

Soil Persistence and Fate of Carbamazepine, Lincomycin, Caffeine, and Ibuprofen from Wastewater Reuse

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The reuse of treated wastewater for groundwater recharge is an effective way to provide advanced treatment and water storage. Contaminants such as human drugs have been identified as a potential problem for use of this water. Gilbert, Arizona maintains a 28.3-ha facility designed to recharge $15,150 \text{ m}^3 \text{ d}^{-1}$ through recharge basins constructed on native soil. The facility averages an infiltration rate of $>5 \text{ cm d}^{-1}$, resulting in the potential of pharmaceutical compounds leaching to groundwater. One 4-ha basin was selected for spatial sampling of four pharmaceutically active compounds (PhACs). The compounds were carbamazepine, lincomycin, ibuprofen, and caffeine. Soils were extracted and analyzed using pressurized liquid extraction and liquid chromatography–mass spectrometry–mass spectrometry. The concentration of ibuprofen was below detection limits in all samples. Lincomycin exhibited no net accumulation from year to year but had significantly higher concentrations from depths of 0 to 5 cm than from depths >10 cm. Carbamazepine had the lowest concentration at 0 to 5 cm ($0.18 \text{ ng g soil}^{-1}$), providing evidence that there is potential degradation of carbamazepine in surface soils. Carbamazepine also exhibited significant accumulation from year to year. Caffeine exhibited net accumulation and had higher concentrations in surface samples. The accumulation of PhACs in the soil beneath recharge basins indicates that PhACs are being removed from the infiltrating water and that, regarding ibuprofen and lincomycin, the treatment is sustainable due to the lack of accumulation. Regarding carbamazepine and caffeine, further investigations are needed to determine possible management and environmental conditions that could prevent accumulation.

IN ARID REGIONS, the reuse of wastewater is often seen as a valuable water resource. Treated municipal wastewater can be reclaimed via many mechanisms, including direct reuse (e.g., irrigation or advanced treatment), recharge to groundwater, or release into surface waters for recapture and reuse downstream. Recently, the presence of pharmaceutically active compounds (PhACs) at very low levels in treated effluent has gained the interest of regulators as well as municipal water providers due to increased analytical capabilities and potentially unknown environmental and health effects. The ability to detect and quantify these compounds at environmentally significant concentrations became widely available at the end of the last century (Jorgensen and Halling-Sorensen, 2000). Some of the earliest reports of finding PhACs in the environment occurred in the early 1980s (Halling-Sorensen et al., 1998). More recently, the detection of numerous PhACs in environmental samples has become commonplace (Kolpin et al., 2002; Ternes, 1998, 2001). It is unknown if the presence of these compounds at very low concentrations in environmental samples is biologically relevant.

Understanding the environmental fate of waste water contaminants found in sewage effluent is becoming more important. Many investigations regarding the fate and transport of pharmaceuticals have focused on river and stream systems and hydrologically connected groundwater (Clara et al., 2004; Löffler et al., 2005; Kolpin et al., 2004; Kolpin et al., 2002). Other studies have investigated the fate of pharmaceuticals in terrestrial settings. Kinney et al. (2006) reported that the use of reclaimed waste water for irrigation of turf resulted in the presence of a number of pharmaceutical compounds in the top 30 cm of soil. They also found that the concentration of the individual compounds investigated were $<15 \text{ } \mu\text{g kg}^{-1}$ in the top 30 cm of soil and that most compounds showed no net accumulation in the soil. This indicates that natural inactivation and removal of the compounds were occurring in the top 30 cm of soil through degradation, sorption, or a combination of both. Williams et al. (2006) reported carbamazepine sorption and desorption coefficients using equilibrium batch techniques for terrestrial

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Abbreviations: HPLC, high-performance liquid chromatography; LC, liquid chromatography; MS, mass spectrometry; OC, organic carbon; PhAC, pharmaceutically active compound; SAT, soil aquifer treatment.

soils. Adsorption and desorption distribution coefficients were determined, resulting in K_D values ranging from 12.6 to 47.8, with adsorption having the lowest K_D and sequential desorption events having the highest.

Reclaimed sewage effluent can be further treated and stored through artificial groundwater recharge (Bouwer, 1996). Conventional water storage requires large surface impoundments, such as reservoirs where stored water is exposed to loss through evaporation. Existing aquifers offer a reliable alternate storage option with adequate storage volume and greatly reduced potential for loss due to evaporation (Bouwer, 1991). Further treatment can be achieved within the saturated and unsaturated zone between the point of infiltration and extraction from the groundwater. Bank filtration and soil aquifer treatment are examples of enhanced treatment of wastewater through infiltration.

