Fates and transport of PPCPs in soil receiving reclaimed water irrigation

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HIGHLIGHTS

- Behaviors of 9 PPCPs in soil were evaluated by model validated with field data.
- Accumulation of PPCPs in the top 20 cm soil layer varied from <1 to about 140 ng g⁻¹.
- Extent that PPCPs were being transported downward by the drainage water was minor.
- Accumulation and leaching of PPCPs were highly dependent on the chemical nature.
- Normal reclaimed water irrigation did not appear to produce undue ecological risks.

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ABSTRACT

Fates and transport of 9 commonly found PPCPs of the reclaimed water were simulated based on the HYDRUS-1D software that was validated with data generated from field experiments. Under the default scenario in which the model parameters and input data represented the typical conditions of turf grass irrigation in southern California, the adsorption, degradation, and volatilization of clofibric acid, ibuprofen, 4-tert-octylphenol, 4-n-nonylphenol, naproxen, triclosan, diclofenac sodium, bisphenol A and estrone in the receiving soils were tracked for 10 years. At the end, their accumulations in the 90 cm soil profile varied from less than 1 ng g⁻¹ to about 140 ng g⁻¹ and their concentrations in the drainage water in the 90 cm soil depth varied from nil to μg L⁻¹ levels. The adsorption and microbial degradation processes interacted to contain the PPCPs entirely within surface 40 cm of the soil profiles. Leaching and volatilization were not significant processes governing the PPCPs in the soils. The extent of accumulations in the soils did not appear to produce undue ecological risks to the soil biota. PPCPs did not represent any potential environmental harm in reclaimed water irrigation.

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1. Introduction

Water has always been reused (Levine and Asano, 2004). As urban water shortages grow and purification technologies advance, the wastewater is being reclaimed and reused in increasing volumes and for more purposes. The water reuses in California for instance increased from 649 million tons in 2003 to 894 million tons in 2009. It is expected to reach 1540 million ton in 2015 and 1880 million ton in 2020 (California Water Planning, 2009). Beijing reused 680 million tons of reclaimed water in 2010 and in 5 years the reuses would expect to exceed 1000 million tons (Yi et al., 2011).

Overwhelming majority of the reclaimed water has been used for irrigation. Potentially harmful compounds if not effectively removed during the treatment may be inadvertently introduced into

the terrestrial environment in this manner. Among those the pharmaceutical and personal care products (PPCPs) are recent concerns (Yang et al., 2011). The PPCPs are not completely and consistently removed during the wastewater treatment processes employed by the publicly owned treatment works and their concentrations in reclaimed water might range from the nano to micro gram per liter levels (Wang et al., 2005; Kim et al., 2007; Nikolaou et al., 2007; Onesios et al., 2009; Reungoat et al., 2011). Both the product water and the municipal sewage sludge are potential sinks for the wastewater borne PPCPs. The behaviors of PPCPs in aquatic ecosystems are alarming (Onesios et al., 2009). The environmental fate and transport of the compounds in receiving soils need to be delineated (Xu et al., 2009b, 2010).

The PPCPs are pervasive in the terrestrial-aquatic environment. Kuroda et al. (2012) examined the city-wide occurrence of selected PPCPs through 50 groundwater samples extracted from the <30 m in depth unconfined and up to 500 m in depth confined aquifers in Tokyo. The PPCPs were detected in 68% and 44% of the samples

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obtained from unconfined and confined aquifers, respectively. The concentrations of PPCPs in groundwater, excluding caffeine, were 1–2 orders of magnitude lower than those of in the sewage treatment plant influents. In selected samples, their concentrations in the wastewater and groundwater were comparable. The extent of their fate and transport are uncertain.

Upon irrigation, the reclaimed water borne PPCP compounds passing along the flow paths in the receiving soils are subject to volatilization, degradation, and plant uptake (Haruta et al., 2008; Xu et al., 2009a). In addition, surface sorption by soil particles may immobilize and retard the chemicals' fate and transport processes. Depending on the nature of chemicals and water fluxes, the remaining PPCPs may leach down the soil profile, resulting in pollution of groundwater (Matamoros et al., 2007; Haruta et al., 2008). The PPCP concentrations of applied water in general were quite low and their fate and transport in the receiving soils would be difficult to track and quantify. Drewes et al. (2003) examined the fate of selected PPCPs during the ground water recharge at two reclaimed water reuse sites and found that diclofenac, ibuprofen, ketoprofen, and naproxen were not detected, while carbamazepine and primidone were found in the recharged aquifer throughout 8 years of operations. Xu et al. (2009a) found that significant amounts of reclaimed water borne PPCP compounds accumulated in the surface 30 cm of the soil profile at an irrigated turf grass field. However, no PPCP compound was detected in the gravity drainage collected at the depth of 100 cm below ground surface. Fang et al. (2012) reported that the gemfibrozil in reclaimed water applied on land might reach the groundwater aquifer underneath. These field-observed results provided a snapshot of the PPCP chemicals in motions, but were unable to delineate the dynamic interactions between the chemicals, hydraulics, and nature of soil environment.

In this research, we studied the environmental behaviors of reclaimed water borne PPCP compounds in the receiving soils based on simulated outcomes of a fate transport model that was validated with experimental data. Their potential ecological risks under long term reclaimed water irrigation were then evaluated.

