ground water

Pharmaceuticals in On-Site Sewage Effluent and Ground Water, Western Montana

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Abstract

Human use of pharmaceuticals results in the excretion and disposal of compounds that become part of municipal and domestic waste streams. On-site waste water disposal and leaking city sewer systems can provide avenues for the migration of effluent to the underlying aquifers. This research assessed the occurrence and persistence of 22 target pharmaceuticals in septic tank effluent and two shallow, coarse-grained aquifers in western Montana. Twelve compounds (acetaminophen, caffeine, codeine, carbamazepine, cotinine, erythromycin-18, nicotine, paraxanthine, ranitidine, sulfamethoxazole, trimethoprim, and warfarin) were detected in a high school septic tank effluent. Three of the 12 compounds, carbamazepine, sulfamethoxazole, and nicotine, were detected in the underlying sand and gravel aquifer after effluent percolation through a 2.0-m thick sand vadose zone. Sampling of a second sand, gravel, and cobble dominated unconfined aquifer, partially overlain by septic systems and a city sewer system, revealed the presence of caffeine, carbamazepine, cotinine, nicotine, and trimethoprim. The presence of carbamazepine and sulfamethoxazole in these aquifers appears to correlate with local usage based on a reported monthly prescription volume. This work highlights the need for expanding geochemical investigations of sewage waste impacted ground water systems to include sampling for selected pharmaceuticals.

Introduction

During the past decade, analytic capabilities to detect organic compounds in water at the sub-part-per-trillion level have advanced. Recent investigations have identified the presence of a wide variety of pharmaceuticals and personal care products in both surface water and ground water (Kolpin et al. 2002; Drewes et al. 2003). The sources of these compounds include human waste (Barber et al. 1995; Christensen 1998; Scheytt et al. 1998; Buser et al. 1999; Hartig et al. 1999; Seiler et al. 1999; McQuillan et al. 2000; Heberer 2002a, 2002b; Kolpin et al. 2002; Buerge et al. 2003; Petrovic et al. 2003; Clara et al. 2004; Kolpin et al. 2004), animal wastes (Halling-Sorensen et al. 1998), landfill leachate (Holm et al. 1995; Eckel et al. 1998), and direct disposal of expired or unused drugs into sewer systems, on-site disposal systems, and landfill waste streams (e.g. Bound and Voulvoulis 2005). Standard municipal sewage treatment plants are not completely removing pharmaceuticals through the treatment process (Ternes 1998; Ternes et al. 1998, 2001; Buser et al. 1999; Heberer 2002b; Buser et al. 2003; Drewes et al. 2003; Lippincott and Stackelberg 2003; Clara et al. 2004). As a result, detectable levels of these compounds are present in rivers and streams receiving waste water treatment plant effluent. The recognition that human and veterinary pharmaceuticals persist in waste water and aquatic environments has raised concerns over human and ecosystem health (Daughton and Ternes 1999).

Only a small number of studies have evaluated the fate of pharmaceutical compounds discharged into on-site waste water treatment systems and the resulting impacts to local ground water quality. Godfrey and Woessner (2004) reported septic tank effluent collected from community and single family septic tanks (SFST) in

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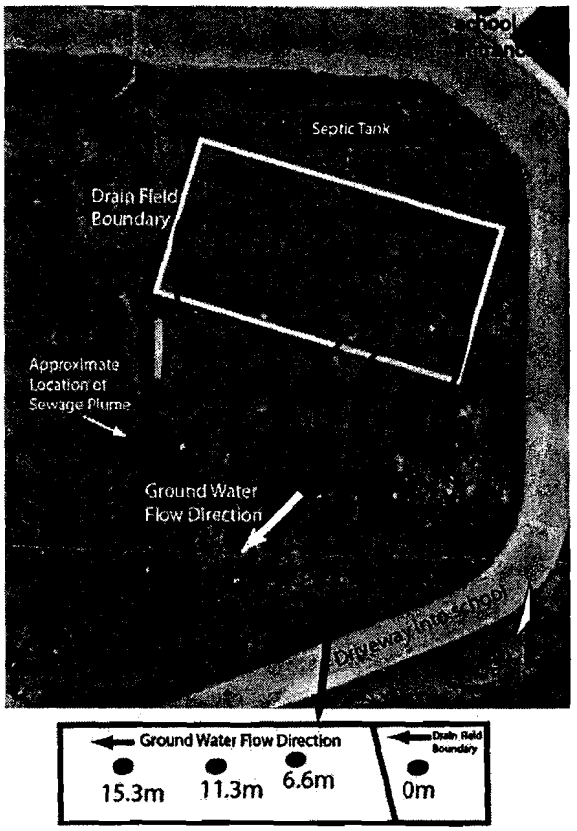