Bank filtration provides treatment that removes biodegradable dissolved organic carbon, trace organics, and pathogens (Grünheid et al., 2005) and is commonly practiced in Europe where favorable hydrologic conditions are present. Generally, the system consists of rivers or lakes with porous banks where extraction wells are located within the groundwater that is under hydrologic influence of the surface water body. Treated effluent is released into the surface water body and infiltrated through the bank to the extraction well. Treatment is achieved by natural attenuation through porous, biologically active zones. Several researchers have demonstrated the utility of bank filtration to remove organic carbon, nutrients, and pathogens (Grünheid et al., 2005; Castillo et al., 2001; Essandoh et al., 2011; Idelovitch et al., 2003; Weiss et al., 2005; Sperlich et al., 2008) such that the extracted water is biologically stable and requires no further disinfection before distribution to drinking water systems (Kuehn, 2003; van der Kooij, 2003). Bank filtration has shown mixed results regarding the removal of trace amounts of pharmaceuticals. In other studies, bank filtration has been shown to reduce a number of different pharmaceuticals, including antibiotics, analgesics, and blood lipid regulators (Grünheid et al., 2005; Heberer et al., 2004; Massmann et al., 2006). However, a number of studies have shown that there is very little attenuation of other pharmaceuticals (e.g., carbamazepine, primidone, and propyphenazone) during bank filtration (Heberer et al., 2004; Massmann et al., 2006).

In arid regions, the use of bank filtration is commonly replaced by the use of spreading basins to infiltrate wastewater that has undergone treatment (Bouwer, 2000; Díaz-Cruz and Barceló, 2008). The infiltrated water receives further treatment, commonly referred to as "soil aquifer treatment" (SAT), during the recharge process (Bouwer, 2002). In addition, large volumes can be stored in groundwater aquifers for future extraction and use. A number of studies have reported the attenuation of pharmaceuticals during SAT (Amy and Drewes, 2007; Díaz-Cruz and Barceló, 2008; Drewes et al., 2003; Laws et al., 2011; Mansell and Drewes, 2004). Laws et al. (2011) found that SAT with a travel time of 60 d provided removal of 86.0 to 99.9% for a number of PhACs. The greatest removal was $\geq 99.9\%$ for Atenolol. Steroidal hormones have also been shown to be removed by SAT. Estrinol and testosterone concentrations were reduced to below detection limits, and 17 β -estradiol was attenuated by 90% (Mansell and Drewes, 2004). Drewes et al. (2003) also found that the analgesics ibuprofen and naproxen were removed to below detection limits by SAT. However, similar to bank filtra-

tion, SAT has been reported to be ineffective at removing carbamazepine and primidone (Drewes et al., 2003; Laws et al., 2011). Laws et al. (2011) also found that phenytoin exhibited negligible removal by SAT and that 74% of sulfamethoxazole remained after SAT treatment, with a travel time of 60 d.

Soil aquifer treatment mechanisms include volatilization, photodegradation, and microbial degradation within the water column before infiltration. After infiltration, further treatment and attenuation can occur via physical filtration, sorption, microbial degradation, chemical reactions, and dilution with groundwater. The soil and vadose zone offers a highly reactive, biologically diverse system where PhACs can be removed or transformed. However, the long-term sustainability of these SAT systems to remove these compounds has not been evaluated. One way to assess sustainability is to examine accumulation rates of PhACs in the soil and vadose zone where recharge is occurring. If PhACs do not accumulate over time, then the system is more likely to be sustainable; however, if PhACs are accumulating, then there is a risk that the system will not be sustainable. The objective of the present research was to measure accumulation rates of four different categories of PhACs over 3 yr at a site with a long-term history of groundwater recharge with treated sewage effluent. The four compounds chosen were carbamazepine (an antiepileptic), caffeine (a stimulant), ibuprofen (an analgesic), and lincomycin (an antibiotic).

Materials and Methods

Caffeine, carbamazepine, ibuprofen, and lincomycin were purchased for analytical standards. The hydrochloride salt of lincomycin was purchased from MP Biomedicals with a purity of $>97\%$. Lincomycin is a white crystalline powder with a molecular weight of 443, a pKa of 7.6, and water solubility of 50 mg mL⁻¹.

Caffeine, carbamazepine, and ibuprofen were obtained from Sigma Co. Caffeine is a white powder with a molecular weight of 194.2, a water solubility of 21.7 g L⁻¹, and a purity 97%. Carbamazepine is a white powder with a molecular weight of 236.3, a water solubility of 17.7 mg L⁻¹, and a purity $>95\%$. Carbamazepine is an established drug for the treatment of seizures caused by epilepsy. Other uses include treatment of bipolar disorder and pain management. Ibuprofen is a white powder with a molecular weight of 206.3, water solubility of 9 mg L⁻¹, and a purity $>98\%$. Ibuprofen is an over-the-counter nonsteroidal anti-inflammatory commonly found in treated sewage effluent.