2. Materials and methods

2.1. Data collection

The experiment was conducted on field-scale lysimeters located at University of California, Riverside. The lysimeters were covered with well established perennial turf grass. Tile drains were installed at 90 cm depth to collect the drainage from each lysimeter. Prior to irrigation, nine PPCPs including clofibric acid, ibuprofen, 4-tert-octylphenol, 4-n-nonylphenol, naproxen, triclosan, diclofenac sodium, bisphenol A and estrone were added and mixed into the stock effluent obtained from a local wastewater treatment plant to reach the concentrations that were comparable to those commonly found in the reclaimed water (see Table 1 for the exact concentrations). The drainage fluxes were collected and PPCPs in the leachates were analyzed regularly. At the end of the experiment, the receiving soils were sectioned and PPCP concentrations of the soils were analyzed (Xu et al., 2009a). Laboratory experiments were conducted to characterize the adsorption and degradation of PPCPs in the soils and the data were used for deriving the parameters for model validation (Xu et al., 2009a).

2.2. Model description

The dynamic interactions of introduced PPCPs and the inherent soil processes were evaluated through model simulations and HYDRUS-1D software package was used to describe movements of

water and solute in the receiving soils (Simunek et al., 2008). The water flows followed the Richards' equation and the solute transport is defined by the convective-dispersive equation. We did not include the solute plant uptake process in the model simulation. The loss of soil-borne PPCPs through plant uptake was relatively small in comparison to losses through the degradation and evaporation pathways (Herklot et al., 2010; Wu et al., 2010). Besides, there was little relevant data available to define the plant uptake parameters. The fate and transport of previously referenced PPCPs in the 0–90-cm soil profile of loamy sand and sandy loam soils were simulated. The soil profile was divided depth-wise into three sections of 20, 30, and 40 cm in which, the chemical reaction rate constants were separately and independently defined. To assure that the chemical' transport in the soil profile approaching the steady states, the simulation ran for a 10-year period.

2.3. Model parameters

With properly defined model parameters and conditions, the fates and transports of PPCPs can be systemically examined under various environmental and operating conditions.

2.3.1. Initial conditions

The initial water contents were set at –200 cm and –500 cm of moisture tension at the top and bottom of soil profile, respectively. For a 10-year simulation, the initial conditions would have negligible impacts on the final simulation outcomes. The initial PPCP concentrations of the soil were set at zero at all depths of soils.

2.3.2. Boundary conditions

Based on the field conditions, the upper and low water flow boundary conditions were set as atmospheric with surface runoff and free drainage, respectively. For the solute, the upper and lower boundary conditions were set as stagnant for volatile solute and zero concentration gradient, respectively. According to Jury and Horton (2004), 0.5 cm was assigned as the stagnant boundary layer.

2.3.3. Soil hydraulic properties

The hydraulic characteristics of the soils were obtained according to the van Genuchten equation (van Genuchten, 1980) in which the equation parameters obtained by Haruta et al. (2008) were adopted. The saturated hydraulic conductivity of the loamy sand soil was 350.2 cm d^{–1}, being one of the highest among those cataloged in the hydraulic property database of Carsel and Parrish (1988). The fate and transport of PPCPs in the loamy sand soil would represent a worst case scenario in terms of groundwater pollution risk. The saturated hydraulic conductivity of the sandy loam soil was 34.32 cm d^{–1}, being situated in the middle among those cataloged in the hydraulic property database of Carsel and Parrish (1988). The fate and transport of PPCPs in the sand loam soil would represent a typical case scenario in terms of the groundwater pollution risk.

2.3.4. Variable boundary conditions

In the model simulation, the time-dependent boundary conditions including precipitation, irrigation evaporation and transpiration must be set. The daily *ET* recorded at a weather station of California Irrigation Management Information System, CIMIS, located at the University of California Field Station in Riverside, California was used and the data were retrieved at www.cimis.water.ca.gov. The cumulative evapotranspiration (*ET_c*) amounted to 1113 mm per year. The turf grass was irrigated three times per week at rates equaled to 1.2 times of the cumulative evapotranspiration loss since the last irrigation. The cumulative

