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Fate and Transport of Fourteen Pharmaceuticals and Personal Care Products in an Irrigated Soil Profile

Lena Wright
University of Nevada, Las Vegas

FATE AND TRANSPORT OF FOURTEEN PHARMACEUTICALS AND

PERSONAL CARE PRODUCTS IN AN IRRIGATED SOIL PROFILE

By

Lena Wright

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Dale Devitt, Ph.D., Committee Chair

Michael Young, Ph.D., Committee Member

David Kreamer, Ph.D., Committee Member

Jacimaria Batista, Ph.D., Graduate College Representative

Tom Piechota, Ph.D., Interim Vice President for Research &
Dean of the Graduate College

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ABSTRACT

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by

Lena Wright

Dr. Dale Devitt, Examination Committee Chair
Professor of School of Life Sciences
University of Nevada, Las Vegas

Use of pharmaceuticals and personal care products (PPCPs) is on the rise and unfortunately, a large percentage passes through the human body. These compounds then find their way into the wastewater stream and into treatment facilities. Only a fraction of these compounds are removed from the stream prior to discharge. An environmentally acceptable alternative to discharging recycled water to rivers, lakes and other bodies of water is to use the water for irrigation of large areas of turfgrass. These PPCPs, of which some may have high mobilities in irrigated soil plant systems, may potentially impact groundwater resources. To determine the movement of 14 PPCPs under turfgrass irrigated conditions, a field based lysimeter study was conducted. The lysimeter study consisted of 24 lysimeters in which eight treatment combinations of soil type (loamy sand or sandy loam), leaching fraction (5 or 25%), and cropping systems (bare or turfgrass) were replicated in triplicate. Lysimeters were irrigated with tertiary treated reclaimed water. After 745 days of monitoring, nine of the 14 compounds were detected in drainage samples. Most of the detections occurred in sandy soils with high leaching fractions, averaging 74% for sulfamethoxazole, 72% for primidone and 40% for carbamazepine versus the lower leaching sandy loams, which had zero or very small detection rates. Factors influencing the movement of these compounds varied based on the compound

and the imposed treatments. In the case of primidone, 94% of the variability in the mass discharge of primidone could be accounted for by taking into account the number of unsaturated pore volumes draining, the percent sand content and the redox potential at 105 cm. The highest mass flux, scaled on a hectare (ha) basis, was recorded for sulfamethoxazole (0.25 g ha^{-1} yr^{-1}). Soil sampling showed nine of the 14 pharmaceuticals in the soil profile. For example, Sulfamethoxazole had the highest average incoming concentration (1600 ng/l) but had only 150 ng/L in the upper most layer of soil with decreasing concentration with depth. Soil concentrations scaled to mass within the soil profile did not fully account for mass lost in the soil profile, with some compounds having greater than 90% unaccounted mass (Diclofenac, Dilantin, Meprobamate, Sulfamethoxazole, Trimethoprim).

Based on our results, restricting the use of recycled water based solely on the presence of PPCP's should only be a consideration at sites where soils are extremely sandy and irrigation regimes are not based on an evapotranspiration feedback approach.

ACKNOWLEDGEMENTS

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Chapter 1

Introduction

The use of recycled water as an irrigation source is gaining greater attention due to the prolonged drought in the arid southwest, the potential for climate change, and increased demand on water resources due to population increases. For example, in 2010 Lake Mead recorded its lowest water level since the lake first began filling in the 1930's (Lake Mead Water Database). With greater uncertainty attached to flow in the Colorado River, communities in the Colorado River Basin, such as Las Vegas, NV, need to expand their water resource portfolios. Using recycled water for irrigation of outdoor landscaping and turfgrass in particular, becomes an important option for water managers. Without changes in how water is used and maintained, and with uncertainty caused by drought and climate change, some theorize that Lake Mead's water level could drop below usable levels by 2021 (Barnett and Pierce, 2008).

One way in which water managers have maintained an adequate supply of potable water for the Las Vegas Valley is through the use of "return-flow credit." Through this system, water treated at a wastewater treatment plant (WWTP) and returned to the Colorado River System provides Nevada with earned credits. When the recycled water is returned to the Colorado River, additional water above Nevada's 300,000 acre-feet allocation, under the Law of the River Compact, can be taken.

There have been some concerns about releasing recycled water to bodies of water, such as Lake Mead, and these concerns have been gaining more attention over the last two decades. One such concern is pharmaceuticals and personal care products (PPCPs). PPCPs are compounds that are used to treat and prevent disease and promote health in

humans and animals. They are used on an increased daily basis for a wide range of other reasons. These PPCPs are washed down the sink or flushed down the toilet as in the case of pharmaceuticals, where as much as 90% are excreted. These PPCPs then make their way into the wastewater treatment process at the wastewater treatment plants (WWTPs). Though some degradation and sorption to sludge occur, a fraction of the compound mass passes through the plant unchanged (Halling-Sorensen et al., 1998; Daughton and Ternes, 1999; Kolpin et al., 2002). Treated waters may then be discharged to bodies of water where they have the potential to negatively affect aquatic organisms.

As mentioned above, the alternative to discharge to Lake Mead, or another body of water is to use the recycled water for irrigation. Thirty of the 53 golf courses in southern Nevada currently use recycled water for irrigating their fairways and greens (Devitt et al., 2007) and new golf courses are required to use recycled water when connections to a distribution system are available. Using this water for irrigation prevents PPCPs from entering the aquatic system directly, but the potential exists for these compounds to reach groundwater sources by downward percolation of water. It is possible that large turfgrass areas would act as a biofilter and possibly reduce PPCP's discharge to groundwater systems (Bower and Chaney, 1974) when this recycled water is used as irrigation.

Many factors can influence the attenuation of pharmaceuticals in the shallow soil subsurface, or move further through the profile to the groundwater system. These factors include, but are not limited to: (1) the physicochemical properties of the compound, including K_{ow} and solubility of the compound; (2) soil structure; (3) the amount of organic material in the soil; (4) the condition of the soil (i.e. aerobic/anaerobic conditions,

soil pH etc.); (5) irrigation cropping system (how a cover crop is maintained and irrigated); and 6) depth to groundwater.

The approach of this study was to monitor selected PPCPs through a soil profile under irrigated conditions, employing meso-scale lysimeters under controlled field conditions. We intend to consider the following three hypotheses:

1. Soil texture will significantly impact the fate and transport of PPCP's, with soils higher in clay content (sandy loam vs. loamy sand) retarding the downward migration of PPCP's to a greater extent.

2. Cover (turfgrass vs. bare) will significantly impact the fate and transport of PPCP's, with turfgrass covered soils retarding the downward migration of PPCP's to a greater extent than bare soil.

3. Irrigation management, especially the imposed leaching fraction (drainage volume/irrigation volume) will significantly impact the fate and transport of PPCP's with the downward migration of PPCP's greater under higher leaching conditions.

With these hypothesis in mind, a lysimeter project was designed to monitor the appearance on PPCPs from recycled water in drainage from lysimeters. The lysimeters were either packed with one of two soils types, one soil type contained higher clay content. They were left bare or covered with turfgrass to monitor the influence of cover on the lysimeters and PPCP appearance in the drainage. Finally, differing leaching fractions were imposed to monitor the different impacts that number of pore volumes may have on the appearance of PPCPs in the drainage. More detailed lysimeter parameters can be seen in Chapter 3.

The experimental set-up for this study began in the summer of 2008, with the first

irrigation of recycled water occurring on 11/18/2008, continuing until December 2010 for

an experimental period of 745 days.

Chapter 2

Literature Review

Overview

PPCPs in the environment are gaining wider attention after detection in lakes, rivers

and streams (Kolpin et al., 2002, Daughton, C.G. and T.A. Ternes, 1999). With the

increase in analytical capabilities, researchers can now detect compounds at lower

concentrations (e.g., ng/l range) and have identified new compounds previously not

detected. In a sizeable study by Kolpin et al. during 2000-2001, the researchers

discovered at least 1 of 95 target organic compounds in approximately 110 streams

(Kolpin et al., 2002), 72 of which were PPCPs. PPCPs found in these bodies of water

were highly variable in concentration. However, this study was biased, choosing

locations where compounds were most likely to be found, downstream of WWTPs, for

example. Differences in the compounds found and their concentrations were attributed to

the life history of the compound. For example, medications excreted or flushed down the

toilet depend on the people living in a specific area and the quantity and dosage of the

medication prescribed and used. Different suites of compounds would thus be found in

different locations based on the types of medication used by the population.

Ecotoxicology

PPCPs that make their way from the wastewater treatment plant to bodies of water

have the potential to affect aquatic life. PPCPs are designed to be biologically active

(Halling-Sorensen et al., 1998; Kummerer, 2010) and resistant to change to impart their

benefits (Santos et al., 2010). These biologically active compounds are continuously

discharged to bodies of water because of their continual use, unlike pesticides that are

sporadically or seasonally used (Daughton and Ternes, 1999). Thus, aquatic species can be continuously and generationally exposed to these compounds (Daughton and Ternes, 1999). Additional concerns relate to the presence of multiple compounds continuously exposing organisms to sub-therapeutic levels (Jones et al., 2004).

Harmful side effects of these compounds can be wide ranging due to the combination of exposures between compounds and organisms. These effects can range from deformation of physical characteristics to reproductive harm to death (Halling-Sorensen et al., 1998; Kummerer, 2010; Santo et al., 2010). Some non-steroidal anti-inflammatory drugs (NSAIDS) have been shown to cause thinning of eggshells, kidney and liver damage (Santo et al., 2010) while lipid medications have caused death among grass shrimp and fish embryos. Hormone medications, primarily estrogenic compounds have caused reproductive harm, including intersex characteristics and feminization of male fish (Santo et al., 2010; Daughton and Ternes, 1999). Significant decline of Oriental white-backed vultures in Pakistan was correlated to diclofenac residues found in the vulture's tissue between 2000-2003 (Oaks et al., 2004).

Ecotoxicological data for many of these compounds are typically obtained through acute exposure experiments with single compounds. They do not generally perform generational testing or mixture effects because of the time required to perform longer experimental runs (Santo et al., 2010). Discharging recycled water to large bodies of waters will nearly always contain mixtures of PPCPs. Not only is there a continuous input of chemicals to the environments where organisms live, but exposing organisms through their entire lifetime. Mixtures of PPCPs can potentially exacerbate the toxicological effects of each individual compound (Santos et al., 2010).

Columns and Field Studies

The alternative to releasing these compounds directly to an aquatic system is to use the water for irrigation purposes. However, to fully understand potential risks of using this water for irrigation, studies need to be undertaken to understand how compounds move through the soil profile. Several approaches have been taken to understand the fate and transport of these compounds in soil environments, including adsorption/desorption studies, small column studies, large column studies and field scale monitoring.

In the field, where water may recharge groundwater, documenting movement of PPCPs has occurred, but the results are not always consistent. For example, Drewes et al. (2003) summarized that, in general, anti-epileptic medications were persistent during groundwater recharge in both aerobic and anaerobic conditions but caffeine, anti-inflammatory and lipid regulators were removed. Carbamazepine (Arye et al., 2011) and sulfamethoxazole (Cordy et al., 2004) are persistent and less reactive, so they tend to move deeper through the soil profile.

Conducting small column studies, generally <10 cm diameter and ≤50 cm height, is one approach taken to look at PPCP migration through soil profiles. Column studies allow experimental control over the soil conditions and easy access to soil water and drainage volumes for subsequent analysis and assessment of PPCP migration. Smaller columns also allow for greater opportunities to pass large numbers of pore volumes through the soil columns. Laboratory column studies also make adsorption/desorption studies possible by passing wastewater through the column and then attempting to desorb PPCPs with distilled or tap water. Small column studies have encompassed many different soil types and different compounds with some varying results (Chefetz et al.,

2008; Oppel et al., 2004; Scheytt et al., 2006; Gibson et al., 2010; Drillia et al., 2005).
Results reported from small column studies varied significantly because of different
protocols followed, such as soil types, amendments and irrigation practices, making
comparisons difficult. In general, sulfamethoxazole, diazepam, and triclosan appear to
have low mobility; carbamazepine, ibuprofen, and diclofenac have low to moderate
mobility; and naproxen has moderate to high mobility. Controlled laboratory
experiments, however, do not simulate natural irrigated field conditions (Diaz-Cruz et al.,
2003) nor do many of these studies include an irrigated crop cover. Conditions in which
crops are grown under irrigated conditions will differ than those without the crop cover.
Crops will potentially add additional organic matter to the system, extract water from the
soil, inhibiting water movement downward, or potentially take up PPCPs or their
daughter products.

   Larger, field-scale lysimeter projects can better predict actual field conditions because
the soil plant system within the lysimeter will undergo the same conditions occurring in
the field with the additional ability to quantify drainage volume. Xu et al. (2009) used
lysimeters to monitor the transport of compounds in soil over a 4 month irrigation period.
They concluded a small threat of contamination from PPCPs after the compounds were
isolated in the upper layers of soil after 4 months of irrigation. PPCP concentrations with
depth revealed higher concentrations deeper in the soil profile of lysimeters irrigated with
higher volumes of water versus those that received lower volumes of irrigation. Xu et al.
(2009) data suggests that areas irrigated for longer periods of time with higher amounts of
recycled wastewater would have the potential to leach compounds toward groundwater.

Field scale experiments are not as prevalent as batch or small column studies. This smaller population of published research is most likely due to the expense and difficulty in conducting a field scale study. A few larger field scale studies were conducted in which soil sampling and/or ground water monitoring have taken place, and some of these attempted to compare field observations with laboratory batch experiments. Snyder et al. (2004) was one such study, in which laboratory batch experiments were compared to field monitoring. Two golf courses and one WWTP was monitored through the use of groundwater well sampling, and tensiometer sampling at one of the two golf courses. Some comparisons between the laboratory column and field scale monitoring were incomplete. However, Snyder et al. (2004) did report several compounds as being rapidly-moderately degraded/adsorbed, including trimethoprim, meprobamate, and gemfibrozil. Carbamazepine was classified as moderate to slowly degraded/adsorbed.

Chapter 3

Material and Methods

A lysimeter study was developed to assess the influence of various parameters on the

potential movement of PPCPs in a soil profile under irrigated conditions. Parameters

included were soil type, irrigation regime, and cover type. Treatment combinations of soil

type (BC or NLV), cover type (bare or turfgrass) and leaching fraction (0.05 or 0.25).

Where leaching fraction (LF) is defined as the ratio of drainage volume/irrigation

volume. Treatment combinations are summarized in Table 1.

Table 1. Treatment combinations for lysimeters

Soil Type	Leaching Fraction	Grass/Bare
BC	0.05	B
BC	0.25	G
BC	0.05	B
BC	0.25	G
NLV	0.05	B
NLV	0.25	G
NLV	0.05	B
NLV	0.25	G

The treatments assigned as turfgrass plots were planted with hybrid Bermuda grass sod.

Buffer areas between all lysimeters were also planted with hybrid Bermuda grass to

minimize an oasis effect (see Figure 1). Plots covered with turfgrass were over-seeded

with ryegrass (Palmer III) during the winter period of each year. Lysimeters were

assigned and placed in a randomized block design and duplicated in triplicate to enable

statistical analysis on treatment combination effects. The study was conducted at the

Center for Urban Horticulture and Water Conservation (Center) in North Las Vegas, NV.

The Center is located in the northern Mojave Desert, with a semi-arid climate, average

annual precipitation of 10 cm and average yearly temperature of 20°C, with maximum

summer highs reaching 44°C and minimum winter lows reaching -5°C.