Figure 2. The Frenchtown High School Site showing an outline of the approximate location of septic effluent impacted ground water (NO_3-N > 1 mg/L) (Lauerman 1999). Inset of PVC monitoring wells sampled (solid dots), with the distances from the initial sample point labeled beginning with the well directly below the drainfield (0 m). Site location is shown in Figure 1.

feeds a drainfield system composed of 26 perforated lateral 10-cm-diameter polyvinyl chloride (PVC) pipes. The pipes are buried in approximately 30-m-long and 0.6-m-deep trenches and surrounded by washed 5-cm-diameter cobbles (Fink 2000; Lauerman 1999) (Figure 2). Approximately 12,000 L of effluent is produced and disposed of daily. Beneath the drain lines is approximately 2 m of naturally occurring fine to medium sand and 8 m of sand and gravel that is underlain by more than 30 m of fine sand and silt. The water table is located approximately 3 m below the land surface, forming a shallow unconfined aquifer. Hydraulic conductivities of the sand and gravel aquifer range from 240 to 300 m/d and ground water velocities range from 1 to 3 m/d (based on bromide tests) (DeBorde et al. 1998; Lauerman 1999) (Figure 2). A previous investigation by Lauerman (1999) installed a network of 32 PVC monitoring wells that were used to characterize the site hydrogeology. Wells were finished at depths of 4 to 6 m with the lower 1.5 to 3.0 m slotted. Ground water flow is to the southwest and is principally two-dimensional as no vertical gradients were observed (Lauerman 1999). Unimpacted ground water is of calcium bicarbonate type with a pH range of 6.6 to 7.2, dissolved oxygen (DO) of 3.4 to 6.4 mg/L, temperature of 6°C to 12°C, and a specific conductance range of 311 to 374 μS/cm. Impacted ground water that is immediately beneath and southwest of the drainfield has a pH range of 6.0 to 6.4, DO of less than 0.1 to 3.0 mg/L, and specific conductance of 323 to 790 μS/cm (DeBorde et al. 1998).

Site 2 City of Missoula and Adjacent Urban Area Site

In the city of Missoula, shallow ground water is produced and served to more than 60,000 residents by municipal wells and to households located outside the municipal distribution system (west of Reserve Street) by individual domestic wells (Figure 1). The unconfined sole source aquifer is composed of approximately 30 to 40 m of sand, gravel, cobbles, and boulders and is underlain by finer-grained sediment. The water table varies from 25 to 2 m (east to west) below the land surface. Ground water flow is from the northeast to the southwest across the valley and is strongly influenced by the perched and recharging Clark Fork River (4 km from the eastern boundary to Reserve Street). Aquifer hydraulic conductivities of the Missoula Aquifer range from 60 to 3650 m/d, and ground water velocities range between 10 and 60 m/d (Miller 1991). More than 30 large production wells pump more than 8000 L/min from the basal 6.5 m of the aquifer. The vadose zone thickness varies from about 10 m at Reserve Street to 2 m near the Bitterroot River.