Table 1
Chemical specific model parameters used for simulation.*

PPCP	C_{irr} ($\mu\text{g L}^{-1}$)	Soil layer (cm)	Loamy sand soil		Sandy loam soil		Henry constant	D_g ($\text{cm}^2 \text{d}^{-1}$)	D_w ($\text{cm}^2 \text{d}^{-1}$)
			$t_{1/2}$ (d)	K_d (L kg^{-1})	$t_{1/2}$ (d)	K_d (L kg^{-1})			
Clofibric acid	1.05	0–20	14.1	2.34	10.1	0.9	4.48×10^{-5}	1063.1	0.57
		20–40	14.3	1.28	56.4	0.6			
		40–90	36.9	0.85	36.9	0.4			
Ibuprofen	8.59	0–20	7.2	0.60	2.0	1.2	3.07×10^{-4}	990.7	0.55
		20–40	11.7	0.33	32.9	0.8			
		40–90	21.0	0.22	21.0	0.6			
4-tert-Octylphenol	2.49	0–20	8.7	8.61	1.7	27.0	1.57×10^{-3}	947.9	0.52
		20–40	13.5	4.70	21.5	18.4			
		40–90	21.1	3.13	21.1	12.3			
4-n-Nonylphenol	4.38	0–20	9.9	198.7	3.0	890.3	5.84×10^{-3}	911.3	0.49
		20–40	12.6	108.4	16.1	607.0			
		40–90	14.0	72.3	14.0	404.7			
Naproxen	13.4	0–20	7.6	1.15	5.9	1.7	6.93×10^{-7}	996.4	0.56
		20–40	7.6	0.63	42.5	1.2			
		40–90	37.3	0.42	37.3	0.8			
Triclosan	3.54	0–20	13.8	13.99	13.2	179.6	3.07×10^{-4}	968.9	0.56
		20–40	15.4	7.63	32.5	122.4			
		40–90	25.1	5.09	25.1	81.6			
Diclofenac sodium	3.41	0–20	3.6	0.87	3.6	4.7	9.67×10^{-9}	945.3	0.56
		20–40	5.0	0.47	5.2	3.2			
		40–90	74.5	0.32	74.5	2.1			
Bisphenol A	2.55	0–20	7.5	9.63	5.2	17.1	2.04×10^{-7}	980.7	0.56
		20–40	7.7	5.25	13.0	11.7			
		40–90	11.8	3.50	11.8	7.8			
Estrone	0.07	0–20	7.7	34.2	4.1	30.8	7.77×10^{-7}	898.9	0.50
		20–40	7.6	18.6	13.7	21.0			
		40–90	13.4	12.4	13.4	14.0			

* C_{irr} is the chemical concentration in irrigation water; $t_{1/2}$ is the degradation half life where the degradation rate (μ, d^{-1}) used in the model is obtained by $0.6932/t_{1/2}$; K_d is the adsorption constant; D_g is the molecular diffusion coefficient in soil air; D_w is the molecular diffusion coefficient in free water.

annual water input was 1336 mm of which, 92 mm came from precipitation.

2.3.5. Chemical specific model parameters

The degradation half-life, $t_{1/2}$, and linear solid-solution distribution coefficient, K_d , of PPCPs reported in Xu et al. (2009b) were adopted (Table 1). The degradation rates were experimentally determined while the PPCP-treated soils were under either septic or aseptic conditions and were exposed to or not exposed to light. The solid-solution distribution coefficient, K_d ($\text{cm}^3 \text{g}^{-1}$), was adjusted to the soil organic carbon content, f_{oc} , of 0.55%, 0.30% and 0.20%, for the 0–20, 20–40 and 40–90 cm layers of the soil profile, where $K_d = K_{oc} * f_{oc}$.

The molecular diffusion coefficients of PPCPs in water, D_w , and in air, D_g , were estimated according to equations suggested by U.S. Environmental Protection Agency (<http://www.epa.gov/athens/learn2model/part-two/onsite/estdiffusion-ext.html>). The dimensionless Henry's law constant, H' , was converted from the dimensional Henry's law constant, H ($\text{atm m}^3 \text{mol}^{-1}$), that $H' = H * 101325/RT$ where R referred to the gas constant of $8.314 \text{ pa m}^3 \text{mol}^{-1} \text{K}^{-1}$ and T referred to the temperature set at 288.15 K.

2.4. Model validation

The model was validated by comparing results obtained from the field lysimeter experiments (Xu et al., 2009a) to simulation outcomes based on the input data and experimentally generated model parameters. During the 4 month summer irrigation season, no PPCP compound was detected in the leachate collected via the underground drains that was in agreement with the simulated

outcomes. Subsequently, the model simulation demonstrated that it required at least one full year of operation for the PPCP chemicals to break through the 90 cm soil profile and reach the underground drainage. At the end of four months of reclaimed water irrigation, PPCPs were found in the surface 30 cm of the soil profiles. Thirty nine cases were examined for model validation. In 50% of the cases, the predicted outcomes were within $\pm 20\%$ of the measured values. Overall, the predicted and observed chemical concentrations were linearly correlated with a coefficient close to 1 (1.054) and a R^2 of 0.687. Given the field variability in soils and in experimental parameters, the model validation results were reasonable. In addition, many studies have been conducted using HYDRUS-1D to simulate transport of various chemicals in soils, such as sulfamethazine (Chu et al., 2013), testosterone and estrogen (Arnon et al., 2008). It have been proved that HYDRUS-1D can be used to qualitatively evaluate the fates and transports of chemicals like PPCPs in soil with satisfied results.

2.5. Model simulation scenarios

The model parameters described in the previous sections depicted the typical conditions of the soils' chemical and hydraulic properties that were being simulated and was designated as the default scenario. In realistic situations, the equation parameters would vary spatially and temporally across the landscape. In addition, the concentration of PPCP chemicals and the irrigation scheduling that defines the PPCP mass inputs were also subject to changes. Once the model was calibrated, we examined the PPCP fate and transport over ranges of chemical and water inputs and model parameters.

