtered effluent sample using a 6-cc, 500-mg HLB sorbant. The ability for the HLB cartridges to capture all target compounds was evaluated by passing one sample through two HLB cartridges in series. Compounds such as acetaminophen, caffeine, cotinine and paraxathine were detected after the second processing of the one-liter samples, while ketoprofen, nicotine and warfarin were not detected (Table 2).

Table 2. Double runs through cartridges. Samples A and B are samples from two septic tanks. A1 and B1 are the results of effluent processed on one HLB cartridge and A 2 and B 2 are processed on a second HLB cartridge. **All values represent minimum concentrations.**

Samples	Acetaminophen	Caffeine	Cotinine	Ketoprofen	Nicotine	Paraxathine	Warfarin
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
A 1	1.09	8.26	Nd	Nd	Nd	67.67	1.81
A 2	0.64	1.39	0.12	Nd	Nd	40.88	Nd
B 1	140.01	60.84	5.36	147.64	0.87	71.84	5.84
B 2	427.73	13.621	2.44	Nd	nd	196.43	Nd

In an effort to examine the reproducibility of our analytical method, nine splits were prepared and analyzed (Table 3).

Table 3. Sample splits. These are reported by compound, total mean % comparisons, number of positive identified compounds ( ). **All values compared represented minimum concentrations**

Compound (n=)	Acetaminophen (9)	Caffeine (9)	Carbamazepine (3)	Cimetidine (2)	Cotinine (8)	Diltiazem (2)
Total mean (%)	88.4	83.2	78.1	91.7	83.9	83.2
Compound (n=)	**Erythromycin-18 (3)**	**Codeine (4)**	**Hydrocodone (1)**	**Ketoprofen (1)**	**Metaformin (3)**	**Nicotine (8)**
Total mean (%)	87.5	90.9	90.4	70.6	87.5	81.7
Compound (n=)	**Paraxathine (9)**	**Ranitidine (1)**	**Sulfamethoxazole (2)**	**Trimethoprim (3)**	**Warfarin (6)**	
Total mean (%)	83.8	69.4	46.0	80.6	70.7	

All compounds exhibited reproducibility above 50% with the exception of sulfamethoxazole, which was only detected in two samples.

During evaporation of the samples, a residue formed in some the test tubes. Visually, these samples were a dark brown color and collected on the bottom and sides of the glass vial. Adding the mobile phase (10-mM ammonium formate/formic acid, pH=3.7) to the near dry sample re-dissolved a portion of the solid phase, but in some samples the solid phase remained in the vial. It is possible that the residue remaining in the sample vial contained target compounds. These conditions may have created analytical results that are lower than actual values for these samples.

These analytical challenges limit the accuracy to report compound concentrations. This study attempted to characterize pharmaceutical concentrations in an environmental compartment for which little data exist (septic tanks). Generally speaking, pharmaceuticals in septic tanks exhibit a wide range of concentrations (from ng/L to high μg/L). While this offers interesting discussion, it must be noted that both the extraction procedure and HPLC-TOF-MS analysis applied in this study were designed to study trace levels of contaminants. Thus, reported concentrations, especially high values, represent a low-end concentration. The actual value cannot be quantitatively determined because phenomenon such as over-loading of SPE cartridges, ionization suppression/enhancement, and detector saturation impact analytical results, especially the determination of high concentrations (Benotti et al. 2003, Godfrey 2004). Although studies to qualify detector saturation and ionization suppression were outside the scope of this project, observation of such phenomenon indicate that concentrations from 10–500-ng/L are within the error of the analysis. Systematic error was assumed to linearly increase for concentrations that exceed 500-ng/L, probably underestimating the highest concentrations.

RESULTS

Single Family and Community Septic Tanks

This study analyzed for 22 pharmaceuticals in each sample. Of those, only 18 were found above their detection limit (Figure 3).

