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Effects of reclaimed water matrix on fate of pharmaceuticals and personal care products in soil

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HIGHLIGHTS

- Common components of reclaimed water were investigated using swine lagoon effluent.
- Soil half-lives of pharmaceuticals, personal care products, and a hormone were quantified.
- Microbial activity caused altered persistence for 7 of 11 tested compounds.
- Dissolved matter caused increased persistence for 6 compounds.
- Particulate matter caused decreased persistence for 7 compounds.

GRAPHICAL ABSTRACT

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ABSTRACT

Reclaimed water is increasingly used to supplement water resources. However, reclaimed water has a complex matrix, which includes emerging chemical contaminants, that is introduced to the soil when this water is used for irrigation. The effects of microbial activity, dissolved matter, nutrients, and particulate matter in reclaimed water on half-life of 11 pharmaceutical and personal care products (PPCPs) in soil were investigated with 7 treatment waters, namely swine lagoon effluent (either unaltered, sterilized, or filtered and sterilized) and nanopure water (either unaltered or with added nitrogen, phosphorus, or potassium). The extractable residues of the parent PPCPs were measured over 35 d. Lagoon microbial activity was significantly ($p \leq 0.05$) related to increased half-life of 4 PPCPs (carbamazepine, fluoxetine, ibuprofen, sulfamethoxazole) by 14–74%, and to decreased half-life of 3 others (caffeine, gemfibrozil, naproxen) by 13–25%. The presence of lagoon dissolved matter was significantly correlated with a 20–110% increase in half-life for 6 PPCPs (caffeine, estrone, gemfibrozil, ibuprofen, naproxen, triclocarban). However, lagoon particulate matter was significantly correlated with 9–52% decrease in half-life for these same compounds, as well as trimethoprim. The levels of nitrogen, phosphorous, and potassium in the lagoon effluent were not significantly related to half-life for most PPCPs, except caffeine. Overall, specific components of reclaimed water matrix had different effects on the soil half-lives of PPCPs, suggesting that the composition of reclaimed water needs to be considered when evaluating PPCP fate after land application.

1. Introduction

Reclaimed water is an important water resource to mitigate increasing water scarcity caused by demands from the expanding

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global population and droughts due to climate change. Water reclamation is growing by 15% each year around the world (Miller, 2006). In 2008, the United States recycled 2.8×10^9 m^3 of treated wastewater (Jiménez and Asano, 2008). Agricultural irrigation using reclaimed water is the most common reclamation practice in the United States (Jiménez and Asano, 2008), such as in California where it accounts for 37% of reclaimed water (Anderson et al., 2010). In addition to supplementing high quality water, field application of manure-containing wastewater generated from animal feeding operations (AFOs) can provide high levels of nutrients and organic matter for plant growth (U.S. Department of Agriculture 2000; U.S. Environmental Protection Agency, 2003). While sewage wastewater in the United States must meet treatment guidelines set by individual states before used for irrigation, regulations do not require AFO wastewaters to be treated before land application.

Both treated sewage wastewater and AFO wastewater can have high levels of dissolved organic matter (DOM), biological and chemical oxygen demand, microbial activity, total Kjeldahl nitrogen (TKN), total phosphorus (TP), and total potassium (TK) (Adeli and Varco, 2001; Barker, 1996; Bolan et al., 2004; Bradford et al., 2008; Greenway, 2005; Heidarpour et al., 2007; Lubello et al., 2004; Ma et al., 2001; McGarvey et al., 2005; Mohammad and Mazahreh, 2003; Neale et al., 2011; Rusan et al., 2007). Levels of each parameter are highly dependent on wastewater sources and treatment processes, causing the matrix of reclaimed water to vary greatly (Burkholder et al., 2007).

Treated wastewaters also contain a variety of emerging chemical contaminants, including pharmaceutical and personal care products (PPCPs) (Anderson et al., 2010; Hutchins et al., 2007; Kinney et al., 2006; Kolodziej et al., 2004; Li et al., 2013; Suárez et al., 2008). When reclaimed water is used for agricultural irrigation, PPCPs may be introduced to the soil (Kinney et al., 2006) and migrate in the soil profile (Chefetz et al., 2008), potentially contaminating groundwater (Avisar et al., 2009) and surface water (Pedersen et al., 2005). Some PPCPs have been shown to alter the metabolism, development, and/or reproduction of fish (Jobling et al., 1998; Sanchez et al., 2011; Schwaiger et al., 2004) and other wildlife (Daughton and Ternes, 1999; Jobling et al., 2004) at environmentally relevant levels. Additionally, previous works have suggested that environmental exposure to PPCPs is inducing the formation of antibiotic-resistance in bacteria, which may represent a major human health risk (Chee-Sanford et al., 2001; Smith, 2009).