2.5.1. Chemical inputs

The accumulation and leaching of PPCPs in soil would be proportional to their respective inputs. In the default scenario, the PPCP concentration of the reclaimed water, C_{irr} , represented the typical level found in the reclaimed water. In practice, the PPCPs concentration of the reclaimed water might vary by one order of magnitude up and down. In addition to the default scenario, the simulations also included scenarios that PPCP concentrations were $0.1 \times$ and $10 \times$ of C_{irr} to cover potentially two extremes of the chemical inputs.

2.5.2. Irrigation practices

The conventional turf grass irrigation practice called for the replenishment of 1.2 times of the cumulative evapotranspiration loss since the previous irrigation (i.e. $1.2 \times ET_c$). Over-irrigation however was common and would increase inputs and subsequently leaching losses of PPCPs. Therefore, we included simulations at two additional irrigation levels, namely $1.5 \times ET_c$ and $1.8 \times ET_c$ to evaluate impacts of over irrigation on fate and transports of PPCPs in the soil profiles. The irrigation frequency kept the same as the default simulation scenario, namely, three times per week.

2.5.3. Chemical specific model parameters

The degradation half-life, $t_{1/2}$, and distribution coefficient, K_d , would affect the fates and transports of PPCPs in soils. In the default scenario, the parameters determined by Xu et al. (2009a) were adopted. The $t_{1/2}$ and K_d of a soil would vary by order of magnitude. In the simulations, scenarios that $t_{1/2}$ and K_d set at

$0.1 \times$ and $10 \times$ of those used in the default scenario were included (Table 1).

3. Results

3.1. Accumulation of PPCP in the surface soil layer

The concentrations of the nine PPCPs in reclaimed water varied from $0.07 \mu\text{g L}^{-1}$ of estrone to $13.4 \mu\text{g L}^{-1}$ of naproxen. Upon irrigation, the chemicals began to accumulate in the soil profile and continued over the 10 year simulation period (Fig. 1). In the 0–20 cm soil layer, where processes determining the fate and transport of chemicals were the most active, the chemicals showed two different accumulation patterns in the reclaimed water irrigated soils. Naproxen, ibuprofen, clofibric acid, and diclofenac sodium despite of relatively weak K_d varying from 0.6 to 2.3 L kg^{-1} in the loamy sand soil and 0.9 – 4.7 L kg^{-1} in the sandy loam soil had accumulated in the surface 20 cm soil layer and their concentrations underwent dynamic changes depending on the irrigation. At the beginning of irrigation season, the inputs of chemicals through irrigation exceeded the losses through degradation, volatilization, and leaching processes that their concentrations in the surface 20 cm soil layer accumulated in proportion to reach respective maxima. Subsequently over the nonirrigation season the accumulated PPCPs were dissipated through the loss processes to reach minima. After the first season, concentrations of the chemicals in the surface 20 cm soil layer oscillated between the minima and maxima coinciding to the beginning and end of the irrigation season and each chemical established its own soil accumulation pattern (Fig. 1a

Fig. 1. Temporal changes of the PPCP concentrations in the 0–20 cm surface soil layers during the course of a 10 year simulation of turf grass irrigation employed reclaimed water.

and c). The maxima for diclofenac sodium, clofibric acid, ibuprofen, and naproxen accumulated in the 0–20 cm soil layer would reach 3.70, 4.27, 7.88 and 23.79 ng g⁻¹, respectively, in the loamy sand soil and 6.82, 1.17, 3.23, and 17.40 ng g⁻¹, respectively, in the sandy loam soil. The minima for diclofenac sodium, clofibric acid, ibuprofen, and naproxen accumulated in the 0–20 cm soil layer would be 1.52, 3.81, 4.18, and 15.46 ng g⁻¹, respectively, in the loamy sand soil and 3.98, 0.52, 0.77 and 8.06 ng g⁻¹ respectively, in the sandy loam soil.

The remaining five chemicals, namely estrone, 4-ter-octylphenol, bisphenol A, triclosan, and 4-n-nonylphenol possessed significantly higher K_d (Table 1) and were expected to be more susceptible to accumulation in the soils (Fig. 1b and d). For 4-ter-octylphenol and bisphenol A, respectively, 6 and 9 years of irrigation were required for their accumulation in the 0–20 cm soil layer to reach the steady state conditions. For triclosan, estrone, and 4-n-nonylphenol, the concentrations in the 0–20 cm soil profile continued to increase over the 10 year simulation period. The rates of accumulation were dependent on interactions between the chemical's annual inputs from reclaimed water irrigation and losses due to degradation and evaporation processes in the receiving soils. Leaching in these cases did not play a significant role. For instance, the 10 year accumulation of estrone in the soil profile was not apparent (Fig. 1b and d) as the input was <0.1 µg L⁻¹ (Table 1). Meanwhile the 10 year accumulation of triclosan in the soil profile reached relatively high levels of 82 and 138 ng g⁻¹ in the loamy sand and sandy loam soils respectively, despite of a relatively moderate input levels indicating the degradation and/or volatilization processes were rather weak. The 4-n-nonylphenol exhibited the highest K_d among this group of PPCPs. Its accumulation in the soil

profile was among the highest at 127 and 136 ng g⁻¹ in the loamy sand and sandy loam soils, respectively.