**Figure 1. Research site at the Center for Urban Horticulture and Water
Conservation.**

Construction of 24 lysimeters began in the summer of 2008. Each column (60 cm

diameter, and 127 cm long was made from PVC pipe (JM Big Blue™). Each column was

capped at the bottom and sealed with resin and fiberglass. The lysimeters were installed

flush to ground surface, but advancing a solid-stem auger (90 cm diameter) to a depth of

125 cm at each of the 24 locations. Lysimeters were arranged within a 20 m by 13 m plot

in a 6 (row) by 4 (column) grid arrangement with approximately 1 m buffer between each

lysimeter (center to center). After placement in each borehole, lysimeters were leveled

using wood and sand and then backfilled around the exterior of the lysimeter with site

material. In the bottom of each column, two 0.5 bar, ceramic soil solution extraction cups

(17 cm long by 4 cm diameter, model 0652X18-B0.5M2, Soilmoisture Equipment, Inc.,

Santa Barbara, CA) were installed in 7 cm of diatomaceous earth, adjusted for 18%

compaction. Tubing for the soil solution extraction cups ran along the inside of the

column and exited a hole drilled near the top of the column to a vacuum line. The

lysimeters were then backfilled in 5 cm increments with either loamy sand soil collected

from a borrow pit in Boulder City, NV (hereafter referred to as BC) or a sandy loam soil

collected at the Center (hereafter referred to as NLV). The BC soil was packed to a bulk

density of 1.7 g cm^{-3}. The NLV was packed to 1.5 g cm^{-3}. The soil properties of each soil

type are shown in Table 2.

Table 2. Soil properties of loamy sand (BC) and sandy loam (NLV).

Soil Type Abbreviation	Soil Classification	Soil Type	% Sand	% Silt	% Clay	CEC (meq/100g soil)	pH	Organic Matter (%)
BC	Arizo Series, a mixed, sandy-skeletal, typic torriorthent	Loamy Sand	86	4	9	11.6	8.0	0.3
NLV	Loamy carbonitic, thermic shallow typic petrocalcid	Sandy Loam	72	8	19	23.2	7.6	0.8

Redox probes were installed in each lysimeter at 15 cm and 105 cm depths. Redox

probes were constructed similarly to those described by Wafer et al. (2004). Briefly, the

redox probes were constructed of a bronze brazing rod cut to the appropriate length with

a 1/16" hole drilled on one end where the platinum tip was soldered. Heat shrink wrap

was added to cover the shaft of the probe. Marine epoxy was used to seal the tip of the

brazing rod. After hardening, the epoxy was sanded smooth and tested with a calomel

electrode using a 0.1 M hydroquinone solution. Redox values greater than ± 10 mV were

rejected because they represented error greater than 5% of the expected value in the

hydroquinone solution. Rejected probes were stripped down and repaired accordingly. An

example of an uncovered redox probe can be seen in Figure 2. In-situ redox

measurements were taken using a pH/millivolt meter (Φ295, Beckman Coulter, Brea,

CA) and a calomel electrode.

Figure 2. Uncovered redox probe.

Soil water content in each lysimeter was measured using profiler probe (PR2/6, Delta T Devices, Cambridge UK). Access tubes were installed at the center of each lysimeter to a depth of 100 cm, with soil water content measurements taken at 10, 20, 30, 40, 60 and 100 cm simultaneously through the profile. Profiler probe and tube are shown in Figure 3.

Figure 3. Profiler access probe to show length and installation into access tube.

All lysimeters were irrigated with post-UV, tertiary treated, recycled water obtained from the Clark County Water Reclamation District on a bimonthly basis. Wastewater

from this plant undergoes primary clarification, including screening of large debris; secondary treatment using aeration and clarification; followed by a tertiary step of dual media filtration and UV disinfection. Further processes can include addition of chlorine before release to the Las Vegas Valley Wash, but the recycled water used in this study was collected before this final chlorination step. The recycled water was pumped into an 1100 liter carboy and transported to and stored at the Center, where it was placed under shade (Figure 4) to inhibit growth of algae.

Figure 4. Tank for storage of post-UV reclaimed water.

Water was sampled immediately after its arrival to the Center. Irrigation samples were collected in 1 liter amber bottles preserved with sodium azide and ascorbic acid to inhibit microbial growth. Bottles were kept at 4^0C until analysis for PPCPs could be performed. Irrigation samples were held until 8-12 drainage samples were collected and sent with the irrigation samples or after a week of holding time, which ever occurred first.

The list of PPCPs are listed in Table 3 along with the compounds general use and some properties associated with each compound; molecular weight, acid dissociation constant (pK_a), octanol-water partition coefficient and solubility in water. The properties of the PPCPs vary widely, from very soluble compounds to only slightly soluble compounds. The acid dissociation constant gives insight into the amount of ionized form versus unionized form of the PPCP. According the Henderson-Hasselbalch equation (Bergstrom et al. 2004), compounds that have pK_a values equal to the pH of the water would imply that the ionized and unionized forms of the compound would be approximately equal. With an average pH of 8.07, Dilantin and Triclosan would both fall into this category where the compound would have approximately equivalent amounts of ionized and unionized forms in solution. Compound that would have more unionized compound would be Atenolol, Fluoxetine, and Primidone because the pK_a value is higher than the pH of the water. The remaining compounds, Atorvastatin, Carbamazepine, Diazepam, Diclofenac, Gemfibrozil, Meprobamate, Naproxen, Sulfamethoxazole, and Trimethoprim, would primarily exist in the ionized form because the pH value of the water was higher than the pK_a of the compound.

Table 3. Pharmaceutical list with general use, chemical formula, molecular weight, acid dissociation constant (pK$_a$), octanol-water partition coefficient (logK$_{ow}$), and solubility in water.

Compound	General Use	Chemical Formula	Molecular Weight (g/mol)	pK$_a$	logK$_{ow}$	Solubility (mg/L)
Atenolol	Beta-blocker	$C_{14}H_{22}N_2O_3$	266.34	9.48[a]	0.16[a]	13300[b]
Atorvastatin	Anticholesteremic	$C_{33}H_{35}FN_2O_5$	558.64	4.46[d]	6.36[b]	0.00112[b]
Carbamazepine	Anticonvulsant	$C_{15}H_{12}N_2O$	236.27	<2[c]	2.30[a]	17.7[b]
Diazepam	Sedative	$C_{16}H_{13}ClN_2O$	284.74	2.4, 1.5 (3.3)[c]	2.82[a]	50[b]
Diclofenac	NSAID	$C_{14}H_{11}Cl_2NO_2$	296.16	4.15[b]	4.51[b]	2.37[b]
Dilantin	Anticonvulsant	$C_{15}H_{12}N_2O_2$	252.27	8.33[b]	2.47[ab]	32[b]
Fluoxetine	Antidepressant	$C_{17}H_{18}F_3NO$	309.33	9.62[a]	4.60[b]	60.3[b]
Gemfibrozil	Antihyperlipidemic	$C_{15}H_{22}O_3$	250.34	4.7[c]	4.77[b]	10.9[b]
Meprobamate	Tranquilizer	$C_9H_{18}N_2O_4$	218.25	<2[c]	0.70[a]	4700[b]
Naproxen	NSAID	$C_{14}H_{14}O_3$	230.26	4.15[ab]	3.18[ab]	15.9[b]
Primidone	Anticonvulsant	$C_{12}H_{14}N_2O_2$	218.26	>13[e]	0.91[b]	500[ab]
Sulfamethoxazole	Antibacterial	$C_{10}H_{11}N_3O_3S$	253.37	2.1, <2, (5.7)[c]	0.89[a]	610[b]
Triclosan	Antibacterial	$C_{12}H_7Cl_3O_2$	289.55	8 (7.9)[c]	4.53[a]	10[b]
Trimethoprim	Antibacterial	$C_{14}H_{18}N_4O_3$	290.32	6.3, 4.0, <2, (7.1)[c]	0.91[a]	400[b]

[a] Sangster

[b] SRC PhysProp Database

[c] Yoon et al. 2007

[d] Wu et al. 2000

[e] Newton and Kluza, 1978

Analysis of PPCPs was performed at the University of California, Riverside by Dr. Jay Gan's laboratory. The procedure was slightly modified to that described by Vanderford and Snyder (2006), where the procedure is described in more detail. Briefly, the procedure for the PPCP analysis is as follows: irrigation or drainage samples were filtered to remove any large particles, the PPCPs were extracted using solid phase extraction (SPE), the PPCPs were eluted off the cartridges and analyzed on a Aquity ultra performance liquid chromatography system coupled with a Trinity triple quadrupole mass spectrometer equipped with an electrospray ionization source (Waters, Millford, MA). Irrigation and drainage samples were also analyzed at UNLV for electrical conductivity (Model RC-20, Beckman Industrial, Fullerton, California), pH (pH 330, WTW, Munich, Germany) and major anions (chloride, nitrate, and sulfate) and cations (sodium, potassium, ammonium, magnesium and calcium) on a Dionex 120 ion chromatograph (Sunnyvale, CA).

Drainage samples were collected through the ceramics located at the bottom of each lysimeter. Water was pulled through the ceramic by placing a vacuum on the connected tubing. Water was collected in 4 liter vessels kept underground to stabilize temperatures and minimize exposure to light. Vacuum was pulled for approximately 1 hour, 6 days a week to prevent samples from staying in contact with diatomaceous earth for long periods of time and to prevent the soil column from becoming saturated. Some lysimeters, mainly those containing the 0.25 NLV soils were evacuated for longer periods of time, because the sandy loam soils hold larger quantities of water. Drainage samples for PPCP analysis were collected when the initial drainage occurred and every 0.5 unsaturated pore volume thereafter, where an unsaturated pore volume is defined as the

amount of water contained in storage that stabilized under the imposed treatment (this will be discussed further below). Drainage samples designated for PPCP analysis were processed in the same manner as those samples collected from the irrigation system. Drainage samples collected for EC, pH major anions and cations were collected regularly, at least on a monthly basis but generally more often. Approximately one year into the study, there were some concerns about adsorption of PPCPs to the sampling material, so stainless steel samplers with teflon caps and tubing were installed in each of the lysimeters at 115 cm and sampled only at the end of the study.

Lysimeters were irrigated to maintain the imposed leaching fractions (LF), where leaching fraction is defined as drainage volume/irrigation volume. Water balance on each lysimeter was closed on a weekly basis, according to equation 1, to estimate evapotranspiration (ET).

$$ET = I - D - \Delta S \qquad\qquad\qquad \textbf{1)}$$

Where ET = evapotranspiration (cm)

I = irrigation and precipitation (cm)

D = drainage (cm)

ΔS = change in storage (cm)

Irrigation depths were then calculated on a weekly basis by incorporating the appropriate LF. Irrigation amounts were calculated using equation 2.

$$I = ET / 1\text{-}LF \qquad\qquad\qquad \textbf{2)}$$

Where I = irrigation and precipitation (cm)

ET = evapotranspiration (cm)

LF = leaching fraction

Environmental demand was assessed using an automated weather station (Campbell Scientific Inc., Logan, UT) within 200 m of the experimental plot. Parameters monitored included temperature, relative humidity, solar radiation, wind speed and rainfall. Daily reference ET was calculated using the Penman Monteith equation (Allen et al., 2006).

Soil samples were collected at the end of the study in increments of 0-15 cm, 15-30 cm, and 30-60 cm, 60-90 cm, and 90-120 cm. Soils within the depth increments were homogenized to obtain representative subsamples. Sub samples from the upper three increments were sent to A&L Laboratories, which used the combustion method (Bisutti et al., 2004) to determine percent organic matter. Soil samples throughout the profile were also analyzed for PPCP analysis, though analyses were limited to soils from the BC lysimeters due to cost and time limitations. Soils were extracted for PPCPs using a Dionex ASE350 (Sunnyvale, CA). The liquid samples containing the PPCPs extracted from the soils were then cleaned using SPE and analyzed similarly to the irrigation and drainage samples.

Approximately halfway through the experimental period, concerns arose to the possible adsorption of PPCPs to materials used to collect the drainage samples. Interference studies were performed by the Southern Nevada Water Authority (SNWA) to determine the extent of PPCP adsorption to some components involved in the collection of the drainage samples, primarily the diatomaceous earth and the ceramic samplers. For the interference studies, material was submerged in water spiked with approximately 50 ng L^{-1} of each the compounds listed in Table 3 except for primidone and dilantin. The diatomaceous earth and the ceramic samplers, along with other components of the sampling system, were left in the spiked solution for 72 hours.

Solution was sampled every 24 hours and then analyzed to determine the remaining PPCP left in solution (i.e., difference in compound mass would imply sorption onto the material). Later in the study a stainless steel sampler with Teflon caps and tubing were similarly tested for PPCP adsorption to sampling components.

Ultimately, the information that we are interested in was the appearance or lack of PPCPs in the drainage and the rate of movement in a soil profile. Retardation factors can give us a numerical was of expressing the speed at which compounds pass through the soil column, with a value of 1 indicating movement with the water front and a value greater than 1 indicating some retardation in the soil. Retardation factors for PPCPs were calculated using two methods. The first was a simple ratio of the velocity of the water front at the first appearance of drainage to the velocity of the first appearance of drainage. Bouwer (1991) afterwards called this observed R_f.

$$R_{fo} = V_w/V_{PPCP} \hspace{4cm} \textbf{3)}$$

where: R_{fo} = retardation factor observed

V_w = velocity of drainage water front (cm day^{-1})

V_{PPCP} = velocity of PPCP (cm day^{-1})

The second method was to use the sorption coefficients to calculate the retardation factors (Bouwer, 1991), afterwards called theoretical R_f.

$$R_{ft} = 1+\rho K_d/n \hspace{4cm} \textbf{4)}$$

where: R_{ft} = retardation factor theoretical

ρ = bulk density (g cm^{-3})

K_d = sorption coefficient (cm^3 g^{-1})

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n = porosity

There are difficulties calculating retardation factor with either method. For equation 3, one must have accurate water and PPCP velocities. For the purpose of calculating the retardation factor from the lysimeters, the first appearance of drainage water was used as the time for calculating V_w. For V_{PPCP}, we used first appearance of the PPCP. If the particular compound did not appear in the drainage water during the experiment, the concentration from the depth profile was used (BC only). If no PPCP was detected in either the drainage or soil, neither approach for calculating retardation factor was used. In addition, for R_{fc}, we assumed steady state conditions in the lysimeters that may not be necessarily valid, but it did allow for a rough estimate of the retardation factor. For R_{ft}, sorption coefficients generated by Jay Gan's laboratory were used (Lin et al. 2011, Lin and Gan 2011, McCullough 2011). The soils used to determine K_d for each compound were the same as used in the lysimeters:;they were not previously exposed to any PPCP prior to the batch experiments.

Data were analyzed using general descriptive statistics, one way ANOVA for repeated measurements, three-way ANOVA and backward stepwise regression (all tests were conducted using SigmaPlot, version 11.0, Systat Software, Inc.). Terms were deleted in the backward regression analysis when p values for the t test exceeded 0.05. To eliminate the possibility of multicollinearity, parameters were included only if variance inflation factors were less than 2 and the sum total was less than 10.

Chapter 4

Results

Evapotranspiration and Irrigation

Final water balance information for all twenty-four lysimeters is reported in Table 4**,** along with reference ET during the 745 day experimental period. Higher ET values were associated with turfgrass lysimeters, averaging 32% higher than bare soil lysimeters (368 cm vs. 251 cm, p<0.05). On sandy loam lysimeters irrigated at 0.05 vs. 0.25, a 40% difference was observed (277 cm vs. 389 cm, p<0.05), with little observed difference in loamy sand lysimeters. Irrigation amount accounted for 90% of the variability in ET (ET $= 1.84 + 0.77$ (I), $R^2 = 0.90$***). When only the turfgrass lysimeters were considered, soil and LF accounted for 89% of the variability in ET (p<0.01) with biomass deleted from the stepwise regression. Biomass was not a major driving force in ET within the turfgrass lysimeters, because the lysimeters always had 100% turfgrass cover and weekly cuttings did not allow for significant changes in plant canopy architecture or aerodynamic resistances.

Table 4. Cumulative Irrigation, Rainfall, Drainage, LF, ET and ET_0 for all Lysimeters from 11/18/08 to 12/2/10.