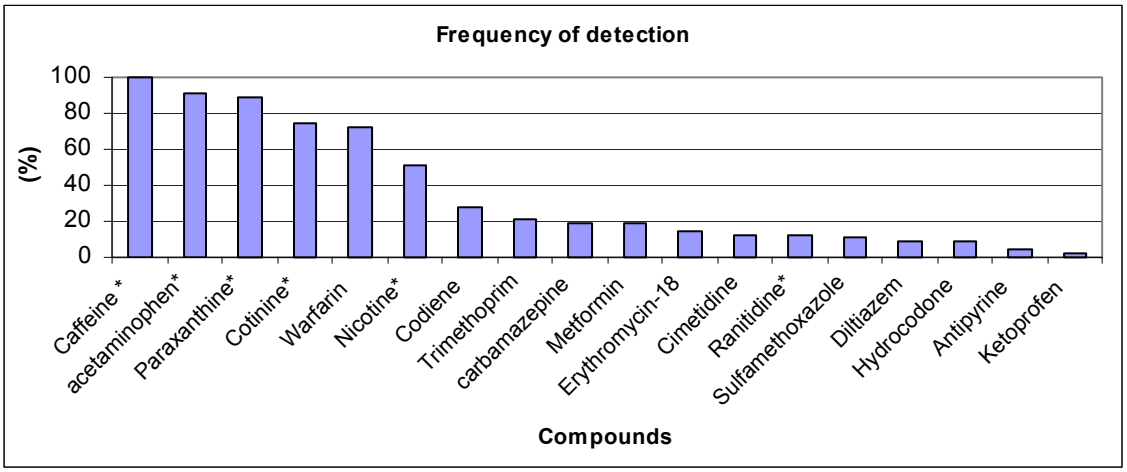

Figure 3. Most frequently detected compounds in raw sewage samples (community, single family and WWTP influent). Marked (*) compounds are nonprescription drugs and/or their metabolites.

Concentration ranges and frequency of occurrence data are provided for all compounds detected in community and single-family septic tank effluent (Figures 4 and 5). Compounds not detected were fenofibrate, fluoxetine, nifedipine and salbutamol. In all community tank effluent the most detected compounds (>60%) were acetaminophen, caffeine, cotinine, paraxanthine and warfarin (Figure 4). In single-family tanks the most detected compounds (>60%) were caffeine, acetaminophen, cotinine, paraxanthine and warfarin (Figure 5).

a. b.

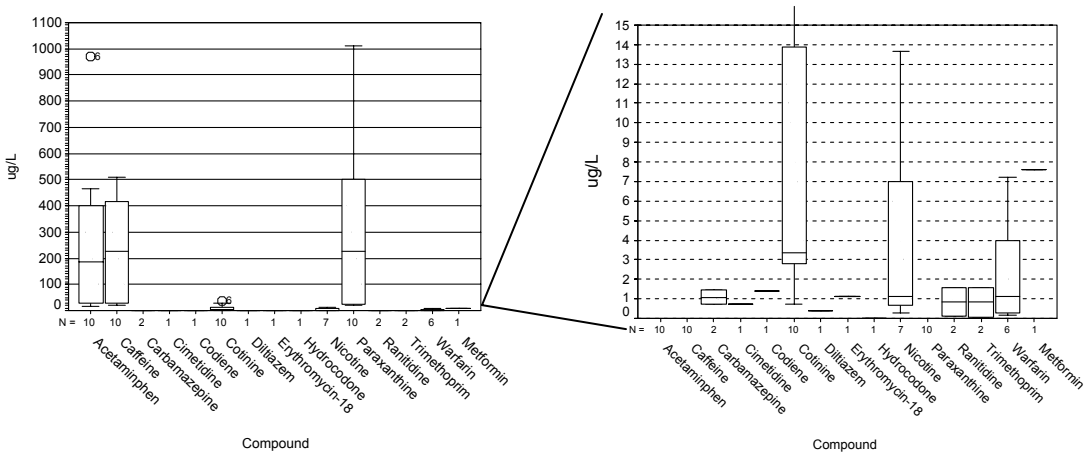

Figure 4. Pharmaceuticals detected in community septic tanks. Box plots report median, 75%, 25% quantities and maximum and minimum values and O_{xx} represent outliers. The numbers of detections in samples are reported above the compound name. Two box plots are used to show all concentration ranges of samples (a) higher concentrations and (b) lower concentrations. **All values represent minimum concentrations.**

a. b.