In all, from <1 ng g⁻¹ to >>100 ng g⁻¹ of the PPCPs might accumulate in the surface 20 cm soil layer of reclaimed water irrigated soils at the end of the 10 year period.

3.2. PPCP distributions in the soil profile

Beyond the surface soil layer, the PPCPs were being transported downward and properties of the soils affected their distributions in the 90 cm soil profile, after they were introduced through the reclaimed water irrigation (Fig. 2). The sandy loam soil exhibited higher K_d for the PPCPs than those for the loamy sand soil denoting stronger tendencies to retain the chemicals. After 10 years of irrigation, PPCPs were rarely detected beyond the 0 to 20 cm soil layer in the sandy loam soil while the PPCPs were detected at soil profile depth beyond 40 cm in the loamy sand soil. In all, the extents that the PPCPs were being transported downward by the drainage water were minor, attributing to the chemicals' adsorption by soil particles and degradation by soil microorganisms.

The K_d of 4-n-nonylphenol was the highest and it exhibited the strongest adsorption by soils relative to other PPCPs. The compound accumulated primarily at the surface few centimeters to concentrations of 589 and 2560 ng g⁻¹ in loamy sand and sandy loam soils, respectively. Beyond the 0–10 cm depth layer in loamy sand soil and 0–6 cm depth layer in sandy loam soil, 4-n-nonylphenol was no longer detectable. Next to 4-n-nonylphenol, triclosan was characterized by relatively lower $t_{1/2}$ and higher K_d . Its concentrations in the soil profile were 106 ng g⁻¹ in the 0–16 cm depth of the loamy sand soil and 642 ng g⁻¹ in the 0–2 cm depth of the

Fig. 2. PPCP distributions in the 90 cm soil profile, following 10 year of simulated reclaimed water irrigation of turf grass fields.

Fig. 3. Temporal changes of PPCP concentrations of drainage water at the 90 cm soil depth under the loamy sand soil during a 10-year simulated reclaimed water irrigation of turf grass fields.

sandy loam soil. In terms of the downward transport, they were followed by bisphenol A and 4-tert-octylphenol, exhibited moderate K_d and degradation rate constants, that were up to 30 ng g^{-1} . With the highest concentration in the reclaimed water, the accumulation of naproxen in soil profile was up to 28.2 ng g^{-1} and 23.4 ng g^{-1} , respectively in the loamy sand soil and sandy loam soil. For the remaining four PPCP chemicals, their accumulations in the soil profile were all $>15 \text{ ng g}^{-1}$, attributed to low concentration in the reclaimed water as in the case of estrone, weak K_d as in the cases of ibuprofen, diclofenac sodium, and clofibric acid, or rapid degradation rate as in the case of clofibric acid.

3.3. Downward leaching of PPCPs in soils

Properties of the soils also affected the leaching of the PPCP chemicals over time and their concentrations in the drainage water at the 90 cm soil depth (Fig. 3). It took at least 1 year for the chemicals to break through the 90 cm soil profile and become detectable in the drainage water. Under the loamy sand soil, only ibuprofen, naproxen, clofibric acid and diclofenac sodium appeared in the drainage water following the 10-year simulation period. These four chemicals possessed the lowest K_d among the 9 PPCPs. The chemicals broke through the soil profile between 2 and 5 years. Once they did, the concentrations in the drainage water reached steady state conditions and underwent annual oscillations thereafter. Annually, the highest concentrations would reach 0.23, 0.21, 0.12, $0.0042 \mu\text{g L}^{-1}$ and the lowest concentrations would reach 0.09, 0.12, 0.11, $0.0019 \mu\text{g L}^{-1}$ for ibuprofen, naproxen, clofibric acid and diclofenac sodium respectively (Fig. 3).

In the sandy loam soil, the simulation outcomes showed that it took 4 to >10 years for the concentrations of diclofenac sodium,

ibuprofen, naproxen, clofibric acid in the drainage water rising up the steady state conditions at which the concentrations were at the negligible levels of $10^{-5} \mu\text{g L}^{-1}$. The simulation outcomes also showed that 4-tert-phenol, triclosan and bisphenol A, they would reach the groundwater at the 90 cm depth; the concentrations in the water however would be less than $10^{-9} \mu\text{g L}^{-1}$. The inherent properties of sandy loam soil would even be more able of preventing PPCPs from leach through the soil profile and reach the groundwater (Table 2).

3.4. Mass balance

At the end of the 10 year simulation period, mass balances showed that the fate and transport of irrigation-introduced PPCPs in the 90 cm soil profile were chemical dependent and for the same chemical soil property dependent (Table 2). Although PPCPs were found in the drainage water collected at the soil depth of 90 cm, leaching did not appeared to be a significant fate and transport pathway for these chemicals. In 10 years, no PCPP lost more than 1.5% of its mass through leaching. In fact, the leaching losses of all PPCPs in the sandy loam soil were negligible and the leaching losses of 5 out of 9 PPCPs were negligible in the loamy sand soil. Except for 4-n-nonylphenol and 4-tert-octylphenol, the evaporative loss of PPCPs did not exceed 1.5% of the total mass. Except for 4-n-nonylphenol and possibly triclosan, degradation was the major fate and transport pathway accounting for the most significant loss of PPCPs in the profile of the sandy loam soil ranging from 27% to 98% of the total mass that were introduced via the reclaimed water irrigation. PPCPs not accounted for by degradation, evaporation, and leaching losses were adsorbed thus retained in the surface 20 and 40 cm of the sandy loam and loamy sand soils, respectively. Adsorption and degradation were the primary pathways for PPCPs that entered the soil through reclaimed water irrigation. Relatively speaking, the percentages of total mass retained were inversely proportional to the percentage of total mass degraded.

