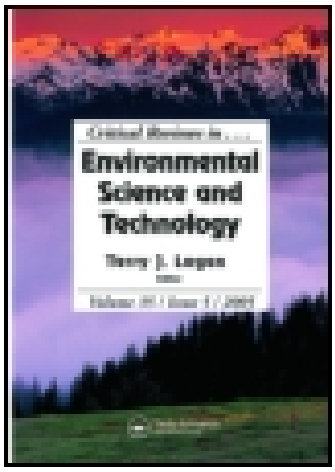


Critical Reviews in Environmental Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/best20

The Fate and Impact of Pharmaceuticals and Personal Care Products in Agricultural Soils Irrigated with Reclaimed Water

Qin Qin[ab], Xijuan Chen[a] & Jie Zhuang[c]

[a] Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Department of Biosystems Engineering and Soil Science, Institute for a Secure and Sustainable Environment, The University of Tennessee, Knoxville, TN 37996, USA

Accepted author version posted online: 09 Sep 2014.

To cite this article: Qin Qin, Xijuan Chen & Jie Zhuang (2014): The Fate and Impact of Pharmaceuticals and Personal Care Products in Agricultural Soils Irrigated with Reclaimed Water, Critical Reviews in Environmental Science and Technology, DOI: 10.1080/10643389.2014.955628

To link to this article: http://dx.doi.org/10.1080/10643389.2014.955628

The Fate and Impact of Pharmaceuticals and Personal Care Products in Agricultural Soils Irrigated with Reclaimed Water

QIN QIN[†,ξ], XIJUAN CHEN[†], JIE ZHUANG[‡,*]

[†]*Key Laboratory of Pollution Ecology and Environmental Engineering, Institute of Applied Ecology，Chinese Academy of Sciences, Shenyang 110016, China*

[ξ]*University of Chinese Academy of Sciences, Beijing 100049, China*

[‡]*Department of Biosystems Engineering and Soil Science, Institute for a Secure and Sustainable Environment, The University of Tennessee, Knoxville, TN 37996, USA*

***Corresponding Author:**

Dr. Jie (Joe) Zhuang

Department of Biosystems Engineering and Soil Science

Institute for a Secure and Sustainable Environment

The University of Tennessee, Knoxville, TN 37996, USA

Email: jzhuang@utk.edu

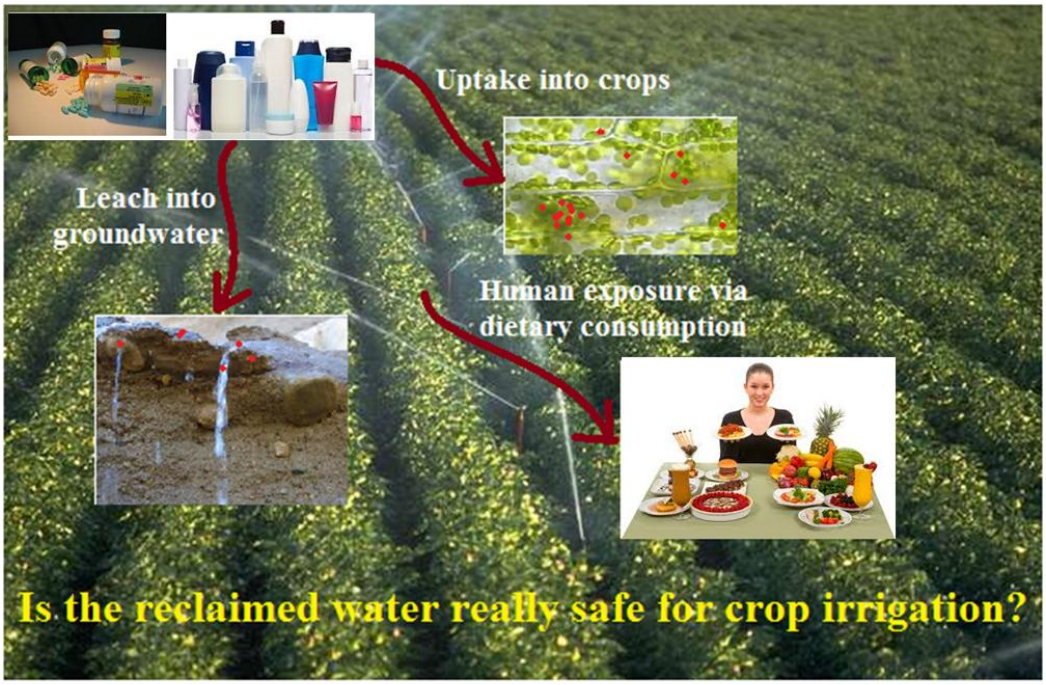
Phone: +1 (865) 974-9467

Fax: +1 (865) 974-4514

ABSTRACT

Reclaimed water is an important source of irrigation and is widely used on agricultural soils throughout the world, particularly in arid and semi-arid regions. However, concerns about the potential risks of this practice are rapidly increasing because reclaimed water may contain various organic pollutants such as pharmaceuticals and personal care products (PPCPs). Trace levels of PPCPs have been found in fields irrigated with reclaimed water, and continual infusion, along with bioaccumulation properties, may result in significant bio-uptake and PPCP contamination in agricultural soils. This review attempts to summarize the literature concerning the fate and behavior of PPCPs in agricultural soils, as well as their adverse effects on soil organisms (including microorganisms and fauna), crops, and even humans via dietary consumption. Strategies and potential technologies for degrading or removing PPCPs from soils are addressed, along with the irrigation strategies and agricultural practices for minimizing PPCP transfer to crops and groundwater. Based on this review, we conclude that the agricultural risks of PPCPs associated with reclaimed water irrigation could be controlled under certain agro-ecological conditions. We suggest developing agro-ecosystem specific practices and regulations for reclaimed water irrigation on the basis of a systematic assessment and modeling analysis of the fate, transport, accumulation, and transformation of PPCPs in soil-crop systems.

KEY WORDS: reclaimed water irrigation, PPCPs, soil, cropland, plants



Agricultural risks of PPCPs

TOC Art

1. INTRODUCTION

Treated wastewater, popularly named reclaimed water or recycled water, is usually directly discharged into rivers, lakes, and oceans.[1] However, in order to meet the water demands of a growing population, increased food production, and urban development, reclaimed water is increasingly used as a sustainable water source for agricultural irrigation, especially in arid and semi-arid areas.[1-5] The percentage of irrigation with reclaimed water increases annually in many countries, such as Germany, the United States, Ireland, and China. [6-10] Thus, increasing attention is being paid to the potential risks of using reclaimed water irrigation, since reclaimed water may contain various emerging organic pollutants, such as pharmaceuticals and personal care products (termed PPCPs) (Figure 1).[11]

PPCPs include a diverse group of chemical substances, which encompass not only prescription drugs and over-the-counter drugs used to prevent or treat human and animal diseases, but also personal care products (such as disinfectants, fragrances, and sun-screens) and household chemical substances used in daily life.[11, 12] During the last decades, PPCPs have been extensively used throughout the world to improve the quality of human life.[11] For instance, in the United Kingdom, there are currently more than 3,000 individual pharmaceutical substances licensed for use.[13] The annual production of polycyclic musks, such as galaxolide and tonalide (used extensively in scented consumer products), was about 1,800 tons in Europe during the 1990s.[14] In China, more than 25,000 tons of antibiotics are consumed annually.[12, 15]

Myriad PPCP substances and their metabolites have been reported discharged into the sewage systems.[6, 16] Unfortunately, the concentrations of many of these emergent organic contaminants (e.g., hydrophilic compound carbamazepine) are only slightly reduced or even unchanged through current treatment processes.[6, 17-19] More than 80% of PPCPs are still detectable in the effluents of at least one municipal sewage treatment plant (STP) (Figure 1).[20] These chemicals could be subsequently released into agricultural soils through reclaimed water irrigation.[21, 22] Due to their very wide range of chemical and physical properties (e.g., chemical structure, aqueous solubility, octanol/water partition coefficient, and Henry's law constant), the removal efficiencies of PPCPs vary with treatment and environmental conditions.[16] It remains unclear how soon sewage treatment technologies could be effectively upgraded to reduce PPCPs in reclaimed water to a level of no harm to biological systems.[16] Based on crop irrigation experiments, Calderón-Preciado et al.[23] reported that the loading mass of the chemicals (including PPCPs) through reclaimed water irrigation ranged from 1.2 g/ha to 121.3 g/ha per crop cycle. Introduced PPCPs are strongly sorbed by soil particles and persistent in top soil (0~30 cm),[2, 24-26] whereas highly mobile chemicals have the potential to move into aquatic systems (such as groundwater and surface water).[12, 26-28] PPCPs are now frequently detected in reclaimed water, surface water, groundwater, and even drinking water as a direct or indirect result of reclaimed water utilization.[29]

The literature documents the persistence of numerous PPCPs, such as antibiotics,

analgesics/anti-inflammatory drugs, antiepileptics, and antiseptics, in agricultural soils at trace levels ranging from nanograms per kilogram up to grams per kilogram.[2, 6, 22, 28] For instance, the concentrations of carbamazepine in soil irrigated with reclaimed water were up to a level of 549 μg/kg dry soil,[2] while triclosan, used as antimicrobial agent, was found to be 16.7 μg/kg dry soil.[30] In spite of their low concentrations, PPCPs could induce multiple adverse effects on soil microbial populations and diversity.[31] In addition, PPCPs are potentially taken up by crops grown on the agricultural soils irrigated with reclaimed water.[32, 33] They can inhibit crop growth, leading to a decrease in crop production.[34] Some types of PPCPs can accumulate in the edible parts of crops, posing a significant threat to human health (e.g., disrupting human endocrine systems and inhibiting growth of human embryonic cells).[4, 33, 35-37]

In recent years, guidelines associated with PPCPs have been issued by the Europe Union, the United States, and other countries due to their potential environmental risks.[10, 21] Although the guidelines might be able to limit the environmental release of these chemicals, the effectiveness of the guidelines may fall short due to the lack of a systemic analysis of the occurrence, distribution, transformation, and mobility of various PPCPs and an assessment of their effects on an agro-system subject to reclaimed water irrigation. Currently, technologies and methods for effective removal of PPCPs from affected farmlands remain extremely limited. In view of the varying range of results reported on the retention, degradation, and impacts of PPCPs, here we present a review of their potential risks for crop production along with strategies and

technologies for minimizing their negative impacts while increasing irrigation with reclaimed water.