Lysimeter	Soil Type	Grass/ Bare	Leaching Fraction	Irrigation (cm)	Rain (cm)	Drainage (cm)	LF	ET (cm)	ET_0 (cm)
8	BC	B	0.05	281.0	18.8	32.7	0.11	226.6	354.3
11	BC	B	0.05	276.8	18.8	52.1	0.18	215.0	354.3
14	BC	B	0.05	251.9	18.8	60.1	0.22	191.5	354.3
6	BC	B	0.25	335.2	18.8	120.6	0.34	212.4	354.3
9	BC	B	0.25	315.6	18.8	90.4	0.27	213.3	354.3
22	BC	B	0.25	386.0	18.8	111.1	0.28	263.8	354.3
1	BC	G	0.05	386.5	18.8	55.5	0.14	329.9	354.3
10	BC	G	0.05	401.3	18.8	34.7	0.08	349.9	354.3
12	BC	G	0.05	420.2	18.8	38.6	0.09	367.5	354.3
13	BC	G	0.25	488.4	18.8	128.2	0.25	343.3	354.3
21	BC	G	0.25	480.5	18.8	123.9	0.25	342.2	354.3
24	BC	G	0.25	509.2	18.8	114.7	0.22	379.0	354.3
2	NLV	B	0.05	278.3	18.8	31.4	0.11	228.9	354.3
4	NLV	B	0.05	235.3	18.8	35.8	0.14	178.8	354.3
7	NLV	B	0.05	275.6	18.8	33.8	0.12	225.4	354.3
16	NLV	B	0.25	423.0	18.8	96.6	0.21	309.6	354.3
19	NLV	B	0.25	504.6	18.8	109.0	0.21	404.1	354.3
20	NLV	B	0.25	460.9	18.8	89.9	0.19	344.1	354.3
15	NLV	G	0.05	419.2	18.8	29.8	0.07	370.9	354.3
18	NLV	G	0.05	401.3	18.8	31.5	0.08	309.0	354.3
23	NLV	G	0.05	411.0	18.8	34.6	0.08	349.1	354.3
3	NLV	G	0.25	548.8	18.8	78.9	0.14	434.6	354.3
5	NLV	G	0.25	549.9	18.8	97.1	0.17	428.1	354.3
17	NLV	G	0.25	541.1	18.8	99.8	0.17	417.2	354.3

Soil Water Content and Soil Water Storage

Soil water content was measured each week to determine the soil water in storage (SWS), in cm of water, on a weekly basis. The change in this soil water storage was used to predict ET and used to obtain irrigation values for the next week to maintain the imposed leaching fraction on each lysimeter. Averaged soil water in storage for each treatment combination is shown in Figure 5. Lysimeter treatments are separated by leaching fraction (LF) and soil type in order to better compare the relationships between

leaching fractions for single cover and soil type. There is not much difference in SWS

between the 0.05 LF and 0.25 LF for the bare loamy sand lysimeters but difference in

SWS can be seen in the remaining treatment combinations. In the turf covered loamy

sand lysimeters the SWS of the 0.05 LF lysimeters is slightly less than the 0.25 LF

lysimeters until the overseed period where lysimeters were all irrigated the same. The

0.05 LF lysimeter reached the same SWS as the 0.25 LF lysimeters and soon surpassed it.

SWS for these lysimeters decrease through the summer months when the 0.05 LF

lysimeters reached similar values to the 0.25 LF lysimeters in mid-summer of 2010. For

both the bare and turf sandy loamy lysimeters the average SWS values of the 0.05 LF

lysimeters compared to the 0.25 LF lysimeters were statistically significant ($p<0.001$)

from 3/1/2009-11/1/2009 when the overseed period began. The 0.05 LF sandy loam

lysimeters SWS began to decline and separate from the 0.25 LF lysimeters around 2/1/10

for the bare lysimeters and 6/1/10 for the turf covered lysimeters. The turf covered sandy

loam lysimeters may have had a 4 month delay compared to the bare because the turf

lysimeters received more irrigations relative to the bare lysimeters to compensate for

evapotranspiration. The soil water storage for each lysimeter needed to reach a certain

value before the lysimeter would begin to drain. The 0.05 leaching fraction sandy loam

lysimeters did not begin to drain until after the overseed period where the soil water in

storage began to approach the values in the 0.25 leaching fraction sandy loam lysimeters.
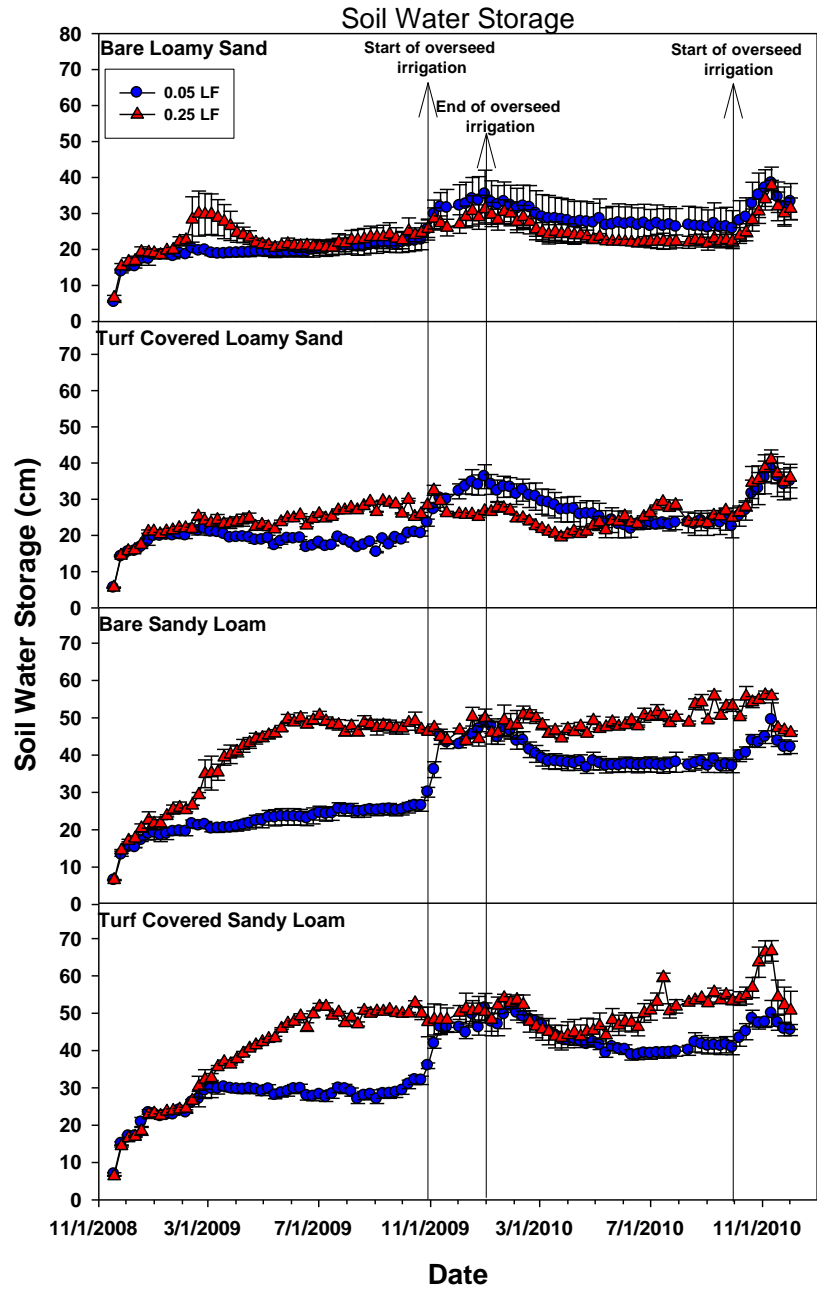
Figure 5. Averaged soil water in storage for each treatment with arrows showing the beginning and end of overseed irrigation.

Soil water content of each lysimeter was not only used to calculate the soil water in storage but to monitor the water content at the lowest depth to aid in determining the time needed for evacuation of the drainage samples. We wanted to maintain unsaturated water contents through the profile, especially at the lowest depths. Averages of the soil water content at the lowest depth (100 cm) can be seen in Figure 6 with the saturation line for each soil type. Saturation of the loamy sand soil is 0.36 m^3 m^{-3} and 0.43 m^3 m^{-3} for the sandy loam soil. The soil water contents at 105 cm for the loamy sand lysimeters were closer in value then the values at 105 cm in the sandy loam lysimeters. There is a clear separation between the 0.05 LF lysimeters and 0.25 LF lysimeters of the sandy loam lysimeters. The sandy loam soils had more clay (19% vs. 9%) in the soils that have a tendency to hold water much tightly then loamy sand soils.
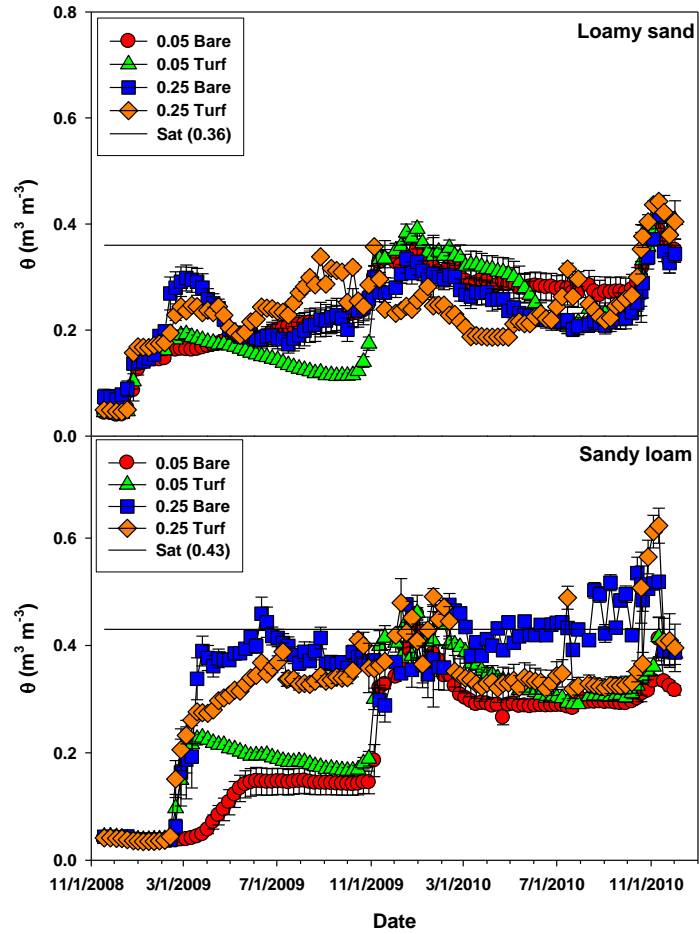
Figure 6. Averaged soil water content at 105 cm for each treatment combination.

In general, soil water contents began to cross the saturated water content line during and immediately after the overseed periods. The only exception was for the bare sandy loam 0.25 LF lysimeters,, which had high irrigations with no turf cover to remove water through evapotranspiration.

Drainage Volume

Cumulative drainage and subsequent LF's are reported in Table 4. Pore volumes of drainage based on unsaturated storage volumes being displaced (Figure 7) were greater in the 0.25 LF loamy sand lysimeters under both turf and bare soil conditions than for other irrigation treatments. Pore volumes of drainage in the 0.25 LF lysimeter for both soil types exceeded 5 pore volumes of drainage after 745 days of experiment. In the bare lysimeters, the 0.05 LF lysimeters had more pore volumes of drainage (2.65) then the 0.25 LF loamy sand lysimeters (2.03). They had similar pore volume until after the overseed period when the 0.05 LF bare loamy sand lysimeters overtook the 0.25 LF bare sandy loam lysimeters. The 0.05 bare sandy loam lysimeters did not reach 1 pore volume of drainage (0.89). The estimated number of days the 0.05 bare sandy loam lysimeters would need to reach 1 pore volume is about 750 days under the overseed period conditions. After the overseed period, the turf 0.25 loamy sand lysimeters and the 0.05 LF sandy loam lysimeters had pore volumes of drainage that were similar. The 0.05 sandy loam turf covered lysimeters also did not reach 1 pore volumes of drainage. The estimated number of days the 0.05 LF turf sandy loam lysimeters would need to reach 1 pore volume of drainage is 764 days. The 0.05 LF sandy loam lysimeters (turfgrass or bare) did not produce any drainage samples until the first overseed period ended, which lasted for approximately 8 weeks.
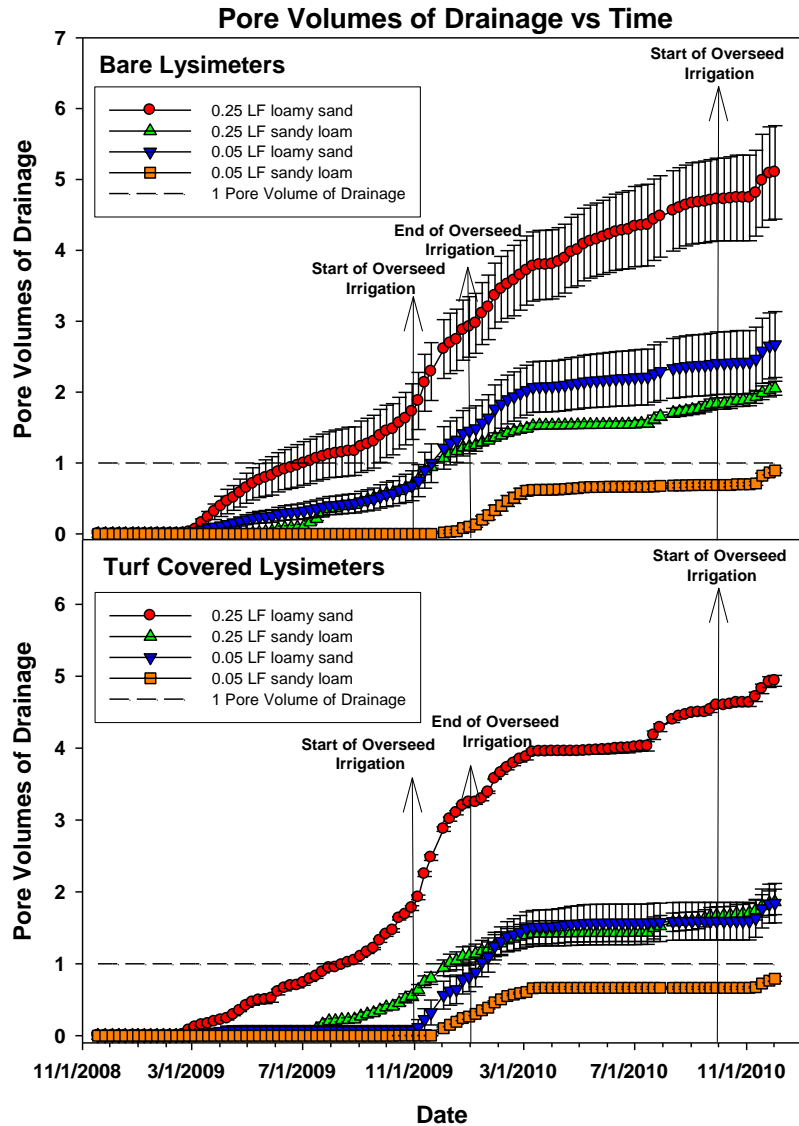
Figure 7. Unsaturated pore volumes of drainage for all lysimeter treatments shown cumulatively over time with arrows showing the beginning and end of overseed irrigation.