3.5. Factors affecting leaching of PPCPs in soils

The fate and transport processes of PPCP were interrelated. If the kinetics of reaction parameters such as K_d and $t_{1/2}$ affected the adsorption of the chemicals by soils, they would also affected the extent of the PPCP leaching down the soil profiles. As the K_d rose, greater proportion of the PPCP entering the soil would be absorbed by the soils and lesser amounts would be leached and/or subject to removals by the degradation. Take the more susceptible loamy sand soil as the examples. Four of the nine PPCPs were detected in the drainage water collected at the 90 cm depth of the soil profile (Table 2). From 0.02% to 1.39% of the diclofenac sodium, naproxen, ibuprofen, and clofibric acid total mass were leached over the 10 year period under the default scenario as the solid-solution

Table 2

Mass balance of PPCPs in surface 90 cm of the soil profile following a 10 year simulation of turf grass irrigation using reclaimed water.

PPCP	Loamy sand soil (% of total mass)				Sandy loam soil (% of total mass)			
	Degradation	Evaporation	Leaching	Storage	Degradation	Evaporation	Leaching	Storage
Clofibric acid	82.24	1.34	1.39	15.05	95.03	1.40	<0.01	3.52
Ibuprofen	95.27	1.10	0.43	3.29	97.93	1.18	<0.01	0.74
4-tert-Octylphenol	53.09	15.32	<0.01	31.65	76.44	14.08	<0.01	9.52
4-n-Nonylphenol	3.16	28.80	<0.01	68.09	6.60	20.65	<0.01	72.76
Naproxen	93.18	1.36	0.23	5.26	95.36	1.41	<0.01	3.26
Triclosan	35.20	1.11	<0.01	63.51	8.81	1.24	<0.01	89.75
Diclofenac sodium	93.11	1.36	0.02	5.51	93.96	1.42	<0.01	4.65
Bisphenol A	64.33	1.36	<0.01	34.34	78.16	1.42	<0.01	20.45
Estrone	26.96	1.36	<0.01	71.73	71.01	1.42	< 10^{-10}	27.60

Fig. 4. Factors influencing leaching of 9 PPCP compounds in the loamy sand soil.

Fig. 5. Factors influencing accumulation of 9 PPCP compounds in the loamy sand soil.

Table 3Predicted no-effect concentrations in soil ($PNEC_{soil}$) of 9 selected PPCPs and their risk characterization ratios (RCR).

PCPP	$PNEC_{water}$ ($\mu\text{g L}^{-1}$)	$PNEC_{soil}$ (mg kg^{-1})	RCR		References
			Loamy sand soil	Sandy loam soil	
Clofibric acid	4.2	5.15	0.0008	0.0002	Ferrari et al. (2003)
Ibuprofen	1.65	0.528	0.0149	0.0061	Martín et al. (2012)
4-Tert-octylphenol	0.12	0.55	0.0459	0.0184	Brooke et al. (2003)
4-n-Nonylphenol	–	2.5	0.0036	0.0039	González et al. (2010)
Naproxen	2.62	1.68	0.0142	0.0104	Martín et al. (2012)
Triclosan	–	0.06	0.0328	0.0554	Amorim et al. (2010)
Diclofenac sodium	9.70	4.66	0.0007	0.0015	Martín et al. (2012)
Bisphenol A	–	3.7	0.0087	0.0061	Staples et al. (2010)
Estrone	0.10	1.82	0.0012	0.0005	Martín et al. (2012)

distribution coefficient was set at $1 \times K_d$. The leaching of all nine PPCPs in the loamy sand soil became negligible when the solid-solution distribution coefficient increased to $10 \times K_d$ (Fig. 4a). Except for 4-n-nonylphenol, all other PPCPs broke through the 90 cm depth soil profile and the total masses leached over the 10 year period were 3.6%, 1.4%, 1.4%, 0.97%, 0.55%, 0.17%, 0.03%, and 0.02% for clofibric acid, ibuprofen, triclosan, naproxen, 4-terl-octylphenol, diclofenac sodium, bisphenol A, and estrone, respectively, when the solid-solution distribution coefficient decreased to $0.1 \times K_d$ (Fig. 4a). Leaching and thus groundwater contamination by PPCPs did not appear to be a significant issue in reclaimed water irrigation.

Variations of the degradation rate constant also had profound impact on the leaching of PPCPs. When the degradation rate constants were increased by 10 folds from those used in the default scenario, i.e. $10 \times t_{1/2}$, the PPCPs did not leached beyond the 90 cm depth soil profile (Fig. 4b). If the degradation rate constants of PPCPs were reduced from those set for the default scenario by 10 folds, i.e. $0.1 \times t_{1/2}$, 35.2%, 49.9%, 41.4%, and 33.4% of clofenac acid, ibuprofen, naproxen and diclofenac total mass, respectively would be leached over the 10 year period (Fig. 4b).