2. FATE AND BEHAVIOR OF PPCPS IN SOIL-CROP SYSTEMS

Figure 2 provides a summary of the possible behaviors of PPCPs in farmlands using reclaimed water irrigation as the main route for introducing PPCPs.[26] The PPCPs in soil could subsequently migrate into water systems (such as surface water, groundwater, and drinking water) and be taken up by plants and animals, thus threatening human health.

2.1 Soil and soil microorganisms

Several investigations described the persistence of PPCPs in arable land irrigated with reclaimed water.[6, 25] Almost all of the PPCP residuals in reclaimed water could be detected in the irrigated soils as shown in Table 1. PPCPs mostly exist in surface soil (0~30 cm),[2, 25] and their concentrations vary with irrigation seasons.[24] The fate and behaviors of these emergent contaminants in soil are complicated and unclear. A certain quantity of PPCPs discharged into soil through reclaimed water irrigation can be degraded or depleted in a short time through sorption, hydrolysis, photolysis, biodegradation, and mineralization.[16] Among these processes, sorption and biodegradation are considered the most important pathways for removal of PPCPs from agricultural soil, particularly for those resistant to photodegradation and/or hydrolysis.[28, 38]

Sorption of many PPCPs in soil, such as clofibric acid, ibuprofen, naproxen, triclosan, diclofenac, and bisphenol A, could be well described with the Freundlich equation.[27] The extent of PPCPs sorbed by soil particles mainly depends on their chemical characteristics, soil organic matter (SOM), soil texture, mineral type, metal oxides, ion exchange capacity, redox condition, and soil pH.[27, 38-41] In the case of gemfibrozil, the sorption capacity is positively related to SOM content.[39] As a result, gemfibrozil is adsorbed in texture-varying soils in a descending order of silt loam > sandy loam > sand.[28] However, the average soil sorption coefficient (k_d) of clofibric acid in four different soils (pH=7) showed a weak correlation with SOM content (R^2=0.0031). Xu et al.[27] inferred that this weak relation resulted from the low pK_a value (2.84) of clofibric acid, as organic acids in soils ($pH>pK_a$) was highly dissociated. Furthermore, the k_d values (0.99~121.88 L/kg) in the same soil varied with compounds with a decrease in the order of triclosan > propranolol > diclofenac > fluoxetine > carbamazepine > sulfamethazine. These results suggest a tendency of strong sorption and minimal mobility of some tested chemicals (e.g., triclosan) in the soil.[42]

To examine the influences of soil and chemical properties, Xu et al.[27] investigated the degradation of six PPCPs (clofibric acid, ibuprofen, naproxen, triclosan, diclofenac, and bisphenol A) in four U.S. agricultural soils irrigated with reclaimed water at a concentration of 100 μg/kg dry soil in the laboratory. Degradation of the compounds in soils generally followed the first-order exponential decay kinetics, with half-lives ranging from 0.81 d (bisphenol A) to

20.44 d (diclofenac). Their degradation rate constants (k) varied with soil characteristics. As an example, 17α-ethinylestradiol in the irrigated soil degraded faster under aerobic conditions (half-life = 1.8 d) than under anaerobic conditions (half-life = 3.0 d).[43] Under the aerobic conditions, the half-life of gemfibrozil was slightly shorter in sandy loam soil (17.8 d) than in silt loam soil (20.6 d).[28] Moreover, the k values of diclofenac were negatively related to SOM content (R^2=0.8).[27] But SOM likely played a dual role in PPCP degradation. Increase in SOM content promoted the degradation rate of ketoprofen, but continuous increases reduced the degradation because incremental adsorption of PPCPs decreased their bioavailability to soil microorganisms.[39] At present, the degradation rates of various PPCPs in soils are not available. Interestingly, Ying et al. [44] found faster aerobic degradation of triclosan (18 d) in comparison with triclocarban (108 d) in the loam soil. This difference is ascribed to a higher loading of triclocarban than triclosan, as well as their different chemical properties, such as faster aerobic biodegradation and easier photolysis of triclosan and stronger sorption of triclocarban ($\log K_{ow}$=6).[2, 44, 45] Besides, the chemical structure of PPCPs appears to have a great influence on their degradation as well. Taking alkylphenols as an example, 4-*n*-Nonylphenol under aerobic conditions was more prone to biodegrade than 4-*tert*-Octylphenol as a result of its straight side chain.[46] Such intricate behavior and associated transformation needs to be clarified in future studies.[6]

Microbial activity controls the degradation of PPCPs in soils in addition to soil

characteristics and PPCP chemistry.[27, 28, 47] Sterilization was found to prolong the half-lives of PPCPs by decreasing their degradation rates in agricultural soils.[27, 39] Ying et al.[44] examined the effect of redox conditions on the biodegradation of two antimicrobial agents (triclocarban and triclosan) in loam soil. The data from laboratory experiments indicated both triclocarban and triclosan with a concentration of 1 mg/kg dry soil could be degraded by microbial processes under aerobic conditions, but they persisted in the soil under anaerobic conditions. In addition, Xu et al.[27] found that increases in the concentrations of tested chemicals in soil from 0.1 mg/kg to 1 mg/kg inhibited the activity of degradation.

To sum up, the fate and transport of PPCPs introduced into soil through reclaimed water irrigation are highly dependent on their sorption and degradation in soil. These two processes are responsible for the fate of approximately 27~98% and 0~70% of the total mass of introduced PPCPs in sandy loam soil, respectively, according to the estimation of Chen et al.[24] Various information indicates that dissipation of PPCP compounds from soil to other media mainly occur through aqueous translocation and food chain scatter.[29]

2.2 Groundwater and surface water

Some PPCP compounds are unexpectedly difficult to mineralize or adsorb in a short time, such as carbamazepine (half-life >125 d).[25] They thus have the potential for long distance transport.[48] The PPCPs that are readily retarded in SOM-rich top soil may have enhanced mobility in

SOM-poor subsurface soil once they break through the top layer.[26] This SOM impact implies that intensive or continuous application of reclaimed water to SOM-low agricultural soils might enhance the transport of a certain type of PPCPs through soil aquifer, causing groundwater contamination.[6, 26, 30] One study demonstrated that gemfibrozil in reclaimed water could reach groundwater through agricultural irrigation.[28] Calculated retardation factors (R_F) of six PPCP chemical substances indicate that ibuprofen (with a low R_F value) has a high risk of being transferred downward into groundwater and other aquatic systems.[27] Figure 2 shows that field runoff and subsurface transport are the two major processes that determine the magnitude of environmental risks of PPCPs in farmland under reclaimed water irrigation.[49] Pedersen et al.[50] reported that agricultural irrigation with reclaimed water has the potential to discharge PPCPs into surface water through field runoff (Figure 2). They detected a variety of human pharmaceuticals (e.g., carbamazepine and gemfibrozil) and personal care product ingredients (e.g., insect repellent and polycyclic musks) in surface water. The PPCPs entering surface water could also be reversibly transferred into groundwater through infiltration.[51, 52] Many PPCPs released into aquatic systems may induce hazardous effects, such as cytotoxicity, on aquatic life at low concentrations.[53] Furthermore, considering that groundwater and surface water are the sources of drinking water,[54] these mobilized compounds may be ultimately introduced into human systems through dietary consumption (Figure 2).

To date, numerous PPCPs have been detected in groundwater below the sites of reclaimed

water irrigation (Table 1). The concentration of some PPCPs, such as gemfibrozil (6,860 ng/L), estriol (1,745 ng/L), and diatrizoate (9,600 ng/L), could reach up to a level of thousands of nanograms per liter in groundwater (Table 1). Nevertheless, the occurrence of PPCPs in groundwater below the application sites of reclaimed water is overall still less common than in surface soil, as reported in a limited number of investigations. Knowledge about the transformation products of PPCPs in groundwater is still missing. Currently, arguments (such as Ternes et al.[6] and Chen et al.[24]) exist concerning the potential mobility of PPCPs to groundwater. Chen et al.[24] estimated leaching losses of PPCPs that entered the soil did not exceed 1.5% of their total mass. These inconsistent findings or perspectives might be due to the varying impacts of surface soil properties on the behaviors of PPCPs as well as their uncertain degradation dynamics.

