LEACHABILITY OF SOME EMERGING CONTAMINANTS IN RECLAIMED MUNICIPAL WASTEWATER-IRRIGATED TURF GRASS FIELDS

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Abstract—Emerging pollutants inherent in reclaimed municipal wastewater, including endocrine-disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs), often have cast uncertainties on the safety of water reuse. We examined the fate and transport behavior of several PPCP and EDC compounds through observations made at experimental turf fields irrigated with naproxen, clofibric acid, diclofenac sodium, ibuprofen, estrone, 4-*tert*-octylphenol, bisphenol A, 4-*n*-nonylphenol, and triclosan latent irrigation water. The potential of the compounds to contaminate underlying groundwater was assessed using three screening protocols that employed the attributes of soils, chemicals, and water fluxes as the estimators. No compound was detected in the leachate draining through the 89-cm profile of a loamy sand soil and a sandy loam soil turf grass field during four months of irrigation according to operations typical of golf courses in southern California (USA). Ibuprofen, naproxen, triclosan, bisphenol A, clofibric acid, and estrone were detected in the surface to 30-cm soil profiles. Higher irrigation rate and coarser textural soil enhanced the downward movement of chemicals in both soils. The pollution risk screenings identified the same six compounds as having the potential to contaminate groundwater, and under conditions of turf grass irrigation, clofibric acid and ibuprofen would be most prone to cause the pollution.

Keywords—Pharmaceutical/personal care products Endocrine-disrupting compounds Turf grass Reclaimed water Leaching

INTRODUCTION

Water reuse has been a common practice worldwide, and the potential for reuse continues to rise as wastewater treatment technology advances [1]. In 2006, an estimated 9.8×10^6 m³/d of treated municipal wastewater, or approximately 7 to 8% of the total generated, was reused in the United States [2]. An overwhelming majority of the reclaimed wastewater is used for irrigation, through which trace amounts of potentially harmful toxic organic compounds, such as pharmaceutical and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs), may be transported off-site via the surface runoff and subsurface drainage [3].

The environmental release of these emerging chemical contaminants in municipal wastewater is currently unregulated. Occurrence of PPCPs and EDCs in wastewater, sewage sludge, surface water, drinking water, groundwater, soil, and sediment is of a growing concern [3–9]. Because of the bioactive nature of PPCPs and EDCs, they may adversely affect the human body and the functions of aquatic ecosystems when exposed at sufficiently high levels and for long enough durations. Potential risks to the exposure include cancers, immune system disturbance, antibiotic resistance, and endocrine-disruptive activity for humans and ecosystem malfunction for other biota. Their fate and transport in the vadose zone following applications of reclaimed wastewater on crops

and landscaping is uncertain and, most likely, compound specific.

Upon irrigation, these compounds in the applied wastewater are subject to volatilization at the surfaces of soils and vegetation, degradation through chemical and biological processes, adsorption by soil organic matter, and plant uptake. The potential ecotoxicological consequences over time should not be overlooked. Pedersen et al. [3] and Kinney et al. [10] reported the presence of PPCPs and EDCs in soils and surface runoff from fields receiving reclaimed wastewater irrigation. It is imperative that the behavior of PPCPs and EDCs in the soil profile underneath irrigated fields be evaluated simultaneously and under conditions more realistic of a field operation in which environmental process parameters may be properly defined.

Southern California (USA) is home to more than 500 golf courses (18-hole equivalent in size). Many golf courses either are being irrigated with reclaimed municipal wastewater or soon will be [11]. According to the U.S. Golf Association, the plant growth media for the root zone of putting greens should consist of at least 90% sand [12]. In the fairway, sandy soils are preferred. This setting allows fast infiltration and percolation of water through the root zone, thus maintaining the ideal conditions for the game. However, it increases significantly the potential for reclaimed wastewater-borne contaminants to move downward, toward the groundwater.

In the present study, we assessed the leaching potential of nine PPCPs and EDCs in irrigated turf grass fields by determining the amount of PPCPs and EDCs found in the soil profiles and leachates, calibrating parameters (e.g., half-

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Table 1. Chemical structure, octanol–water partition coefficient (K_{OW}), and acid dissociation constant (pKa) values of the selected compounds

Compounds	Structure	Log K_{OW}	pKa
Clofibric acid		3.62 [32] ^a	2.84 [33]
Ibuprofen		3.80 [34]	4.90 [33]
4- <i>tert</i> -Octylphenol		4.12 [35]	10.21 [36]
4- <i>n</i> -Nonylphenol		5.76 [35]	10.28 [37]
Naproxen		3.10 [34]	4.15 [33]
Triclosan		4.76 [38]	7.90 [33]
Diclofenac sodium		4.71 [32]	4.00 [33]
Bisphenol A		3.32 [35]	9.73 [39]
Estrone		3.43 [35]	10.40 [36]

^a Reference numbers are in parentheses.

life and organic carbon partition coefficient [K_{OC}] of solute transport using the data obtained, and examining the risks of these compounds in regard to contaminating groundwater.