When the mass inputs of PPCPs varied by either decreasing or increasing their concentrations in the irrigation water by one order of magnitude from the default value, i.e. $0.1 \times C_{irr}$ or $10 \times C_{irr}$ (Fig. 4c), the percentages of the total mass of diclofenac sodium, naproxen, ibuprofen, and clofibric acid leached proportionally decreased or increased, respectively. For estrone, bisphenol A, triclosan, 4-n-nonylphenol, and 4-terl-octylphenol, their inputs were so small, the difference of outcomes in the leachate were realistically not distinguishable.

The clofibric acid, ibuprofen, naproxen, and diclofenac sodium were prone to leaching in the loamy sand soil that was under the typical turf water management practice of irrigating 1.2 times the measured evapo-transpiration demands (i.e. the $1.2 \times ET$ scenario). Increasing the water inputs to $1.5 \times$ and $1.8 \times ET$ would significantly enhanced the leaching losses of these PPCP chemicals. Over irrigations caused the leaching of these chemicals increasing from 1.4%, 0.43%, 0.2%, and 0.02% of the total masses at the $1.2 \times ET$ to 10.8%, 5.5%, 3.7%, and 1.0% of the total masses at the $1.5 \times ET$ and 21.1%, 13.8%, 10.3%, and 4.3% of the total masses at the $1.8 \times ET$, respectively over the 10 year period (Fig. 4d). The added water inputs also enhanced the mobility of PPCPs that were not susceptible to leaching under the typical water management practice. Compounds as much as 5.5%, 1.24%, and 1.7% of the 4-terl-octylphenol, triclosan, and bisphenol A total masses would be leached beyond the 90 cm soil profile of the loamy sand soil when water was applied at the $1.8 \times ET$ level for 10 years (Fig. 4d). Because of their low input levels, 4-n-nonylphenol and estrone remained contained in the 90 cm depth soil profile.

3.6. Factors affecting PPCP accumulation in soils

In the soil, the chemical specific reaction constants, K_d and $t_{1/2}$, would govern the extent of PPCP's fate and transport. The degradation and leaching losses of PPCP in the receiving soils would increase as the chemical solid-solution distribution coefficient of the soil, K_d , became lower and more PPCP remained in the solution phase subjecting to leaching and degradation attacks (Fig. 5a). When K_d was reduced by 10 folds, from that in the default scenario (i.e. $1 \times K_d$) to $0.1 \times K_d$, the PPCP retained in the loamy sand soil decreased across the board from 4.4 folds for ibuprofen to 9.7 folds for 4-n-nonylphenol. For ibuprofen, its storage in soil during the 10-year simulation period decreased from 3.36% to 0.76%, while it changed from 68.09% to 7.01% for 4-n-nonylphenol. Conversely, when K_d was increased by 10 folds, from that in the default scenario (i.e. $1 \times K_d$) to $10 \times K_d$, the PPCP accumulation in soil increased across the board from 1.3 folds for 4-n-nonylphenol to 7.7 folds for naproxen (Fig. 5a).

The degradation process reduced the PPCP mass available for adsorption by the soil. Holding all model parameters at default levels, the PPCP accumulations in the soil increased from 0.04 fold for 4-n-nonylphenol to 5.3 folds for diclofenac sodium when the degradation rate constant was reduced from that at the default (i.e. $1 \times t_{1/2}$) by 10 folds to $0.1 \times t_{1/2}$ (Fig. 5b). Conversely, the PPCP accumulation in the soil decreased across the board by 1.4 folds for 4-n-nonylphenol to 10.6 folds for diclofenac sodium when the rate constant was increased from that at the default by 10 folds to $10 \times t_{1/2}$ (Fig. 5b). Ten folds up and down variations of reaction rate parameters such as K_d and $t_{1/2}$ were common under the realistic environmental conditions as the ambient temperature, moisture content, and soil properties in the field changed temporally and spatially.

Besides the soil properties and the natures of chemicals, the mass inputs of PPCPs and water also affected their accumulation in the soil profiles. When the mass inputs of PPCPs varied by either decreasing or increasing their concentrations in the irrigation water by one order of magnitude from the default value, i.e. $0.1 \times C_{irr}$ or $10 \times C_{irr}$ (Fig. 5c), the percentages of the total mass of lost through degradation, evaporation, and leaching proportionally decreased or increased, respectively. As a result, their storage percentages in soil kept unchanged, and their residual concentration would increased or decreased by 10 folds correspondingly. When the irrigation water inputs were increased from the default 1.2 times of measured evapotranspiration demand (i.e. $1.2 \times ET$) to $1.5 \times$ and $1.8 \times ET$, the PPCP mass inputs as well as the water inputs increased by 25% and 50%, respectively (Fig. 5d). The interactions of enhanced water and mass inputs resulted in significantly greater extent of chemicals' leaching as showed in Fig. 4. Overall, the increase of input was greater than that of leaching. Therefore,

accumulation of PPCPs in soil increased under over-irrigation conditions as illustrated by Fig. 5d. Storage of PPCPs in soil increased by 1.002 times for clofibric acid to 1.32 times for nonylphenol under case of $1.5 \times ET$, by 1.002 times for clofibric acid to 1.66 times for nonylphenol under case of $1.8 \times ET$. In general, the impacts of irrigation practice on accumulation of PPCPs in soil were limited.