The town of Gilbert, Arizona operates a 27.2-ha groundwater recharge facility (33°21'44.31" N, 111°44'5.63" W) consisting of seven individual basins (Fig. 1). The basins are part of a wildlife preserve that incorporates walking trails and riparian habitat. Recharge operations began in 1998. The facility was designed to recharge 30,283 m³ d⁻¹ of treated municipal waste water, and the depth to groundwater was initially 51.2 m. As of December 2010, a total of 4.56 $\times 10^7$ m³ of water has been recharged, and depth to groundwater has risen to 45.4 m below the ground surface. Each basin is operated to maximize infiltration. Recharge occurs by applying water to a depth of 0.31 m. The water is allowed to completely infiltrate, followed by refilling and infiltration. The refill cycle continues for 3 to 4 wk, at which time the basin is allowed to drain and dry until a tractor and disc harrow can till the basin to remove the organic clogging layer that develops on the surface



Fig. 1. The Gilbert Riparian Preserve located in the Town of Gilbert, Arizona (33°21'44.31" N, 111°44'5.63" W). The building in the upper left corner is a regional library with a permanent lake that has a water-tight liner. Seven irregular shaped infiltration basins and the associated habitat are also visible. Basin 7 is labeled.

of the basin. The basin is then refilled, and the cycle is repeated. Each basin is deep ripped (1.3 m) once or twice annually to help maintain infiltration rates.

Basin 7 (Fig. 1) was selected for sampling in April 2009 and 2010 and in March 2011. The basin has an irregular shore line and has a surface area of 3.9 ha. Sample cores were taken after dry down as soon as a tractor with a hydraulic sampler could drive on the basin, before harrowing. Cores were collected in plastic sleeves (7.5 cm diameter by 100 cm length). Cores were capped and stored at 4°C until further sectioning and sampling. A total of 55 core locations were sampled throughout the basin (Fig. 2). In 2009, each location was recorded using differential GPS. Sampling in 2010 and 2011 occurred within 30 cm of the 2009 location. After core removal, the resulting hole was backfilled with a similar textured soil that had never been exposed to treated sewage effluent.

In the laboratory, the plastic sleeve for each core was removed by cutting longitudinally while leaving the soil core intact. Soil cores were sectioned in 5-cm increments to 25 cm and then in 25-cm increments to the bottom of the core. Once sectioned, the outside 2 cm of each core segment was carefully removed and saved for texture and organic carbon analysis. The interior 3.5 cm of each core was saved separately for pharmaceutical analysis. During the sectioning and dissecting of the cores, care was taken to prevent cross contamination of each section. Internal core samples were frozen and freeze dried before drug extraction. Pharmaceutically active compounds were analyzed from the 0- to 5-, 10- to 15-, and 25- to 50-cm sections.

Soils were extracted for PhAC analysis by accelerated solvent extraction (ASE-300, Dionex). Dry soil and Hydromatrix (Agilent Technologies) were mixed (15 g soil per 2 g Hydromatrix) well and poured onto 1 cm of sand in a 34-mL stainless steel extraction cell. The remainder of the extraction cell was filled with sand.

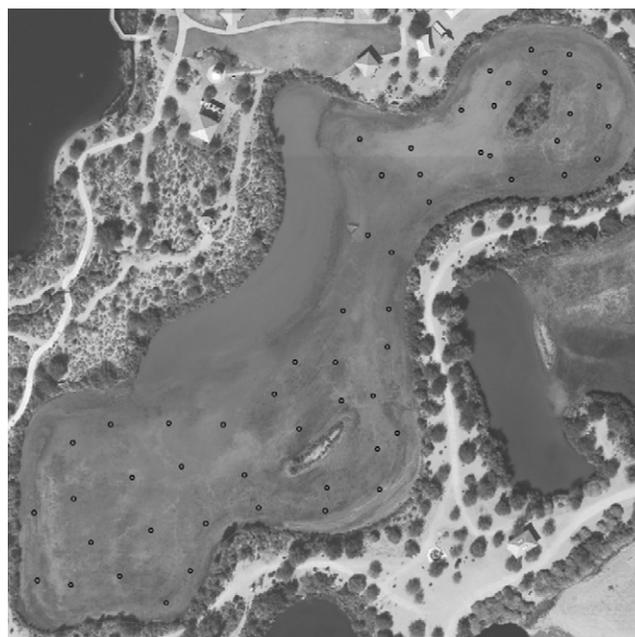


Fig. 2. Close-up view of Basin 7 with sample locations marked within the basin.

Glass fiber filters were placed at both ends of the extraction cell and sealed with high-pressure end caps. The packed cells were then extracted using three static cycles with 75:25 (v/v) water:methanol at 100°C and 10,340 kPa. Each cycle was 5 min long, and the final flush was 60% of the pore volume.

The solution for the ASE extraction (60–70 mL) was diluted with nano-pure water (~400 mL) so that the organic solvent content was <5%. The resulting solution was passed through a conditioned Strata-X (Phenomenex) solid-phase extraction cartridge followed by three 20-mL rinses of nano-pure water. The cartridge was dried for 2 min and eluted with 3 mL of 1:1 methanol:water. The solvent was evaporated to dryness under N₂ at 35°C, and samples were reconstituted with 100 µL of methanol followed by 900 µL of nano-pure water. Samples were transferred to high-performance liquid chromatography (HPLC) vials for liquid chromatography (LC)–mass spectrometry (MS) analysis.