2.3 Volatilization and rain water

Although the concentrations of PPCPs in agricultural soils can be diluted during wetting events (e.g., rainfall), the fragrance chemicals could volatilize into the atmosphere when the soil gets dry (Figure 2).[55] Multiple PPCPs, such as bisphenol A, alkylphenols, alkylphenol ethoxylates, phthalates, flame retardants, and synthetic musk compounds, have been detected in rainwater samples with concentrations ranging from low ng/L to thousands of ng/L.[56] This finding suggests that these pollutants, which were previously volatilized into the atmosphere, could be brought

back into farmland and surface water via atmospheric deposition. Fortunately, many pharmaceuticals have low volatility, and their dissipation into the atmospheric environment would thus be rather limited.[57] Based on the HYDRUS-1D software, Chen et al.[24] analyzed the fate and transport of nine commonly detected PPCPs in reclaimed water. They found evaporative loss of all PPCPs in soils (sandy loam soil and loamy sand soil) was less than 1.5% in ten years.

2.4 Uptake by plants and other organisms

Numerous PPCPs, especially hydrophobic chemicals, have been detected in the plants grown on the reclaimed water irrigated fields,[32, 33, 58] suggesting moderately hydrophobic PPCPs released into farmlands are most likely to be taken up and dissipated into plants (Figure 2).[59] A greenhouse experiment conducted by Wu et al.[60] was used to investigate the uptake of three pharmaceuticals (carbamazepine, diphenhydramine, and fluoxetine) and two personal care products (triclosan and triclocarban) in soils by soybeans (*Glycine max [L.] Merr*). Carbamzepine, triclosan, and triclocarban were mainly accumulated into soybean roots and subsequently transferred into leaves and beans, but the accumulation and translocation of diphenhydramine and fluoxetine was limited.[60] Differences in plant uptake of PPCPs may be caused by their different physicochemical properties, such as hydrophobicity and extent of ionization.[42] Table 1 shows the physicochemical properties of various PPCPs. In comparison with previous studies, Carter et al.[42] investigated the fate and uptake of seven PPCPs in soil-plant

systems using radish (*Raphanus sativus*) and ryegrass (*Lolium perenne*) at relatively realistic exposure concentrations (no observed effect on plants at 1 mg/kg). Results of pot experiments showed that diclofenac with extensive ionization (>99%) in the test soil was highly concentrated in both soil and pore water but less dissipated in plants. There was up to 600 times less uptake of the large ionized diclofenac, fluoxetine, and propranolol (>99%) in the ryegrass, compared to the neutral carbamzepine (low $\log K_{ow}$ value). Uptake of neutral PPCPs in roots was positively related to $\log D_{ow}$ (pH corrected $\log K_{ow}$), whereas translocation from roots to leaves was negatively correlated with $\log D_{ow}$.[61] For instance, neutral triclosan and triclocarban with higher $\log D_{ow}$ values (4.74 and 4.90, respectively) likely contributed to their extensive accumulation in hydroponic plant roots (1.4~3.1 mg triclocarban/$kg_{dry\ weight}$; 3.2~5.6 mg triclosan/$kg_{dry\ weight}$) at a concentration of 0.5 μg/L, whereas the root uptake of acetaminophen might be negligible due to its low $\log D_{ow}$ (0.46).[61] The uptake of these PPCP compounds in the tested soil also varied with crop species (e.g., 52 μg carbamazepine/g dry radish, 3.3 μg carbamazepine/g dry ryegrass) due to their differences in lipid content and plant physiology (e.g., root growth, transpiration rate, and the size and shape of the leaf material).[42, 61] Furthermore, PPCP chemicals in irrigation water seemed to be more bioavailable for uptake and translocation than in land-applied biosolids.[60] Overall, the uptake of PPCPs by plants is a complex process and influenced by a combination of multiple factors, including soil properties, plant species, and PPCP chemistry (e.g., hydrophobicity and the extent of ionization).[42, 62, 63]

Existing studies have shown that PPCPs could be transferred into biological systems as a result of direct exposure of soil earthworms and microorganisms to reclaimed water during irrigation and secondary exposure experienced by mammals and birds via dietary consumption of PPCP-containing animals and plants (Figure 2).[4, 61, 64] According to average daily consumption of leafy vegetables (0.54 $g_{wet\ weight}/kg_{body\ weight}$-day) derived from the U.S. Environmental Protection Agency, Wu et al.[61] calculated the annual exposure of a 70-kg person to two levels of PPCPs (0.5 μg/L and 5 μg/L) through dietary absorption. The exposure ranged from 0.08 μg to 150 μg for lettuce and 0.04 μg to 350 μg for spinach cultivated in hydroponic solution. However, the factors influencing the uptake of PPCPs by non-plant organisms from reclaimed water are much less understood.[65]

3. IMPACTS OF PPCPS ON SOIL-CROP SYSTEMS

3.1 Soil microorganisms

Understanding the effects of PPCPs on terrestrial organisms, including soil organisms (e.g., microorganisms and fauna), crops, and humans, is rather critical but extremely limited.[66] The concentrations of PPCPs detected in farmlands are usually low. However, little is understood regarding their chronic effects on terrestrial organisms if they are sufficiently bioavailable and/or significantly bioaccumulated.[11, 16] A few studies demonstrate that PPCPs at trace levels exert adverse effects on soil microorganisms or fauna (e.g., destroy their population structure and

diversity). The results are mostly confined to antibiotic agents. For example, the addition of oxytetracycline hydrochloride and penicillin at 10 μg/g could reduce soil bacterial biomass.[67] The structure of soil microbial communities could be broken down by antibiotic agents.[68] Similarly, Harrow et al.[31] found that short-term exposure to triclosan not only influenced microbial population but also decreased microbial diversity, while the total number of heterotrophic microorganisms in soil irrigated with reclaimed water did not show significant change. PPCPs in soil may also potentially affect soil microbial activities (e.g., enzyme activities, nitrification, biodegradation, and soil respiration) and functional biodiversity.[66, 69, 70] For instance, Conkle and White[71] evidenced the ability of two antibiotics (ciprofloxacin and sulfamethoxazole) at environmentally relevant concentrations (150 μg/kg) to inhibit respiration. Antibiotic triclosan at more than 1 mg/kg in sandy soil can influence the nitrification and disturb the soil nitrogen cycle.[66] The toxic effects of PPCPs at environmentally relevant concentrations appear to be only detectable with chronic exposure due to their bioaccumulation properties. So, much higher concentrations than those detected in real soil environments are used in the majority of acute toxicity tests on soil microorganisms for better observation of their adverse effects in the short-term.

The microbial effect is determined by the stability and bioavailability of PPCPs. A study has shown that the sorption potentials of PPCPs (negatively correlated to the magnitude of impact) in soil could be used as an indicator of their bioavailability.[66] For instance, sulfamethoxazole with a

lower sorption potential (higher bioavailability) exerted larger influence on microbial activity in comparison to ciprofloxacin and tetracycline.[71] The biological impacts of PPCPs also depend on soil texture. For instance, soil respiration decreased by the addition of triclosan at 50 mg/kg to a clayey soil, whereas no similar influence was observed in a sandy soil.[66] These results suggest that the sorption alone is insufficient to indicate the difference in bioavailability of PPCPs in different types of soils. Accurate assessment of PPCPs' impact on soil microbial activity must consider soil conditions (e.g., organic carbon, clay, and aggregates) and the length of exposure time.

However, recent studies indicate that reclaimed water irrigation seemed not to bring undue ecological risk to agricultural soil microorganisms.[24] Investigation on paddy soil was performed by Liu et al.[69] and shows that the addition of triclosan increased the utilization of carbon sources and there was no adverse effect on the functional diversity of the soil microbial community. Triclosan obviously inhibited soil respiration at concentrations larger than 10 mg/kg dry soil and phosphatase activity at concentrations larger than 100 μg/kg dry soil in the initial two days, but the effect quickly declined afterward.[69] The analysis of antibiotic resistance (AR) and antibiotic resistance genes (ARG) in reclaimed water irrigated soils indicates that the overall levels of AR bacteria and ARG in soils were similar and sometimes even lower than in fresh water irrigated soils,[84] suggesting that massive resistant bacteria that enter the soils from the reclaimed water are not competitive for survival in their receiving soil and ARG does not apparently enhance soil

bacteria.

At present, most of studies focus on the short-time effects of PPCPs on microorganisms in reclaimed water irrigated soil. Understanding of the long-term influences of PPCPs on microorganisms is insufficient. The primary types of PPCPs studied for microbial effects are antibiotic agents. The microbial bioavailability and toxicity of other PPCPs at environmentally relevant concentrations have not been well addressed.[72]

3.2 Soil fauna

The majority of studies of the effects of PPCPs on animals are focused on aquatic life (e.g., bivalves and fish),[53, 73, 74] and few have been performed on soil fauna, such as earthworms, predatory mites, and springtails.[48] A series of toxicity experiments of triclosan were conducted to figure out the potential effects of PPCPs on soil fauna by Amorim et al.[58] using different invertebrates, such as *Eisenia andrei*, *Enchytraeus albidus*, and *Folsomia candida*. The results showed that triclosan at 0.6~7.0 mg/kg in soil could inhibit reproduction in the invertebrates. Among the three invertebrate species, earthworms (*E. andrei*) were most sensitive to triclosan.[58] Earthworms, a common soil species playing a crucial role in adjusting the soil's ecological function, account for 60~80% of the total soil biomass.[75] The potential harmfulness of PPCPs to soil earthworms has been addressed in a number of research studies. Lin et al.[76] analyzed biochemical responses, ecotoxicity, and potential genotoxicity of triclosan on earthworms

(*Eisenia fetida*). Their data show that the activity of antioxidative enzymes, such as catalase (CAT) and glutathione-S-transferase (GST), was inhibited at the highest tested dose of triclosan after prolonged exposure. The activities of CAT and GST reduced the levels of control to 47% and 33%, respectively. Additionally, the comet assay verified that triclosan treatments resulted in dose-dependent DNA damage of *E. fetida* after exposures of 7~14 d, suggesting a sublethal effect of triclosan on *E. fetida*.