MATERIALS AND METHODS

Chemical standards and reagents

The PPCP and EDC compounds that we selected have all been detected in surface and groundwater susceptible to the influence of wastewater treatment plant effluents [4–8]. Naproxen (>98%), clofibric acid (>99%), and diclofenac sodium salt (>98%) were purchased from MP Biomedicals. Estrone (>99%) and ibuprofen (99%) were purchased from Acros Organics (percentages in parentheses are purity at which the compound was obtained). In addition, 4-*tert*-octylphenol (97%), bisphenol A (>99%), and the derivatizing reagent *N*-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) were purchased from Sigma-Aldrich. Both 4-*n*-nonylphenol (>99%) and triclosan (>97%) were purchased from Sigma-Aldrich as well. The surrogate standard, 2,4-dichlorophenylacetic acid, and the internal standard, 4,4'-dibromooctafluorobiphenyl, were purchased from Spex CertiPrep. Table 1 summarizes the structures and properties of the chemicals involved. Reagents of acetone, ethyl acetate, and dichloromethane (all pesticide grade) were purchased from Fisher. Anhydrous sodium sulfate (Fisher) was of analytical grade and was baked at 400°C for 4 h, then stored in a sealed container.

Experimental field

The field study was conducted at the University of California–Riverside turf grass facility under the setting of experimental lysimeters. The field was constructed in 1991 and consisted of 24 plots (3.66 × 3.66 m) laid out in a 3- × 8-plot, side-by-side arrangement. Plots were separated by plywood from the surface down for approximately 1 m. The plots were equally divided and filled with either an Arlington fine sandy loam soil (70.3% sand, 19.4% silt, and 10.3% clay) with organic carbon content (f_{OC}) of 0.55% or a Hanford loamy sand soil (83.4% sand, 9.5% silt, and 7.1% clay) with a f_{OC} of 0.44% [11]. Both soils were deemed to be suitable for golf courses and were conducive to water moving through the soil profile. The lysimeter assembly inside each plot, consisting of five metal cylinders (inner diameter, 56 cm; combined surface area, 1.23 m²), was preassembled and then evenly spaced and planted each plot. The top 89 cm of the cylinder were hand-packed to the same bulk density as the external surrounding soils, whereas the bottom 7.5-cm layer was filled with pea gravel. The soil water drained under gravity, and the leachate flowed through a conduit and collected in a receptacle for volume measurement and sample acquisition. The plots were planted with a hybrid Bermuda grass (*Cynodon dactylon* × *transvaalensis*) in 1994 and professionally maintained. Each plot was equipped with four pop-up sprinklers situated at the corners and a separate timer; thus, the volume and scheduling of the water application could be individually controlled.

Table 2. Measured and calculated pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs) accumulated in soils underneath reclaimed wastewater-irrigated turf grass field

Compounds	Irrigation water ($\mu\text{g/L}$)			Total chemical applied ($\mu\text{g/plot}$) ^a		Recovered (% of total applied) from high ET_0 input plots			
						Loamy sand soil		Sandy loam soil	
	Maximum	Minimum	Mean	Low ET_0	High ET_0	Measured	Calculated ^b	Measured	Calculated ^b
Clofibric acid	1.25	0.86	1.05	2,906	3,980	8	20	9	15
Ibuprofen	9.12	7.39	8.59	23,773	32,559	7	10	6	4
4- <i>tert</i> -Octylphenol	2.63	2.39	2.49	6,891	9,438	0	12	0	3
4- <i>n</i> -Nonylphenol	5.11	4.07	4.38	12,122	16,601	0	15	0	4
Naproxen	14.63	12.64	13.40	37,084	50,790	4	10	6	8
Triclosan	4.41	3.17	3.54	9,797	13,418	7	16	9	16
Diclofenac sodium	4.06	3.15	3.41	9,437	12,925	0	6	0	6
Bisphenol A	3.14	2.11	2.55	7,057	9,665	5	10	6	8
Estrone	0.11	0.05	0.07	194	265	4	10	4	7

^a ET_0 = potential evapotranspiration.