A single water sample was taken in April 2010 to confirm the presence of the PhACs under investigation. Two 1-L amber glass bottles were filled with treated effluent taken from a splitter box structure before distribution to the recharge basins. In the lab, approximately 500 mL of each bottle was mixed together in a volumetric flask. The resulting composite sample was passed through a conditioned Strata-X solid-phase extraction cartridge. The volumetric flask was washed with three successive 100-mL aliquots of nano-pure water, the cartridge was dried for 2 min and eluted with 3 mL of 1:1 methanol:water, and the solvent was evaporated to dryness under N₂ at 35°C. Samples were reconstituted with 100 µL of methanol followed by 900 µL of nano-pure water and transferred to HPLC vials for LC-MS analysis.

Lincomycin, caffeine, and carbamazepine analysis was performed using LC-MS-MS electrospray (+). Separation was performed using a Waters 2.1 × 30 mm XTerra MS C18 column with a 2.5-µm stationary phase (Waters Co.). Operating conditions of the LC were: a mobile phase flow rate of 0.25 mL min⁻¹ with a binary mobile phase of 0.1% formic acid in acetonitrile

and 0.1% formic acid in water. Initial conditions were 10:90 acetonitrile:water, followed by isocratic flow for 1.5 min. At 1.5 min, a linear gradient from 10:90 acetonitrile:water to 90:10 acetonitrile:water was applied over 5 min, followed by 1.5 min isocratic flow at 90:10 acetonitrile:water. Lincomycin eluted at 2.2 min and was quantified using the transition 407.2 (m/z)→126.2 (m/z), caffeine eluted at 3.7 min and was quantified using the transition 194.9 (m/z)→137.9 (m/z), and carbamazepine eluted at 5.3 min and was quantified using the transition 237.1 (m/z)→194.06 (m/z).

Ibuprofen analysis was performed using LC-MS-MS electrospray (-). Separation was performed using a Waters 2.1 × 30 mm XTerra MS C18 column with a 2.5- μm stationary phase (Waters Co.). Operating conditions of the LC were: a mobile phase flow rate of 0.25 mL min⁻¹ with a binary mobile phase of 0.1% NH₄OH in acetonitrile and 0.1% NH₄OH in water. Initial conditions were 10:90 acetonitrile:water, followed by isocratic flow for 1.5 min. At 1.5 min, a linear gradient from 10:90 acetonitrile:water to 90:10 acetonitrile:water was applied over 5 min, followed by 1.5 min isocratic flow at 90:10 acetonitrile:water. Ibuprofen eluted at 5.0 min and was quantified using the transition 205.1 (m/z)→161.1 (m/z).

Texture was determined using the hydrometer method (Gee and Bauder, 1986). Total organic carbon was determined using a Shimadzu total organic carbon analyzer with a solid sample module (Shimadzu Scientific Instruments). Organic matter was oxidized in an oxygen stream at 950°C, and CO₂ was analyzed using an infrared detector.

Analysis of covariance was performed using StatView 5.1 (SAS Institute). A split-plot design was used with the entire basin being the main plot and each year being a subplot with depth as the main effect. The mobility of organic compounds can also be affected by clay content and soil organic carbon content. Therefore, organic carbon content and percent clay were used as covariates.

Results

Organic carbon (OC) content of the soil in the basin decreased with depth from the surface (Fig. 3). The average OC content was 4.3 g kg⁻¹ for the 0- to 5-cm layer, 2.5 g kg⁻¹ for the 10- to 15-cm layer, and 1.7 g kg⁻¹ for the 25- to 50-cm layer. The typical OC content for the surface layer of soils in the area is <2.5 g kg⁻¹. This would indicate that the application of treated wastewater increased the OC of the top 5 cm but did not increase OC in the lower layers. The increase in OC is due to the continual growth and deposition of floating aquatic vegetation during recharge. Additionally, the spatial variability of OC within the basin was very small for each depth, and OC remained constant from year to year. The increase in OC can provide a site for increased sorption of the PhACs as well as a nutrient source for direct metabolism or co-metabolism of the PhACs.

Clay content of the basin was more spatially variable than OC and had a general increase with depth (Fig. 4). Average clay content was 409 g kg⁻¹ at the surface and 419 g kg⁻¹ in the 25- to 50-cm layer. Statistically there was no net increase in the clay content with depth. The increase in clay with depth is expected due to accumulation of clays leached from the surface. This accumulation of clay may result in the loss of infiltration in the future; therefore, further monitoring of clay accumulation would be warranted.

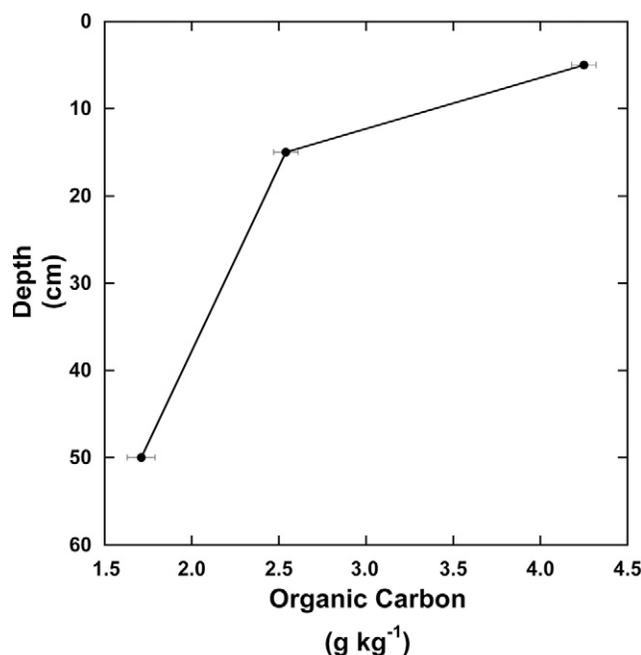


Fig. 3. Plot of percent organic carbon versus depth for Basin 7 at the Gilbert Riparian Preserve. Error bars represent ± 1 SEM.