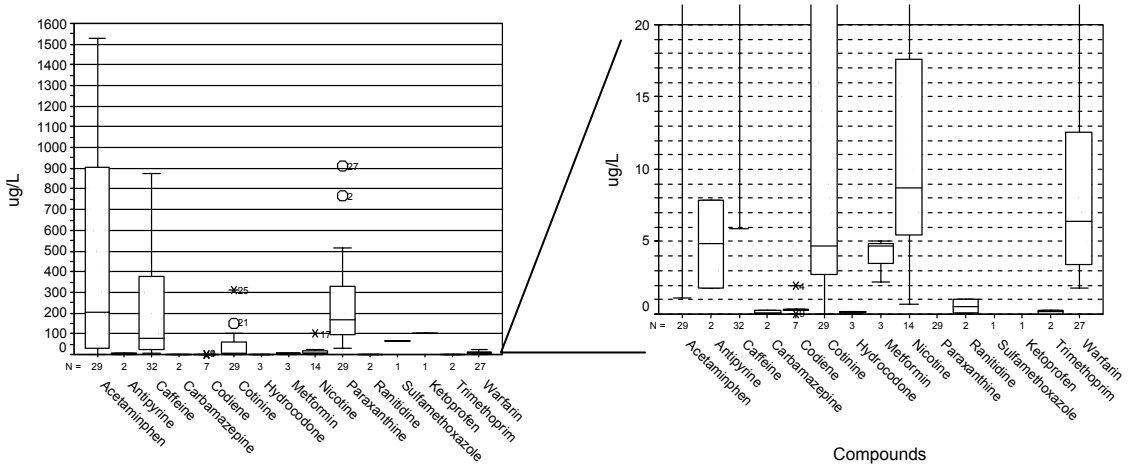

Figure 5. Pharmaceuticals detected in single-family septic tank. Box plots report median, 75%, 25% quantities and maximum and minimum values. O_{xx} and represent outliers and $*_{xx}$ represent extreme values. The numbers of detections in samples are reported above the compound name. Two box plots are used to show all concentration ranges of samples (a) higher concentrations and (b) lower concentrations. **All values represent minimum concentrations.**

Wastewater Treatment Plant

Comparisons of pharmaceutical concentrations from influent and effluent sewage of the city's WWTP are reported, including concentrations of before and after ultraviolet treatment (Figure 6). Acetaminophen, diltiazem, nicotine, paraxathine and warfarin were not detected in the outflow of the WWTP.

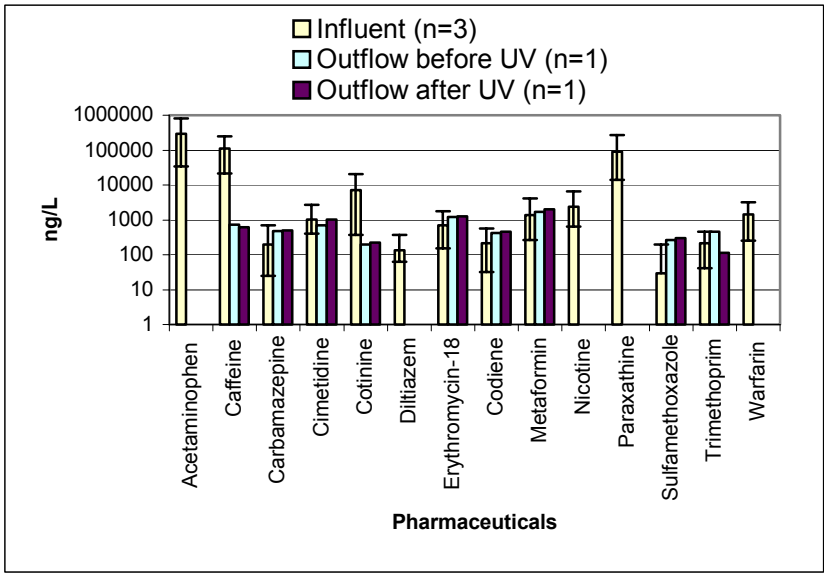

Figure 6. Concentrations of pharmaceuticals at the WWTP. Error Bars in the influent column represent a range of three separate sampling periods. Two concentrations are plotted of outflow samples before and after ultraviolet treatment. **All values represent minimum concentrations.**

DISCUSSION

Effluent samples
(Community, single family and WWTP samples)

Non-prescription drugs

Non-prescription drugs examined in this study include acetaminophen, caffeine, nicotine, ranitidine, paraxanthine (caffeine metabolite), and cotinine (nicotine metabolite). Five of these compounds were among the most frequently detected compounds in sewage (Figure 3). In community and single-family tanks acetaminophen, caffeine and paraxanthine were detected most frequently, with concentrations estimated at greater then 1530-ug/L, 877-ug/L, and 1010-ug/L, respectively (Figures 4 and 5). High concentrations detected in WWTP were lower than those found in septic effluent (acetaminophen at 525-ug/L, caffeine at 137-ug/L, and paraxanthine at 183-ug/L).

Concentrations of target compounds in septic systems appear to be more variable (have a larger range) than samples from the WWTP. Variations in concentrations are likely the result of the septic tank effluent's susceptibility to fluctuation and/or perturbations based on homeowner pharmaceutical use. It is likely that WWTP's have more stable concentrations and fluctuations are subtle as the waste integrates pharmaceutical use by a large diverse population.

The greater frequency of detection and higher concentrations of non-prescription drugs compared to prescription drugs in both septic waste and WWTP influent is related to their suspected greater annual use (Kolpin et al. 2002). Kolpin et al. (2002) observed similar findings when testing streams and rivers across the US. They report that non-prescription drugs were detected more frequently than other organic contaminants such as antibiotics, prescription drugs and reproductive hormones. They also frequently detected concentrations of drug metabolites and noted the importance of expanding analysis to include the possible degradates of parent compounds (Kolpin et al. 2002). For example, there are more than 20 metabolites of caffeine produced in the human liver (Buerge et al. 2003).