Six 15.1-cm-diameter PVC monitoring wells (wells 1 to 6) and one 15.1-cm-diameter steel-cased monitoring well (well 8), all maintained by the Missoula Water Quality District, were sampled (Figure 1). These wells are generally perforated over 3 to 6 m and finished with the top of the perforations extending about 2 m above the low water table elevation. Well 8 is located north of the Clark Fork River in the Rattlesnake Creek Valley, where the vadose zone is approximately 15 m thick. The surrounding area contains individual homes using septic systems for waste disposal (0.25 to 0.5 ha lots). In the area between Russell and Reserve Streets west of the main Missoula urban area, some individual homes use septic systems for household waste disposal while all homes west of Reserve Street are on septic systems (more than 4000 on-site disposal systems). Ground water is of calcium bicarbonate type with a pH range of 6.7 to 7.9, a temperature of 6°C to 13°C, and a specific conductance range of 205 to 272 μS/cm (Woessner 1988).

Methods

Selection of Pharmaceutical Compounds for Evaluation

The group of pharmaceuticals selected for evaluation fit one or more of three criteria: (1) commonly used in North America; (2) previously detected in natural water; and (3) compatibility with selected analytic methods. Targeted compounds included 20 pharmaceuticals (prescription and nonprescription drugs) and two metabolites (Table 1).

Field Sampling

At the Frenchtown High School site, septic tank effluent and ground water samples were collected within

solids remained in the sample after reduction. All septic effluent samples were diluted with Milli-Q to a 10% solution prior to analysis. Compounds were measured by time-of-flight, high-performance liquid chromatography coupled with mass spectrometry (HPLC-TOF-MS, Waters HPLC system) at the Marine Sciences Research Center Laboratory at Stony Brook University, the State University of New York (Benotti et al. 2002; Cahill et al. 2004).

Pharmaceutical standards were obtained from Aldrich and prepared by the personnel of the Marine Sciences Research Center Laboratory. We used available laboratory and instrument methods, recognizing that analytic methodologies are yet to be standardized for pharmaceutical analysis in environmental matrices (Godfrey and Woessner 2004). Effluent sample preparation may have resulted in overloaded SPE cartridges when some compounds were present in high concentrations. In addition, when effluent sample concentrations exceeded the maximum sample standards of 500 ng/L, values were estimated by linear extrapolation of calibration curves. In matrix-rich samples, certain compounds are susceptible to suppression in the electrospray source (Lindsey et al. 2001). Effluent analysis was completed using the same sample preparation, analysis methods, and instrument as reported by Benotti et al. (2002). All lab blanks were nondetect.

Ground water sample concentrations were within the range of our standards, 1.5 to 500 ng/L. Method recoveries for the six compounds detected in ground water were as follows: caffeine (101%), carbamazepine (72%), cotinine (106%), nicotine (120%), sulfamethoxazole (38%), and trimethoprim (12%). Method detection limits (MDLs) for compounds that were detected in ground water were as follows: caffeine 3.33 ng/L, carbamazepine 0.17 ng/L, cotinine 0.63 ng/L, nicotine 1.02 ng/L, sulfamethoxazole 0.63 ng/L, and trimethoprim 0.11 ng/L. MDLs for effluent samples were not determined as the focus of this study was on ground water. Reported concentrations in this paper are (1) greater than the MDL; (2) not corrected for recovery; and (3) not corrected for possible matrix suppression. Thus, they likely represent a slight underestimation of the environmental concentration. Analytic results are viewed as screening level.

Results

Frenchtown High School Site

Twelve of the 22 target compounds were detected in the school septic tank effluent (Figure 3). Concentrations of pharmaceuticals in the septic tank effluent had comparable concentrations between the two sampling periods. During the 7-d sampling interval, 5 school days, approximately 60,000 L of effluent passed through the septic tank (Lauerman 1999). Concentrations of pharmaceutical compounds found in single family septic tank (SFST) effluent sampled in 2004 (Godfrey and Woessner 2004) and the results of this study were compared in Figure 3 and are generally considered similar.

Erythromycin-18, which was detected in the high school septic effluent at concentrations of 5.7 and 18 ug/L, was not detected in the SFST effluent samples.