Redox Potential

Averaged redox potential for each treatment is shown in Figures 8 and 9 for the 745

day experimental period. After the first overseed period, a distinct downward shift in

redox potential began to occur at the 15 cm depth under turfgrass, regardless of the soil type or LF being imposed. Nine of the 12 turfgrass covered lysimeters showed a downward shift below 300 mV, and one bare lysimeter also showed this downward shift. Redox potentials below 300 mV have been linked to denitrification of nitrate, indicating reducing conditions in the soil (Wodarczyk, 2000; Sparks, 2003). Redox values at the 105 cm depth were more varied but values in 14 of the 24 lysimeters dropped below 300 mV for periods of time. Negative redox potentials were recorded in 5 of 6 lysimeters with 0.25 LF in the sandy loam soil, a clear indicator of poor aeration at the deepest depth.

In the 0.05 LF loamy sand lysimeters the redox values at 15 cm tracked each other around 538.3±59.3 mV until after the first overseed period (starting 11/1/09) where the turf redox values dropped to an average of 266.3±196.8 mV (statistically significant p<0.001). A similar shift downward occurred in the 0.25 LF loamy sand lysimeters at the 15 cm depth for the turf lysimeters 479.4±133.7 mV vs. 179.8±131.0 mV after the drop in redox potential (p<0.001). At the 105 cm depth in the loamy sand 0.05 LF lysimeters, there are two downward shifts in redox potential. The first is for the turfgrass lysimeters around 4/1/10 and the second for the bare lysimeters around 7/15/10. Then both the turf and bare lysimeters average around 233.0±214.0 mV. The 0.25 LF turf loamy sand lysimeters have a slight downward shift in redox potential after the first overseed period, with the bare lysimeters remaining mostly constant.
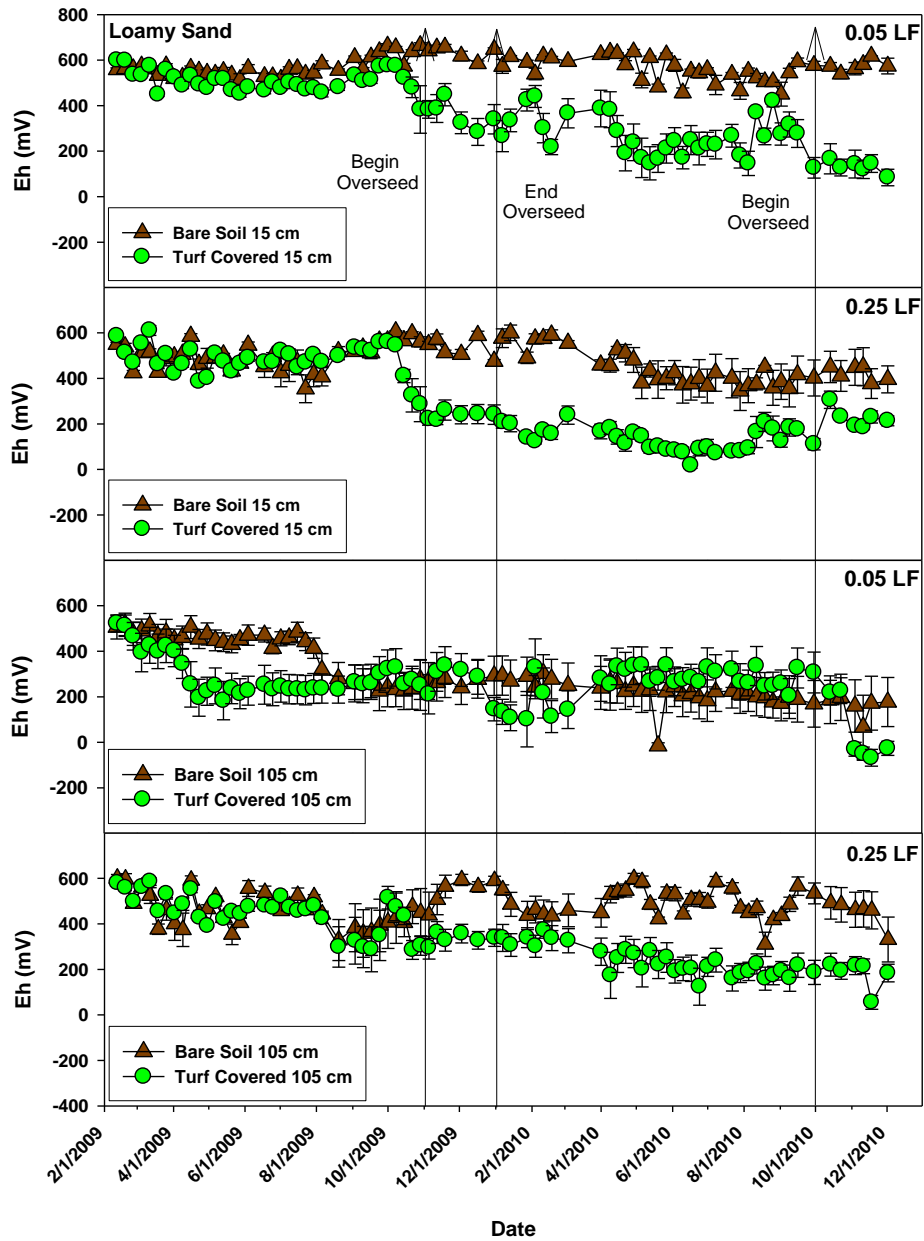
Figure 8. Loamy sand average redox potential over time with arrows indicating the beginning and ending of the overseen periods.

The 0.05 and 0.25 LF sandy loam lysimeters also show the downward shift in redox

potential at 15 cm in the turf covered lysimeters after the first overseed period. The redox

potentials of the 0.05 LF sandy loam lysimeters at the 105 cm depth have slightly higher

redox potentials in the bare lysimeters but around 4/1/10, the values begin the track each

other. The 105 cm redox potential of the 0.25 LF lysimeters of both the bare and turf

lysimeters drop sharply from about (Value) to (value) around 5/1/10. These low redox

potentials are an indicator of poor aeration at the lowest depth in the 0.25 LF sandy loam

lysimeters.
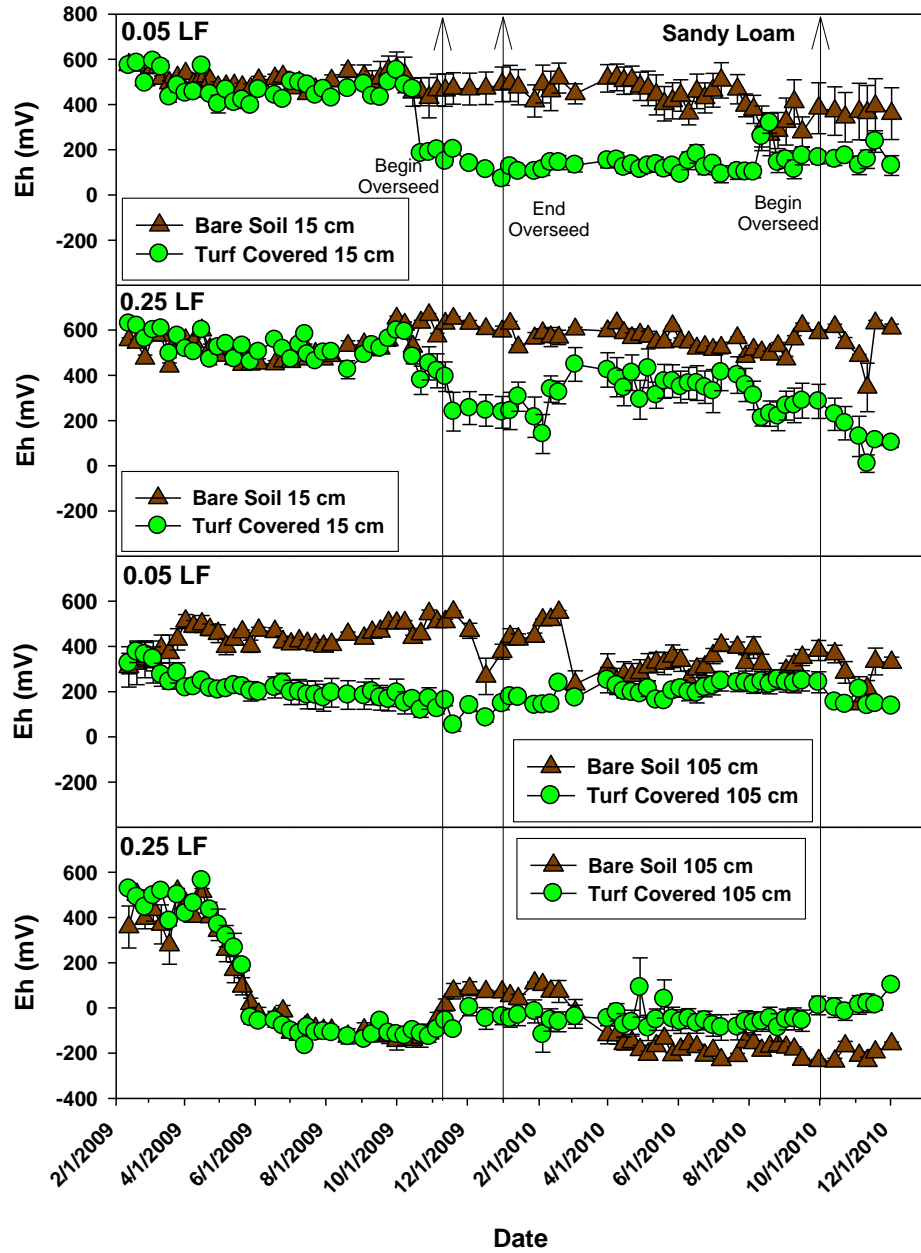
Figure 9. Sandy loam average redox potential over time with arrows indicating the beginning and ending of the overseen periods.

Chloride Concentrations in Irrigation and Drainage Water

Chloride can be useful as a comparative ion to the PPCPs because the chloride ion generally does not interact with the soil profile. As a conservative tracer, chloride should move with the water front in the soil profile and give a basis for comparisons when assessing the movement of the PPCPs. In the irrigation water, the average chloride concentration was 7.05 ± 0.97 mE L^{-1}. Chloride concentrations in the drainage water varied in each soil type (Table 5). Chloride concentrations, in general are higher in the sandy loam soils than the loamy sand soils. This may be due to the higher initial chloride concentrations in the sandy loam soils versus the loamy sand soils (13.51 mEq L^-1 vs. 7.25 mEq L^{-1}) as determined by soil saturation extract.

Table 5. Average chloride concentrations (mEq L^{-1}) in the drainage water.

Treatment	Ave	SD	CV
BC 0.05 B	17.64	10.37	0.59
BC 0.05 G	26.64	14.23	0.53
BC 0.25 B	12.71	7.31	0.58
BC 0.25 G	18.00	11.27	0.63
NLV 0.05 B	29.30	15.60	0.53
NLV 0.05 G	43.00	35.87	0.83
NLV 0.25 B	27.58	20.31	0.74
NLV 0.25 G	25.24	10.55	0.42

PPCP in Irrigation Water

Average PPCP concentrations, standard deviations (SD) and coefficients of variation (CV) in the irrigation water are reported in Table 6. The compound with the lowest

average concentration was diazepam with a concentration of 4.41±1.99 ng L^{-1} and the

highest was sulfamethoxazole at 1611.62±250.00 ng L^{-1}. The remainder of the compound

fell in between these two concentrations. Seven of the 14 PPCPs showed low variability

(CV≤ 0.45) (carbamazepine, diazepam, diclofenac, dilantin, meprobamate, primidone and

sulfamethoxazole). Five PPCPs had moderate variability (0.45 > CV < 1.05) (atenolol,

atorvastatin, naproxen, triclosan, and trimethoprim), while gemfibrozil showed high

variability (CV > 1.05).

Table 6. Concentration of PPCPs in Post-UV reuse water in ng L^{-1}

Analyte	Average	SD	CV
Atenolol	143.59	139.96	0.97
Atorvastatin	16.44	13.79	0.84
Carbamazepine	256.71	80.98	0.32
Diazepam	4.41	1.99	0.45
Diclofenac	70.76	19.28	0.27
Dilantin	13.03	3.36	0.26
Fluoxetine	33.90	9.04	0.27
Gemfibrozil	19.86	33.03	1.66
Meprobamate	395.87	100.91	0.25
Naproxen	21.84	16.57	0.76
Primidone	26.01	11.63	0.45
Sulfamethoxazole	1611.62	250.00	0.16
Triclosan	62.96	34.33	0.55
Trimethoprim	35.44	36.60	1.03

SD = standard deviation
CV = coefficient of variation

Variability in concentration was most likely linked to variable concentrations of

PPCPs entering the waste water treatment plant (WWTP) based on changes in PPCP

usage on a community-wide basis, or increased or decreased removal rates at the WWTP,

although no significant changes in plant operations were noted by personnel. Concentrations over time for primidone, carbamazepine and diclofenac can be seen in Figure 10, revealing a general increasing or decreasing trend over time (R^2=0.26-0.45, $p<0.05$). The remaining compounds did not show any significant trends over time.
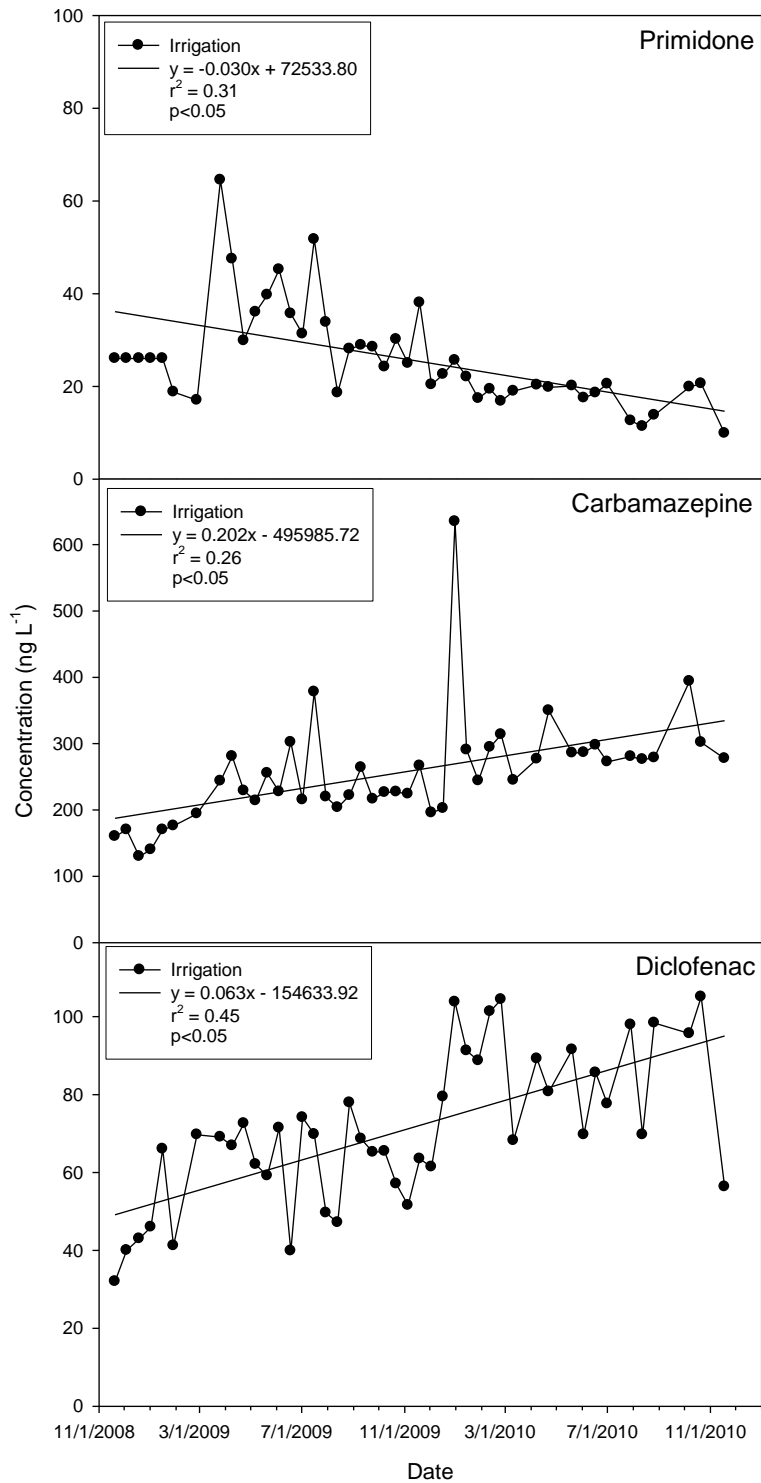
Figure 10. Primidone, carbamazepine and diclofenac concentration (ng L^{-1}) in irrigation water, revealing a downward or upward trend in concentration over time.