Römbke et al.[77] investigated the chronic effects of a veterinary drug (ivermectin, an anthelminthic) on three invertebrate species, including earthworms (*E. fetia),* springtails (*F. candida*), and predatory mites (*Hypoaspis aculeifer*) at laboratory levels according to OECD (Organization for Economic CO-operation and Development) and ISO (International Organization for Standardization) protocols. The results showed that survival and reproduction of springtails (LC_{50}≥8.4 mg/kg dry soil; $NOEC_{repro}$=0.3 mg/kg dry soil) were significantly influenced, whereas the predatory mites (LC_{50}≥31.6 mg/kg dry soil; $NOEC_{repro}$=3.2 mg/kg dry soil) reacted less sensitively. With regard to the earthworm (LC_{50}≥10 mg/kg dry soil; $NOEC_{repro}$=2.5 mg/kg dry soil), its survival and reproduction were affected by the same order of magnitude as the predatory mites. These results imply that the effects of ivermectin on soil invertebrates, especially springtails, cannot be excluded in the assessment of the field risks of PPCPs.

3.3 Crops

Reclaimed water contains a large amount of nutrients necessary for plant growth like nitrogen and phosphorus.[78, 79] However, PPCP residuals in reclaimed water can be potentially taken up by crops if it is used for agricultural irrigation. The reclaimed water with trace levels of PPCPs could promote crop growth,[33, 34, 69, 80] but their accumulation in crops may also produce morphological and physiological effects to a certain extent.[81, 82] Young seedlings of plants are more accessible to PPCPs than mature ones.[83] For instance, bisphenol A at 10 mg/L and 50 mg/L could induce significant morphological anomalies while reducing seedling biomass of hydroponic crops (e.g., broad bean, tomato, and lettuce), though no inhibition of germination occurred at any dose of bisphenol A.[81] Triclosan at 10 mg/kg in a silt loam soil could distinctly inhibit root elongation of rice plants grown in a climate chamber.[69] Increasing the concentration of triclosan to 50 mg/kg significantly retarded root elongation and shoot growth of rice and cucumber plants.[69] When soybean seedlings cultured in 1/2 strength Hoagland solution in a greenhouse were exposed to bisphenol A at relatively high levels (e.g., >7.0 mg/L), the chlorophyll content significantly decreased, leading to a decline in photosynthesis.[34, 84] Retardation of crop growth can be ascribed to the physiological toxicity of bisphenol A. These experiments were mostly conducted under hydroponic conditions, and thereby the observed toxicity of PPCPs was likely higher compared with that in the soil, considering the sorption and biodegradation of PPCPs in soil. For instance, triclosan at 10 μg/L could decrease the root length

and surface area of wetland plants in a flow-through system,[85] whereas no effect on plants cultivated in silt loam soil were observed at 1 mg/kg (dry weight).[86] Further studies of the influence of PPCPs on plants should thus necessarily focus on the soil-plant systems under natural field conditions and at relevant environmental concentrations.[34, 81]

PPCPs also show potential genotoxicity effects on plants.[81] For instance, treatment with bisphenol A at 10 mg/L and 50 mg/L significantly increased the number of micronuclei in the root-tip cells of broad bean and tomato plants, indicating that bisphenol A has a clastogenic effect on crops.[81] Similarly, 0.005% bisphenol A could induce chromosomal aberration in the roots of *Allium cepa*, and an increase in exposure concentration (≥0.005%) remarkably decreased the value of the Mitotic Index (MI).[87] In addition, bisphenol A at 100 mg/L could derange interphase and mitotic Microtube (MT) arrays.[82] Since MT arrays are the basis of plant cell division and morphogenesis, interference of MT arrays by bisphenol A could ultimately result in negative effects on plant growth (e.g., inhibiting cell division and elongation).[81, 82] Meantime, an increase in the number of macrotubes was observed during the exposure to bisphenol A.[82] This increase might be a defensive response intrinsically exhibited in plants, though they eventually could not withstand the toxic effect. Cell damage may potentially affect the whole organism and even lead to its death.[87] Unfortunately, current acute toxic tests of plants are mainly focused on concentrations higher than those detected in real field soil. The adoption of unrealistic concentrations mostly aims to observe significant effects in the short term and test the high-level

risks of the bioaccumulation of PPCPs in plants under continuous irrigation of reclaimed water. Therefore, caution must be paid to the use of data obtained at environmentally irrelevant concentrations. The chronic genotoxicity of PPCPs and their metabolites on plant cells under real environmental scenarios should be the focus of future studies.

3.4 Uncertainty of agriculturally derived PPCP risks to human health

Pharmaceuticals are specifically designed to target certain metabolic and molecular pathways in humans and animals. However, they usually have serious side effects as well.[29] PPCPs in soils could be taken up by crops and subsequently transferred to humans through dietary consumption.[4, 22, 61] A few studies have reported that the consumption of the edible parts of crops grown on soils irrigated with reclaimed water adversely effected human health.[4, 35] According to Calderón-Preciado's estimation,[35] consumption of 400 g fresh weight per day of the studied crops, like carrots, lettuce, and green beans, could lead to an average daily intake of 0.4~20 μg of each target compound. It is reported that low concentrations of PPCPs in humans may disrupt metabolic systems and hormone homeostasis.[88] However, recent reports indicate that even the highest estimates of annual exposure to PPCPs by consuming leafy vegetables could not reach the quantity of a single medical dose (typically in the range of 20~200 mg).[4, 61] Therefore, in some cases, dietary intake of PPCPs by humans might not induce adverse endocrine activity.[4, 61] Further, approximately 70~80% of some PPCPs (e.g., the psychiatric drug oxazepam) absorbed

into bodies can be transformed and excreted through the urine and feces.[89] Nevertheless, worth noting is that a certain quantity of these compounds may be persistent due to their bioaccumulation property and continual infusion, in spite of the low level of PPCPs observed in a short time.[90] Adults appear not to be significantly impacted by short-term acute exposure to PPCPs/EDCs (endocrine disrupting compounds) in foods, whereas long-term chronic exposure even at extremely low concentrations might be harmful. Furthermore, PPCPs like triclosan have been found in human plasma and milk, suggesting a potential risk to infants during lactation.[88] Fetuses *in utero* and young children are especially susceptible to the effects of these pollutants. Therefore, large acute doses or chronic exposure to PPCPs may affect children much more than adults. Thus far, neither the toxicity effects of PPCP metabolites nor the long-term effects of PPCPs on humans through dietary consumption have been clarified. A biological test on a single PPCP compound cannot reflect the interactive effects of various PPCPs on human health.[4] The health risk caused by the toxicity of the mixture of different PPCPs needs to be assessed, based on real scenarios (e.g., crop production/consumption and transport pathways) in a systematic manner.

4. STRATEGIES FOR REDUCING PPCPS IN SOIL-CROP SYSTEMS

In the past decades, wastewater treatment technologies have advanced significantly, including activated carbon,[91] magnetic nanoparticles coated zeolite adsorption,[92] reverse osmosis,[93]

ozonation and advanced oxidation processes,[93, 94] membrane filtration,[93, 95] and constructed wetlands.[17, 37] However, these technologies are still not effective at removing all PPCPs from the waste water. In view of the increasing demand for reclaimed water for crop irrigation, scenario-based management strategies are needed for reducing the potential risks of PPCPs.

There are two general strategies for mitigation of PPCPs in soil or their availability to crops. One is simply to decrease the concentrations of PPCPs before the reclaimed water is irrigated into agricultural soil. The other is to increase the degradation of PPCPs in soil. For the first strategy, a variety of techniques, such as biofilm systems and constructed wetlands, have been adopted in series with the existing technologies in STPs. In a laboratory-scale sand column experiment, Onesios et al.[96] observed that biofilm-based systems (e.g. soil aquifer treatment and slow sand filtration) have the potential to effectively remove PPCPs from reclaimed water. The removal rates of ten PPCPs (biphenylol, p-chloro-m-cresol, chlorophene, 5-fluorouracil, gemfibrozil, ibuprofen, ketoprofen, naproxen, triclosan, and valproic acid) could reach 95%. Bekele et al.[97] infiltrated reclaimed water through a 9 m-thick calcareous vadose zone in a field trial. They found a significant removal of residual oxazepam and temazepam from reclaimed water except for carbamazepine. Reyes-Contreras et al.[17] discharged reclaimed water directly into two constructed wetlands (a surface flow wetland and a subsurface flow wetland) in series. The overall removal rate of PPCPs was more than 70%. A study by Reyes-Contreras et al.[17] demonstrated that the removal rates of some PPCPs like carbamazepine varied substantially with

the season, whereas phthalate esters and fragrance substances were steady. These investigations, along with many not described here, suggest that current technologies, such as biofilm systems and artificial wetlands, could still not meet the requirement of complete removal of PPCPs from reclaimed water.