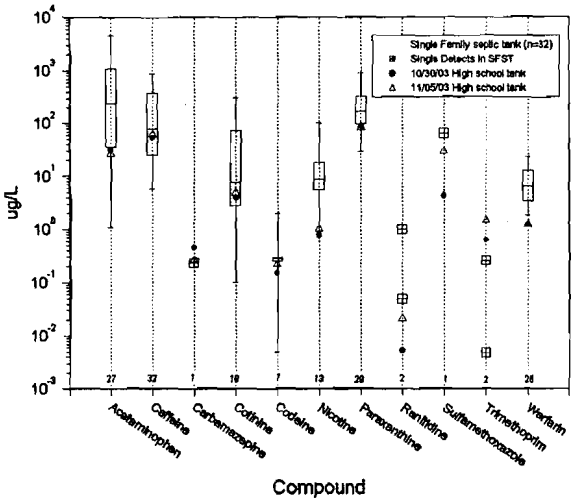

Figure 3. Box plots represent ranges of concentrations of positive detects out of 32 SFST samples. The single box represents one detection in all the SFST. Numbers above the x-axis represent the number of positive detects out of 32 SFST effluent samples. Concentrations in the high school septic effluent sampled on October 30, 2003, and November 5, 2003, are shown as black dots and hollow triangles, respectively.

Compounds that were not detected in the high school septic effluent, but were detected in the SFST effluent samples, were metformin, hydrocodone, antipyrine, and ketoprofen. Compounds that were tested for and not detected in either single family or high school septic tank effluent samples were cimetidine, diltiazem, fenofibrate, fluoxetine, nifedipine, and salbutamol.

The high school ground water sample directly below the drainfield contained measurable concentrations of 2 of the 12 compounds observed in the tank effluent (Figures 4A and 4B). Effluent infiltrated through a 2-m-thick sand vadose zone with an average saturation of 65% (Fink 2000). Concentrations of carbamazepine were detected in the septic tank effluent at 250 and 450 ng/L, while ground water concentrations ranged from 60 to 210 ng/L. Sulfamethoxazole septic tank effluent concentrations were 4200 and 29,000 ng/L, while ground water concentrations ranged from 10 to 450 ng/L. Measurable concentrations of carbamazepine and sulfamethoxazole were detected for each sampling event at all wells. Nicotine was detected once at the well farthest from the drainfield at a concentration of 50 ng/L. No other compounds were detected in ground water at the Frenchtown High School site. Each sample is a "snapshot" of what is present in the system at the time of sampling; thus, the levels of nicotine detected 15 m from the drainfield most likely represent an input prior to the initiation of our sampling.

Missoula City and Urban Area Site

A single ground water sampling event at site 2 found concentrations of pharmaceuticals generally present at quantifiable concentrations in the less than 25 ng/L range, with the consistent exception of caffeine, which was found at a maximum concentration of 206 ng/L (Figure 5).

reported carbamazepine in waste water treatment effluent under both oxic and anoxic conditions. Clara et al. (2004) examined both lab-scale and the full-scale effects of the waste water treatment processes on carbamazepine and reported no significant degradation or adsorption. Heberer (2002b) evaluated the fate of carbamazepine in waste water treatment plants in Berlin, Germany, and found only an 8% removal rate. Drewes et al. (2003) reported that carbamazepine persisted in an alluvial aquifer that harbored both anoxic and oxic ground water conditions for up to 8 years. In the case of carbamazepine, medicinally, it is used as an anticonvulsant, antimanic, and antidepressant drug, and it is often detected in trace concentrations in sewage-impacted water (Ternes 1998; Heberer 2002a, 2002b; Clara et al. 2004; Benotti 2006). Generally, it is highly metabolized (Ternes 1998; Seiler et al. 1999); however, individual doses are large (hundreds of mg/dose) and at reported excretion rates of 2% to 7% enough of the compound apparently enters the waste stream to yield detectable concentrations in receiving water. It has been suggested that investigators should also look for the primary human metabolite of carbamazepine, 10,11-epoxide, which is pharmacologically active and likely to occur in much higher concentrations than carbamazepine (Miao et al. 2005).

This study's observations at site 2 found the presence of 5 of the 22 target compounds at measurable concentrations in the ground water. Low levels of one or more of caffeine, carbamazepine, cotinine, nicotine, and trimethoprim were detected in the ground water (Figure 5). These compounds most likely percolated from a sewage effluent source through the 2- to 10-m sand, gravel, and cobble vadose zone common in the western unsewered portion of the Missoula Valley. The likely source of these compounds is septic effluent in this portion of the valley. A second possible source may be effluent leaking from damaged sewer lines located east of Reserve Street (Figure 1).