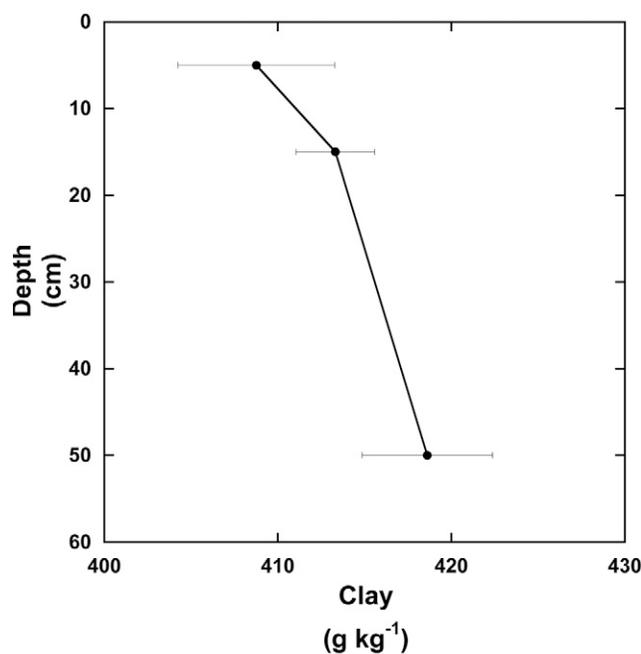


Fig. 4. Plot of percent clay versus depth for Basin 7 at the Gilbert Riparian Preserve. Error bars represent ± 1 SEM.

Ibuprofen

None of the samples taken from the recharge basin had quantifiable amounts of ibuprofen (Table 1). Some of the chromatograms from the 0- to 50-cm sections showed peaks for ibuprofen, but none of the peaks was large enough to quantify. The method detection limit for ibuprofen was 1.0×10^{-3} ng soil⁻¹. Ibuprofen concentration in the single water sample was 16.0 ng L⁻¹, indicating that the source water contained ibuprofen. However, because this was a single “snap-shot” of the applied water, no further inferences can be drawn. Others have also reported that ibuprofen was

Table 1. Soil concentration of pharmaceutically active compounds in the Gilbert Riparian Preserve Basin 7.

	Soil concentration			
	2009	2010	2011	Avg.
	ng g ⁻¹ soil			
Ibuprofen	b.d.†	b.d.	b.d.	n.a.‡
0–5 cm	b.d.	b.d.	b.d.	n.a.
10–15 cm	b.d.	b.d.	b.d.	n.a.
25–50 cm	b.d.	b.d.	b.d.	n.a.
Lincomycin	5.4 × 10 ⁻³ (2.9 × 10 ⁻⁴)§	7.6 × 10 ⁻³ (4.6 × 10 ⁻⁴)	2.4 × 10 ⁻³ (1.3 × 10 ⁻⁴)	5.1 × 10 ⁻³ (2.1 × 10 ⁻⁴)
0–5 cm	9.3 × 10 ⁻³ (4.5 × 10 ⁻⁴)	1.3 × 10 ⁻² (9.7 × 10 ⁻⁴)	4.2 × 10 ⁻² (2.0 × 10 ⁻⁴)	8.8 × 10 ⁻³ (4.6 × 10 ⁻⁴)
10–15 cm	4.2 × 10 ⁻³ (2.5 × 10 ⁻⁴)	5.5 × 10 ⁻³ (2.6 × 10 ⁻⁴)	1.8 × 10 ⁻³ (1.1 × 10 ⁻⁴)	3.8 × 10 ⁻³ (1.8 × 10 ⁻⁴)
25–50 cm	2.7 × 10 ⁻³ (2.2 × 10 ⁻⁴)	4.5 × 10 ⁻³ (3.0 × 10 ⁻⁴)	1.2 × 10 ⁻³ (1.0 × 10 ⁻⁴)	2.8 × 10 ⁻³ (1.7 × 10 ⁻⁴)
Carbamazepine	0.21 (1.5 × 10 ⁻³)	0.21 (1.3 × 10 ⁻³)	0.29 (1.6 × 10 ⁻³)	0.24 (8.8 × 10 ⁻³)
0–5 cm	0.14 (1.2 × 10 ⁻²)	0.16 (1.2 × 10 ⁻²)	0.25 (1.4 × 10 ⁻²)	0.18 (8.3 × 10 ⁻³)
10–15 cm	0.24 (2.6 × 10 ⁻²)	0.27 (2.3 × 10 ⁻²)	0.35 (2.9 × 10 ⁻²)	0.29 (1.5 × 10 ⁻²)
25–50 cm	0.24 (3.5 × 10 ⁻²)	0.21 (2.7 × 10 ⁻²)	0.28 (3.6 × 10 ⁻²)	0.24 (1.9 × 10 ⁻²)
Caffeine	0.77 (3.4 × 10 ⁻²)	0.88 (3.5 × 10 ⁻²)	1.2 (5.9 × 10 ⁻²)	0.96 (2.7 × 10 ⁻²)
0–5 cm	0.89 (5.0 × 10 ⁻²)	1.1 (8.1 × 10 ⁻²)	1.7 (9.6 × 10 ⁻²)	1.2 (5.2 × 10 ⁻²)
10–15 cm	0.97 (6.7 × 10 ⁻²)	0.88 (3.4 × 10 ⁻²)	1.4 (9.4 × 10 ⁻²)	1.1 (4.3 × 10 ⁻²)
25–50 cm	0.46 (2.1 × 10 ⁻²)	0.66 (3.8 × 10 ⁻²)	0.66 (5.6 × 10 ⁻²)	0.59 (2.5 × 10 ⁻²)