Prescription Drugs

Prescription drugs in effluent were detected less than 30% of the time, with the exception of warfarin, which was detected in approximately 77% of the samples (Figure 3). The highest concentrations of prescription drugs found in both single-family and community tank effluent were estimated to be greater than 6.4-ng/L for carbamazepine, 64-ug/L for sulfamethoxazole, 1.5-ug/L for trimethoprim, and 23-ug/L for warfarin (Figures 4 and 5). The apparent lower concentrations and frequency of detection for prescription drugs could be the result of their limited use and accessibility. Heberer (2002a) states that a reliable predictor of environmental concentrations of pharmaceuticals is the overall consumption and the fate of individual compounds in the human body. This study supports the fact that overall consumption of drugs plays a major role in the concentrations of pharmaceuticals found in the environment.

Wastewater treatment plant

The effluent samples at the WWTP were taken synoptically. However, pharmaceutical concentrations entering the plant were generally higher than levels leaving the plant (Figure 6). Ultraviolet treatment did not seem to significantly alter the apparent pharmaceutical concentrations (Figure 6). Acetaminophen, diltiazem, nicotine, paraxanthine and warfarin were below detection limits in WWTP outflow samples. This could be the result of degradation processes by microorganisms, elimination by the wastewater treatment process or the stated analytical recovery issues. Ternes (1998) noted the lack of acetaminophen in surface water due to high removal efficiencies by WWTP's. Buerge et al. (2003) and Heberer et al. (2002b) reported ~99.3% and 99.9% removal rates of WWTP for caffeine, respectively.

Analytical Difficulties

There are thousands of tons of pharmaceuticals produced and used in human and veterinary medicinal practices (Daughton and Ternes 1999). This can lead to potentially thousands of different molecules belonging to different chemical classes, structures and behaviors that could re-enter the environment. It would be unrealistic and costly to produce analytical methods for measuring all pharmaceuticals in the environment. To date no

single analytical procedure has been set as an accepted method to measure quantities of pharmaceuticals in the environment (Castiglioni et al. 2004).

Due to the analytical difficulties mentioned earlier, this study reports a range of concentrations for septic tank effluent samples (Figures 4 and 5) with the exception of demonstrating analytical changelings with the HLB cartridges (Table 2). Reasons for error include: 1) over saturation of the 500-mg, 6-cc HLB sorbant by sewage effluent samples; 2) loss of target compounds during filtration 3) loss of target compounds to the glass vial; and 4) concentrations of target compound over saturating the detector, causing suppression of ions during analysis.

Recovery data for raw sewage effluent matrix are not reported in this paper, yet Ternes et al. (2001) reports a limited number of recoveries of pharmaceuticals from a raw sewage effluent matrix. Ternes et al. (2001) reported 70% recovery of caffeine in sewage treatment plant effluent with other pharmaceuticals ranging from 30-142% recovery. Clearly, additional effort is needed to standardize analytical techniques.

FURTHER RESEARCH

The presence of pharmaceuticals in our waterways and ground water is a growing concern. With increased sensitivity of analytical equipment, we are able to report concentrations in the low ng/L range (Benotti et al. 2003). This low level of detection requires a methodology to ensure clean glassware and proper sample preparation in a raw sewage matrix are in need. In addition, other compounds that may be important to evaluate in ground water and wastewater include: primidone, naproxen, gemfibrozol, and metoprolol (Scheytt 1998; Ternes 1998; Drewes et al. 2003; Heberer 2002a; Castiglioni et al. 2004). Certainly a follow up study of Missoula's ground water that more clearly quantifies the occurrence and concentration of pharmaceuticals and personal care products should be conducted. This screening level study should be used to design such an effort.

CONCLUSION

Based on the analysis of all sewage effluent samples, 18 of the 22 compounds studied were detected above the detection limit. These 18 compounds include both prescription and non-prescription drugs, with prescription drugs being most frequently detected. This is most likely the result of greater annual use by the general population.

Acknowledgements

This work was supported by a grant from the Montana Water Center and the University of Montana. We would like to recognize the assistance of Professor Bruce J. Brownawell and Ph.D. student Mark Benotti of the Marine Science Research Center, Stony Brook University, at the State University of New York. They provided us access to their environmental laboratory and equipment. We greatly appreciate their assistance without which this project could not have been completed. Thanks also to Dr. Traugott Scheytt for his frank discussions regarding our results.

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