The observations that carbamazepine and sulfamethoxazole are occurring in shallow ground water in western Montana, at other study sites around North America, and in Europe led us to examine a link between the presence of selected pharmaceuticals in shallow ground water and the mass prescribed in a region. With the cooperation of a pharmacy that served approximately 7% of the Missoula population, the amount of prescription drugs distributed over a 4-week period was compiled (Figure 6). Interestingly, of the 13 prescription drugs evaluated, the mass of sulfamethoxazole and carbamazepine prescribed ranked second and third, respectively. An estimate of the yearly use (prescriptions) of sulfamethoxazole and carbamazepine for the entire Missoula area population (100%) yields more than 74,000 g/year and more than 56,000 g/year, respectively. Possibly, such usage in the study area correlates with the observed occurrence of these compounds in septic tank effluent and shallow ground water.

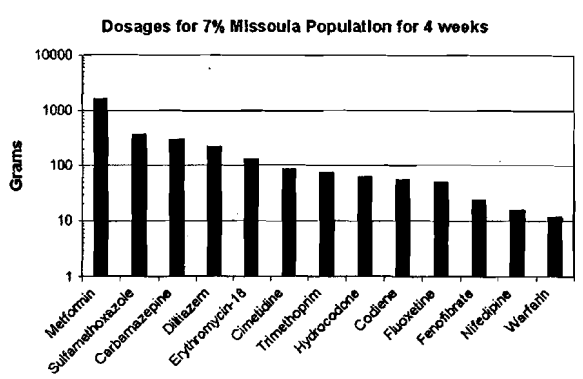

Figure 6. Quantity of drugs prescribed over a 4-week period in the Missoula area as represented by a pharmacy estimated to serve 7% of the Missoula Valley population.

The presence of detectable target compounds in shallow, unconfined, coarse-grained aquifers suggests that infiltrating sewage waste water has the potential to impact shallow ground water. Though ground water concentrations were typically at the nanogram per liter level, compounds such as carbamazepine and sulfamethoxazole, and to some degree of caffeine, cotinine, nicotine, and trimethoprim, appear to remain detectable once they pass through a sewage system, the vadose zone, and shallow ground water. Though this work was limited in scope, other researchers have suggested that additional compounds may also prove to be useful indicators of on-site effluent impacted ground water, including primidone, naproxen, gemfibrozol, metoprolol, ibuprofen, and furosemide (Scheytt et al. 1998; Ternes 1998; Heberer 2002b; Drewes et al. 2003; Castiglioni et al. 2005).

During this study, it was recognized that a formalized methodology addressing preparation and analysis of effluent and water samples using HPLC-TOF-MS method was needed. Fortunately, since the completion of this study, Cahill et al. (2004) published methods for analyzing compounds using HPLC. As the methods we applied were considered to be at a screening level, a followup study of our sites that more accurately quantifies the occurrence and concentration of pharmaceuticals in septic tank effluent and the underlying ground water should be completed to support or modify these preliminary results.

Conclusions

Our research supports observations and conclusions of a small number of previous studies that suggest some pharmaceutical compounds found in on-site system effluent leave the holding tanks, percolate to the underlying shallow ground water, and are transported in aquifers at measurable concentrations (Dejong et al. 2004; Godfrey and Woessner 2004; Szabo et al. 2004; Verstraeten et al. 2004). As we found 12 of our 22 prescription and nonprescription drugs, and metabolites (acetaminophen, caffeine, codeine, carbamazepine, cotinine, erythromycin-18, nicotine, paraxanthine, ranitidine, sulfamethoxazole, trimethoprim, and warfarin) in a community septic tank serving 350 users, it is likely that measurable concentrations of these compounds will be observable in on-site waste water from similar sources. These compounds are apparently used frequently enough and at sufficient dosages in a high school population to enter the waste stream

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