^b Results were calculated using the first-order decay equations of each compound.

Additional information regarding this experimental facility may be found in Wu et al. [11] and Gan et al. [13].

Climatic conditions

The climatic data were obtained from an official California Irrigation Management Information System (CIMIS) weather station on site. During the course of the experiment, rainfalls were recorded on January 4, 5, 6, and 7, 2008, in amounts of 2.8, 19.1, 20, and 0.4 mm, respectively. The average daily maximum and minimum air temperatures were 22.2 and 9.4°C, respectively, and the average daily soil temperature was 14.6°C. The daily average maximum, minimum, and mean relative humidities were 68, 29, and 48%, respectively. The warm and dry conditions resulted in high potential evapotranspiration (ET_0) and irrigation demands for the turf grass [13].

The drainage took place following the first irrigation event and occurred in a steady and regular manner.

Irrigation water

A reclaimed municipal wastewater that contains known amounts of all test chemicals would be an ideal irrigation water source for the present experiment. The occurrences and concentrations of chemicals in any water source, however, are subject to temporal variations [14]. To insure all of the compounds being tested were present and their concentrations were comparable to those reported in the literature, we added chemicals to the irrigation water so that the concentrations would remain constant for the duration of the present study. The water and the stock solutions (in ethyl acetate) of the chemicals were mixed in an approximately 22,000-L, polyethylene storage tank for 4 h using a vortex mixer and then withdrawn for irrigation as needed. One tank of water may last for approximately 10 to 15 d, depending on the daily evapotranspiration. The irrigation water was routinely sampled and assayed for the concentrations of the compounds (Table 2).

Irrigation schedule and sample collection

The field study was conducted from September 15, 2007, to January 10, 2008. Sixteen of the 24 plots ($n = 8$ for each soil type) were employed. Within each soil type, three plots were irrigated three times weekly (in the early morning of Monday, Thursday, and Saturday) at the typical rate of 1.1- to 1.2-fold

the ET_0 , consistent with practices of golf courses in southern California. These plots are designated hereafter as the low-water treatment plots. Three plots were irrigated three times weekly at 1.5- to 1.6-fold of ET_0 , representing the worst-case scenario in terms of leaching. These plots are designated hereafter as the high-water treatment plots. Over the experimental period, a total of 214 and 293 mm of irrigation water were applied to plots at the low- and high-water treatment, respectively. Two remaining plots were striped of the sod and irrigated at 1.1- to 1.2-fold the ET_0 to test the role of turf grass on the fate and transport of these compounds.

The experimental plots were irrigated from September 15, 2007, to January 10, 2008. The leachate, consisting of drainage from the lysimeters of each plot, was collected in 4-L, amber-glass jugs and retrieved three times weekly. The chemical contents were analyzed within 12 h of the recovery. Soils of the 0- to 89-cm profile were sampled at the end of the experiment using a coring device (inner diameter, 5 cm) and then sectioned into nine segments—namely, the soil depths of 0 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 30, 30 to 40, 40 to 50, 50 to 70, and 70 to 89 cm. The samples from plots receiving the same treatment were combined and mixed according to the depth segment to obtain a composite sample and then stored at -20°C until analysis. On April 3, 2008, which was 84 d from the end of the experiment, the irrigation resumed with water free of the spiked chemicals, and leachates were again collected to determine if the chemicals accumulated in the soils would be mobile.

Sample analysis

The PPCPs and EDCs in soil and leachate samples were determined according to procedures outlined elsewhere [15]. Briefly, leachates were concentrated with solid-phase extraction, followed with elution by ethyl acetate. Soil samples were sonicated with acetone-ethyl acetate solution, followed with solid-phase extraction cleanup and analysis with a gas chromatograph/mass selective detector (GC/MSD; Agilent 6890N GC coupled with 5975C MSD). Before GC/MSD analysis, all sample extracts were derivatized with MTBSTFA.

Seven-point calibration curves were prepared by spiking appropriate amounts of target compounds into 500 ml of deionized water. The spiked-water samples were analyzed according to the procedure described above. A water sample with addition of a blank soil extract was analyzed to provide a calibration blank. Limits of quantification (LOQs) were set as

the second-lowest calibration point within the linear correlation curve, with a signal to noise ratio of at least 10 using the baseline in the chromatogram. The method recovery for test compounds in leachate samples was between 81 to 118%, and the LOQ ranged from 6 to 75 ng/L, depending on the compounds. The LOQ of the method in dry-soil samples was 0.2 ng/g for ibuprofen; 2.4 ng/g for 4-*tert*-octylphenol; 0.4 ng/g for clofibric acid, 4-*n*-nonylphenol, naproxen, triclosan, and bisphenol A; and 1.2 ng/g for diclofenac sodium salt and estrone [15].

