Pharmaceuticals and Personal Care Product Impacts to Groundwater from the Land Application of Treated Wastewater Effluent: A Comparison of Three Land Application Systems

By

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Abstract

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Pharmaceuticals and Personal Care Products (PPCPs) represent a division of contaminants known as Contaminants of Emerging Concern (CECs), which are often not removed during traditional wastewater treatment processes. Through various procedures, wastewater treatment plants (WWTPs) play an essential role in the elimination of harmful contaminants for safe water use. Although traditional WWTPs are often effective in removing harmful contaminants, many PPCPs are often not removed in the process. Traditional WWTPs typically discharge treated wastewater effluent directly into nearby surface waters. Although, due to the potential harmful ecological impacts associated with discharging wastewater effluent directly into surface wasters, and lack of available fresh water in many areas, many WWTPs instead discharge treated wastewater effluent onto various approved lands. This review aims to identify and summarize PPCP concentrations in wastewater effluent and groundwater at three wastewater land application sites (LASs) across the United States in order to further evaluate the fate and transport of PPCPs originating from the land application of treated wastewater.

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Introduction

As human populations grow, effective municipal wastewater treatment continues to be essential for the health and safety of the natural environment and human population (NRC. 2012). Traditional wastewater treatment plants (WWTPs) are vital to providing effective means of dealing with human generated wastewater and treat the majority of municipal wastewater throughout the United States (McEachran et al. 2016). Treated wastewater effluent is typically discharged into various approved surface waters or land areas. Certain contaminants are often not removed from municipal wastewater by WWTPs and can result in negative impacts to the environment. Chemicals associated with pharmaceuticals and personal care products (PPCPs) represent a significant group of contaminants of emerging concern (CECs), that often remain in treated municipal wastewater and enter the environment (McEachran et al. 2018). These PPCPs can have various harmful effects in receiving surface waters. PPCPs can represent a significant ecological hazard for a variety of organisms in environments that receive waters from WWTPs and are currently not regulated by the federal government (McEachran et al. 2017).

Pharmaceuticals are used primarily to prevent or treat human and animal disease, whereas personal care products are used to improve the quality of daily life and include products such as moisturizers, lipsticks, shampoos, hair colors, deodorants, and toothpastes (Boxall et al. 2012). 4,000 pharmaceuticals are currently in use, and many types of chemicals are used in personal care products (Boxall et al. 2012). Although reported concentrations are generally low, many PPCPs have been detected in a variety of hydrological, climatic, and land-use settings and some can persist in the environment for months to years (Monteiro and Boxall 2009).

Once in the environment, PPCPs can result in detrimental effects on aquatic wildlife. Natural and synthetic estrogen compounds, including 17β-estradiol, estrone, and 17α-ethynylestradiol, have been reported to cause decreased fecundity in flathead minnows (Panter et al. 1998) and reduced testicular development in trout (Jobling et al. 1996), among other negative reproductive effects in fish (McEachran et al. 2016). Furthermore, inhibition of growth and development of secondary sexual characteristics in *Daphnia magna*, an important indicator species in aquatic ecosystems, was reported after exposure to a variety of endocrine-active chemicals (McEachran et al. 2016). Other commonly used compounds that are persistent in wastewater treatment effluent are nonsteroidal anti-inflammatory drugs. These compounds, including ibuprofen and naproxen, have been reported in the environment at concentrations of 300 ng/L in surface waters (Antonic and Heath 2007), and they elicit negative reproductive effects on aquatic organisms at low, but potentially environmentally relevant, concentrations (Heckmann et al. 2007). To combat rising concerns over the ecological hazards of discharging treated wastewater effluent containing a multitude of PPCPs directly into surface waters, researchers continue to investigate the potential benefits of wastewater land application systems (LASs).

Land Application Background

Land application reuse of municipal wastewater represents one method in which WWTPs release treated wastewater into the environment. Land application systems (LASs) are water reuse systems that treat and recycle wastewaters through soil infiltration and groundwater recharge (Crites 1984; USEPA 1972). The applied wastewater infiltrates the soil column and discharges to surface water as groundwater via base flow (Barton et al. 2005; Hutchins et al. 1985). Although wastewater LASs filter nutrients from wastewater to acceptable levels before reaching surface water sources, the fate and transport of PPCPs from wastewater application to ground waters and surface waters is often unknown (McEachran et al. 2016). Further discovery and assessment of PPCPs in soil and groundwater as a result of the land application of wastewater effluent is necessary due to their potential harmful ecological effects.

In the United States, land application technologies were implemented in the 1970s with the introduction of the National Environmental Policy Act and amendments to the Federal Water Pollution Control Act of 1972 (US Congress, FWPCA 1972). This technology involves the irrigation of municipal wastewater onto agricultural or forested lands; the treatment of wastewater may vary from no treatment to tertiary treatment before actual irrigation onto land (McEachran et al. 2016). This review explores PPCP concentrations from the application of wastewater effluent after primary and secondary treatment has occurred. There are around 600 communities in the United States reusing effluent from municipal WWTPs for surface irrigation (Davis and Cornwell 1998). Wastewater reuse via land application has been shown to mitigate PPCP concentrations in groundwater and receiving surface waters through several processes including soil infiltration, soil sorption, biodegradation, photodegradation, and other biogeochemical processes.

Following primary and secondary treatment of wastewater, wastewater effluent is applied to soil. Application to soil can occur in a variety of methods. Common application techniques include the use of installed sprinkler heads, pivot irrigation systems, or other installed water distribution systems. Treated wastewater effluent is generally applied to either agricultural lands or approved non-agricultural lands, typically forest systems or grasslands. When compared with mechanical and lagoon treatment systems that treat 19,000 $m^3\ d^{-1}$ of municipal wastewater or less, slow-rate LASs have lower costs (capital, energy, and user), high removal of nutrients and organic materials (biological oxygen demand), more employment (staff) per plant capacity, and the lowest odor potential (Muga and Mihelcic, 2008). Determining effective approaches to municipal wastewater treatment and disposal is critical to the future of societal and environmental health. Therefore, determining how land application of minimally treated municipal wastewater may lead to environmental input of pharmaceuticals is crucial to the greater understanding of wastewater treatment options and development (McEachran et al., 2016).

Study Areas

Wastewater influent at the three reviewed LASs undergoes a variety of primary and secondary treatment processes including screening, grit removal, settling, and chlorine contact depending on the site. In North Carolina, the city of Jacksonville's 6,300-acre LAS consists of 10 acres of biological treatment lagoons, 90 acres of storage lagoons, and over 2,300 acres of natural grass and planted pine forests (Jacksonville NC, Gov. 2019). Since its establishment in 1998, the site now contains more than 18,000 sprinklers and can treat up to 6 million gallons of wastewater per day (Jacksonville NC, Gov. 2019). Treated wastewater is land-applied onto approximately 2,300 acres of temperate forested land within the 6,300-acre site with application rates averaging 5.1 million gallons per day (McEachran et al. 2018). The land application area receives approximately 1200 mm of wastewater and 1300 mm of precipitation annually (McEachran et al. 2017). PPCPs analyzed in this review at the Jacksonville LAS include 17-β estradiol, estrone, 17-α ethynylestradiol, estriol, ibuprofen, acetaminophen, naproxen, triclosan, trimethoprim, sulfamethoxazole, and caffeine.