Interference with Sampling Material

Atorvastatin, fluoxetine and triclosan had 92-100% removal of the compound when in contact with a rubber stopper (a component of the drainage sampling system). Atorvastatin had 100% reduction when in contact with the tubing for 3 days. Other compounds that had more than 20% removal when in contact with the tubing were fluoxetine and triclosan. Fluoxetine had 94% removal when in contact with the diatomaceous earth, while atorvastatin had 25% removal. Atorvastatin, atenolol, fluoxetine, and trimethoprim revealed 100% reduction when in contact with a ceramic sampler. Compounds with more than 20% removal when in contact with a Teflon collar for 3 days included atorvastatin, fluoxetine, naproxen, triclosan, and trimethoprim. However, atorvastatin, atenolol, diclofenac, fluoxetine, meprobamate, naproxen, triclosan and trimethoprim revealed a reduction between 14 and 95% after 3 days of contact with stainless steel (Table 7).This suggests that either degradation and/or adsorption of the compound occurred. These values represented worst-case scenarios, as drainage samples would not have been allowed to remain in contact with drainage components for more than 24 hours. Compounds that had more than three occurrences of greater than 20% reduction were atorvastatin, fluoxetine, triclosan and trimethoprim. Even with preservation techniques, some compounds can degrade or be adsorbed to various surfaces. Two compounds of note for which there is no preservation techniques recommended, atenolol and fluoxetine, can degrade more than 15% in an amber bottle (Vanderford et al. 2011), even preserved using sodium azide at 4^0C. For fluoxetine, this could be an explanation as to why there was so much removal during the interference studies.

Table 7. Percent reduction of PPCP in solution after 3 days when in contact with soil water sampler components.

	Collar (Teflon)	Stainless Steel	Diatomaceous Earth	Tubing	Stopper	Ceramic
Atenolol	11	14	5	2	0	100
Atorvastatin	100	23	25	100	100	100
Carbamazepine	4	4	6	8	0	0
Diazepam	0	0	2	6	16	36
Diclofenac	0	24	0	14	0	10
Fluoxetine	89	95	94	35	92	100
Gemfibrozil	9	14	6	10	0	0
Meprobamate	19	28	0	0	0	0
Naproxen	25	35	0	20	0	5
Sulfamethoxazole	5	0	0	9	0	4
Triclosan	36	56	13	51	100	11
Trimethoprim	33	24	2	6	0	100

Stainless steel samplers were placed at the 110 cm soil depth at the end of year one in all lysimeters and sampled only at the end of the experiment. Results from the samples collected from the stainless steel samplers revealed no detection of atorvastatin, atenolol, fluoxetine, or trimethoprim, suggesting that these four compounds had not yet arrived at the 110 cm depth, perhaps as a result of undergoing significant adsorption interactions within the soil profile. We compared the PPCPs results obtained from the stainless steel samplers with those obtained from the existing lysimeter sampling system at the end of the experiment. Seven compounds were detected, of which five showed no statistical difference in the results ($p>0.05$) (primidone, sulfamethoxazole, carbamazepine, triclosan, and naproxen). Only in the cases of diazepam and diclofenac was a statistical difference observed, and in both cases, they were associated with no detections in the stainless steel samplers. Although we cannot rule out the possibility that system

interference reduced the concentration of some compounds, the results suggest that it was a potential issue only under the experimental conditions of this study for carbamazepine (possible 6% reduction in diatomaceous earth) and diazepam (possible 36% reduction in contact with the ceramic samplers), recognizing that concentrations of atorvastatin, atenolol, fluoxetine, and trimethoprim would have also been affected by the sampling system had they arrived at the depth of the samplers (no detection with the stainless steel samplers). It should also be noted that the results reported in Table 7 are for percent reduction after a 72 hour period. Significantly lower reduction values were obtained after only 24 hours, which was the typical contact time for drainage water in the diatomaceous earth at the bottom of the lysimeters.

PPCP in Drainage Water

Drainage sampling for PPCP analyses was based on unsaturated pore volumes being displaced from the lysimeters. Drainage samples were collected at the first appearance of drainage and every half unsaturated pore volume thereafter. Because lysimeters were irrigated based on imposed leaching fractions, high leaching fraction loamy sand lysimeters were sampled more often than the low leaching fraction sandy loam lysimeters. For example, loamy sand lysimeters under the 0.25 LF treatment (bare and turfgrass) were sampled between 8 and 12 times during the experiment, whereas sandy loam lysimeters under the 0.05 LF treatment (bare and turfgrass) sampling occurred only 2 to 4 times during the experiment. The percentage of lysimeters that showed PPCPs in the drainage varied. Primidone and sulfamethoxazole were detected in 100% (Figure 11) of the loamy sand lysimeters with lower numbers of detection in the sandy loam soil (approximately 65% and 50% of lysimeters, respectively). Other PPCP's were detected

fewer times, such as the 50% detection of carbamazepine (Figure 11) and 40% detection of meprobamate in loamy sand lysimeters, with no detections in the sandy loam lysimeters. Gemfibrozil, atorvastatin, trimethoprim, fluoxetine, and atenolol were not detected in the drainage of any lysimeters (though as noted above, interference with sampling material was a possibility for some compounds).
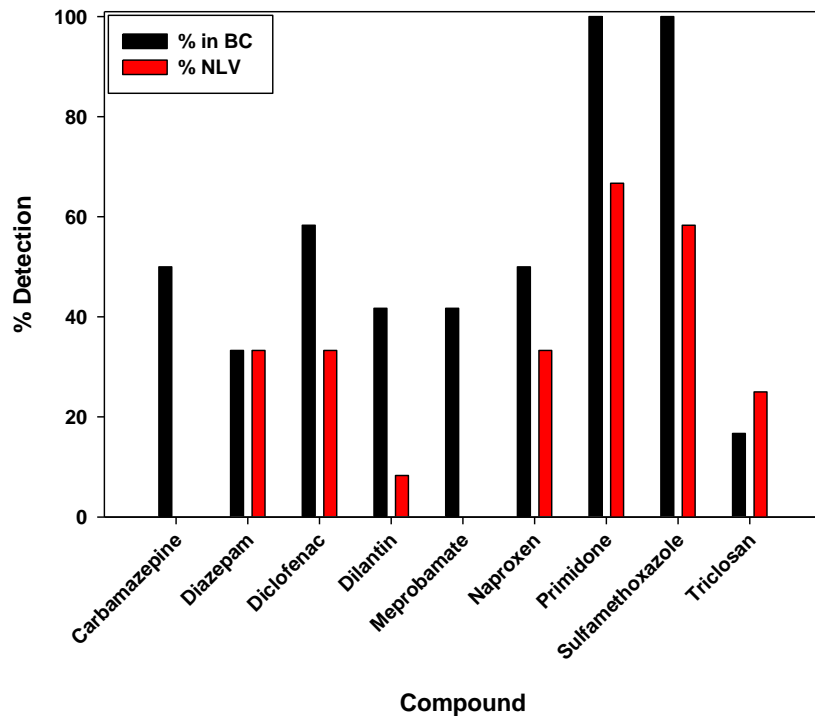
Figure 11. Percentage of lysimeters with at least one detection of compound in the drainage.

Primidone, sulfamethoxazole and carbamazepine had overall higher detection rates in the drainage water than all other compounds. The detection rates varied based on soil type, cover and LF ($p<0.05$). In the 0.25 LF loamy sand lysimeters, the detection rate averaged 74% for sulfamethoxazole, 72% for primidone and 40% for carbamazepine. A break down by compound and treatment can be seen in Figure 12.
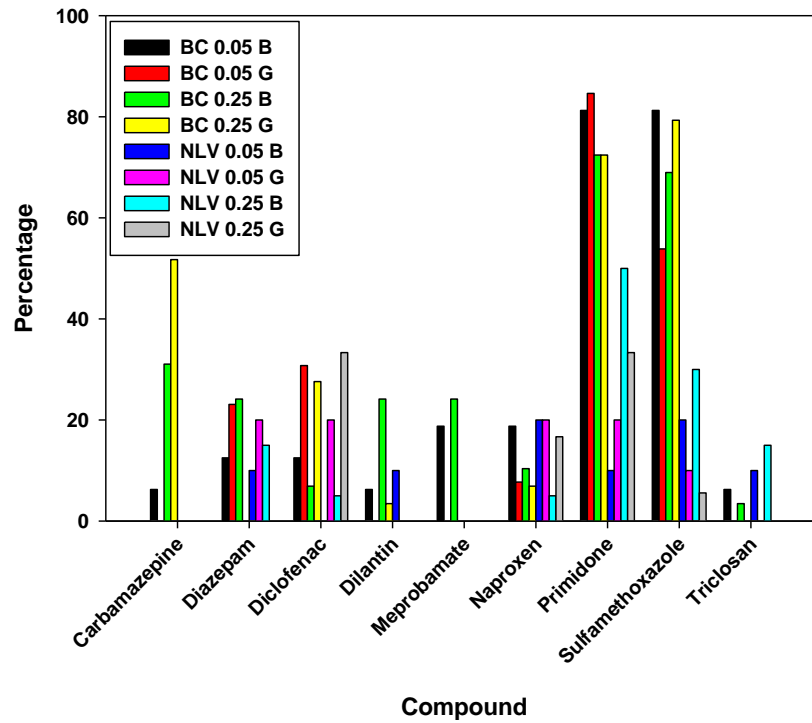
Figure 12. Average percent detection for each compound broken down by treatment type.

ANOVA's indicated significant soil x LF interactions ($p<0.05$) on the number of detections during the experiment for both sulfamethoxazole (7.2 sampling detections in

the loamy sand at 0.25 LF vs. 3.3 detections at 0.05 LF) and carbamazepine (4.0

sampling detections in the loamy sand at 0.25 LF vs. 0.2 detections at 0.05 LF), whereas

primidone revealed no interactions but did reveal significant main effects for both soil

(5.5 sampling detections in the loamy sand vs. 1.2 detections in the sandy loam) and LF

(4.3 sampling detections at 0.25 LF vs. 2.3 detections at 0.05 LF).

Concentration values of the PPCPs in the drainage waters had high variability. There

was a time lag associated when the PPCPs were first detected in the drainage water.

ANOVA's were also run on the final drainage concentrations at the end of the

experiment, with results varying by compound. Primidone revealed only a soil effect,

with least square means at 14.3 ng l^{-1} for the loamy sand and 7.0 ng l^{-1} for the sandy loam

soil. Carbamazepine and dilantin both revealed soil x LF interactions ($p<0.05$), while

meprobamate revealed a soil x cover interaction ($p<0.05$). Sulfamethoxazole, which had a

very high detection rate, revealed no separation in drainage concentration at the end of

the experiment based on main treatment or interaction effects.

PPCP Concentrations in Soil

Soil samples collected at the end of the study were analyzed for PPCPs. Due to

prohibitive cost, soil analysis was limited to replicates of each treatment for the five

depths of the loamy sand lysimeters only. The concentration of PPCPs for 9 of the 14

compounds at depth varied depending on compound and concentration in the irrigation

water. The remaining five compounds (atenolol, atorvastatin, fluoxetine, naproxen, and

triclosan) are not shown due to either unusual concentrations (i.e. mass balances in the

soil higher than the total incoming mass) in the soil profile or non-detects. The

concentrations of each compound were not statistically significant (ANOVA) between

treatments (Figure 13) except in the case of meprobamate (Figure 14). The meprobamate

concentrations between the bare and turf grass covered lysimeters showed a statistically

significant difference ($p<0.05$) at the 0-15, 15-30 and 30-60 cm depths. There was no

difference at the 60-90 and 90-120cm depth where concentration values were all close to

zero. This clear separation between the grass and bare soil may indicate that the turf

covered lysimeters are playing a part in removing or limiting movement of Meprobamate.
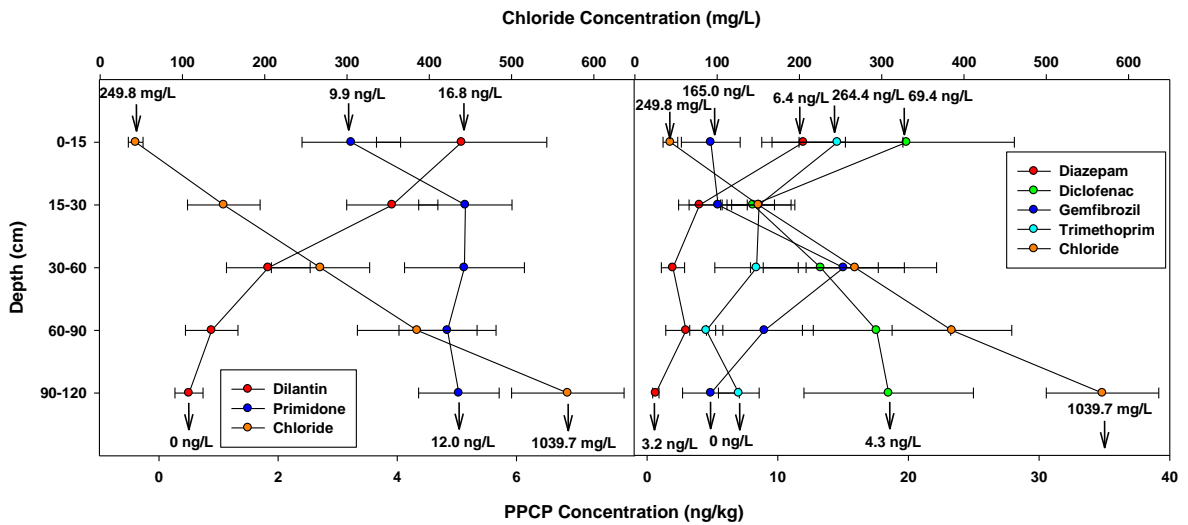
Figure 13. Average treatment concentrations (ng kg^{-1}) with depth for Dilantin, Primidone, Diazepam, Diclofenac, Gemfibrozil, Trimethoprim and Chloride (mg L^{-1}) with associated ingoing and outgoing final concentrations indicated with arrows.
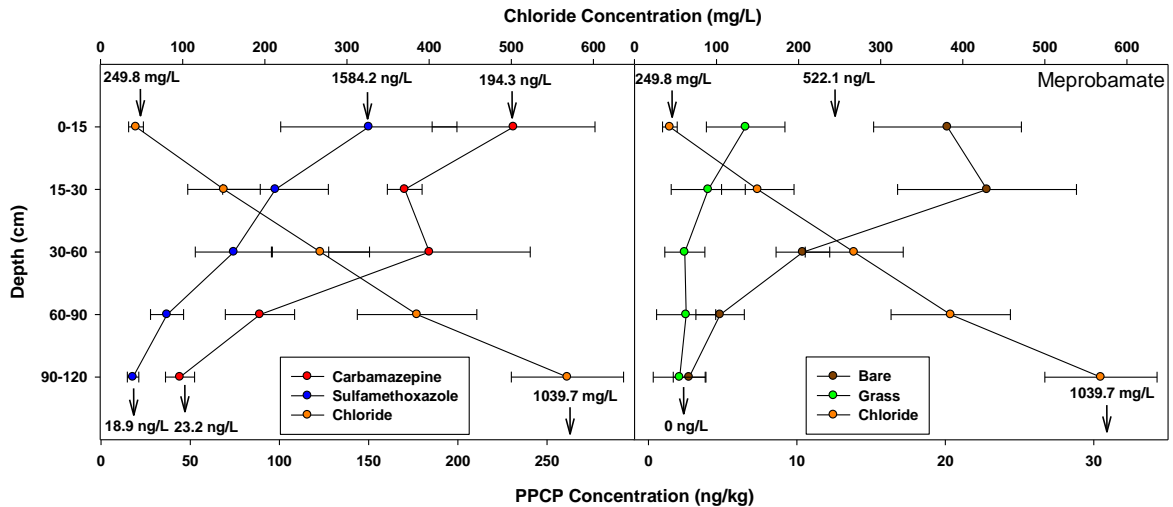
Figure 14. Average treatment concentrations (ng kg^{-1}) with depth for Carbamazepine, Sulfamethoxazole, Meprobamate (separated by bare and turf lysimeters) and Chloride (mg L^{-1}) with associated ingoing and outgoing final concentrations indicated with arrows.