Degradation study

Soils were obtained from the experimental field, air-dried, and allowed to pass through a sieve with 2-mm openings. Aliquots (0.5 ml) of the chemicals in ethyl acetate solutions (10 mg/L) were mixed with 10 g of prepared soils. Acetone was added to ensure the spiked compounds were evenly distributed in the soil. The solvents were evaporated by exposing the mixtures at room temperature ($20 \pm 2^\circ\text{C}$) in a darkened fume hood for 15 h. The spiked samples were then thoroughly mixed with 40 g of untreated soil to attain the desired concentration of 100 ng/g. Five grams of the preparation were placed in a 50-ml, screw-capped, Teflon® centrifuge tube, and deionized water (distilled water further deionized using a Milli-Q® filter assembly [Millipore]) was added to maintain moisture contents at 70% of the soil's water-holding capacity and then divided evenly into three experimental groups: Those treated with 0.1% HgCl_2 to suppress the microbial activities, those covered completely with aluminum foil to prevent exposure to light, and those that remained untreated, mimicking the ambient soils. These groups were incubated at room temperature, and sets of two were retrieved at days 0, 1, 3, 5, 8, 12, 16, 23, 30, and 45 following commencement of incubation for chemical analyses according to previously described protocols. The degradation half-lives were calculated accordingly.

Adsorption study

The batch equilibrium method was followed. Aliquots (5 g dry-wt equivalent) of soils at the field moisture contents were each mixed with 10 ml of 0.01 M CaCl_2 plus 0.1% HgCl_2 solution containing chemicals at concentrations of 0, 0.5, 1.0, 2.5, 5.0, and 10 $\mu\text{g/ml}$ in 50-ml, Teflon centrifuge tubes. The soil suspensions were continuously mixed by shaking and equilibrated for 24 h at room temperature ($20 \pm 2^\circ\text{C}$), and the contents were then centrifuged at 10,000 rpm for 10 min to separate the solid and aqueous phases (mean $\pm$ standard deviation). The remaining soil phase was extracted according to procedures described above to obtain the concentration of the adsorbed phase (C_s ; $\mu\text{g/g}$). The decanted supernatants were extracted with dichloromethane. The organic dichloromethane phase was dried over anhydrous Na_2SO_4 , concentrated, derivatized with MTBSTFA, and examined using GC/MSD analysis to obtain the aqueous-phase concentration (C_w ; $\mu\text{g/ml}$). Preliminary experiments showed that the recovery rate of the liquid-liquid extraction procedure was at least 78% for the chemicals of concerns. The C_w versus C_s were fitted to a linear equation to estimate the partition coefficient (K_d), and $K_{OC} = K_d/f_{OC}$.

Leaching potential assessment

Three screening models were adopted to assess the leaching potential of selected chemicals in soils.

Cohen et al. [16] postulated that organic chemicals, such as pesticides, fitting the following chemical profile pose high risks for contaminating groundwater. Namely, they were chemicals that had a negative charge at ambient pH, a K_{OC} of less than 300 to 500 cm^3/g , and a half-life ($t_{1/2}$) of the soil of greater than two to three weeks.

Gustafson [17] differentiated the leachable and nonleachable pesticides by considering their mobility and persistence in soil according to their groundwater ubiquity scores (GUS):

$$\text{GUS} = \log t_{1/2} \cdot (4 - \log K_{OC}) \quad (1)$$

where $t_{1/2}$ is the degradation half-life in the soil (d). Leachable chemicals have GUS scores equal to or greater than 2.8, whereas nonleachable chemicals have GUS scores of less than 1.8. Chemicals with GUS scores of between 2.8 and 1.8 are transitional, and their leaching potentials are not certain.

Jury et al. [18] screened organic chemicals, such as pesticides, for their potentials to contaminate groundwater under the dynamic and interactive processes of water movement and chemical and biological reactions. Chemicals were judged to pose an insignificant groundwater hazard when

$$K_{OC} > a[t_{1/2}(\text{soil})] - b \quad (2)$$

where

$$a = 0.235J_w / [0.693(L + r^{-1})B_d f_{OC}] \quad (3)$$

$$b = \theta / B_d f_{OC} \quad (4)$$

and K_{OC} is in terms of cm^3/g , J_w is the drainage rate (m/year), L is the surface zone (m), r is the depth constant (1/m), B_d is the soil bulk density (kg/m^3), and θ is the water content.