First installed in 1913, the Pennsylvania State University 605-acre LAS (PSU LAS), known as the Living Filter, is comprised of two irrigation sites known as the Gamelands and Astronomy sites (Kibuye et al. 2019; Franklin et al. 2018). The Gamelands site makes up approximately half of the total Living Filter area and consists of primarily forested lands comprised of white oak and other mixed hard woods (Andrews et al. 2016). The Astronomy site is comprised of cropped lands rotated with wheat, corn, rye, soybeans, and sorghum-sundagrass (Kibuye et al. 2019). More than 3,000 spray heads distribute an average of 1.5-2.0 million gallons of treated wastewater per day when school is in session, to 0.5 million gallons per day during holiday breaks (Kibuye et al. 2019; Franklin et al. 2018). PPCPs analyzed in this review at the PSU LAS include acetaminophen, caffeine, naproxen, sulfamethoxazole, and trimethoprim.

In West Texas, the 6,000-acre Lubbock, TX LAS treats approximately 21 million gallons of wastewater per day, of which an estimated 13 million gallons of treated effluent is applied daily to land plots (Karnjanapiboonwong et al. 2011). For more than 70 years, Pivot irrigation systems have been employed to apply the effluent to what has grown to be 31 treatment plots corresponding to 2,538 acres, which are seeded with grasses, cotton, and legume species (Karnjanapiboonwong et al. 2011). PPCPs analyzed in this review at the Lubbock LAS include 17-β Estradiol, Estrone, 17-α Ethynylestradiol, Estriol, ibuprofen, triclosan, and caffeine.

Methods

From August 2018 to April 2019, scientific literature pertaining to wastewater LASs and CECs was reviewed with a focus on the fate and transport of land applied PPCPs in wastewater effluent, soil, and groundwater. Three LASs from different regions across the United States were chosen from the literature review to focus on and are described previously.

The North Carolina State Universities (NCSUs) Web of Science and Agricultural and Environmental Science literature search databases were used to identify scientific literature from 2019 and prior. The following key words were used when conducting literature review searches: *wastewater, wastewater treatment, WWTP, land treatment, land application, spectrometry, chemicals of concern, pharmaceuticals, PPCP, reuse, soil, groundwater, effluent, fate, and transport.* Articles were selected for review if the abstract identified PPCP impacts to soil and or groundwater as a result of the land application of treated wastewater effluent. A total of 16 articles were found with 7 being primarily used in this assessment (Table 3). Articles were also reviewed from the references of applicable articles.

The articles identified were grouped into 2 categories for organizational purposes: PPCP concentrations in treated wastewater effluent and soil, and PPCP concentrations in treated wastewater effluent and groundwater. The objective of this review is to further examine the fate and transport of PPCPs from treated wastewater effluent to groundwater. A total of 11 PPCPs were analyzed in this review (Table. 1).

Results

Jacksonville LAS Wastewater

Several studies have assessed LAS efficiency, hydrologic impacts, and resulting PPCP concentrations in wastewater effluent and groundwater at the Jacksonville LAS (McEachran et al. 2016, 2017, 2018; Birch et al. 2016). Overall, the most abundant PPCPs in wastewater were predominated by the prescription and over-the-counter drug, non-steroidal anti-inflammatory drug (NSAID), and antibiotics/antimicrobials chemical groups (McEachran et al. 2017). Of the analyzed PPCPs in this review, the most abundant PPCPs by average concentration in wastewater effluent at the Jacksonville LAS included trimethoprim (573 ng/L), sulfamethoxazole (380 ng/L), ibuprofen (200 ng/L) and Caffeine (145 ng/L) (Table. 4).

Jacksonville LAS Soil

PPCP concentrations in soil at the Jacksonville LAS have been well documented by McEachran et al. (2017). PPCP concentrations were greater in samples taken from irrigated areas versus samples taken from non-irrigated areas and generally, PPCP concentrations were greater in surface soils compared to deeper soils. Concentrations of PPCPs ranged from less than 1 ng/g to 5 ng/g wet weight for irrigated soils. Of the analyzed PPCPs in this review, 17-α Ethynylestradiol was the only one detected with any significance at the Jacksonville LAS. Surface soils often had twice the organic carbon content as their deeper soils, thus often resulting in higher sorption and attenuation of PPCPs (McEachran et al. 2017). Organic carbon content, along with other biogeochemical interactions throughout the soil column likely contributed to the very low detection of the majority of the PPCPs in this review. Overall research at the Jacksonville LAS has demonstrated the role soil can serve as a natural filter for PPCPs through biodegradation processes.

Jacksonville LAS Groundwater

When the highest average wastewater effluent concentrations are compared to the highest average groundwater concentrations of 17-β estradiol (13.8 ng/L), sulfamethoxazole (4.2 ng/L), and Triclosan (2.93 ng/L), it is apparent that the Jacksonville LAS is extremely successful at reducing PPCP concentrations from wastewater effluent to groundwater (Fig. 1). These compounds, although detected at low concentrations, generally have lower log Kow values and greater water solubility which indicates increased likelihood of downward movement through soil and into groundwater. Sulfamethoxazole was present throughout the majority of groundwater samples and has been well documented in groundwater at other sites by Barnes et al. (2008) and McEachran et al. (2016, 2017). Although PPCP infiltration to groundwater was observed at the Jacksonville LAS, concentrations were well below those found in applied effluent and do not represent an acute ecological threat.

PSU LAS Wastewater

PPCP concentrations at the Penn State LAS have been well documented by Kibuye et al. (2019) and Franklin et al. (2018). Overall, effluent samples generally had lower PPCP concentrations than influent samples, which suggests partial degradation or transformation during primary and secondary treatment (Kibuye et al. 2019). The highest average concentrations in wastewater effluent at the PSU LAS throughout the year ranged from 1,102 ng/L to 3,765,070 ng/L, with naproxen (3,765,070 ng/L), sulfamethoxazole (34,330 ng/L), and caffeine (23,230 ng/L) representing the most abundant PPCPs detected (Table. 5). Average PPCP concentrations from wastewater to groundwater observed in this review demonstrates the effectiveness of the system to mitigate PPCPs entering the environment.

Overall, the literature has shown that PPCP concentrations in the fall and winter are generally higher than concentrations in the spring and summer due to increased human consumption rates in the colder months and increased biodegradation, photodegradation, and other biogeochemical interactions in the warmer months (Kibuye et al. 2019). Although the concentrations in seasonal trends are similar to those reported in other wastewater studies (Hedgespeth et al. 2012; Sui et al. 2011), PPCP concentrations in effluent at the PSU LAS have been shown to correspond directly to when students are in session (Kibuye et al. 2019). During the fall and spring the number of residents is at its highest, which often means higher usage of PPCPs, which correlates directly to higher concentrations in wastewater. In the summer months, the majority of students leave campus and PPCP concentrations in effluent are, correlatively, lower (Franklin et al. 2018).