The second strategy involves a broad range of agricultural practices that have the potential to lower the amount of PPCPs and/or their bioavailability. Some agricultural practice, such as SOM accrual and reclaimed water application along with biosolids, can effectively retard the transport of PPCPs in soil to reduce their exposure to terrestrial organisms.[98] For example, Shenker et al.[99] found a negative correlation between the concentrations of carbamazepine in cucumber fruits and leaves and SOM content in the soil irrigated with reclaimed water. Borgman et al.[100] reported that biosolid application on farmland with reclaimed water could increase the retardation of pharmaceutical compounds, but biosolids may simultaneously bring other potentially harmful materials into the soil, including PPCPs. To sum up, a system strategy, including pre-filtration and on-site degradation, might be a wise choice for minimizing the level of PPCPs in agricultural soil before PPCP-effective wastewater treatment technologies become available. The agricultural risks of reclaimed water irrigation could be reduced by 1) avoiding utilization of the reclaimed water that is produced in the seasons with high releases of PPCPs, 2) avoiding adoption of irrigation methods that could increase direct contact of PPCP-containing reclaimed water with the edible parts of crop, such as spray irrigation for non-root vegetables

(e.g., watermelon, cabbage, and celery) and drip irrigation for root vegetables (sweet potato, carrots, and beets), 3) applying the reclaimed water to SOM-rich soils or those with advance application of manure, 4) applying the reclaimed water along with inorganic fertilizers to promote microbial degradation, and 5) adding PPCP-adsorptive nano-fluids to the reclaimed water. These strategies could be integrated into a comprehensive practice, but a life-cycle assessment is necessary for achieving the highest efficiency in PPCP mitigation.

5. CLOSING REMARKS AND FUTURE DIRECTIONS

Our analysis reveals that PPCPs introduced into soil via irrigation are mainly accumulated in surface soil, and certain types of PPCPs could be leached into groundwater under intensive or long-term irrigation. The residual PPCPs in soil could negatively affect the functions of soil organisms (microorganisms and fauna), crops, and even humans. However, a short-term harmful effect requires relatively high concentrations, bioavailability, and/or specific toxicity (e.g., receptor-mediated effects). The majority of studies thus-far have been focused on potential acute effects, but PPCPs at trace levels in soil are more likely to cause chronic effects. The chronic effects at environmentally relevant concentrations on terrestrial organisms (including microorganisms, fauna, and crops) need a systematic study in relation to the potential transformation of PPCPs. It is worth noting that the toxic effects of some PPCPs, such as antibiotic triclosan, on plants cultivated in solution could be approximately 100 times higher than

those in soil.[85, 86] This suggests that the environmental risks of PPCPs depend on specific environmental conditions (e.g., hydroponic and soil environments). Multiple mechanisms are responsible for the toxicity reduction in soil relative to solution, such as microbial degradation and interfacial adsorption of PPCPs. Currently, data are insufficient to clarify the contribution of individual soil component (e.g., minerals and organic matter) to the change in PPCP toxicity. Furthermore, the majority of studies have addressed the parent compounds of PPCPs, but very few have considered the nature and amount of unidentifiable transformation products, which might persist in soil with increased or decreased biotoxicity.[101]

The extent of groundwater pollution by PPCPs depends on not only soil properties (e.g., organic matter, clay content, and soil texture) but also the chemical properties of PPCPs (e.g., hydrophobicity and half-life). There are increasing arguments on the leaching risks of various PPCPs from soil to groundwater. Their clarification requires quantifying the leaching potentials of PPCP compounds with respect to their different affinity on soil or sediments and degradation rate during transport. For instance, compounds with longer half-life (e.g., carbamazepine) are more readily to pollute the groundwater system due to their accumulation in soil and continued downward migration. However, the factors and mechanisms controlling PPCP mobility from soil to groundwater have not been sufficiently addressed in the context of practical scenarios. The potential ecotoxicological effects of PPCPs on groundwater at environmentally relevant levels should be examined using microbial biomarkers and considering anaerobic degradation and

colloid-mediated transport.

Currently, considerable uncertainty exists regarding the potential risks of PPCPs and their transformation products to agricultural and environmental health. The incomplete data, particularly on the toxicity and environmental fate of transformation products, may increase the inaccuracy of risk assessment of reclaimed water irrigation. In view of the increasing irrigation with reclaimed water, conservative practices (such as low-pollution irrigation and low-uptake crop management) are urgently needed to minimize the potential threats of PPCPs on the environmental health. Current regulations for reclaimed water irrigation, such as threshold concentrations of PPCPs, should be amended based on real scenario investigations on the fate and impact of PPCPs in different parts of soil-crop systems.

In closing, human and ecological demands for water resources require a substantial increase in reclaimed water irrigation for agriculture at no risk to food quality and human health. This goal is very likely achievable if we could make clear what, where, when, and how the reclaimed water should be applied to soil-crop systems at both technical and policy levels.

ACKNOWLEDGEMENTS

This work was financially supported by the strategic priority research program of the Chinese Academy of Sciences (Grant No. XDB14020204).

REFERENCES

[1] Plumlee, M. H., Gurr, C. J., Reinhard, M. (2012). Recycled water for stream flow augmentation: benefits, challenges, and the presence of wastewater-derived organic compounds. *Science of the Total Environment,* 438, 541-548.

[2] Kinney, C. A., Furlong, E. T., Werner, S. L., Cahill, J. D. (2006). Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. *Environmental Toxicology and Chemistry,* 25, 317-326.

[3] Hamilton, A. J., Stagnitti, F., Xiong, X., Kreidl, S. L., Benke, K. K., Maher, P. (2007). Wastewater Irrigation: The State of Play. *Vadose Zone Journal,* 6, 823-840.

[4] Dodgen, L. K., Li, J., Parker, D., Gan, J. J. (2013). Uptake and accumulation of four PPCP/EDCs in two leafy vegetables. *Environmental Pollution* 182, 150-156.

[5] Chen, W., Lu, S., Jiao, W., Wang, M., Chang, A. C. (2013). Reclaimed water: A safe irrigation water source? *Environmental Development,* 8, 74-83.

[6] Ternes, T. A., Bonerz, M., Herrmann, N., Teiser, B., Andersen, H. R. (2007). Irrigation of treated wastewater in Braunschweig, Germany: an option to remove pharmaceuticals and musk fragrances. *Chemosphere,* 66, 894-904.

[7] Davis, M. L., Cornwell, D. F. (1998). *Itroduction to Environmental Engineering (3rd Ed)*. New York :McGraw-Hill Higher Education.

[8] Anderson, P., Denslow, N., Drewes, J. E., Olivieri, A., Schlenk, D., Snyder, S. (2010). *Final*

Report Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water; State Water Resources Control Board: California.

[9] Avnimelech, Y. (1993). Irrigation with sewage effluents: the Israeli experience. *Environmental Science & Technology,* 27, 1278-1281.

[10] Chang, D., Ma, Z. (2012). Wastewater reclamation and reuse in Beijing: Influence factors and policy implications. *Desalination,* 297, 72-78.

[11] Daughton, C. G., Ternes, T. A. (1999). Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environmental Health Perspectives,* 107, 907-938.

[12] Bu, Q., Wang, B., Huang, J., Deng, S., Yu, G. (2013). Pharmaceuticals and personal care products in the aquatic environment in China: A review. *Journal of Hazardous Materials,* 262, 189-211.

[13] Ayscough, N. J., Fawell, J., Franklin, G., Young W. (2000). *Review of Human Pharmaceuticals in the Environment*; UK Environmental Agency, Bristol.

[14] Rimkus, G. G. (1999). Polycyclic musk fragrances in the aquatic environment. *Toxicology Letters,* 111, 37-56.

[15] Xu, W. H., Zhang, G., Zou, S. C., Li, X. D., Liu, Y. C. (2007). Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry. *Environmental Pollution,* 145, 672-679.

[16] Jones, O., Voulvoulis, N., Lester, J. (2001). Human pharmaceuticals in the aquatic environment a review. *Environmental Technology,* 22, 1383-1394.

[17] Reyes-Contreras, C., Matamoros, V., Ruiz, I., Soto, M., Bayona, J. M. (2011). Evaluation of PPCPs removal in a combined anaerobic digester-constructed wetland pilot plant treating urban wastewater. *Chemosphere*, 84, 1200-1207.

[18] Tauxe-Wuersch, A., De Alencastro, L. F., Grandjean, D., Tarradellas, J. (2005). Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment. *Water Reaserch,* 39, 1761-1772.

[19] Andreozzi, R., Marotta, R., Pinto, G., Pollio, A. (2002). Carbamazepine in water persistence in the environment, ozonation treatment and preliminary assessment on algal toxicity. *Water Reaserch,* 36, 2869-2877.

[20] Ternes, T. A. (1998). Occurrence of drugs in German sewage treatment plants and rivers. *Water Research,* 32, 3245-3260.

[21] Esplugas, S., Bila, D. M., Krause, L. G., Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials*, 149, 631-642.

[22] Karnjanapiboonwong, A., Suski, J. G., Shah, A. A., Cai, Q., Morse, A. N., Anderson, T. A. (2011). Occurrence of PPCPs at a Wastewater Treatment Plant and in Soil and Groundwater

at a Land Application Site. *Water, Air, & Soil Pollution,* 216, 257-273.

[23] Calderón-Preciado, D., Jiménez-Cartagena, C., Matamoros, V., Bayona, J. (2011). Screening of 47 organic microcontaminants in agricultural irrigation waters and their soil loading. *Water research,* 45, 221-231.

[24] Chen, W., Xu, J., Lu, S., Jiao, W., Wu, L., Chang, A. C. (2013). Fates and transport of PPCPs in soil receiving reclaimed water irrigation. *Chemosphere,* 93, 2621-2630.