RESULTS AND DISCUSSION

PPCPs and EDCs of leachates

From commencement of the field test on September 15, 2007, to January 10, 2008, the concentrations of the target chemicals in leachate were less than the LOQ of the respective chemicals, whereas regular and steady subsurface drainage was observed. Similarly, Gan et al. [13], employing the same experimental facility, found that *N*-nitrosodimethylamine, a disinfection by-product chemical of the reclaimed municipal wastewater, was detected in 4 of 200 leachate samples at concentrations barely greater than the method detection limit. Casey et al. [19] investigated the fate and transport of 17 β -estradiol and testosterone in a field lysimeter. Approximately 1.3 and 0.02% of 17 β -estradiol and testosterone, respectively, were recovered from lysimeter effluent. The absence of chemicals in the lysimeter drainages or leachates may be the result of elimination, either via sorption or via transformation during the soil aquifer passage. Ternes et al. [20] analyzed lysimeter effluents and groundwater samples from arable land receiving treated wastewater irrigation continuously for more than 45 years. Of 52 PPCPs, only four could be found in the wells, and six were identified in the aqueous lysimeter samples, which excluded acidic pharmaceuticals, musk fragrances, estrogens, and β -blockers. Williams et al. [21] also attributed the low leaching potential of carbamazepine to the adsorption of irrigation water by the soil profile. Under the circumstances of low concentrations of the compounds and reactive processes of attenuation in soils, the amounts leached would be less than the detectable levels when the field was irrigated with reclaimed wastewater.

Table 3. First-order kinetic constants (1/d) in different experimental treatments^a

Compounds	Loamy sand				Sandy loam
	Nonsterile and lighted	Nonsterile and dark	Sterile	Sterile and dark	Nonsterile and lighted
Clofibric acid	0.0493 (14.1)	0.0486 (14.3)	0.0188 (36.9)	0.0123 (56.3)	0.0686 (10.1)
Ibuprofen	0.0963 (7.2)	0.0593 (11.7)	0.033 (21.0)	0.0211 (32.8)	0.3491 (2.0)
4- <i>tert</i> -Octylphenol	0.0799 (8.7)	0.0514 (13.5)	0.0328 (21.1)	0.0322 (21.5)	0.412 (1.7)
4- <i>n</i> -Nonylphenol	0.0697 (9.9)	0.0549 (12.6)	0.0494 (14.0)	0.0431 (16.1)	0.228 (3.0)
Naproxen	0.0911 (7.6)	0.0907 (7.6)	0.0186 (37.3)	0.0163 (42.5)	0.1167 (5.9)
Triclosan	0.0501 (13.8)	0.0449 (15.4)	0.0276 (25.1)	0.0213 (32.5)	0.0527 (13.1)
Diclofenac sodium	0.1924 (3.6)	0.1392 (5.0)	0.0093 (74.5)	0.009 (77.0)	0.1951 (3.6)
Bisphenol A	0.0929 (7.5)	0.0897 (7.8)	0.0588 (11.8)	0.0534 (13.0)	0.1325 (5.2)
Estrone	0.090 (7.7)	0.0907 (7.6)	0.0517 (13.4)	0.0506 (13.7)	0.1694 (4.1)

^a Half-lives (d) are given in parentheses.

For 84 d following the switch from the PPCP and EDC latent to the PPCP and EDC free irrigation water, none of the targeted chemicals was detected in the subsequent leachates collected.

Degradation

The field lysimeter experiments showed that the targeted chemicals were resistant to leach-out of the 89-cm soil profile. The PPCPs and EDCs added with the irrigation water were retained in the soil profiles, dissipated during the downward migration, or both. To trace the fates of these chemicals, their residual in the soil profile was measured, and their degradation in soil was studied through laboratory batch experiments. The time-dependent disappearance of the targeted chemicals in the bench-top experiment was fitted to the first-order kinetics equation. The results are summarized in Table 3.

The soil recoveries of the targeted chemicals under different treatments were less than 10% (Table 4). The levels of three chemicals—4-*t*-octylphenol, 4-*n*-nonylphenol, and diclofenac sodium—were less than the respective LOQ. These results indicated that most of the chemicals added with the irrigation water were dissipated through degradation, volatilization, or other pathways.