PSU LAS Soil

Soil sample data was averaged from samples collected during 3 sampling periods at two locations from the PSU LAS agricultural site only. Soil sampling period one occurred prior to the first spray irrigation, with the most recent spray irrigation taking place seven months prior. Soil sampling period two was collected after a single 12-hour spray irrigation period. Soil sampling period three took place after ten weeks of weekly 12 hour irrigation events (Franklin et al. 2018). Sample events two and three were each taken at a summit (highest elevation) location and a depression (lowest elevation) location. Sample period one was only taken at the summit location.

Of the analyzed PPCPs in this review, sulfamethoxazole and trimethoprim were detected in soil samples at an average of 0.24 ng/g and 0.02 ng/g respectively. Overall, sulfamethoxazole was the most commonly detected PPCP throughout all soil depths with the highest concentrations generally remaining in the top 0-5 cm of soil (Franklin et al. 2018). Trimethoprim was only detected at low concentrations, primarily in the upper 30 cm of soil samples after ten weeks of weekly wastewater irrigation (Franklin et al. 2018). The disappearance of this compound in the soil and water environment may be due to strong interactions within the soil profile, formation of complexes that do not allow it to be extracted completely, or rapid degradation within the soil system (Franklin et al. 2018).

PSU LAS Groundwater

The highest average concentrations in groundwater throughout the PSU LAS were naproxen (37,700 ng/L), caffeine (2,650 ng/L), and sulfamethoxazole (1,111 ng/L) (Table. 5). Groundwater results conclude that Naproxen was the most mobile compound throughout soil and was detected at the highest concentrations in groundwater samples. Trimethoprim was the lowest detected in groundwater of the targeted PPCPs at the PSU LAS and is not expected to represent acute risk groundwater systems. Caffeine and sulfamethoxazole were also among the most frequently detected PPCPs in other groundwater studies (Ayers et al. 2017; Barnes et al. 2008; Fram and Belitz, 2011; McEachran et al. 2017; Vulliet and Cren-Olivé, 2011) and similar low detection frequencies for trimethoprim have been observed by Vulliet and Cren-Olivé (2011).

Minimal variations in concentration were observed in sample wells located in irrigated and non-irrigated areas of the PSU LAS. Interestingly, the highest concentrations observed were generally found in a well which does not receive direct wastewater irrigation (Kibuye et al. 2019). Overall, similarities in concentrations at the sites may be expected due to the influence of groundwater flow at the site leading to flow from irrigated areas impacting wells in non-irrigated areas and the multi-decadal history of wastewater irrigation activities (Kibuye et al. 2019). Although higher than PPCP concentrations observed at the Jacksonville and Lubbock LASs, groundwater concentrations were reduced significantly compared to wastewater effluent (Fig. 2). Based on the ratio of the average concentrations between wastewater effluent and groundwater in this review, the land application of wastewater at the PSU LAS is an effective option to reduce PPCP concentrations in groundwater.

Lubbock LAS Wastewater

In general, PPCP concentrations in effluent were lower than concentrations in influent. This supports the literature that certain compounds can partially be removed or transformed from wastewater during primary and secondary treatment processes. At the Lubbock LAS, significant differences in concentrations between wastewater effluent and groundwater were observed (Fig. 3). Average concentrations of PPCPs in wastewater effluent ranged from 50 ng/L to 20,793 ng/L, with estriol (20,793 ng/L), estrone (642 ng/L), 17-β estradiol (443 ng/L), and triclosan (155 ng/L) representing the most abundant PPCPs by average concentration of all effluent samples (Table. 6).

Seasonal variations in PPCP concentrations were observed with higher concentrations generally being recorded during the December and March sampling events and lower concentrations during the June and September sampling events (Karnjanapiboonwong et al. 2011). Lower total PPCP concentrations with warmer daily temperatures may reflect chemical, biological, and physical PPCP dissipation in the open-air reservoirs due to enhanced photodegradation through increased sunlight intensity, algal growth, and microbial activity (McEachran et al. 2017). Occasionally Estrone, 17β-estradiol, Estriol, and 17α-ethynylestradiol were detected in effluent at higher concentrations than influent (Karnjanapiboonwong et al. 2011). This suggests that these compounds may not be easily degraded or the inactive conjugates of estrogens may be deconjugated during the wastewater treatment process resulting in the release of the active parent compound to produce higher effluent concentrations (Kirk et al. 2002; Anderson et al. 2003; D'Ascenzo et al. 2003).

Lubbock LAS Soil

Soil samples were taken during the months of March, June, and September at depths of 0-6", 12-18", and 24-30" at four sampling locations, two of which were within wastewater irrigation and two outside wastewater irrigation. Overall average PPCP concentrations of both irrigated and non-irrigated soil ranged from 0 to 73.5 ng/g. Except for caffeine, target PPCPs in this review were detected both inside and outside irrigated areas, indicating that PPCPs are being transported via runoff (Karnjanapiboonwong et al. 2011). Overall, PPCP concentrations in soil were varied and unpredictable throughout different sample depths (Karnjanapiboonwong et al. 2011).

Average PPCP concentrations over the seven-month sampling period identified ibuprofen with the highest concentration of 73.5 ng/L (Table. 7). Although Estrone was not detected at high levels in wastewater effluent, it was the most detected of all the targeted estrogens in soil. Several studies have reported that 17β-estradiol is biotransformed to Estrone rapidly under both aerobic and anaerobic conditions in soils (Colucci et al. 2001; Jacobsen et al. 2005; Ying and Kookana 2005; Xuan et al. 2008). This biotransformation of 17β-estradiol to Estrone in soil is a likely cause for the higher Estrone concentrations throughout the soil samples. Although Estriol was the most detected compound of all the PPCPs in wastewater and groundwater, it was detected at relatively low concentrations in soil. The lower concentrations of Estriol in soil compared to that of Estrone is likely due to higher soil mobility of Estriol, resulting in less Estriol adsorbed to soil (Karnjanapiboonwong et al. 2011).

Lubbock LAS Groundwater

Average PPCP concentrations in groundwater ranged from 0 to 570 ng/L. The most prevalent PPCPs identified in groundwater by average concentration were estriol (570 ng/L), caffeine (39 ng/L), 17-α ethynylestradiol (30 ng/L), and 17-β estradiol (27 ng/L) (Table. 6). Ibuprofen was not detected in any groundwater samples, while Estriol was detected at the highest concentrations of all targeted PPCPs. Ibuprofens high concentration in soil and lack of concentration in groundwater is likely due to its high log Kow (3.97) and tendency to sorb to soil. With Estriol representing the highest concentrations in both wastewater effluent and groundwater, but not soil, it is likely that Estriol has higher attenuation in soil. The extent of PPCPs in groundwater can also be affected by sorption and biodegradation of these compounds throughout the soil-water interface (Kreuzinger et al. 2004b; Mansell et al. 2004; Snyder et al. 2004; Osenbrück et al. 2007). Overall, biogeochemical interactions in soil at the Lubbock LAS likely contributed to drastically reducing PPCP concentrations from wastewater effluent to groundwater (Fig. 3).