Chloride concentration with depth was not significantly different based on treatments and was therefore averaged for comparison with the PPCP concentrations with depth (Figure 13 and Figure 14). Chloride concentration, with depth, increased down through the profile, unlike many of the PPCPs. Compounds that decreased with depth include Dilantin, Diazepam, Carbamazepine, Sulfamethoxazole, and Meprobamate (bare). These compounds also saw a general decrease in the drainage concentration as compared to the irrigation concentration. Primidone, Diclofenac, Gemfibrozil, Trimethoprim, and Meprobamate (in turf covered lysimeters) had consistent average concentrations through the soil profile. In some cases, the drainage concentration was comparable to the concentration in the lowest depth (90-120 cm) for dilantin, primidone, diazepam, diclofenac, gemfibrozil, sulfamethoxazole, carbamazepine and meprobamate. This is

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good evidence that the diatomaceous earth and ceramic samplers played a relatively small part in removal of compounds between the lowest depth of soil and the drainage sampler but we cannot entirely rule out the possibility that some removal of compounds by the diatomaceous earth and the ceramic sampler were occurring.

PPCP Mass Discharge

Mass discharge estimates for PPCP's required weighting the irrigation and drainage volumes with their respective concentrations. In one lysimeter, no PPCP's were detected at any time during the study (lysimeter 18, sandy loam, 0.05 LF, grass cover). In other lysimeters, PPCP's were detected but the drainage volumes were quite small. Mass discharge in all loamy sand lysimeters were greater than zero for primidone, sulfamethoxazole, carbamazepine, diazepam, naproxen, diclofenac, dilantin, meprobamate and triclosan, whereas zero mass discharge occurred for gemfibrozil, trimethoprim, fluoxetine, and atenolol in both soils (Figure 15.)
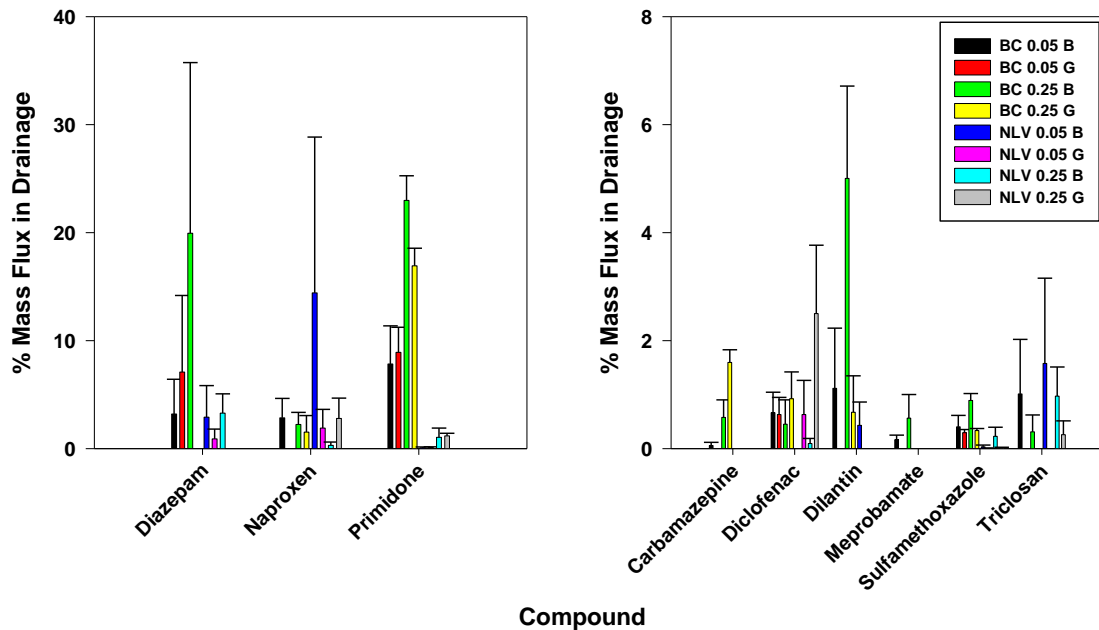
Figure 15. Percent mass discharge in drainage for all treatments.

The highest average percent mass in the drainage occurred for diazepam, naproxen and

primidone, with primidone in the drainage reaching almost 23% of the irrigation mass

that was applied as irrigation to the high leaching loamy sand with no cover. Conversely,

sulfamethoxazole, which had the highest incoming concentration, only reached as high as

0.9% mass discharge in the drainage for the same treatment. One general trend that was

observed from the average percent mass discharge draining, was the higher percentages

in the loamy sand vs. the sandy loam lysimeters. This was easily seen for most

compounds but one example was carbamazepine, where there was some detection of the

compound in the drainage for the loamy sand lysimeters but no detection in the sandy

loam lysimeters (p = 0.006). The other very general trend was the higher percent mass

discharge in the draining of the high leaching fraction vs. the low leaching fraction lysimeters, such as with the draining of primidone. The percent mass discharge of primidone in the drainage of the low leaching loamy sand lysimeters was 7.8% and 8.9% for bare and turf respectively while the high leaching fraction lysimeters average was 23.0% and 16.9% for bare and turf respectively (p = 0.001).

Mass discharge for all three compounds was found to be significantly correlated to the number of unsaturated pore volumes that had drained. In the case of primidone (Figure 16), a clear separation was found between the two soil types, with up to 28% of the applied primidone being detected in the drainage of one of the 0.25 LF loamy sand lysimeters. Results indicated that 82% of the variation in the percentage of primidone discharged from the loamy sand lysimeters could be accounted for based on the number of unsaturated pore volumes drained. A clear separation in the mass discharge of the sulfamethoxazole was also observed based on soil types and unsaturated pore volumes drained ($R^2 = 0.52***$, Figure 16). However, maximum discharge in the drainage of 0.25 LF lysimeters was less than 1.2%. Carbamazepine revealed a curvilinear relationship ($R^2=0.71***$) between mass discharge and unsaturated pore volumes drained, with no mass discharge observed from the sandy loam soils even at the higher LF (Figure 16). Although other factors may be at play with carbamazepine transport in the sandy loam soil, these results suggest that the number of unsaturated pore volumes drained was too small, as even within the loamy sand lysimeters, detection did not occur until more than 2.5 unsaturated pore volumes drained.
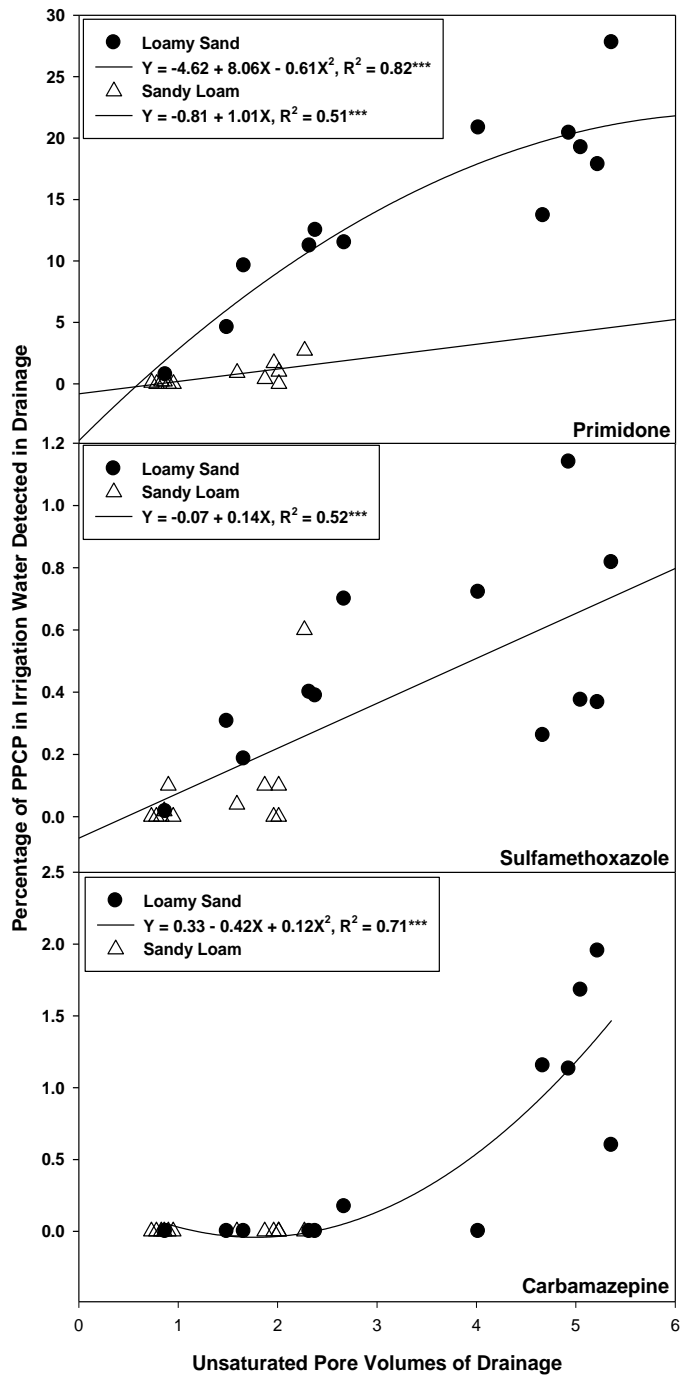
Figure 16. Percentage of PPCP detected in drainage water for carbamazepine, primidone and sulfamethoxazole as a function of unsaturated pore volumes of drainage.

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Mass discharge of PPCPs draining was scaled on a per hectare basis (Appendix A). Scaling from lysimeter (2800 cm^2) to a per hectare basis allowed for a field estimate related to the size of golfcourse fairways. In the 0.05 bare lysimeters, comparing loamy sand lysimeters as compared to sandy loam lysimeters, the average mass discharges are less in the sandy loam lysimeters, with the exception of naproxen and triclosan. Both, however, have high standard deviations and coefficient of variation values indicating large variability within replicates.

Factors Influencing Fate and Transport of PPCP's

As one might expect each PPCP compound responded differently under the experimental conditions imposed in this experiment. Many of the compounds did not behave consistently enough to generate statistically significant results using ANOVA. In fact, only primidone, sulfamethoxazole, carbamazepine and dilantin demonstrated significant main treatment or treatment interaction effects. With respect to the percentage of primidone collected in the drainage water, only a soil x LF interaction was observed ($p<0.05$), while sulfamethoxazole revealed a soil effect and a cover x LF interaction ($p<0.05$). Carbamazepine revealed a soil x cover effect ($p<0.05$), while dilantin revealed both a soil x cover and soil x LF effect ($p<0.05$). In all cases, the results supported higher PPCP leaching from soil profiles in the loamy sand lysimeters and at higher LF's. Although leaching losses were almost always higher under bare soil conditions, carbamazepine revealed the highest leaching losses in the loamy sand 0.25 LF lysimeters under turfgrass.

Significant variations in the percentage of mass discharge of PPCP's were revealed using multiple regression analysis with a mix of soil, plant, and water variables.

However, only seven of the thirteen PPCPs could be analyzed using this approach due to limited PPCP results. The variables selected for testing included the number of unsaturated pore volumes drained; ET; Irrigation plus precipitation (I); cover type; percent sand; biomass; average redox potential during the downward shift period at 15 and 105 cm depths; the percent organic matter (OM) content in the 0-15 cm depth; and the average percent OM in the 0-60 cm depth. Properties of the compounds, pKa, Kow and solubility, were rejected by the multiple regression analysis. Table 8 reports the variables accepted in the regression analysis, along with R^2 and p values. The degree of variation, accounted for using these variables, ranged from a low of 17 % with diclofenac to 94% with primidone. Because many compounds were not detected or detected only on a few occasions, only with three compounds could we account for greater than 50% of the variation in the percentage of the compound drained, specifically primidone, sulfamethoxazole and carbamazepine. In the case of primidone, 94% of the variation in the amount leached could be described by the number of unsaturated pore volumes drained, the percent sand in the soil and the average redox potential during the downward shift period at the 105 cm depth. We note that redox was a significant variable for four of the seven compounds, with primidone mass discharge increasing with redox potential at 105 cm depth, and increased mass discharge of dilantin as redox potentials increased at depths of both 15 and 105 cm. However, with both naproxen and triclosan, when redox potential increased at the 15 cm depth, leaching losses decreased. Only in the case of carbamazepine was percent OM (0-15 cm depth) accepted as a significant variable in the regression analysis, with increased leaching losses associated with higher percent OM, substantiating the higher leaching losses associated with the turfgrass lysimeters.

Table 8. Results of Multiple Regression Analysis Describing the Influence of Soil Plant Water Variables on Percent Discharge of PPCPs.

PPCP	Variables Accepted	R^2	p value
Primidone	Y=-27.9 + 0.008 Redox 105 cm + 0.317 % Sand + 3.69 PV	0.94	0.001
Carbamazepine	Y=-1.068 + 0.314 PV + 1.086 % OM	0.73	0.001
Sulfamethoxazole	Y= 0.037 – 0.001 Biomass + 0.145 PV	0.67	0.001
Dilantin	Y= -2.26 +0.003 Redox 15 cm + 0.003 Redox 105 cm +0.577 PV	0.46	0.001
Naproxen	Y= -4.87 -0.41 Redox 15 cm + 15.142 Cover	0.35	0.01
Triclosan	Y= -1.12 – 0.004 Redox 15 cm + 2.002 Cover	0.28	0.05
Diclofenac	Y= 0.251 +0.003 Biomass	0.17	0.05

Cover assigned as Bare = 2 or Turf = 1

% Sand = content of sand in soil

Biomass = amount of turfgrass removed from lysimeter (g)

% OM = Average organic matter through profile

PV = pore volumes of drainage

Redox = redox values at either 15 or 105 cm (mV)

Mass Balance

Based on the mass of compounds being applied to the lysimeters, the mass exiting the lysimeters, and from the mass on the soil particles a mass balance was closed for each compound in the loamy sand (BC) lysimeters. The percentage of mass that was unaccounted for was also obtained (Table 9). The unaccounted mass (Table 9) for several of the compounds in many of the treatments was very high (> 90% unaccounted). The only compound that had low (<40%) unaccounted mass was diazepam in all but the high leaching turf covered lysimeters. The loss of the compounds could be for a variety of reasons. Their concentrations could have decreased by chemical or biological processes or taken up by the turfgrass. Using similar parameters as the above analysis of percent mass discharge, we looked at the influence of soil plant water variables on the percent unaccounted mass for each loamy sand lysimeter. Only in seven of the compounds could the percent mass unaccounted be described by the soil plant and water variables (Table 10).

Table 9. Average (Avg), Standard Deviation (SD) and Coefficient of Variation (CV) for unaccounted mass percentage of each PPCP for each treatment of the Loamy Sand Soil (BC).