[25] Durán-Álvarez, J. C., Prado-Pano, B., Jiménez-Cisneros, B. (2012). Sorption and desorption of carbamazepine, naproxen and triclosan in a soil irrigated with raw wastewater: Estimation of the sorption parameters by considering the initial mass of the compounds in the soil. *Chemosphere,* 88, 84-90.

[26] Chefetz, B., Mualem, T., Ben-Ari, J. (2008). Sorption and mobility of pharmaceutical compounds in soil irrigated with reclaimed wastewater. *Chemosphere,* 73, 1335-1343.

[27] Xu, J., Wu, L., Chang, A. C. (2009). Degradation and adsorption of selected pharmaceuticals and personal care products (PPCPs) in agricultural soils. *Chemosphere*, 77, 1299-1305.

[28] Fang, Y., Karnjanapiboonwong, A., Chase, D. A., Wang, J., Morse, A. N., Anderson, T. A. (2012). Occurrence, fate, and persistence of gemfibrozil in water and soil. *Environmental Toxicology and Chemistry,* 31, 550-555.

[29] Fent, K., Weston, A. A., Caminada, D. (2006). Ecotoxicology of human pharmaceuticals.

Aquatic toxicology, 76, 122-159.

[30] Gibson, R., Duran-Alvarez, J. C., Estrada, K. L., Chavez, A., Jimenez Cisneros, B. (2010). Accumulation and leaching potential of some pharmaceuticals and potential endocrine disruptors in soils irrigated with wastewater in the Tula Valley, Mexico. *Chemosphere,* 81, 1437-1445.

[31] Harrow, D. I., Felker, J. M., Baker, K. H. (2011). Impacts of Triclosan in Greywater on Soil Microorganisms. *Applied and Environmental Soil Science*, 2011, 1-8.

[32] Herklotz, P. A., Gurung, P., Vanden Heuvel, B., Kinney, C. A. (2010). Uptake of human pharmaceuticals by plants grown under hydroponic conditions. *Chemosphere,* 78, 1416-1421.

[33] Karnjanapiboonwong, A., Chase, D. A., Cañas, J. E., Jackson, W. A., Maul, J. D., Morse, A. N., Anderson, T. A. (2011). Uptake of 17 α-ethynylestradiol and triclosan in pinto bean, *Phaseolus vulgaris*. *Ecotoxicology and Environmental Safety,* 74, 1336-1342.

[34] Qiu, Z., Wang, L., Zhou, Q. (2013). Effects of bisphenol A on growth, photosynthesis and chlorophyll fluorescence in above-ground organs of soybean seedlings. *Chemosphere,* 90, 1274-1280.

[35] Calderón-Preciado, D., Matamoros, V., Savé, R., Muñoz, P., Biel, C., Bayona, J. (2013). Uptake of microcontaminants by crops irrigated with reclaimed water and groundwater under real field greenhouse conditions. *Environmental science and pollution research*

international, 20, 3629-3638.

[36] Ashton, D., Hilton, M., Thomas, K. V. (2004). Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. *Science of the Total Environment*, 333, 167-184.

[37] Zhang, D., Gersberg, R. M., Ng, W. J., Tan, S. K. (2014). Removal of pharmaceuticals and personal care products in aquatic plant-based systems: A review. *Environmental Pollution,* 184, 620-639.

[38] Estevez, E., Hernandez-Moreno, J. M., Fernandez-Vera, J. R., Palacios-Diaz, M. P. (2014). Ibuprofen adsorption in four agricultural volcanic soils. *Science of the Total Environment,* 468-469C, 406-414.

[39] Xu, J., Wu, L., Chen, W., Chang, A. C. (2009). Adsorption and degradation of ketoprofen in soils. *Journal of Environmental Quality,* 38, 1177-1182.

[40] Drillia, P., Stamatelatou, K., Lyberatos, G. (2005). Fate and mobility of pharmaceuticals in solid matrices. *Chemosphere,* 60, 1034-1044.

[41] Balogh, T., Revitt, D. M., Jones, H., Lundy, L. (2011). *Factors influencing the infiltration of pharmaceuticals through soils*, 12th International Conference on Urban Drainage: Porto Alegre/Brazil.

[42] Carter, L. J., Harris, E., Williams, M., Ryan, J. J., Kookana, R. S., Boxall, A. B. (2014). Fate and uptake of pharmaceuticals in soil-plant systems. *Journal of Agricultural and Food*

Chemistry, 62, 816-825.

[43] Carr, D. L., Morse, A. N., Zak, J. C., Anderson, T. A. (2010). Microbially mediated degradation of common pharmaceuticals and personal care products in soil under aerobic and reduced oxygen conditions. *Water, Air, & Soil Pollution*, 216, 633-642.

[44] Ying, G. G., Yu, X. Y., Kookana, R. S. (2007). Biological degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modelling. *Environmental Pollution*, 150, 300-305.

[45] Cha, J., Cupples, A. M. (2009). Detection of the antimicrobials triclocarban and triclosan in agricultural soils following land application of municipal biosolids. *Water Research,* 43, 2522-2530.

[46] Ying, G. G., Kookana, R. S. (2005). Sorption and degradation of estrogen-like-endocrine disrupting chemicals in soil. *Environmental Toxicology and Chemistry,* 24, 2640-2645.

[47] Lin, K., Gan, J. (2011). Sorption and degradation of wastewater-associated non-steroidal anti-inflammatory drugs and antibiotics in soils. *Chemosphere,* 83, 240-246.

[48] Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P., Ingerslev, F., Holten Lützhøft, H., Jørgensen, S. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment-A review. *Chemosphere,* 36, 357-393.

[49] Sangsupan, H. A., Radcliffe, D. E., Hartel, P. G., Jenkins, M. B., Vencill, W. K., Cabrera, M. L. (2006). Sorption and transport of 17 β-estradiol and testosterone in undisturbed soil

columns. *Journal of Environmental Quality,* 35, 2261-2272.

[50] Pedersen, J. A., Soliman, M., Suffet, I. (2005). Human pharmaceuticals, hormones, and personal care product ingredients in runoff from agricultural fields irrigated with treated wastewater. *Journal of Agricultural and Food Chemistry,* 53, 1625-1632.

[51] Lapworth, D., Gooddy, D., Allen, D., Old, G. (2009). Understanding groundwater, surface water, and hyporheic zone biogeochemical processes in a Chalk catchment using fluorescence properties of dissolved and colloidal organic matter. *Journal of Geophysical Research: Biogeosciences (2005–2012)*, 114.

[52] Lapworth, D. J., Baran, N., Stuart, M. E., Ward, R. S. (2012). Emerging organic contaminants in groundwater: A review of sources, fate and occurrence. *Environmental Pollution*, 163, 287-303.

[53] Schnell, S., Bols, N. C., Barata, C., Porte, C. (2009). Single and combined toxicity of pharmaceuticals and personal care products (PPCPs) on the rainbow trout liver cell line RTL-W1. *Aquatic toxicology*, 93, 244-252.

[54] Alder, A., McArdell, C., Golet, E., Kohler, H. P., Molnar, E., Thi, N. A. P., Siegrist, H., Suter, M. F., Giger, W., (2004). *Environmental exposure of antibiotics in wastewaters, sewage sludges and surface waters in Switzerland*. Springer.

[55] Zhang, X., Brar, S. K., Yan, S., Tyagi, R. D., Surampalli, R. Y. (2013). Fate and transport of fragrance materials in principal environmental sinks. *Chemosphere,* 93, 857-869.

[56] Peters, R. J., Beeltje, H., Van Delft, R. J. (2008). Xeno-estrogenic compounds in precipitation. *Journal of Environmental Monitoring,* 10, 760-769.

[57] Liu, J. L., Wong, M. H. (2013). Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China. *Environment international,* 59, 208-224.

[58] Amorim, M. J., Oliveira, E., Soares, A. M., Scott-Fordsmand, J. J. (2010). Predicted no effect concentration (PNEC) for triclosan to terrestrial species (invertebrates and plants). *Environment international,* 36, 338-343.

[59] Dietz, A. C., Schnoor, J. L. (2001). Advances in phytoremediation. *Environmental Health Perspectives,* 109, 163-168.

[60] Wu, C., Spongberg, A. L., Witter, J. D., Fang, M., Czajkowski, K. P. (2010). Uptake of pharmaceutical and personal care products by soybean plants from soils applied with biosolids and irrigated with contaminated water. *Environmental Science & Technology,* 44, 6157-6161.

[61] Wu, X., Ernst, F., Conkle, J. L., Gan, J. (2013). Comparative uptake and translocation of pharmaceutical and personal care products (PPCPs) by common vegetables. *Environment international,* 60C, 15-22.

[62] Briggs, G. G., Bromilow, R. H., Evans, A. A. (1982). Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. *Pesticide Science,* 13, 495-504.

[63] Pilon-Smits, E. (2005). Phytoremediation. *Annual Review of Plant Biology,* 56, 15-39.

[64] Reiss, R., Lewis, G., Griffin, J. (2009). An ecological risk assessment for triclosan in the terrestrial environment. *Environmental Toxicology and Chemistry,* 28, 1546-1556.

[65] Boxall, A. B., Rudd, M. A., Brooks, B. W., Caldwell, D. J., Choi, K., Hickmann, S., Innes, E., Ostapyk, K., Staveley, J. P., Verslycke, T. (2012). Pharmaceuticals and personal care products in the environment: what are the big questions? *Environmental Health Perspectives*, 120, 1221-1229.

[66] Waller, N. J., Kookana, R. S. (2009). Effect of triclosan on microbial activity in Australian soils. *Envrionmental Toxicology and Chemistry,* 28, 65-70.