3.7. Potential ecological risks of PPCPs

When PPCPs accumulated in the soils, they might potentially be toxic to the soil biota. We evaluated the potential ecological risks by comparing the cumulative levels of the PPCPs in the soils to their respective potential no-effect concentrations in soil ($PNEC_{soil}$). When the $PNEC_{soil}$ were unavailable, it might be derived from the $PNEC_{water}$ (predicted no effect concentration in water based on aquatic toxicity data) through the equilibrium partition method (ECHA, 2008) as $PNEC_{soil} = 1000 * PNEC_{water} * K_d / (\rho * (1 + FC_{water}))$, where ρ is the soil bulk density, and FC_{water} is the field water content. When more than one $PNEC_{soil}$ or $PNEC_{water}$ was reported, the lowest would be selected. Table 3 summarized the derived PNEC values from the references and calculated the risk characterization ratios (RCR) which was the ratio of cumulative PPCP concentration in the top 0–20 cm soil layer at the end of 10 year simulation with respect to the respective $PNEC_{soil}$. The resulted RCRs in the two types of soil were all far than 1 varying from 0.0002 to 0.0459, indicating that the 9 selected PPCPs did not exhibit any potential harm to the soil biota. Furthermore, the concentrations of 9 selected PPCPs in the drainage water if appeared were all less than their respective $PNEC_{water}$ under the default simulation, suggesting that if the drainage water was discharged into surface water bodies, they would not pose potential harm to the aquatic biota upon dilutions in the receiving water bodies. The same would be true in case the leaching affected the groundwater. In all, the PPCP accumulation in the receiving soils of reclaimed water irrigation did not appear to produce undue ecological risks to soil biota.

4. Discussion and conclusions

For decades, trace organic contaminants of the water such as the PPCPs and disinfection byproducts have been concerns of environmental researchers. Municipal wastewater and its treated effluents have been the primary sources of their presence in the aquatic and terrestrial environment. Because both the frequency of detection and their concentrations were low, their presence and mobility in the terrestrial environment were difficult to track. Field observations so far have not yielded conclusive results, because the investigations were constrained by time periods and range of conditions covered.

In this study, we employed the solute transport modeling process and collected field observation data and laboratory-defined rate constants to validate the model that was then adopted to simulate the paths of 9 PPCPs in reclaimed water irrigated turf fields over a 10 year period. In this manner, the environmental fate and transport of PPCP trace organics in terrestrial environment might be comprehensively evaluated over a wide range of conditions.

In the examinations, we evaluated nine PPCPs of varying chemical properties, frequency of occurrence and concentrations in the reclaimed water under typical turf grass water management scenario for two types of soils. The soils, sandy loam and loamy sand, possessed the textures most suitable for turf grass in golf fields. Because they were conducive to water movement and light in clay content, the soils would be more prone to leaching of trace organic chemicals than the heavier textured soils thus representing worse case scenarios. The PPCPs we examined, on the other hand, covered a wide spectrum of chemical properties that defined their

environmental fate and transport. The solution versus soil distribution coefficients (K_d) of the PPCPs varied by three orders of magnitudes from <1 to 199 L kg^{-1} and <1 to 890 L kg^{-1} in loamy sand and sandy loam soils, respectively; their degradation half life ($t_{1/2}$) varied by two orders of magnitudes from 3.6 to 74.5 d and 1.7 to 77 d for loamy sand and sandy loam soils, respectively; and their dimensionless Henry's Law constant (K') varied by six orders of magnitudes from 9.67×10^{-9} to 5.84×10^{-3} (Table 1). As the reactive processes of adsorption, degradation, and volatilization were taken places simultaneously in the soil profile, the environmental fate and transport scenarios represented by this group of would be broad based. Besides, the water flux that defined the leaching potential of chemicals included not only the typical for turf grass irrigation but also considered over irrigations by 25% and 50%, respectively. In all, this study considered the environmental fate and transport of PPCPs in a comprehensive manner (Figs. 1–5).

The outcomes of our study appeared to reassure that PPCPs present in the reclaimed water when used for irrigation would not cause significant contamination of groundwater and accumulation in the receiving soils. Under default conditions, the PPCP accumulations in the surface 20 cm soil layer varied from less than 1 ng g^{-1} to about 140 ng g^{-1} (Fig. 1). The potentials for leaching through the soil profile were weak and after 10 years the PPCPs were not detectable below the surface 40 cm of the soil profile (Fig. 2). Even when, the environmental fate and transport parameters, K_d , $t_{1/2}$, and C_{irr} were allowed to vary by $\pm 10\times$, the expected range of variations in field situations, their accumulations in the soils and potentials for leaching through the soil profile dynamically changed with the boundary conditions (Figs. 4 and 5). Only in extreme scenarios when the K_d of the chemical was weak, the soil was lighter (i.e. loamy sand), and over irrigated did selected PPCPs breached the 90 cm soil profiles we examined, as illustrated by Fig. 4, in some scenarios, the leaching loss can be more than 10%.

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