Discussion

Soils have been shown to aid in the removal and dissipation of many PPCPs through a variety of methods. Organic matter and microbial activity can cause dramatic changes to the dissipation of PPCPs in soils resulting in increases and decreases in dissipation rate (Dodgen and Zheng, 2016). The contribution of organic matter to soils from wastewater irrigation may have enhanced PPCP biodegradation and sequestration in forest-water reuse soils (Dalkmann et al., 2014), thus lowering observed PPCP concentrations (McEachran et al. 2017). In the soil environment, sorption is believed to be an important process governing the mobility of organic compounds including PPCPs (Drillia et al. 2005; Boxall 2008), whereas volatilization and degradation are processes governing the elimination of these compounds (Karnjanapiboonwong et al. 2011). Photodegradation may be a pathway for the removal of target PPCPs on surface soil exposed to sunlight since these compounds can be degraded by wavelengths in the environmental UV spectrum (Phillips et al. 1990; Lin and Reinhard 2005; Aranami and Readman 2007; Belden et al. 2007; Mazellier et al. 2008; Nakada et al. 2008; Matamoros et al. 2009).

Although PPCPs can be volatilized and dissipated through various biogeochemical interactions in soil, certain soil-water interactions that take place over time can potentially increase PPCP concentrations in groundwater. Factors such as the presence of preferential flow paths (Assadian et al., 2005; Gall et al., 2016) and clogged soil pores (De Vries, 1972) can impact soil-water interactions, hence minimizing pollutant removal (Kibuye et al. 2019). Eventually, under frequent, long-term irrigation, the soil's capacity to act as an effective biogeochemical filter for pollutants may be reduced, leading to increased pollutant levels in groundwater over time (Ramirez-Fuentes et al., 2002).

Although research has shown that soil can act as an effective natural filter for PPCPs applied from wastewater, not all PPCPs are often able to be removed. Thus, with wastewater application over time, PPCP impacts to groundwater can occur. As with soil, groundwater can play an important role in

PPCP mitigation to surface waters. Many factors come into play when evaluating PPCP impacts and residence times in groundwater. Wastewater application rates, precipitation amounts, chemical properties, groundwater recharge times, and the shape of subterranean hydrological systems will all determine the fate and transport of PPCPs in groundwater. As described in (Boxall 2008), PPCPs can be transported from soil to other aquatic systems and groundwater, the extent of which is dependent on various factors including the solubility, sorption behavior, and persistence of the contaminant as well as climate conditions and physiochemical properties of the soil. Evaluating the efficacy of LASs to mitigate nonregulated and emerging contaminants requires a quantitative assessment of the hydrological system (Ruiz et al. 2002), but few studies have evaluated the connectivity between groundwater and local surface water LAS sites (Crites, 1984; Hutchins et al., 1985; Sabourin et al., 2009). Overall, research has shown that continued release of wastewater onto soil over time, coupled with the mixtures of relatively small amounts of many different PPCPs, can result in groundwater contamination.

Conclusions

Several similarities were observed at the reviewed LASs. Analyzed PPCPs in this review were detected in wastewater effluent and groundwater across all three LASs (Table. 8). Throughout all three systems, partial removal or transformation of PPCPs was observed for many of the PPCPs during primary and secondary treatment, prior to wastewater irrigation. Beginning with applied wastewater effluent, common seasonal variations in PPCP concentrations were observed. With few exceptions, concentrations in wastewater and soil were generally higher in winter months due to increased usage of pharmaceuticals and lower degradation rates associated with colder temperatures. Although this is a well-documented correlation between PPCP concentrations and changes in temperature, other factors can influence PPCP concentrations at LASs. The log Kow and water solubility of PPCPs played an important role in the seasonal and average concentrations observed throughout wastewater effluent, soil, and groundwater at the reviewed LASs (Table. 2). PPCPs with lower log Kow values and higher water solubility such as caffeine, acetaminophen, and sulfamethoxazole were found to move more readily from wastewater to groundwater and represent the highest concentrations observed in groundwater in this assessment. PPCPs with higher log Kow values and lower water solubility such as Ibuprofen tended to sorb to soil more readily and were observed at higher concentrations in soil but not groundwater (Table 7). Research conducted at the PSU LAS demonstrated that areas with large population fluctuations throughout the year may result in correlatively variable PPCP concentrations present at the receiving LAS. Even during some warmer months at the PSU LAS, PPCP concentrations were often highest, possibly due to the large population of students and faculty in session at the University.

Several soil-water interactions with PPCPs were likely taking place at the reviewed LASs. Often dependent on the physiochemical properties of the compounds, photodegradation, organic carbon content in soil, and groundwater recharge rates, PPCP movement from wastewater effluent to groundwater can vary. Although the movement of PPCPs from treated effluent to groundwater was detected at the reviewed LASs, concentrations were significantly lower between wastewater effluent and groundwater. As wastewater reuse becomes increasingly common worldwide, the presence of PPCPs known to persist in treated wastewater effluent has raised concerns about their potential impacts to ecosystems and human health (Kibuye et al. 2019).

Based on the averages of wastewater effluent samples and groundwater samples across the three reviewed sites (Table. 8), average groundwater concentrations were always lower than effluent concentrations (Fig. 4). Of the PPCPs analyzed in this review, naproxen was detected at the highest concentrations in both wastewater effluent and groundwater. While naproxen was only detected in groundwater at 1.3 ng/L at the Jacksonville LAS, it was detected in groundwater at 37,700 ng/L at the PSU LAS. The overall higher concentrations observed at the PSU LAS compared to the Jacksonville and

Lubbock LASs may be attributed to the overall increase in usage associated with the large population of students and faculty the PSU LAS receives wastewater from. The higher concentrations observed at the PSU LAS are also likely due to its smaller size compared to the Jacksonville and Lubbock LASs. At approximately one fourth the size of the other two LASs and still receiving up to 2 million gallons of wastewater effluent per day, the higher concentrations of PPCPs observed at the PSU LAS could be expected (Table. 2). Although the PSU LAS has been shown to effectively mitigate a substantial percentage of PPCPs before reaching groundwater, further assessment and monitoring is recommended due to the significantly greater amount of PPCPs detected comparted to the other two LASs. Even while naproxen was detected at a relatively high average concentration in groundwater comparted to other PPCPs across the reviewed LASs, the PPCPs analyzed in this review represent little to no acute toxicity risk based on their concentrations in groundwater. Chronic exposure to the observed relatively small amounts of many different chemicals, however, requires further research and assessment.

While PPCP concentrations detected in groundwater at the Lubbock LAS were generally slightly higher than at the Jacksonville LAS, both saw groundwater concentrations at much lower concentrations than the PSU LAS (Table. 2). The higher concentrations of PPCPs observed at the Lubbock LAS and even higher concentrations observed at the PSU LAS, comparted to the lower observed concentrations at the Jacksonville LAS is likely partly due to how long these facilities have been releasing wastewater effluent. While the Jacksonville LAS has been land applying wastewater effluent since 1998, both the PSU LAS and Lubbock LAS have been operational for over 70 years. The continued discharge of wastewater for 50 years longer than the Jacksonville LAS is likely correlated to the increased observed PPCP concentrations at those sites. Although often dependent on the populations and usage rates of PPCPs which WWTPs receive wastewater from, Overall, this review has assessed that soil can act as an effective natural filter for the removal and mitigation of PPCPs from wastewater to groundwater and proves to be a useful alternative to the direct discharge of wastewater effluent into surface waters. Further research and assessment are necessary to determine chronic risks associated with exposure to relatively small concentrations of many different PPCPs.

Tables and Figures

Table 1 – Analyzed PPCPs at each LAS by log Kow.