† Below method detection limit (1.0 × 10⁻³).

‡ Not applicable (no average could be calculated).

§ Values are averages for all locations and depths. Numbers in parentheses are SEM.

very degradable under aerobic field conditions (Rauch-Williams et al., 2010 and references therein). Due to the wet–dry operational regime of the recharge basin, ibuprofen would have ample opportunity to be exposed to aerobic conditions conducive to degradation. Thus, over a 3-yr period, the concentration of ibuprofen did not accumulate, and the soil appeared to be capable of removing any ibuprofen applied in the recharge water.

Caffeine

The concentration of caffeine in the single water sample was 47.6 ng L⁻¹. Caffeine content of the soil was higher than any of the other PhACs measured (Table 1). Caffeine concentration decreased with increasing depth from the surface (Fig. 5). Results from ANOVA indicate that there was a significant difference in the downward movement of caffeine (*p* < 0.01). The average caffeine concentration for all years in the 0- to 5-cm layer was 1.2 ng g soil⁻¹, and the average caffeine concentration was significantly lower at depth (1.1 ng g soil⁻¹ for 10–15 cm; 0.6 ng g soil⁻¹ for 25–50 cm). Analysis of variance also indicated that caffeine concentration was independent of soil clay content and OC content. The lack of correlation between clay and OC content and caffeine content is consistent with results from Karnjanapiboonwong et al. (2010). They found that the sorption of caffeine was dominated by organic matter in soils having an OC content of 1.3 and 2.5% but was significantly reduced in a soil with very little OC sorption. Soils from the riparian preserve had very low OC contents of <0.45%.

Over 3 yr, caffeine accumulated significantly (*p* < 0.01) within the profile from an average soil concentration of 0.8 ng g soil⁻¹ in 2009 to 1.2 ng g soil⁻¹ in 2011. Caffeine concentrations in the 0- to 5-cm and the 10- to 15-cm layers were higher in 2011 than in 2009 and 2010. However, at 25 to 50 cm, the concentrations of caffeine in 2010 and 2011 were similar but significantly greater than in 2009. The findings presented here

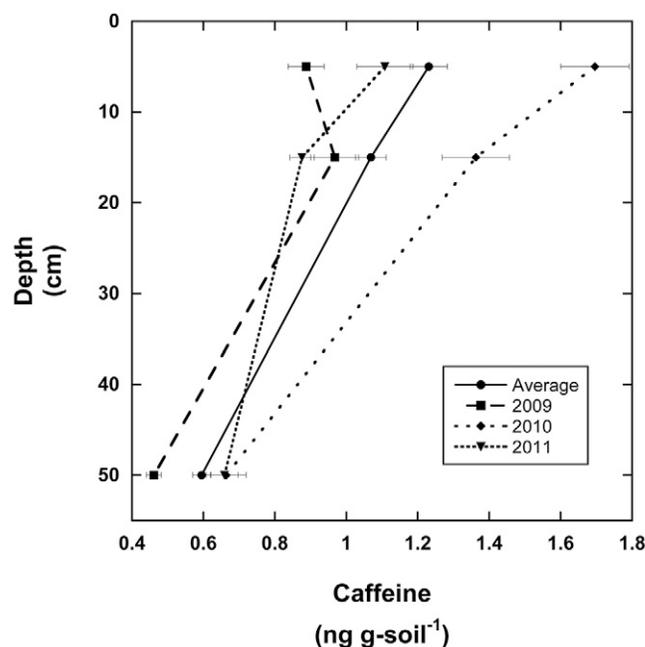


Fig. 5. Plot of soil caffeine concentration versus depth for Basin 7 at the Gilbert Riparian Preserve. The solid line is the average for all samples. The broken lines are the average concentration for each individual year. Error bars represent ±1 SEM.

are in agreement with Laws et al. (2011), who reported that caffeine was essentially removed from infiltrated water during SAT. The results presented here also indicate that the caffeine removed from infiltrating water is accumulating in the soil layer underlying the recharge basin. Whether that accumulation will continue depends on the native soil biology and the ability to degrade caffeine. All indications are that caffeine is biodegraded during sewage treatment. Froehner et al. (2011) reported that sewage treatment plants reduced caffeine concentrations from

5 to 10 $\mu\text{g L}^{-1}$ before treatment to $<0.02 \mu\text{g L}^{-1}$ after treatment. This indicates that, as the mass of caffeine in the soil increases, there will be a critical concentration at which point biological degradation will begin to remove caffeine from the soil profile. Caffeine metabolites were not measured and may have very different behavior and distribution; therefore, metabolite accumulation may or may not be greater than caffeine.