The chemicals disappeared under both the septic and the aseptic conditions. Judging from the degradation half-life, the chemicals were more stable under the sterile environment, illustrating that the soil microorganisms played major roles in degradation of the chemical (Table 3). The degradation rate caused by photodegradation, as depicted by the $t_{1/2}$ of the sterile treatment, was significantly ($p < 0.05$) lower than the microbial decomposition, as depicted by the $t_{1/2}$ of the dark and nonsterile treatment. The presence of light had little effect

on the disappearance of several compounds—namely, clofibric acid, 4-*n*-nonylphenol, naproxen, bisphenol A, and estrone—and would enhance the degradation of remaining chemicals—namely, ibuprofen, 4-*tert*-octylphenol, triclosan, and diclofenac sodium—when the two nonsterile treatments were compared. For the light-sensitive chemicals, the microbial degradation and photodegradation processes acted simultaneously. Although photodegradation could be an important loss mechanism for selected pharmaceutical pollutants in surface waters [22–24], microbial degradation played a dominant role in the soil matrices. When the influences of the soils were considered, the test chemicals invariably disappeared faster in the sandy loam than in the loamy sand soils (Table 3). Because the conditions of the experiments were identical, the enhanced biodegradation in the slightly heavier textured, sandy loam soil might be a result of the higher organic carbon and nutrient accumulation and the greater surface area of the soil particles.

Assuming that interception and absorption by plants were negligible, the amounts of chemicals accumulated in the soil profiles should be comparable to the calculated residues because of degradation. If degradation in the soil was the only pathway, then based on measured degradation rate constants and residence time, approximately 12, 15, and 6% of the total applied 4-*tert*-octylphenol, 4-*n*-nonylphenol, and diclofenac sodium, respectively, would have remained in the loamy sand soil. In the sandy loam soil, 3, 4, and 6% of the total applied 4-*tert*-octylphenol, 4-*n*-nonylphenol, and diclofenac sodium, respectively, would have remained in the soil profile. These three compounds, however, were not detected in both the soil profile and leachates. These discrepancies demonstrated that degradation, though by far the most

Table 4. Physical and chemical properties and their respective screening model predictions for the nine selected compounds in the two test soils

Compounds	Loamy sand					Sandy loam				
	Distribution coefficient (K_d) (cm ³ /g)	r^2	Organic carbon partition coefficient (K_{OC}) (cm ³ /g)	Groundwater ubiquity score (GUS)	Jury's inequality (cm ³ /g)	K_d (cm ³ /g)	r^2	K_{OC} (cm ³ /g)	GUS score	Jury's inequality (cm ³ /g)
Clofibric acid	2.3	0.9997	426	1.6	282	0.9	0.9699	205	1.7	493
Ibuprofen	0.6	0.9935	109	1.7	130	1.2	0.9947	275	0.5	142
4- <i>tert</i> -Octylphenol	8.6	0.9607	1,566	0.8	163	26.9	0.9707	6,132	0.1	82
4- <i>n</i> -Nonylphenol	198.7	0.9739	36,126	−0.6	189	890.3	0.8436	202,332	−0.6	170
Naproxen	1.2	0.9887	209	1.5	139	1.7	0.9930	389	1.1	168
Triclosan	13.9	0.9945	2,544	0.7	276	179.6	0.9934	40,809	−0.7	493
Diclofenac sodium	0.9	0.9881	158	1.0	50	4.7	0.9976	1,066	0.9	85
Bisphenol A	9.6	0.9889	1,751	1.6	136	17.1	0.9971	3,886	0.7	116
Estrone	34.2	0.8654	6,211	0.7	141	30.8	0.9661	7,002	0.3	170

important process, might not be the only pathway for the target chemicals to disappear in the turf grass fields. The same also may be said for the other targeted compounds (Table 2). In unsaturated soils under open-field conditions, volatilization may occur after the water application, because chemical transport may occur in both the solution and gas phases and the chemical may volatilize readily at the soil-air interface into the atmosphere [13]. For example, nonylphenol and octylphenol have shown their potential for volatilization, being detected at levels of up to 70 and 1.0 ng/m³, respectively, in coastal sites atmospheric samples [25–27]. Volatilization of targeted compounds was not measured in the present study; however, it is expected to be one of the dissipation pathways for some compounds, such as nonylphenol and octylphenol, in soils. Another factor that should be considered is the irreversible binding of compounds on soil humic substances, which may decrease the compound recovery from the soils. Other considerations, for example, interception of compounds by aboveground foliage and plant root uptake [13] could be potential removal pathways as well.

PPCPs and EDCs in soil profiles

The profile distributions of the targeted chemicals along the 89 soil profiles are illustrated in Figure 1. None of the recovered chemicals was detected beyond the surface 30-cm soil depth. Three compounds—namely, 4-*tert*-octylphenol, 4-*n*-nonylphenol, and diclofenac sodium—were not detected in any of the soils examined. Because they were not found in the leachate, other processes, such as volatilization and degradation, might have contributed to their disappearance in the soils.