Jacksonville LAS	PSU LAS	Lubbock LAS	log Kow
Caffeine	Caffeine	Caffeine	-0.07
Acetaminophen	Acetaminophen		0.46
Sulfamethoxazole	Sulfamethoxazole		0.89
Trimethoprim	Trimethoprim		0.91
Estriol		Estriol	2.45
Naproxen	Naproxen		3.18
17-β Estradiol		17-β Estradiol	3.28
Estrone		Estrone	3.43
17-α Ethynylestradiol		17-α Ethynylestradiol	3.67
Ibuprofen		Ibuprofen	3.97
Triclosan		Triclosan	4.76

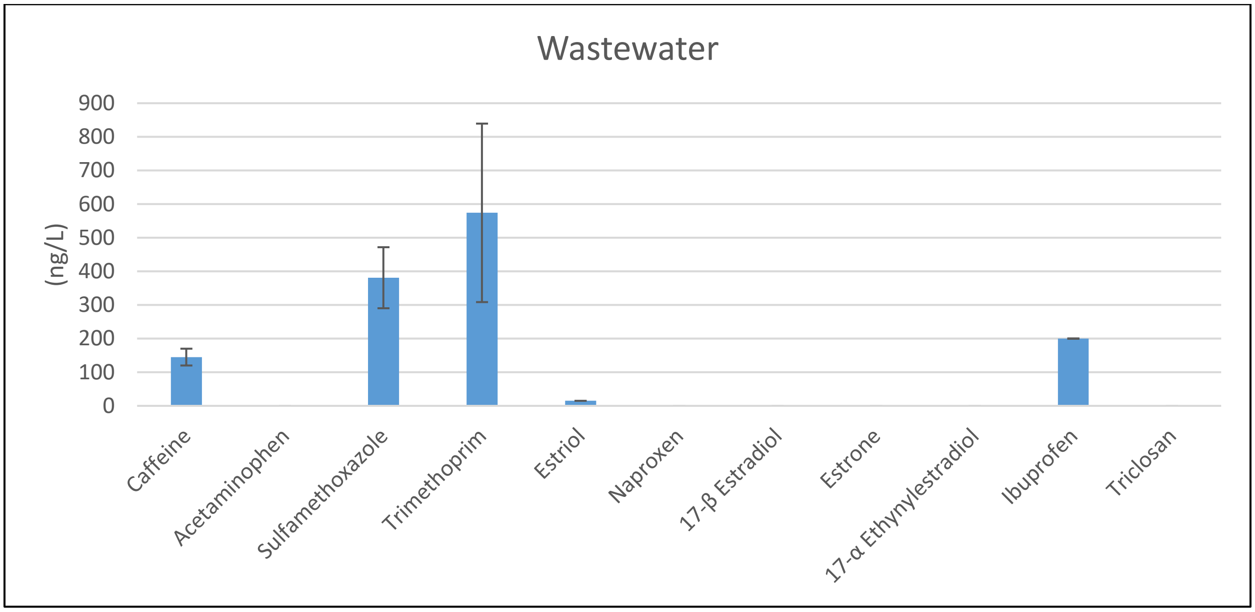
Table 2 – Background information for each LAS and overall average PPCP concentrations in order of log Kow values.

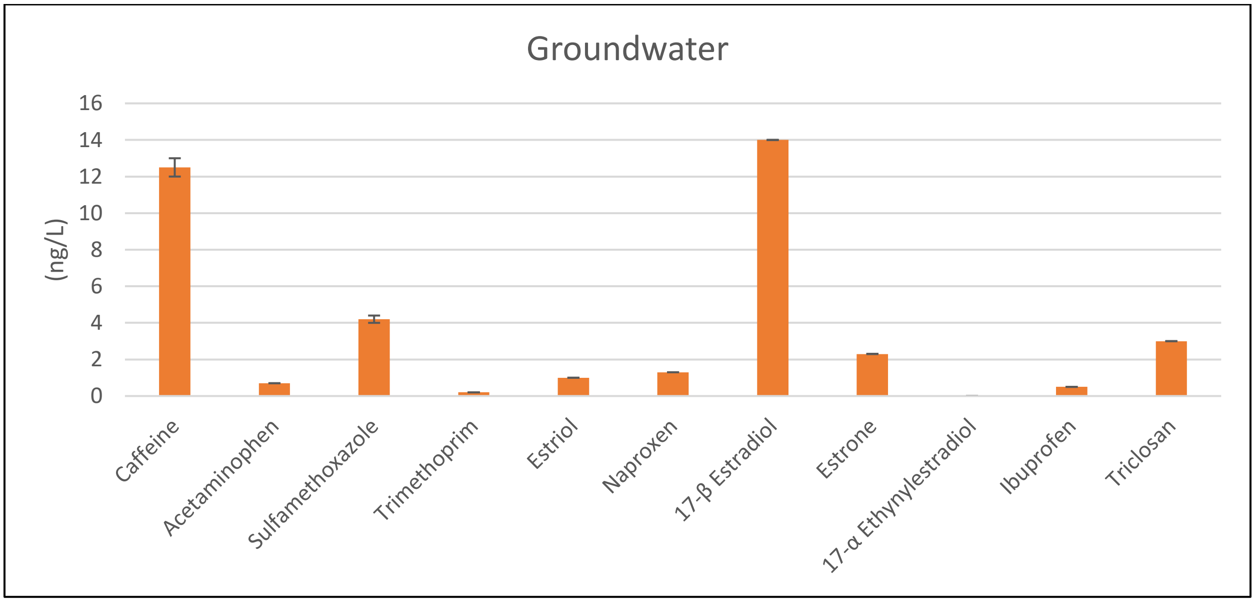
	Jacksonville LAS	PSU LAS	Lubbock LAS
Site Location	Jacksonville, North Carolina	State College, Pennsylvania	Lubbock, Texas
Acreage	2,300	605	2,538
Land Type	Pine Forest and Natural Grass	Mixed Hardwood Forest and Cropped Fields	Copped Land Plots
Method of Wastewater Application	Stationary Spray Head Sprinklers	Stationary Spray Head Sprinklers	Pivot Irrigation Sprinklers
Average Applied GPD	5.1 Million	0.5 - 2.0 Million	13 Million
Average Overall Concentrations (ng/L) in Wastewater and Groundwater at Each Site (WW / GW)			
Caffeine	145 / 12.5	23,230 / 2,650	64 / 40
Acetaminophen	0 / 0.7	5,830 / 420	
Sulfamethoxazole	381 / 4.2	34,330 / 1,111	
Trimethoprim	574 / 0.2	1,103 / 307	
Estriol	15 / 1		20,793 / 570
Naproxen	0 / 1.3	3,765,070 / 37,700	
17-β Estradiol	0 / 14		443 / 28
Estrone	0 / 2.3		642 / 18
17-α Ethynylestradiol	0 / 0		91 / 31
Ibuprofen	200 / 0.5		51 / 0
Triclosan	0 / 3		155 / 12

Table 3 – List of primary articles utilized for Sample data at the three compared LASs.