[67] Colinas, C., Ingham, E., Molina, R. (1994). Population responses of target and non-target forest soil organisms to selected biocides. *Soil Biology and Biochemistry,* 26, 41-47.

[68] Westergaard, K., Müller, A., Christensen, S., Bloem, J., Sørensen, S. (2001). Effects of tylosin as a disturbance on the soil microbial community. *Soil Biology and Biochemistry*, 33, 2061-2071.

[69] Liu, F., Ying, G. G., Yang, L. H., Zhou, Q. X. (2009). Terrestrial ecotoxicological effects of the antimicrobial agent triclosan. *Ecotoxicology and Environmental Safety,* 72, 86-92.

[70] Girardi, C., Greve, J., Lamshoft, M., Fetzer, I., Miltner, A., Schaffer, A., Kastner, M. (2011). Biodegradation of ciprofloxacin in water and soil and its effects on the microbial communities. *Journal of Hazardous Materials*, 198, 22-30.

[71] Conkle, J. L., White, J. R. (2012). An initial screening of antibiotic effects on microbial respiration in wetland soils. *Journal of Environmental Science and Health, Part A,* 47, 1381-1390.

[72] Thiele-Bruhn, S., Beck, I. C. (2005). Effects of sulfonamide and tetracycline antibiotics on soil microbial activity and microbial biomass. *Chemosphere,* 59, 457-465.

[73] Gagné, F., Blaise, C., Fournier, M., Hansen, P. D. (2006). Effects of selected pharmaceutical products on phagocytic activity in Elliptio complanata mussels. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology,* 143, 179-186.

[74] Gagné, F., Blaise, C., Andre, C. (2006). Occurrence of pharmaceutical products in a municipal effluent and toxicity to rainbow trout (*Oncorhynchus mykiss*) hepatocytes. *Ecotoxicology and Environmental Safety,* 64, 329-336.

[75] Li, X. Y., Luo, Y. R., Yun, M. X., Wang, J., Wang, J. J. (2010). Effects of 1-methyl-3-octylimidazolium bromide on the anti-oxidant system of earthworm. *Chemosphere,* 78, 853-858.

[76] Lin, D., Zhou, Q., Xie, X., Liu, Y. (2010). Potential biochemical and genetic toxicity of triclosan as an emerging pollutant on earthworms (*Eisenia fetida*). *Chemosphere,* 81, 1328-1333.

[77] Römbke, J., Krogh, K. A., Moser, T., Scheffczyk, A., Liebig, M. (2010). Effects of the veterinary pharmaceutical ivermectin on soil invertebrates in laboratory tests. *Archives of*

environmental contamination and toxicology, 58, 332-340.

[78] Feigin, A., Vaisman, I., Bielorai, H. (1984). Drip irrigation of cotton with treated municipal effluents: II. Nutrient availability in soil. *Journal of Environmental Quality,* 13, 234-238.

[79] Vaisman, I., Shalhevet, J., Kipnis, T., Feigin, A. (1981). Reducing ground-water pollution from municipal waste-water irrigation of rhodes grass grown on sand dunes. *Journal of Environmental Quality,* 10, 434-439.

[80] Shore, L. S., Kapulnik, Y., Ben-Dor, B., Fridman, Y., Wininger, S., Shemesh, M. (1992). Effects of estrone and 17 β-estradiol on vegetative growth of *Medicago sativa. Physiologia Plantarum,* 84, 217-222.

[81] Ferrara, G., Loffredo, E., Senesi, N. (2006). Phytotoxic, clastogenic and bioaccumulation effects of the environmental endocrine disruptor bisphenol A in various crops grown hydroponically. *Planta,* 223, 910-916.

[82] Adamakis, I. D., Panteris, E., Cherianidou, A., Eleftheriou, E. P. (2013). Effects of bisphenol A on the microtubule arrays in root meristematic cells of *Pisum sativum* L. *Mutation research,* 750, 111-120.

[83] Wei, X., Wu, S. C., Nie, X. P., Yediler, A., Wong, M. H. (2009). The effects of residual tetracycline on soil enzymatic activities and plant growth. *Journal of Environmental Science and Health, Part B,* 44, 461-471.

[84] Chia, T. F., He, J. (1999). Photosynthetic capacity in *Oncidium* (Orchidaceae) plants after

virus eradication. *Environmental and Experimental Botany,* 42, 11-16.

[85] Stevens, K. J., Kim, S. Y., Adhikari, S., Vadapalli, V., Venables, B. J. (2009). Effects of triclosan on seed germination and seedling development of three wetland plants: *Sesbania herbacea*, *Eclipta prostrata*, and *Bidens frondosa*. *Environmental toxicology and chemistry,* 28, 2598-2609.

[86] Liu, F., Ying, G. G., Tao, R., Zhao, J. L., Yang, J. F., Zhao, L. F. (2009). Effects of six selected antibiotics on plant growth and soil microbial and enzymatic activities. *Environmental Pollution*, 157, 1636-1642.

[87] Jadhav, V., Jadhav, A., Chandagade, C., Raut, P. (2012). Genotoxicity of bisphenol A on root meristem cells of *Allium cepa*: a cytogenetic approach. *Asian Journal of Water, Environment and Pollution*, 9, 39-43.

[88] Allmyr, M., Adolfsson-Erici, M., McLachlan, M. S., Sandborgh-Englund, G. (2006). Triclosan in plasma and milk from Swedish nursing mothers and their exposure via personal care products. *Science of the Total Environment*, 372, 87-93.

[89] Carballa, M., Omil, F., Lema, J. M. (2008). Comparison of predicted and measured concentrations of selected pharmaceuticals, fragrances and hormones in Spanish sewage. *Chemosphere*, 72, 1118-1123.

[90] Mustafa, M., Wondimu, B., Hultenby, K., Yucel-Lindberg, T., Modéer, T. (2003). Uptake, distribution and release of ^{14}C-triclosan in human gingival fibroblasts. *Journal of*

Pharmaceutical Sciences, 92, 1648-1653.

[91] Delgado, L. F., Charles, P., Glucina, K., Morlay, C. (2012). The removal of endocrine disrupting compounds, pharmaceutically activated compounds and cyanobacterial toxins during drinking water preparation using activated carbon--a review. *Science of the Total Environment,* 435, 509-525.

[92] Salem Attia, T. M., Hu, X. L., Qiang, Y. D. (2013). Synthesized magnetic nanoparticles coated zeolite for the adsorption of pharmaceutical compounds from aqueous solution using batch and column studies. *Chemosphere,* 93, 2076-2085.

[93] Lee, C. O., Howe, K. J., Thomson, B. M. (2012). Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. *Water Research,* 46, 1005-1014.

[94] Ternes, T. A., Stüber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M., Teiser, B. (2003). Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Research,* 37, 1976-1982.

[95] Snyder, S. A., Wert, E., Lei, H. D., Westerhoff, P., Yoon, Y. (2007). *Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes,* American Water Works Association Research Foundation (AWWARF): Denver, Colorado, USA

[96] Onesios, K. M., Bouwer, E. J. (2012). Biological removal of pharmaceuticals and personal care products during laboratory soil aquifer treatment simulation with different primary

substrate concentrations. *Water Research,* 46, 2365-2375.

[97] Bekele, E., Toze, S., Patterson, B., Higginson, S. (2011). Managed aquifer recharge of treated wastwater: water quality changes resulting from infiltration through the vadose zone. *Water Research*, 45, 5764-5772.

[98] Unold, M., Kasteel, R., Groeneweg, J., Vereecken, H. (2009). Transport and transformation of sulfadiazine in soil columns packed with a silty loam and a loamy sand. *Journal of Contaminant Hydrology,* 103, 38-47.

[99] Shenker, M., Harush, D., Ben-Ari, J., Chefetz, B. (2011). Uptake of carbamazepine by cucumber plants--a case study related to irrigation with reclaimed wastewater. *Chemosphere*, 82, 905-910.

[100] Borgman, O., Chefetz, B. (2013). Combined effects of biosolids application and irrigation with reclaimed wastewater on transport of pharmaceutical compounds in arable soils. *Water Research,* 47, 3431-3443.

[101] Bedoux, G., Roig, B., Thomas, O., Dupont, V., Bot, B. L. (2012) Occurrence and toxicity of antimicrobial triclosan and by-products in the environment. *Environmental science and pollution research interantional*, 19, 1044-1065.

[102] Nakada, N., Tanishima, T., Shinohara, H., Kiri, K., Takada, H. (2006). Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. *Water Research,* 40, 3297-3303.

[103] Wang, Y., Hu, W., Cao, Z., Fu, X., Zhu, T. (2005). Occurrence of endocrine-disrupting compounds in reclaimed water from Tianjin, China. *Analytical and bioanalytical chemistry,* 383, 857-863.

[104] Vieno, N., Tuhkanen, T., Kronberg, L. (2007). Elimination of pharmaceuticals in sewage treatment plants in Finland. *Water Research,* 41, 1001-1012.

[105] Zorita, S., Martensson, L., Mathiasson, L. (2009). Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden. *Science of the Total Environment,* 407, 2760-2770.

[106] Flint, S., Markle, T., Thompson, S., Wallace, E. (2012). Bisphenol A exposure, effects, and policy: a wildlife perspective. *Journal of environmental management,* 104, 19-34.

[107] Xu, J., Wu, L., Chen, W., Jiang, P., Chang, A. C. S. (2009). Pharmaceuticals and personal care products (PPCPs), and endocrine disrupting compounds (EDCs) in runoff from a potato field irrigated with treated wastewater in southern California. *Journal of Health Science,* 55, 306-310.