For each soil, more chemicals were detected and distributed to deeper depths with higher irrigation water inputs of 1.5- to 1.6-fold the ET_o than at the lower and more typical irrigation water inputs of 1.1- to 1.2-fold the ET_o. For instance, ibuprofen, naproxen, triclosan, and bisphenol A were found to a depth of 0 to 10 cm when the loamy sand soil was irrigated at the rate of 1.1- to 1.2-fold the ET_o. Two additional compounds, clofibric acid and estrone, were detected as well. The detectable chemicals spread to the 0- to 30-cm soil depth when irrigated at the higher water inputs, whereas clofibric acid and estrone were not detected in the soil profile under the low irrigation inputs.

Similar patterns were observed in the profiles of the sandy loam soils, and the three-way interactions of irrigation volume, chemical, and soil characteristics were apparent (Fig. 1). At an irrigation rate of 1.1- to 1.2-fold the ET_o, ibuprofen, triclosan, bisphenol A, and clofibric acid were detected in the surface to 15-cm soil depth, whereas naproxen spread to the surface to 30-cm soil depth. When the irrigation rate was at 1.5- to 1.6-fold the ET_o, estrone was detected in addition to the above-referenced chemicals, and the profile distribution expanded to the surface to 30-cm soil depth.

According to the laboratory-determined degradation rates (Table 3), test compounds degraded much more quickly in the sandy loam soil; thus, concentrations of compounds in the sandy loam soil should be lower than concentrations of the respective counterparts in the loamy sand soils. However, the opposite was observed based on the field data. More of the detected chemicals accumulated in the profile of the sandy loam soil compared with the loamy sand soil. For example, naproxen concentrations of that soil profile were the highest among the detected chemicals. The highest naproxen levels

of the 1.1- to 1.2-fold the ET_o soil profiles were 10.3 and 12.7 ng/g for the loamy sand and sandy loam, respectively. At an irrigation rate of 1.5- to 1.6-fold the ET_o, maximum soil levels of naproxen were 6.9 and 9.6 ng/g for loamy sand and sandy loam, respectively. For the chemicals present in soils, higher profile concentrations denoted slower degradation. In addition, other causes might have affected the outcomes. It was reported that the root density of turf grass grown in the loamy sand was significantly higher than that in the sandy loam soil [11]. The degradation of test chemicals would be higher in the loamy sand soil because of enhanced rhizospheric activities induced by the higher root density [28–30].

Leaching potential of PPCPs and EDCs

We employed the information summarized in the previous sections to assess the risks of PPCPs and EDCs in regard to contaminating the underlying groundwater aquifer when reclaimed municipal wastewater is used in irrigating turf grass. The K_{OC} and $t_{1/2}$ (Tables 3 and 4) are critical input parameters for the assessment protocols summarized previously. Because the K_d and K_{OC} are linearly correlated, the retardation of solute transport in the soil profile indicated by these two models is valid even when the K_{OC} values of some chemicals were rather low.

Based on the information in Tables 3 and 4, the targeted compounds may be divided into the following categories: High leaching potential ($K_{OC} < 300$ cm³/g and $t_{1/2} > 21$ d; no compound is in this category), medium-high leaching potential ($K_{OC} < 300$ cm³/g or $t_{1/2} > 21$ d), medium leaching potential ($K_{OC} = 300$ –500 cm³/g and $t_{1/2} = 14$ –21 d), medium-low leaching potential ($K_{OC} > 500$ cm³/g or $t_{1/2} < 14$ d), and low leaching potential ($K_{OC} > 500$ cm³/g and $t_{1/2} < 14$ d). The chemicals were categorized as shown in Table 5. None of the targeted chemicals appeared specifically prone to leaching even in the most susceptible soils, such as the loamy sand and sandy loam soils. Among the group, ibuprofen, clofibric acid, diclofenac sodium, and naproxen were most likely to leach, because either their K_{OC} was less than 300 cm³/g or their $t_{1/2}$ was greater than 21 d. The chemicals 4-*tert*-octylphenol, 4-*n*-nonylphenol, bisphenol A, and estrone had moderately low potential for leaching, because either their K_{OC} was greater than 500 cm³/g or their $t_{1/2}$ was less than 14 d. Triclosan would be the compound most resistant to leaching in the group that had K_{OC} greater than 500 cm³/g and $t_{1/2}$ less than 14 d. However, because of the relatively small chemical inputs, together with the expected rapid degradation rates, the targeted compounds are not expected to remain in the soil profile for long.