Jacksonville LAS		PSU LAS		Lubbock LAS	
McEachran et al. 2016	Pharmaceutical occurrence in groundwater and surface waters in forests land-applied with municipal wastewater	Franklin et al. 2018	Assessment of soil to mitigate antibiotics in the environment due to release of wastewater treatment plant effluent	Karnjanapiboonwong et al. 2010	Occurrence of PPCPs at a wastewater treatment plant and in soil and groundwater at a land application site
Birch et al. 2016	Hydrologic impacts of municipal wastewater irrigation to a temperate forest watershed	Kibuye et al. 2019	Fate of pharmaceuticals in a spray-irrigation system: From wastewater to groundwater		
McEachran et al. 2017	Pharmaceuticals in a temperate forest-water reuse system				
McEachran et al. 2018	Comparison of emerging contaminants in receiving waters downstream of a conventional wastewater treatment plant and a forest-water reuse system				

Figure 1 - **Average concentrations of PPCPs in wastewater and groundwater at the Jacksonville LAS in order based on log Kow values. Wastewater and groundwater PPCP concentrations averaged from sample data from McEachran et al. 2016, 2017, and 2018. Error bars represent one standard deviation from the sample set.**





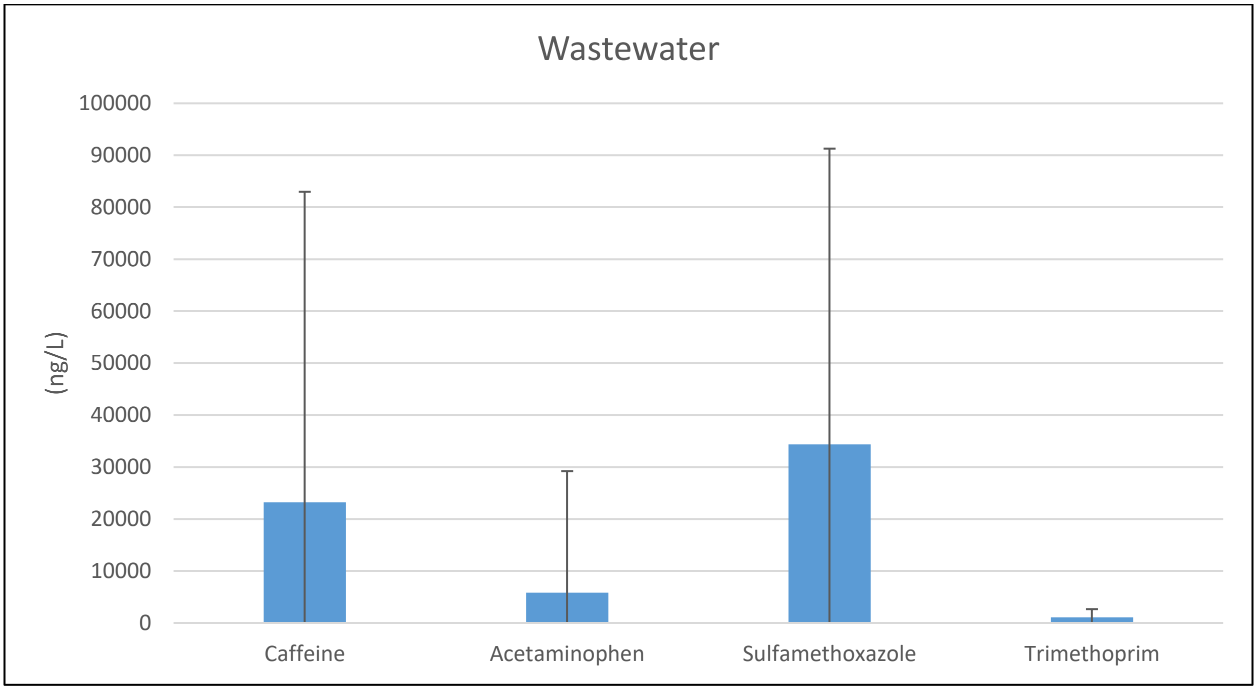
<u>Table 4</u> – Average wastewater and groundwater concentrations (ng/L) of reviewed PPCPs at the Jacksonville LAS in order of log Kow values. Wastewater and groundwater PPCP concentrations averaged from sample data from McEachran et al. 2016, 2017, and 2018. Note: PPCPs with detected concentrations and 0 STDEV represent the only available sample and have no STDEV.

PPCP	Wastewater	Standard Deviation
Caffeine	145	25
Acetaminophen	0	0
Sulfamethoxazole	381	90.75
Trimethoprim	574	265.37
Estriol	15	0
Naproxen	0	0
17-β Estradiol	0	0
Estrone	0	0
17-α Ethynylestradiol	0	0
Ibuprofen	200	0
Triclosan	0	0
PPCP	**Groundwater**	**Standard Deviation**
Caffeine	12.5	0.5
Acetaminophen	0.7	0
Sulfamethoxazole	4.2	0.2
Trimethoprim	0.2	0
Estriol	1	0
Naproxen	1.3	0
17-β Estradiol	14	0
Estrone	2.3	0
17-α Ethynylestradiol	0	0
Ibuprofen	0.5	0
Triclosan	3	0

<u>Table 5</u> – Average wastewater and groundwater concentrations (ng/L) of reviewed PPCPs at the PSU LAS in order of log Kow Values. Wastewater and groundwater PPCP concentrations averaged from sample data from Kibuye et al. 2019 and Franklin et al. 2018.

PPCP	**Wastewater**	**Standard Deviation**
Caffeine	23,230	59,760
Acetaminophen	5,830	23,380
Sulfamethoxazole	34,330	56,963
Trimethoprim	1,103	1,554
Naproxen	3,765,070	9,925,960
PPCP	**Groundwater**	**Standard Deviation**
Caffeine	2,650	4,730
Acetaminophen	420	2,190
Sulfamethoxazole	1,111	2,690
Trimethoprim	307	812
Naproxen	37,700	29,770

<u>Figure 2</u> – Average concentrations of PPCPs between wastewater effluent and groundwater at PSU LAS in order of log Kow values. Note: Naproxen was detected at significantly higher concentrations and was not included in this figure (see table 5). Wastewater and groundwater PPCP concentrations averaged from sample data from Kibuye et al. 2019 and Franklin et al. 2018. Error bars represent one standard deviation from the sample set.