Carbamazepine

The carbamazepine concentration in the effluent sample was 31.1 ng L^{-1} , and the distribution within the soil profile is shown in Fig. 6. Carbamazepine concentration increased in the entire soil profile from $0.21 \text{ ng g soil}^{-1}$ in 2009 to $0.29 \text{ ng g soil}^{-1}$ in 2011 (Table 1). Carbamazepine has been shown to be highly recalcitrant in the environment (Amy and Drewes, 2007; Laws et al., 2011; Massmann et al., 2006; Snyder et al., 2004; Teijon et al., 2010; Ternes 1998). Additionally, neither bank filtration nor SAT has been successful at reducing carbamazepine during aquifer replenishment. Heberer et al. (2004) reported a slight decrease in carbamazepine concentration during bank filtration, and Drewes et al. (2003) reported that the carbamazepine concentration found in groundwater monitoring wells downgradient from waste water recharge basins showed no significant reduction after travel times of approximately 2 yr. Recently it was reported that SAT removed approximately 49% of the carbamazepine present in recharge water. However, when taking into account the loss of concentration due to dilution, there was only negligible removal (Laws et al., 2011).

Carbamazepine concentration was significantly lower ($p < 0.01$) in the 0- to 5-cm layer ($0.18 \text{ ng g soil}^{-1}$) than in the 10- to 15-cm ($0.29 \text{ ng g soil}^{-1}$) or the 25- to 50-cm layer ($0.24 \text{ ng g soil}^{-1}$). One possible explanation for the surface having a lower carbamazepine concentration than the lower depths is increased degradation in the surface. Even though carbamazepine is highly recalcitrant, researchers have reported that specific environmental conditions can lead to removal. A number of researchers have reported that carbamazepine can be degraded through photolysis (Chiron et al., 2006; Pereira et al., 2007). The maximum depth of water applied to the infiltration basin is 0.31 m, followed by complete infiltration. This assures that the carbamazepine present in the wastewater is continually exposed to sunlight and potential photodegradation. In addition to photodegradation, Reungoat et al. (2011) recently reported that a pilot-scale biofilter was capable of removing $>90\%$ of applied carbamazepine under aerobic conditions. The surface layer of the recharge basin could be considered a highly effective aerobic biofilter due to the development of an algal mat at the infiltration surface with frequent aerobic conditions due to repeated exposure to the atmosphere in between the filling cycle of the basin. Every 3 to 4 wk, the basin is dried and the top 10 cm is harrowed to mix the surface organic layer, which can seal the surface and prevent infiltration into the top 10 cm of soil. This provides further aeration and access to sunlight for potential degradation of carbamazepine. Finally, Heberer and Adam (2004), using a recharge basin configuration, found that carbamazepine was reduced by 9% over a travel distance of approximately 50 m. This is consistent with some carbamazepine removal in a zone near the point of infiltration followed by trans-

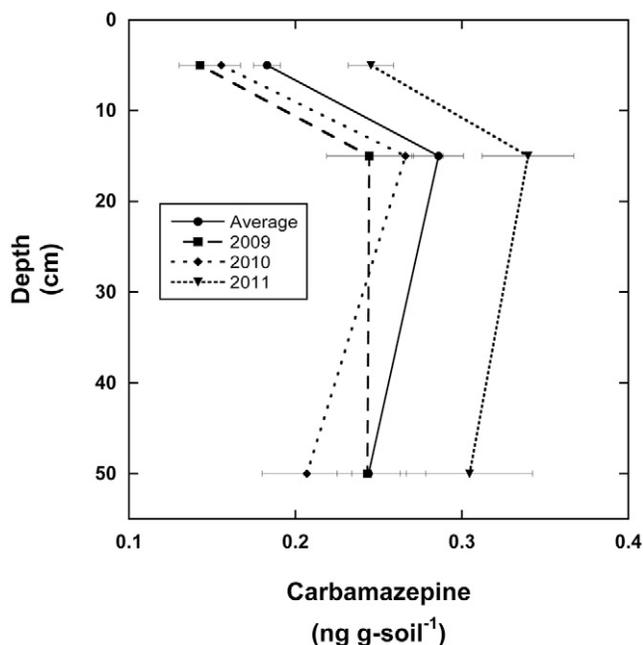


Fig. 6. Plot of soil carbamazepine concentration versus depth for Basin 7 at the Gilbert Riparian Preserve. The solid line is the average for all samples. The broken lines are the average concentration for each individual year. Error bars represent ± 1 SEM.

port of the majority of the carbamazepine unattenuated through the remainder of the distance.