According to the Gustafson criteria, the GUS of all tested PPCPs and EDCs were judged as nonleachers, because the GUS scores for both soils were less than 1.8 (Table 4).

For Jury's inequality of $K_{OC} > a[t_{1/2}(\text{soil})] - b$, the leaching water flux (J_w) was estimated by the difference between the water inputs (sum of irrigation and precipitation) and the evapotranspiration, which was approximately 0.43 m/year. Other parameters were defined as follows: Surface zone, $L = 0.5$ m; depth factor, $r = 3$ m; soil bulk density, $B_d = 1,550$ kg/m³ for loamy sand soil and 1,500 kg/m³ for sandy loam; fractional content of organic carbon, $f_{OC} = 0.0055$ for loamy sand and 0.0044 for sandy loam; and average volumetric water content, $\theta = 0.25$. Consequently, $a = 0.0221$ and $b = 0.0293$ for the loamy sand soil, and $a =$

Fig. 1. Distribution of the nine selected pharmaceuticals and personal care products and endocrine-disrupting compounds levels in the soil profiles at the end of a four-month irrigation: (a) loamy sand soil with an irrigation rate of 1.1- to 1.2-fold the potential evapotranspiration (ET_0), (b) loamy sand soil with an irrigation rate of 1.5- to 1.6-fold the ET_0 , (c) sandy loam soil with an irrigation rate of 1.1- to 1.2-fold the ET_0 , (d) sandy loam soil with an irrigation rate of 1.5- to 1.6-fold the ET_0 , (e) bare sandy loam soil with an irrigation rate of 1.1- to 1.2-fold the ET_0 , and (f) bare loamy sand soil with an irrigation rate of 1.1- to 1.2-fold ET_0 .

0.0285 and $b = 0.0379$ for the sandy loam soil. In this regard, ibuprofen in the loamy sand soil and clofibric acid in the sandy loam soil have the potential of leaching to the groundwater, whereas other chemicals conformed to the inequality showing the improbable contamination risk (Table 4).

Results of the field experiment showed that when present in the irrigation water, clofibric acid, naproxen, ibuprofen, triclosan, bisphenol A, and estrone could accumulate in the surface to 30-cm soil layer at low levels. Among them, clofibric acid and naproxen appeared at higher concentrations than the remainders. Whereas the model

assessments and the field measurements were not completely in agreement, the general trends appeared to be analogous. Outcomes based on the three assessment models indicated that clofibric acid and ibuprofen would have greater leaching potential compared with the rest of the group. The profile distributions showed that clofibric acid and ibuprofen were consistently detected and spread to the farthest extent of the surface to 30-cm soil depth. Oppel et al. [31] reported that the leaching potential of clofibric acid exceeded that of ibuprofen, again in agreement with the findings of the present assessments.

Table 5. Leaching potential of test chemicals according to criteria of Cohen et al. [16]

Leaching potential	Loamy sand soil	Sandy loam soil
High	None	None
Medium-high	Ibuprofen, naproxen, diclofenac sodium	Clofibric acid, ibuprofen
Medium	Clofibric acid	None
Medium-low	4- <i>tert</i> -Octylphenol, 4- <i>n</i> -nonylphenol, bisphenol A, estrone	4- <i>tert</i> -Octylphenol, 4- <i>n</i> -nonylphenol, naproxen, diclofenac sodium, bisphenol A, estrone
Low	Triclosan	Triclosan

CONCLUSION

Even under the most susceptible conditions in irrigation, the PPCPs and EDCs in the reclaimed wastewater were not likely to contaminate the underlying groundwater. Outcomes of field experiments showed that three of nine targeted compounds—namely, 4-*tert*-octylphenol, 4-*n*-nonylphenol, and diclofenac sodium—were not detected in the soil profile and leachates. Less than 9% of the remaining six targeted compounds—namely, naproxen, clofibric acid, ibuprofen, estrone, bisphenol A, and triclosan—were recovered in the soil profile and deposited in the surface 30-cm of the soil depth. Whereas microbial degradation was by far the most important process affecting the fate and transport of these compounds, the roles of volatilization during the water application, interception by foliage, and absorption by plant roots may not be ruled out completely.

Outcomes of the field experiment were employed to test the validity of three commonly used models for assessing the groundwater contamination potential of organic chemical compounds. It demonstrated that these models, though unable to provide quantitative estimates, were accurate in predicting the leaching potentials of the compounds and that their conclusions agreed with one another.

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