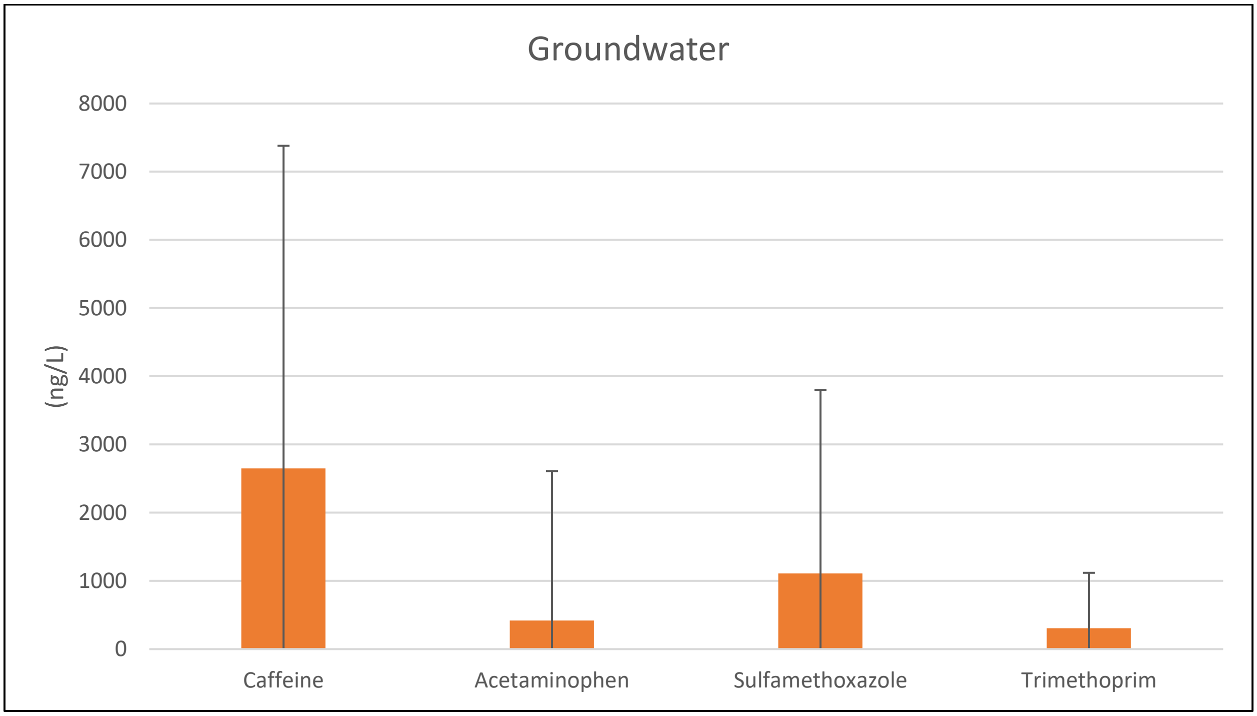
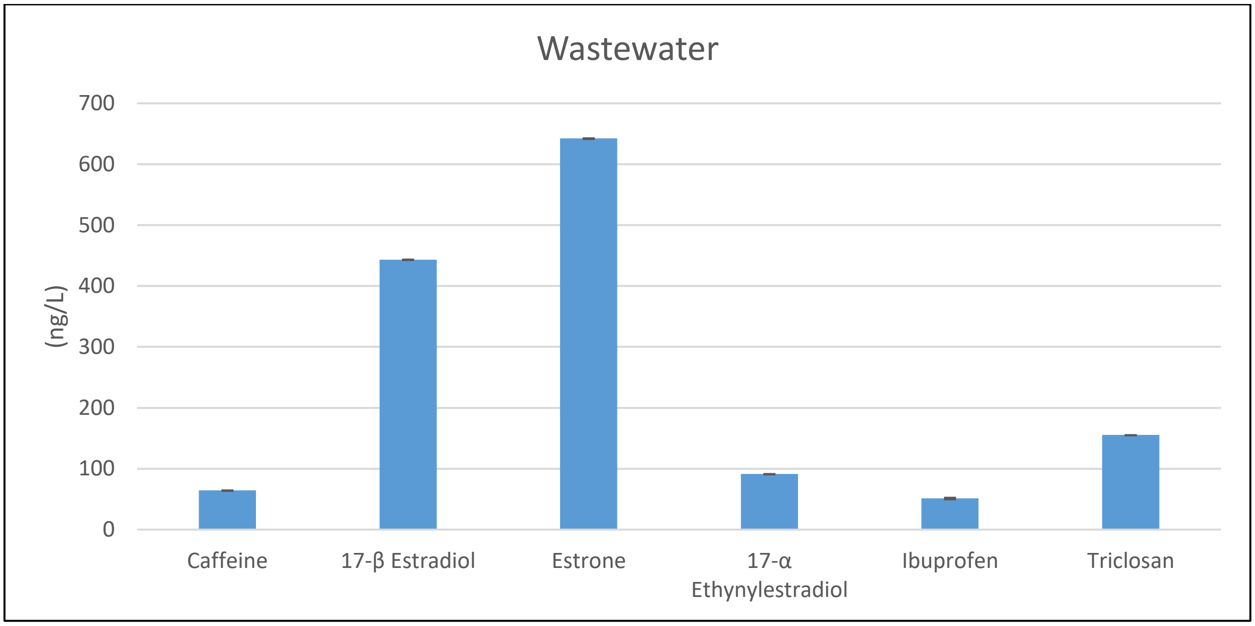


Figure 3 – Average concentrations between wastewater effluent and groundwater at Lubbock LAS in order of log Kow values. Note: Estriol was detected at significantly higher concentrations and was not included in this figure (see table 6). Wastewater and groundwater PPCP concentrations averaged from sample data from Karnjanapiboonwong et al. 2011. Error bars represent one standard deviation from the sample set.



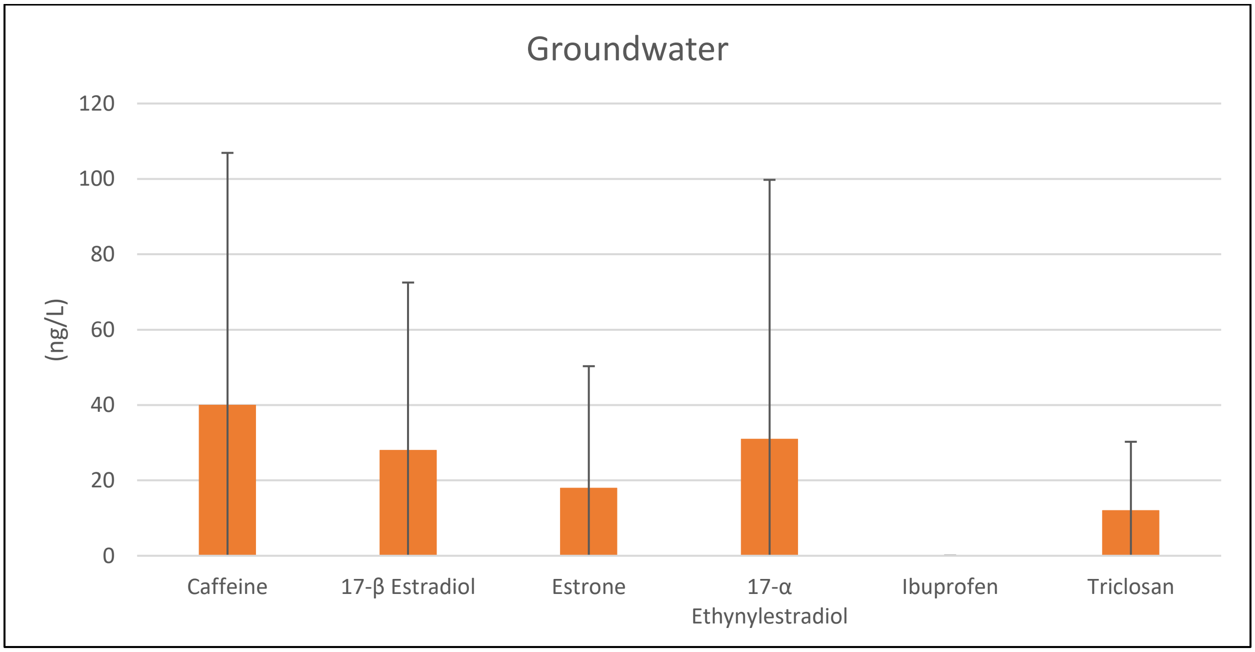


Table 6 – Average wastewater and groundwater concentrations (ng/L) of reviewed PPCPs at the Lubbock LAS in order of log Kow values. Wastewater and groundwater PPCP concentrations averaged from sample data from Karnjanapiboonwong et al. 2011.