In soil, the fate of PPCPs is greatly affected by microbial activity (Carr et al., 2011; Nowak et al., 2013; Smith and Riddell-Black, 2007; Thiele-Bruhn, 2003). Soil microorganisms can directly or indirectly metabolize PPCPs (Benotti and Snyder, 2009; Gabriel et al., 2005). DOM can also affect persistence of organic contaminants in soils, by serving as substrate for microorganisms (Schwarzenbach et al., 2003), but it can also adsorb PPCPs and reduce their availability for microbial metabolism (Drillia et al., 2005; Stevens-Garmon et al., 2011; Thiele-Bruhn, 2003). The effect of biosolids amendment on PPCP soil persistence has been investigated. Some studies have reported decreased soil persistence of PPCPs due to increased microbial activity, while other studies have found increased persistence due to DOM-enhanced sorption of PPCPs (Jacobsen et al., 2005; Monteiro and Boxall, 2009; Al-Rajab et al., 2009). However, few studies have assessed the effect of reclaimed water matrix on PPCP fate in soils.

During agricultural irrigation with reclaimed water, PPCPs are introduced to the soil simultaneously with the water matrix. In this study, different treatment waters were created to examine the impact of wastewater matrix on the fate of 11 PPCPs in soil. These targeted PPCPs were selected based on frequent detections in reclaimed water, potential ecosystem impacts, and physicochemical parameters (e.g., pK_a and K_{ow}) (Anderson et al., 2010; Kinney et al., 2006; Li et al., 2013). Since reclaimed waters vary greatly in quality, a systematic understanding of the interactions between water matrix components and PPCPs is necessary in order to evaluate PPCP fate in soil and their ecosystem risk under different irrigation scenarios.

2. Materials and methods

2.1. Chemicals

Analytical standards of caffeine, carbamazepine, estrone, gemfibrozil, ibuprofen, naproxen, sulfamethazine, sulfamethoxazole, triclocarban, and trimethoprim were purchased from Restek (Bellefonte, PA, USA) and fluoxetine was purchased from Sigma-Aldrich (St. Louis, MO, USA). Isotope standards of $^{13}C_3$-caffeine, D_{10}-carbamazepine, $^{13}C_6$-estrone, D_6-fluoxetine, D_6-gemfibrozil, $^{13}C_3$-ibuprofen, $^{13}C_4$-naproxen, $^{13}C_6$-sulfamethazine, $^{13}C_6$-sulfamethoxazole, $^{13}C_6$-triclocarban, and $^{13}C_3$-trimethoprim were purchased from Cambridge Isotope (Andover, MA, USA). All analytical and isotopic standards were of 97% purity or greater. Other chemicals and solvents were purchased from Fisher Scientific (West Chester, PA, USA). Nanopure water (>18 MΩ cm) was produced by a Labconco Water Pro Plus system (Kansas City, MO, USA).

2.2. Treatment waters and soil

Swine lagoon effluent was collected from the Swine Research Center at the University of Illinois Urbana-Champaign (Champaign, IL, USA). Lagoon water was sampled from the liquid layer via installed piping, stored at 4 °C, and a homogenous subsample sent to a commercial lab (Midwest Laboratories, NE, United States) for nutrient analysis. Nutrient levels and other parameters of the effluent are listed in Table 1.

Seven treatment waters were created to examine the impact of microbial activity, particulate matter, dissolved matter, and inorganic nutrients in the lagoon effluent. A treatment water composed of unaltered swine lagoon effluent ("Lagoon") represented a real-life application of reclaimed water and the water was used without any processing. Sterilized lagoon effluent ("Sterile Lagoon") was created by autoclaving a subsample of effluent at 121 °C for 60 min a total of three times. Filtered and sterilized lagoon water ("Filtered + Sterile Lagoon") was created by filtering lagoon water through 0.45 μm PVDF filters (Millipore, MA, USA) and then sterilizing as stated above. Nanopure treatment water ("Nanopure Water") served as a control to determine PPCP half-life in soil without effects from reclaimed water matrix. In order to

Table 1
Lagoon effluent and soil characteristics.

Swine lagoon effluent		Knox farm soil	
pH	7.75	Clay (%)	12
Conductance (mS/cm)	3.54	Silt (%)	54
Calcium (mg/L)	105	Sand (%)	34
Copper (mg/L)	No detection	Organic carbon (%)	2.15
Iron (mg/L)	1.9	Organic matter (%)	3.7
Manganese (mg/L)	0.3	pH	6.0
Magnesium (mg/L)	61.0	Cation exchange capacity (meq/100 g)	14.9
Nitrogen (mg/L)	265	Water holding capacity (%)	79.9
Phosphorus (mg/L)	10.3		
Potassium (mg/L)	108		
Sodium (mg/L)	73.1		
Sulfur (mg/L)	11.9		
Zinc (mg/L)	0.1		