Compound	BC 0.05 B			BC 0.05 G			BC 0.25 B			BC 0.25 G		
	Ave	SD	CV	Ave	SD	CV	Ave	SD	CV	Ave	SD	CV
Carbamazepine	54.5	19.4	0.4	76.7	4.1	0.1	66.1	16.0	0.2	83.2	3.6	0.0
Diazepam	37.9	9.7	0.3	28.2	13.1	0.5	31.7	28.6	0.9	84.1	8.1	0.1
Diclofenac	86.7	16.6	0.2	81.1	3.3	0.0	90.7	7.8	0.1	86.6	2.7	0.0
Dilantin	93.5	1.4	0.0	92.9	3.6	0.0	79.0	6.1	0.1	95.0	1.0	0.0
Gemfibrozil	49.1	43.5	0.9	70.1	25.3	0.4	71.2	43.3	0.6	79.3	17.1	0.2
Meprobamate	97.9	0.4	0.0	99.6	0.4	0.0	98.0	1.0	0.0	99.8	0.2	0.0
Primidone	84.3	6.1	0.1	82.4	2.5	0.0	61.7	7.1	0.1	74.9	3.8	0.1
Sulfamethoxazole	91.2	10.6	0.1	97.4	1.1	0.0	97.1	2.1	0.0	97.7	1.2	0.0
Trimethoprim	90.7	2.8	0.0	87.7	6.6	0.1	84.8	2.2	0.0	84.1	7.1	0.1

Table 10. Results of Multiple Regression Analysis Describing the Influence of Soil Plant Water Variables on Percent of Unaccounted Mass for Loamy Sand (BC) Lysimeters.

Compound	Parameters Accepted	R^2	p-value
Meprobamate	Y = 101.349 - 1.696 Cover	0.73	0.05
Carbamazepine	Y = 63.215 + 109.182 LF - 3.195 NO_3-N	0.64	0.05
Trimethoprim	Y = 67.104 - 54.427 LF + 9.807 Cover + 45.823 % OM_{Avg}	0.59	0.05
Gemfibrozil	Y = -108.727 - 203.046 % OM_{Avg} + 14.276 I_M	0.52	0.05
Primidone	Y = 90.823 - 4.431 PV	0.46	0.05
Diazepam	Y = -16.837 + 124.786 % $OM_{Surface}$	0.43	0.05
Dilantin	Y = 94.820 - 0.985 NO_3-N	0.41	0.05

Cover assigned as Bare = 2 or Turf = 1

LF = actual leaching fraction

NO_3-N = drainage nitrate nitrogen (g)

I_M = Mass of compound applied as Irrigation

% OM_{avg} = Average organic matter through profile

% $OM_{surface}$ = Organic Matter at the upper 15 cm

PV = pore volumes of drainage

We could account for 72.3% of the variation in the unaccounted percent mass discharge of meprobamate based simply on cover (bare vs. turfgrass).This is logical when one thinks back to the concentration with depth for Meprobamate. The compound had a significant difference in concentration for the upper 60 cm. With a negative correlation with cover, higher unaccounted mass will occur in the bare soils versus the turf covered soil, which is also highlighted in the concentration with depth graph. Carbamazepine also had a higher correlation coefficient with variability accounted for by knowing the leaching fraction and mass of nitrate-nitrogen discharged in the drainage.

Retardation Factors

In a soil profile, two main processes that often determine the fate of compounds are sorption and degradation. Retardation of compounds in a soil profile may be a combination of these two processes. Neither process was examined directly in these experiments but side experiments completed in Gan's laboratory (Lin et al. 2011, Lin and Gan 2011) using the same soils as those in the lysimeters for this project and with many of the same PPCP's gives some indication of how certain compounds would undergo sorption and degradation. Gan (Lin et al. 2011, Lin and Gan 2011, McCullough 2011) reported specific sorption coefficients. Those sorption values were used to calculate retardation factors (R_{ft}, Equation 4) to compare to the observed retardation factors (R_{fo}, Equation 3) from this lysimeter study (Appendix B). Retardation factors (R_f) give an indication of the rate at which compounds will pass through a soil column in relation to the water front. A factor of 1 indicates movement with the water front and values higher indicate some retardation of the compound of interest. The observed retardation of compounds in the lysimeters, in most cases, was different from the predicted retardation

from the laboratory batch studies. This may be related to the "virgin" nature of the soil, the shorter laboratory experiments and/or that the longer field experiments allowed more time for degradation to occur in the soil profile.

The average R_{fo} for sulfamethoxazole was 3.19 which was not significantly different ($p<0.05$) from the theoretically calculated value of 2.70 in the BC soil. The average retardation factor for the NLV soil was less than that of the BC soil at 2.14, which was greater than the theoretical value of approximately one. Primidone did not have any sorption coefficients with which to calculate the R_{ft} but was reported by Lin et al. (2011) to have no significant sorption to soil particles. This was confirmed based on the low average R_{fo} in the lysimeters for both the BC and NLV soil types; 2.72 and 2.77 respectively. This was also similar to the R_f values calculated by Schaffer et al. (2012) for primidone (1.2) in a very sandy soil. Overall, primidone and sulfamethoxazole appeared in the drainage of many lysimeters, suggesting only slight retardation in both soil types.

Diazepam, diclofenac, and naproxen were all compounds that, under the observed conditions, had higher retardation in the BC soil than the NLV soil. For diazepam, the average R_{fo} for the BC soil was 11.78 which was statistically significant ($p<0.05$) from the theoretical value. The average R_{fo} for the NLV soil was 2.63 as compared to the theoretical value of 35.88 ($p<0.001$). Both theoretical values would predict that the retardation in the soil profiles should limit or prevent detection of diazepam in the drainage samples, however, this was not the case. Naproxen has a similar pattern to diazepam, in which the BC R_{fo} values were higher than the NLV values, 7.06 vs. 2.48 respectively. Naproxen had a very high R_{ft} value for both the BC and NLV lysimeters. For both, diazepam and naproxen the R_{ft} values would suggest that the compounds

should have been moderately to strongly retarded in the lysimeters. Diclofenac had similar observed retardation factors as naproxen but with lower theoretical values in both the BC and NLV soils. In the BC soil, we observed an average R_{fo} value of 5.73 which was significantly different (p<0.05) from the theoretical value of 3.08. The NLV value for diclofenac was 2.98, which was not significantly different from the theoretical value of 2.40. These theoretical values, especially in the BC soil, would predict less retardation in the soil profile than observed.

The remaining compounds, carbamazepine, dilantin, gemfibrozil, meprobamate and trimethoprim had R_{fo} values that were lower in the BC soils then the NLV soil or not observed at all in the NLV soil. Carbamazepine had an average 5.09 retardation factor, that was not significantly different from the 4.21 theoretical value. Carbamazepine was not detected in the drainage samples of the sandy loam soil, so an observed R_f could not be calculated. Not observing carbamazepine in the NLV soil but observing it in the BC soil corresponds well to the high retardation factor in the NLV soil and low retardation factor in the BC soil that was theoretically possible from the lab experiments. The theoretical R_f values also better reflect the observed values, or lack thereof, than many of the other compounds. Dilantin and meprobamate both had observed average retardation factors that were significantly higher (p<0.05) then their theoretical values. Both compounds were expected to appear in the drainage due to their low sorption in the laboratory experiments, but this was not the case in the lysimeters. This may be due to the nature of the compound and the field conditions, which allowed for increased adsorption and/or a greater likelihood of degradation. Dilantin and meprobamate were degraded more in aerobic conditions in the BC soil, in the anaerobic or sterilized conditions, so

perhaps it was degraded more and this slowed its appearance in the BC soils. The response of Trimethoprim was opposite of dilantin and meprobamate, in the BC soil. The average observed retardation factor was significantly lower in the BC soil than the theoretical value (7.36 vs. 35.94). Trimethoprim, however, was also not detected in the drainage samples.

Chapter 5

Discussion

Our results suggest that PPCP interactions in soil-plant-irrigated systems are complex, with many factors influencing the fate and transport of these compounds. At the same time, we also state upfront that our approach and interpretations were limited to the analysis of the parent compounds and not degradation products, daughter products or metabolites. Compounds detected consistently in the drainage water for the loamy sand soil were primidone, sulfamethoxazole and carbamazepine; whereas in the sandy loam soil; compounds consistently detected were primidone and sulfamethoxazole, but only at the higher LFs. Detection was strongly coupled to the number of unsaturated pore volumes draining from the soil profile. Even with the higher LFs, the earliest detection of the PPCPs did not occur until approximately 6 months into the monitoring period. By comparison, chloride (data not shown), a conservative tracer, was detected at elevated concentrations in the first drainage samples collected after 2 months of monitoring.

Detection rates in the drainage water associated with the sandy loam soil were lower when compared to the loamy sand soil (11% vs. 27%, respectively) which also differed significantly in the clay content (19% in the sandy loam vs. 9% in the loamy sand) which may have contributed to sorption or even possible exchange reactions as suggested by Gibson et al. (2010). Slightly higher percentages of organic matter measured in the sandy loam soil versus the loamy sand soil, especially at shallower soil depths may have contributed to higher rates of carbon-PPCP sorption reactions (Rauch-Williams, 2010). The only compound that did not follow this pattern was carbamazepine, in which higher mobility was associated with higher organic matter content, as higher % OM may

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compete with PPCPs for sorption sites (Navon *et al.*, 2011). Understanding all of the processes and interactions with soil and organic matter, however, are complicated to predict (Pan *et al.,* 2009).

Redox measurements taken during the experiment indicated the aerobic status within each lysimeter. Redox values less than 300 mV have been suggested (Fiedler *et al.*, 2007) to indicate a shift from aerobic to anaerobic conditions. In general, the redox potential at 15 cm decreased for the turfgrass covered lysimeters while it remained more constant in the bare lysimeters. This downward redox potential shift in the turfgrass lysimeters could be associated with increased microbial activity in the rootzone of the turfgrass lysimeters (Fiedler *et al.* 2007), associated with increased root mass (carbon as an electron donor) during the first year of establishment. Redox values at 105 cm were not distinctly different between turfgrass and bare soils but they did show a large downward shift for the high leaching fraction treatment in sandy loam lysimeters. This downward redox potential shift was associated with increased soil moisture at the lowest depth for the sandy loam soil, which would support an anaerobic environment in which less oxygen would be available for redox reactions (Fiedler et *al.* 2007).

Summary of high (>4.00) octanol-water partitioning compounds

Atorvastatin, diclofenac, fluoxetine, gemfibrozil and triclosan are all compounds that have the highest (>4.00) octanol-water partitioning coefficients (6.36, 4.51, 4.60, 4.77 and 4.53 respectively) and lower solubility (0.00112, 2.37, 60.3, 10.9 and 10 mg L^{-1} respectively). With only this information, these compounds would seem unlikely to pass through the soil profile, highly likely to sorb to components of the system (soil, organic matter, ceramic sampler, etc) and not occur in the drainage. In some instances these two

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factors, high octanol-water partitioning coefficient and low solubility did seem to predict the behavior of the compound in the lysimeter study but not in all cases. Atorvastatin and fluoxetine did not appear in any drainage samples and the soil samples had unusually high concentrations, exceeding the amount that was applied to the system. Gemfibrozil was not detected in any of the drainage samples but mass balance of the soil portion did not exceed the amount applied as irrigation. Gemfibrozil concentrations from the soil profile were further examined because they did not exceed the amount applied as irrigation. The concentrations in the soil for the loamy sand lysimeters were not statistically different so they were combined. When averaged by depth, gemfibrozil did not show any trend towards decreasing concentration with depth despite the high incoming concentration and zero discharge concentration. Gemfibrozil had a moderate amount of compound (~70%) unaccounted for in the soil profile but only about 52% of the variation from the backwards-stepwise regression analysis could be accounted for using average organic matter in the soil profile of the loamy sand lysimeters and the mass of gemfibrozil applied as irrigation. This unaccounted for mass may have been chemically or biologically degraded in the loamy sand lysimeters. Lin et al (2011) reported gemfibrozil did degrade under aerobic conditions, which may help explain why there was some unaccounted mass and higher retardation factors. Triclosan was the only personal care product examined in the study. Triclosan does have a high potential for contamination due to its presence in a wide variety of products including but not limited to hands soaps, cleaning solutions, and incorporated into office supplies (EPA factsheets). Triclosan was detected less than 20% of the time in drainage samples. Diclofenac was detected at least once in all treatments except for the low leaching loamy sand lysimeters

(20% of the samples from all lysimeters). The concentration of diclofenac was uniform in the soil profile, but the mass detected in the drainage of the lysimeters was less than 3% of the mass applied as irrigation, indicating that there was a significant amount of adsorption or degradation occurring within the soil profile, which limited the amount of compound discharged in the drainage. The plant, soil and water factors only accounted for 17% of the variability in the percent of diclofenac detected in the drainage. Atorvastatin and fluoxetine were never detected in the drainage water but both had total masses within the soil profile higher than was applied from the irrigation.

Summary of moderate (2.00-4.00) octanol-water partitioning compounds

Carbamazepine, diazepam, dilantin and naproxen all had moderate (2.00-4.00) octanol-water partitioning coefficients (2.30, 2.82, 2.47, 3.18 respectively) and only slightly higher solubility than the high K_{ow} compounds (17.7, 50, 32, and 15.9 mg L^{-1}). With lower K_{ow} and solubility values, one might expect to see these compounds more often in the drainage than triclosan, atorvastatin, diclofenac, fluoxetine and gemfibrozil.

Diazepam had low potential interference with the drainage sampling system components so one would expect to see it in the drainage samples. However, the low incoming concentration from the irrigation water could have potentially made detections in drainage and soil samples difficult. The total percentage of detections in the drainage samples was around 20% and the mass discharge detected in the drainage ranged from 0-20% of the mass of diazepam applied as irrigation. The theoretical retention factors for diazepam for both soil types were very high indicating strong adsorption to soil particles. The observed retention factors in the loamy sand lysimeters were also high, but were

lower in the sandy loam lysimeters. Some of these seemingly contradictory statements make determining whether diazepam will be mobile under irrigated conditions difficult.

Based on dilantin's similar K_{ow} and solubility, it should be similar to diazepam in the soil profile. Unfortunately, we do not have any information on interference with the sampling material for dilantin. Dilantin overall had less detections (5.5% average) in the drainage for all the lysimeters than diazepam but more detection in the drainage then trimethoprim, which had a lower K_{ow}. The concentrations of dilantin in the soil profile however did show an interesting decrease with increasing depth corresponding to less detection in the drainage. This indirectly shows a retardation of dilantin in the soil profile which was confirmed by the higher (>8) retardation factors calculated by equation 3. The theoretical retardation factors however would predict movement of the compound at a much faster rate (R_f = 1-1.45) than was actually observed in the soil profiles. The factors that increased the downward migration of dilantin were aerobic conditions and high pore volumes. This high difference between the observed and theoretical retardation factors could be a reflection of degradation in the more established lysimeter soils compared to the native soil used in the laboratory studies. Dilantin did degrade more under aerobic conditions in the loamy sand than the sandy loam soil (Lin et al. 2011). Degradation in the soils could contribute to lack of compound detection in both the drainage samples and the soil (Cordy et al. 2004). Only 46% of the variability of the data could be accounted for using these factors, which implied there were more factors at play in the movement of dilantin through the soil profile before discharge in the drainage.

Naproxen also had similar interference with the components of the sampling system as diclofenac. Detections in the drainage for all the lysimeters averaged 13.1% with

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average mass discharge <10%. The one exception was for the low leaching bare sandy loam (NLV) lysimeters, which had approximately 20% of the mass of naproxen in the irrigation water end up in the drainage. This was a slightly higher drainage mass discharge than observed for diclofenac. Xu et al. (2009) however did not detect naproxen in the drainage of lysimeters with similar soils (loamy sand, 83.4% sand and sandy loam, 70.3% sand). However, when they sectioned the soil in their lysimeters after four months of irrigation, they did detect both compounds at depths of 25 cm below the surface; unlike Xu et al (2009), our study was conducted over a 745 day period with 120 cm soil profiles. Naproxen concentrations, for our experiment, in the soil profile were not included because the mass in the soil were greater than the mass applied as irrigation. In general, naproxen movement was similar to diclofenac but the factors that increased the percentage of mass in drainage were anaerobic conditions and bare lysimeter cover. The factors only accounted for 35% of the variability in the mass discharge of drainage, similar to diclofenac's lower coefficient of determination. Such results would indicate that other factors beyond the soil, plant and water variables included in the backward stepwise regression were controlling the fate and transport of naproxen.