PPCP	Wastewater	Standard Deviation
Caffeine	64	0.19
Estriol	20793	30.1
17-β Estradiol	443	0.45
Estrone	642	0.61
17-α Ethynylestradiol	91	0.14
Ibuprofen	51	1.34
Triclosan	155	0.11
PPCP	**Groundwater**	**Standard Deviation**
Caffeine	40	66.9
Estriol	570	606
17-β Estradiol	28	44.5
Estrone	18	32.3
17-α Ethynylestradiol	31	68.75
Ibuprofen	0	0
Triclosan	12	18.25

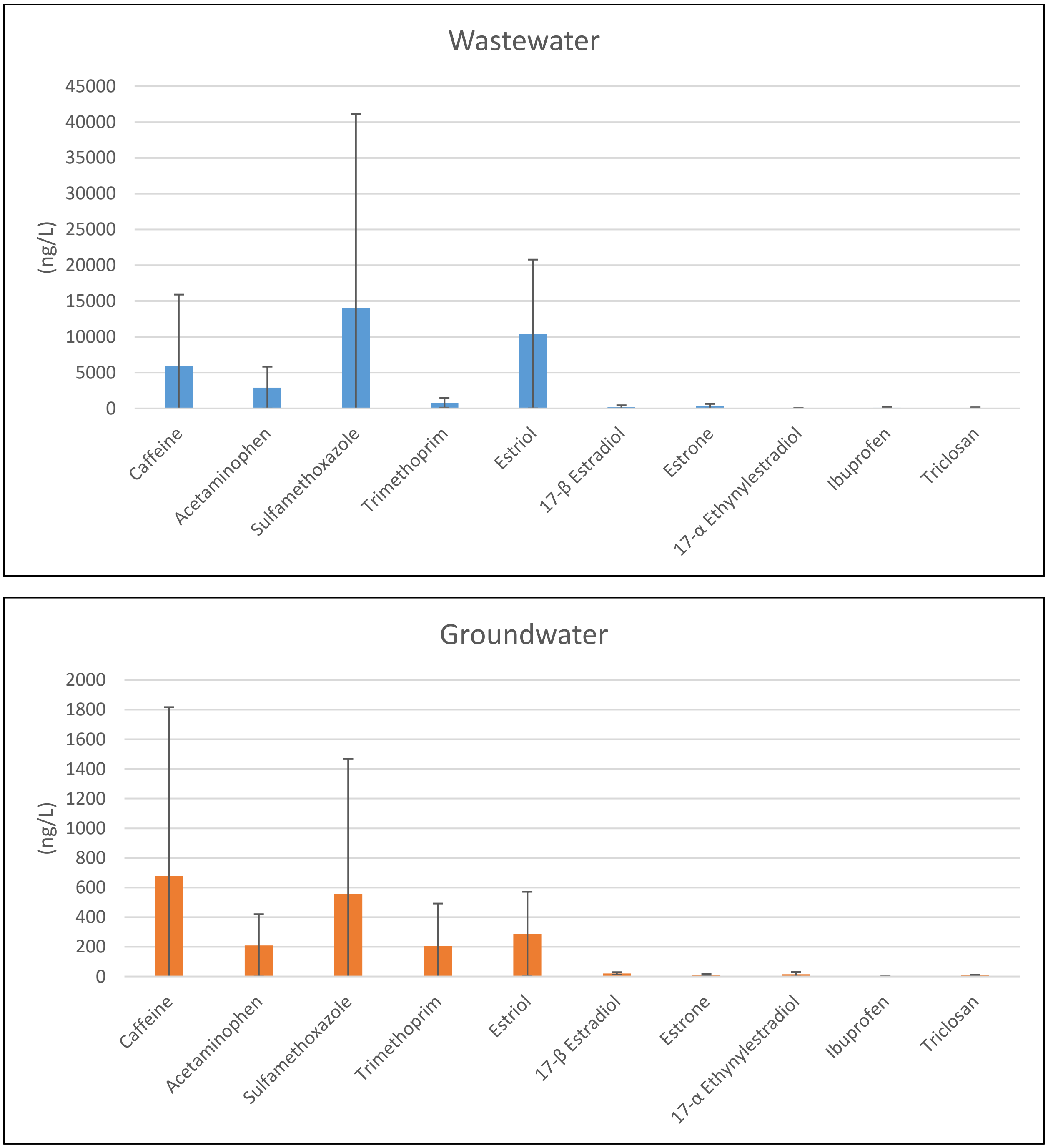
Table 7 – Average soil concentrations (ng/g) of reviewed PPCPs at the Lubbock LAS in order of log Kow values. Soil PPCP concentrations averaged from sample data from Karnjanapiboonwong et al. 2011.

PPCP	Concentration	Standard Deviation
Caffeine	0	0
Estriol	1.2	0.46
17-β Estradiol	0.6	0.26
Estrone	10.7	5.1
17-α Ethynylestradiol	0.2	0.13
Ibuprofen	73.5	16.84
Triclosan	1.5	1

Table 8 – **Average wastewater and groundwater concentrations (ng/L) of analyzed PPCPs across all three reviewed LASs in order of log Kow values. Wastewater and groundwater PPCP concentrations averaged from sample data from McEachran et al. 2016, 2017, 2018 (Jacksonville LAS data); Kibuye et al. 2019, Franklin et al. 2018 (PSU LAS data); Karnjanapiboonwong et al. 2011 (Lubbock LAS data).**

PPCP	Wastewater	Standard Deviation
Caffeine	5,896	10,008
Acetaminophen	2,915	2,915
Sulfamethoxazole	13,961	27,170
Trimethoprim	785	673
Estriol	10,404	10,389
Naproxen	1,882,535	1,882,535
17-β Estradiol	222	222
Estrone	321	321
17-α Ethynylestradiol	46	46
Ibuprofen	125	75
Triclosan	78	78
PPCP	**Groundwater**	**Standard Deviation**
Caffeine	679	1,138
Acetaminophen	210	210
Sulfamethoxazole	558	909
Trimethoprim	205	287
Estriol	286	285
Naproxen	18,851	18,849
17-β Estradiol	21	8
Estrone	10	8
17-α Ethynylestradiol	15	15
Ibuprofen	0.2	0.2
Triclosan	7.5	5

__Figure 4__ **– Average wastewater and groundwater concentrations (ng/L) of analyzed PPCPs across all three reviewed LASs in order of log Kow values. Wastewater and groundwater PPCP concentrations averaged from sample data from McEachran et al. 2016, 2017, 2018 (Jacksonville LAS data); Kibuye et al. 2019, Franklin et al. 2018 (PSU LAS data); Karnjanapiboonwong et al. 2011 (Lubbock LAS data). Note: Naproxen was detected at significantly higher concentrations and was not included in this figure (see table 6). Error bars represent one standard deviation from the sample set.**



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