The carbamazepine concentration below 10 cm is significantly ($p < 0.01$) higher than the surface layer and indicates that no further attenuation occurs and accumulation begins. In addition, carbamazepine concentration was more variable at depth than the other compounds, resulting in larger standard errors. The larger standard error was related to a few sample locations that are some distance apart having consistently higher carbamazepine concentrations. This indicates that carbamazepine may be more susceptible to preferential flow. Alternatively, this is a public area with thousands of yearly visitors who could have inadvertently contaminated those sites such that carbamazepine was incorporated into the soil, and the concentration will decline as the source dissipates. Accumulation of carbamazepine occurred during the 3 yr that were monitored, indicating some removal from the aqueous phase; however, the annual increase was only on the order of $33.3 \text{ pg g soil}^{-1}$. Combined, these results indicate that there are potential management scenarios that could provide additional treatment of carbamazepine during groundwater recharge.

Lincomycin

Lincomycin had the lowest concentration in the effluent water sample (5.0 ng L^{-1}) of any of the PhACs investigated. The lincomycin distribution in the soil profile is plotted in Fig. 7. The concentration of lincomycin was two orders of magnitude lower (Table 1) than carbamazepine and was significantly higher in the surface 0- to 5-cm layer ($8.8 \times 10^{-3} \text{ ng g soil}^{-1}$) than in the deeper layers (3.8×10^{-3} and $2.8 \times 10^{-3} \text{ ng g soil}^{-1}$ for 10–15 and 25–50 cm, respectively). There were significant differences in lincomycin concentration from year to year, with 2010 having the highest concentration ($7.6 \times 10^{-3} \text{ ng g soil}^{-1}$) and 2011 having the lowest ($2.4 \times 10^{-3} \text{ ng g soil}^{-1}$). The overall

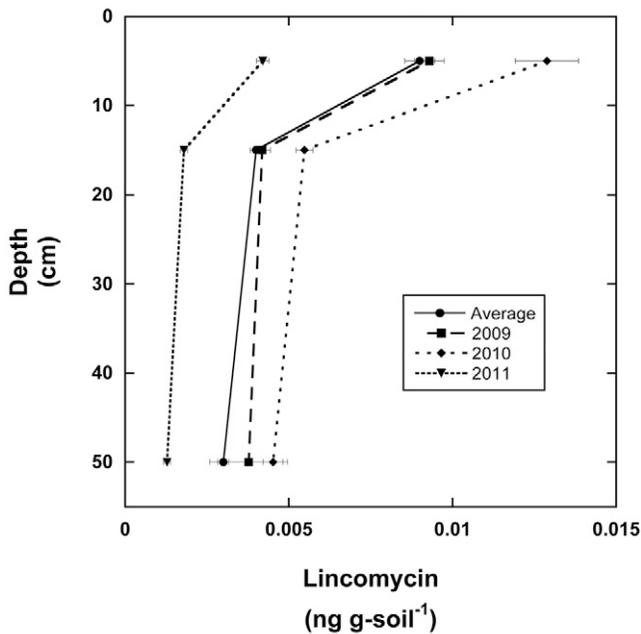


Fig. 7. Plot of soil lincomycin concentration versus depth for Basin 7 at the Gilbert Riparian Preserve. The solid line is the average for all samples. The broken lines are the average concentration for each individual year. Error bars represent ± 1 SEM.

low level of lincomycin in the soil can be attributed to two factors: (i) the low concentration of lincomycin in the effluent sample and (ii) the occurrence of lincomycin degradation. Degradation is expected because lincomycin is a naturally occurring compound produced by soil microorganisms (Hornish et al., 1987). It also appears that no overall accumulation of lincomycin occurred over the 3 yr because the concentration in 2011 was the lowest measured.

Conclusions

The accumulation of four PhACs in soil was measured in a basin designed to recharge groundwater with treated sewage wastewater. Over a 3-yr period, no net accumulation of ibuprofen or lincomycin was observed. However, caffeine and carbamazepine exhibited significant accumulation. On average, the mass accumulated over 3 yr; in the top 50 cm of the 1.4-ha basin, 32 g of carbamazepine and 155 g of caffeine were detected. The soil concentration of ibuprofen was below detection limits in all soil samples. Lincomycin and caffeine had the highest concentration in the surface and reduced concentrations related to increasing depth. Carbamazepine was unlike any of the other compounds, with significantly lower concentrations at the surface than at depth, providing evidence that potential management strategies might be found to help reduce or eliminate the mass of carbamazepine reaching groundwater. Overall, our results indicate that recharge of treated wastewater to groundwater is sustainable in the case of ibuprofen and lincomycin and potentially sustainable in the case of carbamazepine. In the case of caffeine, the research presented here is inconclusive regarding the sustainability of groundwater recharge. Caffeine accumulated over 3 yr; however, it is unclear whether it will continue to accumulate or if there is a threshold concentration above which biological degradation will occur.

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