One might expect to see carbamazepine in the drainage samples with similar regularity to dilantin. However, carbamazepine detections were seen more often than dilantin in the loamy sand lysimeters and carbamazepine was never detected in the sandy loam lysimeters. The percent mass discharge in the drainage for the loamy sand lysimeters for carbamazepine and diazepam were both <2% except for the high leaching bare loamy sand lysimeters for dilantin (5%). Pore volumes of drainage and the percentage of organic matter in the soil influenced the percent mass discharge in

drainage. Higher pore volumes of drainage and higher organic matter content increased the percent mass discharge in the drainage, however, Chefetz et al. (2008) suggested that carbamazepine would be retarded by organic carbon rather than enhanced by it. The concentration profile of carbamazepine was also interesting showing a decrease towards zero, from a higher concentration in the upper soil layers. This suggests some impaired movement of carbamazepine in the soil profile, which was supported by the retardation factors in the loamy sand soil, as well as the backward step regression analysis of the percent mass unaccounted.

Summary of low (<2.00) octanol-water partitioning compounds

Atenolol, meprobamate, primidone, sulfamethoxazole and trimethoprim had the lowest octanol-water portioning values (0.16, 0.70, 0.91, 0.89 and 0.91 respectively) and the highest solubilities (13300, 4700, 500, 610 and 400 mg L^{-1} respectively). We would expect to see these compounds in the drainage water because of a higher likelihood of dissolving and preferentially entering the aqueous phase.

Atenolol was not detected in any of the drainage samples and the concentration in the soil samples exceeded the amount applied as irrigation. We unfortunately do not have any data on the half-lives or degradation coefficients for atenolol in the soil types used in this experiment so we cannot speculate on whether there was any possible degradation of this compound. Scaffer et al. (2012) reported 80% degradation of atenolol under small column studies using a very sandy soil around pH 8. They also calculated higher retardation factors for atenolol, under varying pH values than would be expected from its low octanol-water partitioning coefficient. There was some interference with the sampling material after contact for 3 days but sampling was completed with more

regularity in our lysimeters than the interference studies, so contact with the material would have been on the orders of hours rather than days.

Trimethoprim was not detected in any of the drainage samples over the 745 day experimental period. The theoretical retention factor for each soil type was very high indicating strong sorption to soil particles. Trimethoprim also had high (~86%) unaccounted for mass in the loamy sand lysimeters, which indicated some degradation of compound was occurring. We could account for approximately 60% of the variation in the unaccounted mass of trimethoprim based on the leaching fraction, cover and average % organic matter in the soil profile.

Meprobamate has a very low K_{ow} and high solubility in water, which suggests that it will move through a soil profile much faster than many of the other compounds. Meprobamate also did not reveal interference with components of the drainage sampling system so one might expect to see the compound in the drainage samples more often than other compounds with higher Kow's and/or that revealed interference with the sampling system. Meprobamate was detected in only the bare loamy sand lysimeter (0.05 and 0.25 BC Bare). Detection rates were 18.7 and 24.4% respectively for the 0.05 and 0.25 loamy sand bare lysimeters. The concentration of meprobamate in the soil showed a significant split ($p<0.05$) in concentration between the bare and grass lysimeters. The bare lysimeters had a decrease in concentration with depth but the concentrations were more uniform and lower in the turf covered loamy sand lysimeters. This deviation in concentrations between the bare and turf lysimeters was confirmed by the backward stepwise regression analysis for the unaccounted mass of meprobamate (73.3% accounted for based on cover, higher under bare conditions).

Sulfamethoxazole also had little interference with all the components of the drainage sampling system. This compound was detected 74% of the time in the drainage samples. After sulfamethoxazole was first detected in the drainage, nearly all subsequent samples also had sulfamethoxazole. The percent mass discharge of sulfamethoxazole in the drainage was very low (<2%) as compared to the high incoming concentration (1600 ng L^{-1}). The primary factor driving the amount of sulfamethoxazole mass discharged from the soil profile was the number of pore volume passing through the profile. However, this large discrepancy between the high mass applied in the irrigation, low concentrations in the soil and low mass in the drainage resulted in a large amount of mass unaccounted which could not be explained by the soil, water and plant parameters in our backward step regression analysis. There may be some other chemical or biological degradation occurring in the soil.

Average detection rate of primidone (72%) was very similar to sulfamethoxazole in all the samples collected from the lysimeters. Unlike sulfamethoxazole, primidone had a mass discharge in the drainage as high as 23% in the high leaching loamy sand lysimeters and an average of 7.4% for all lysimeters. The calculated retardation factors were the lowest overall. Primidone also had the highest mass discharge accounted for using the soil, plant and water parameters in the backward stepwise regression analysis (94%). Backwards stepwise regression analysis, using the plant, soil and water parameters, accounted for 45% of the variability of the unaccounted for mass of primidone in the soil system.. This would indicate that other parameters not measured in this study had a greater influence on the final fate and transport of primidone.

Chapter 6

Conclusions

The interactions between PPCPs and an irrigated soil profile are often complex. Estimation of adsorption within soil profiles based on compound properties can give an incomplete picture of actual field conditions. Values of octanol-water partition coefficients, solubility, and dissociation constants did not accurately portray how these compounds moved in the soil profile under the experimental conditions imposed. Nine of the 14 PPCP's were detected in the drainage of some lysimeters under different soil, LF and cover combinations; however, these detections were associated with small mass discharge in the drainage over the 745 day period. The highest mass flux, scaled on a hectare basis, was recorded for sulfamethoxazole (518 mg per ha per 745 days, equivalent to 0.25 g ha^{-1} yr^{-1}). However, in the case of primidone, as much as 28% of primidone entering the soil/plant system was detected in drainage water. Fortunately, primidone concentrations averaged only 26 ng L^{-1} in the irrigation water, as opposed to the highest concentration of 1600 ng L^{-1} for sulfamethoxazole. In most cases, higher mass flux was observed in the higher sand content soil under higher leaching conditions. Under golfcouse irrigated conditions in southern Nevada, where many fairways have significantly higher clay contents than the two soils investigated in this study, and in which low LF's are typically employed (Devitt *et al.*, 2007), using recycled water for irrigation represents a far more acceptable environmental alternative than returning these waters directly to river and/or lake systems. As noted in our study, irrigating turfgrass used 28% more water than would occur if the water was simply sprayed on bare soils as a disposal method. Based on our results, restricting the use of recycled water based solely

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on the presence of PPCP's should only be a consideration at sites where soils are extremely sandy and irrigations are not based on an ET feedback approach (Devitt *et al.*, 2007).

APPENDIX A. ACKNOWLEDGEMENTS FOR FUNDING

APPENDIX B: PHARMACEUTICAL MASS DISCHARGE PER HECTARE

Appendix B. Pharmaceutical mass discharge on a per hectare basis over the 745 day experimental period.

0.05 Bare Loamy Sand				0.05 Bare Sandy Loam			
Analyte	**Average (mg)**	**SD (mg)**	**CV**	**Analyte**	**Average (mg)**	**SD (mg)**	**CV**
Carbamazepine	3.76	6.51	1.73	Carbamazepine	<RL	<RL	<RL
Diazepam	3.73	6.47	1.73	Diazepam	3.40	5.89	1.73
Diclofenac	12.39	11.86	0.96	Diclofenac	<RL	<RL	<RL
Dilantin	3.41	5.91	1.73	Dilantin	1.46	2.54	1.73
Meprobamate	17.36	15.72	0.91	Meprobamate	<RL	<RL	<RL
Naproxen	12.74	13.94	1.09	Naproxen	54.97	95.21	1.73
Primidone	53.06	41.62	0.78	Primidone	0.51	0.89	1.73
Sulfamethoxazole	173.28	152.40	0.88	Sulfamethoxazole	14.89	25.79	1.73
Triclosan	19.54	33.84	1.73	Triclosan	26.67	46.20	1.73

0.05 Turf Loamy Sand				0.05 Turf Sandy Loam			
Analyte	**Average (mg)**	**SD (mg)**	**CV**	**Analyte**	**Average (mg)**	**SD (mg)**	**CV**
Carbamazepine	<RL	<RL	<RL	Carbamazepine	<RL	<RL	<RL
Diazepam	12.83	22.22	1.73	Diazepam	1.59	2.75	1.73
Diclofenac	18.42	16.25	0.88	Diclofenac	18.80	32.56	1.73
Dilantin	<RL	<RL	<RL	Dilantin	<RL	<RL	<RL
Meprobamate	<RL	<RL	<RL	Meprobamate	<RL	<RL	<RL
Naproxen	<RL	<RL	<RL	Naproxen	11.77	18.59	1.58
Primidone	90.34	39.44	0.44	Primidone	1.09	1.13	1.04
Sulfamethoxazole	191.14	59.99	0.31	Sulfamethoxazole	3.94	6.82	1.73
Triclosan	<RL	<RL	<RL	Triclosan	<RL	<RL	<RL

<RL = less then reportable limits

<RL for replicate calculated as zero for average and standard deviation

Appendix B (continued). Pharmaceutical mass discharge on a per hectare basis over the 745 day experimental period.

0.25 Bare Loamy Sand

Analyte	Average (mg)	SD (mg)	CV
Carbamazepine	54.79	56.19	1.03
Diazepam	28.36	39.53	1.39
Diclofenac	10.16	17.60	1.73
Dilantin	22.23	15.56	0.70
Meprobamate	85.25	118.94	1.40
Naproxen	12.74	11.06	0.87
Primidone	200.75	36.48	0.18
Sulfamethoxazole	518.33	185.31	0.36
Triclosan	7.94	13.75	1.73

0.25 Bare Sandy Loam

Analyte	Average (mg)	SD (mg)	CV
Carbamazepine	<RL	<RL	<RL
Diazepam	6.40	5.78	0.90
Diclofenac	3.15	5.45	1.73
Dilantin	<RL	<RL	<RL
Meprobamate	<RL	<RL	<RL
Naproxen	2.16	3.74	1.73
Primidone	13.32	19.08	1.43
Sulfamethoxazole	181.27	240.74	1.33
Triclosan	31.25	31.80	1.02

0.25 Turf Loamy Sand

Analyte	Average (mg)	SD (mg)	CV
Carbamazepine	205.35	48.01	0.23
Diazepam	<RL	<RL	<RL
Diclofenac	32.65	29.84	0.91
Dilantin	4.28	7.41	1.73
Meprobamate	<RL	<RL	<RL
Naproxen	11.61	20.10	1.73
Primidone	208.80	29.91	0.14
Sulfamethoxazole	267.34	44.34	0.17
Triclosan	<RL	<RL	<RL

0.25 Turf Sandy Loam

Analyte	Average (mg)	SD (mg)	CV
Carbamazepine	<RL	<RL	<RL
Diazepam	<RL	<RL	<RL
Diclofenac	97.65	85.62	0.88
Dilantin	<RL	<RL	<RL
Meprobamate	<RL	<RL	<RL
Naproxen	22.61	25.97	1.15
Primidone	16.51	6.15	0.37
Sulfamethoxazole	11.56	20.02	1.73
Triclosan	9.43	16.33	1.73

<RL = less then reportable limits

<RL for replicate calculated as zero for average and standard deviation

APPENDIX C: RETARDATION FACTORS

Appendix C. Retardation factors calculated from water and PPCP velocities (R_{fo}) and sorption factors (R_{ft}) averaged for each treatment combination.

Treatment			Sulfamethoxazole		Primidone		Carbamazepine	
			R_{fo}	R_{ft}	R_{fo}	R_{ft}	R_{fo}	R_{ft}
BC	0.05	B	1.84	2.70	1.38	1[a]	3.13	4.21
BC	0.05	G	4.98	2.70	3.54	1[a]	6.25	4.21
BC	0.25	B	3.19	2.70	3.19	1[a]	6.87	4.21
BC	0.25	G	2.76	2.70	2.76	1[a]	4.11	4.21
NLV	0.05	B	2.02	1[a]	2.02	1[a]	ND	25.77
NLV	0.05	G	1.96	1[a]	2.02	1[a]	ND	25.77
NLV	0.25	B	2.44	1[a]	4.20	1[a]	ND	25.77
NLV	0.25	G	ND	1[a]	2.85	1[a]	ND	25.77

Treatment			Diazepam		Diclofenac		Dilantin	
			R_{fo}	R_{ft}	R_{fo}	R_{ft}	R_{fo}	R_{ft}
BC	0.05	B	14.71	29.33	5.58	3.08	8.18	1[a]
BC	0.05	G	6.20	29.33	5.88	3.08	9.23	1[a]
BC	0.25	B	7.01	29.33	17.67	3.08	7.04	1[a]
BC	0.25	G	19.21	29.33	5.19	3.08	30.19	1[a]
NLV	0.05	B	2.02	35.88[b]	ND	2.40	2.02	1.45
NLV	0.05	G	1.96	35.88[b]	1.96	2.40	ND	1.45
NLV	0.25	B	3.90	35.88[b]	4.41	2.40	ND	1.45
NLV	0.25	G	ND	35.88[b]	2.58	2.40	ND	1.45

Treatment			Trimethoprim		Gemfibrozil		Meprobamate	
			R_{fo}	R_{ft}	R_{fo}	R_{ft}	R_{fo}	R_{ft}
BC	0.05	B	3.25	3.25	3.25	3.55	3.25	1.52
BC	0.05	G	6.49	6.49	6.25	3.55	6.25	1.52
BC	0.25	B	9.32	9.32	9.32	3.55	9.32	1.52
BC	0.25	G	8.23	8.23	8.23	3.55	11.89	1.52
NLV	0.05	B	ND	ND	ND	9.72	ND	2.74
NLV	0.05	G	ND	ND	ND	9.72	ND	2.74
NLV	0.25	B	ND	ND	ND	9.72	ND	2.74
NLV	0.25	G	ND	ND	ND	9.72	ND	2.74

Treatment			Naproxen	
			R_{fo}	R_{ft}
BC	0.05	B	2.90	48.22[b]
BC	0.05	G	6.07	48.22[b]
BC	0.25	B	8.96	48.22[b]
BC	0.25	G	8.04	48.22[b]
NLV	0.05	B	1.02	35.88[b]
NLV	0.05	G	1.52	35.88[b]
NLV	0.25	B	3.58	35.88[b]
NLV	0.25	G	3.43	35.88[b]

[a]Value calculated with Kd = zero, no significant sorption
[b]Value calculated with Kd = 10 but adsorption was significantly high
ND; value not determined

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CURRICULUM VITAE

LENA WRIGHT

8545 West Hammer Ln, Las Vegas, NV 89149 | 702-575-8790 |
lewright@unlv.nevada.edu

EDUCATION

University of Nevada, Las Vegas
M.S. Water Resource Management

2008-current

University of Nevada, Las Vegas
B.S. Chemistry   **2001-2006**

AWARDS

Dean's List Fall 2004 – Spring 2006
Harold and Mayme Stoker Chemistry Award - 2006
Student Award from The American Institute of Chemists Foundation and UNLV
Chemistry Department - 2006

PUBLICATIONS AND PAPERS

Wright, L., D.A. Devitt, M.H. Young, J. Gan, B.J. Vanderford, S.A. Snyder, M. McCullough, and L. Dodgen. 2012. "Fate and transport of thirteen pharmaceuticals and personal care products in a controlled irrigated turfgrass system." *Agronomy Journal*. 104(5):1244-1254.

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