[108] Chen, F., Ying, G. G., Kong, L. X., Wang, L., Zhao, J. L., Zhou, L. J., Zhang, L. J. (2011). Distribution and accumulation of endocrine-disrupting chemicals and pharmaceuticals in wastewater irrigated soils in Hebei, China. *Environmental Pollution,* 159, 1490-1498.

[109] Liu, F., Ying, G. G., Yang, J. F., Zhou, L. J., Tao, R., Wang, L., Zhang, L. J., Peng, P. A. (2010). Dissipation of sulfamethoxazole, trimethoprim and tylosin in a soil under aerobic

and anoxic conditions. *Environmental Chemistry,* 7, 370-376.

[110] Yang, J. F., Ying, G. G., Zhou, L. J., Liu, S., Zhao, J. L. (2009). Dissipation of oxytetracycline in soils under different redox conditions. *Environmental Pollution,* 157, 2704-2709.

[111] Wu, C., Spongberg, A. L., Witter, J. D. (2008). Determination of the persistence of pharmaceuticals in biosolids using liquid-chromatography tandem mass spectrometry. *Chemosphere,* 73, 511-518.

[112] Yu, Y., Liu, Y., Wu, L. (2013). Sorption and degradation of pharmaceuticals and personal care products (PPCPs) in soils. *Environmental Science and Pollution Research,* 20, 4261-4267.

[113] Sanchez-Brunete, C., Miguel, E., Tadeo, J. L. (2009). Determination of tetrabromobisphenol-A, tetrachlorobisphenol-A and bisphenol-A in soil by ultrasonic assisted extraction and gas chromatography-mass spectrometry. *Journal of Chromatography A,* 1216, 5497-5503.

[114] Chase, D. A., Karnjanapiboonwong, A., Fang, Y., Cobb, G. P., Morse, A. N., Anderson, T. A. (2012). Occurrence of synthetic musk fragrances in effluent and non-effluent impacted environments. *Science of the Total Environment,* 416, 253-260.

TABLE 1. Occurrence of PPCPs in reclaimed water, irrigated agricultural soils, and groundwater in different locations.

Classification	Compounds	Physicochemical properties*		Half-life in soil (days)	Location	Reclaimed water (μg/L)	Soil (ng/g)	Groundwater (ng/L)	Reference
		Water solubility (mg/L)	logK_{ow}						
Lipid-regulating drugs	Clofibric acid	583	2.57	56.4[24]	Braunschweig, Germany	0.12	ND[a]	<25	6
					California, Riverside, USA	1.05	4.27	ND	24
					California, Riverside, USA	0.26	ND	188	107
	Fenofibric acid	9.114	4.0	//	Braunschweig, Germany	0.13	ND	<25	6
	Bezafibrate	1.224	4.25	//	Braunschweig, Germany	0.13	ND	<25	6
	Gemfibrozil	4.964	4.77	20.6	Texas ,USA	19.4	ND	6,860	28
					Colorado, USA	0.094	0	ND	2
Analgesics/Anti-inflammatory drugs	Ibuprofen	21	3.97	121.9[43]	Texas, USA	4.06	318.5	UD[b]	22
					California, Riverside, USA	8.59	7.88	ND	24
					California, Riverside, USA	1.15	ND	213	107
					Braunschweig, Germany	0.13	ND	<25	6
	Naproxen	15.9	3.18	42.5	California, Riverside, USA	13.4	23.79	ND	24
					California, Riverside, USA	0.15	ND	93	107
	Ketoprofen	51	3.12	27.61[39]	California, Riverside, USA	0.14	ND	97	107
	Diclofenac	2.37	4.51	20.44[27]	Braunschweig, Germany	1.3	ND	<25	6
					California, Riverside, USA	0.11	ND	71	107
	Diclofenac sodium	2425	4.51	74.5	California, Riverside, USA	3.41	6.82	ND	24

	Acetaminophen	1.4×10^4	0.46	//	Colorado, USA	0.65	1,640	ND	2
	Salicylic acid	2240	2.26	11[27]	Cangzhou, He Bei, China	0.0078	4.5	ND	108
					Baoding, He Bei, China	0.0064	9.1	ND	
					Shijiazhuang, He Bei, China	0.041	10.7	ND	
Antiseptics	Triclosan	10	4.76	32.5[24]	Texas,USA	0.35	8.16	53	22
					California, Riverside, USA	3.54	138	ND	24
					California, Riverside, USA	0.56	ND	95	107
					Cangzhou, He Bei, China	0.0018	<1.58	ND	108
					Baoding, He Bei, China	0.11	1.8	ND	
					Shijiazhuang, He Bei, Chia	0.066	<1.58	ND	
Antibiotics	Ciprofloxacin	3.0×10^4	0.28	//	Texas,USA	0.3	0.68	0.27	22
	Trimethoprim	400	0.91	4[109]	Braunschweig, Germany	0.34	ND	<25	6
					Colorado, USA	0.042	60	ND	2
					Cangzhou, He Bei, China	0.0033	<2.15	ND	108
					Baoding, He Bei, China	0.03	2.6	ND	
					Shijiazhuang, He Bei, China	0.050	<2.15	ND	
	Sulfamethoxazole	610	0.89	2[109]	Braunschweig, Germany	0.62	ND	110	6
					Colorado, USA	0.059	332	ND	2
	Erythromycin	1.44	3.06	//	Braunschweig, Germany	0.62	ND	<25	6
					Colorado, USA	0.61	6,270	ND	2
	Oxytetracycline	313	0.9	56[110]	Cangzhou, He Bei, China	0.013	6.2	ND	108
					Baoding, He Bei, China	0.013	7.5	ND	

ACCEPTED MANUSCRIPT

					Shijiazhuang, He Bei, China	1.6	212	ND	
	Tetracycline	231	1.3	>77[111]	Cangzhou, He Bei, China	0.013	<2.67	ND	108
					Baoding, He Bei, China	0.012	6.9	ND	
					Shijiazhuang, He Bei, China	1.50	19.9	ND	
Antiepileptic	Carbamazepine	17.7	2.45	125[25]	Braunschweig, Germany	2.1	ND	570[b]	6
					Colorado, USA	0.094	549	ND	2
	Primidone	500	0.91	//	Cangzhou, He Bei, China	UD	<1.11	ND	108
					Baoding, He Bei, China	0.017	3.3	ND	
					Shijiazhuang, He Bei, China	UD	UD	ND	
Endocrine-disrupting chemicals	Bisphenol A	120	3.32	14.4[112]	California, Riverside, USA	2.55	31	ND	24
					California, Riverside, USA	0.46	ND	144	107
					Cangzhou, He Bei, China	0.092	3.33	ND	108
					Baoding, He Bei, China	0.15	<3.4	ND	
					Shijiazhuang, He Bei, China	0.27	2.7	ND	
					Madrid, Spain	ND	4.6	ND	113
	4-Nonylphenol	6.35	5.76	16.1[24]	Cangzhou, He Bei, China	0.46	36.9	ND	108
					Baoding, He Bei, China	3.17	25.8	ND	
					Shijiazhuang, He Bei, China	4.88	55.4	ND	
					California, Riverside, USA	4.38	136	ND	24
					California, Riverside, USA	0.33	ND	163	107

ACCEPTED MANUSCRIPT

Steroid hormones	Estrone(E1)	13	3.13	13.7[24]	Texas, USA	1.82	135.9	79	22
					California, Riverside, USA	0.063	ND	75	107
	17β-estradiol (E2)	13	4.01	2.3[43]	Texas, USA	1.37	3.33	147	22
					California, Riverside, USA	<0.075	ND	<75	24
	17α-ethynyle stradiol(EE2)	4.8	3.67	3.0[43]	Texas, USA	0.39	2.7	230	22
					California, Riverside, USA	0.048	ND	25	107
	Estriol(E3)	13	2.45	1.7[43]	Texas, USA	83.43	7.73	1,745	22
Psychomotor stimulants	Caffeine	2.1×10^4	-0.07	//	Texas, USA	0.34	UD	166	22
					Braunschweig, Germany	0.22	ND	<25	6
					Colorado, USA	0.017	317	ND	2
Antidepressants	Fluoxetine	60.3	4.05	//	Colorado, USA	0.0054	376	ND	2
Betablockers	Warfarin	17	2.60	//	Colorado, USA	0.073	2, 770	ND	2
Synthetic musk fragrance	Galaxolide	1.75	5.90	//	Texas, Lubbock , USA	3.94	1.98	<5	114
					Braunschweig, Germany	0.73	ND	<25	6
	Tonalide	1.25	5.70	//	Texas, Lubbock, USA	0.67	5.46	72	114
					Braunschweig, Germany	0.1	ND	<25	6
Flame retardants	Tetrabromobi sphenol A	0.001002	7.20	//	Madrid, Spain	ND	0.3	ND	113
	Tetrachlorobi sphenol A	0.09158	6.22	//	Madrid, Spain	ND	UD	ND	113
X-ray contrast media	Diatrizoate	8.885	1.37	//	Braunschweig, Germany	3.3	ND	9,600	6
	Iopamidol	61.08	-2.42	//	Braunschweig, Germany	1.9	ND	110	6

ACCEPTED MANUSCRIPT

[a]ND: not detected; [b]UD: undetectable

*Physicochemical properties were found from the following online data base: http://www.syrres.com/ese and http://logkow.cisti.nrc.ca/logkow/search.html.

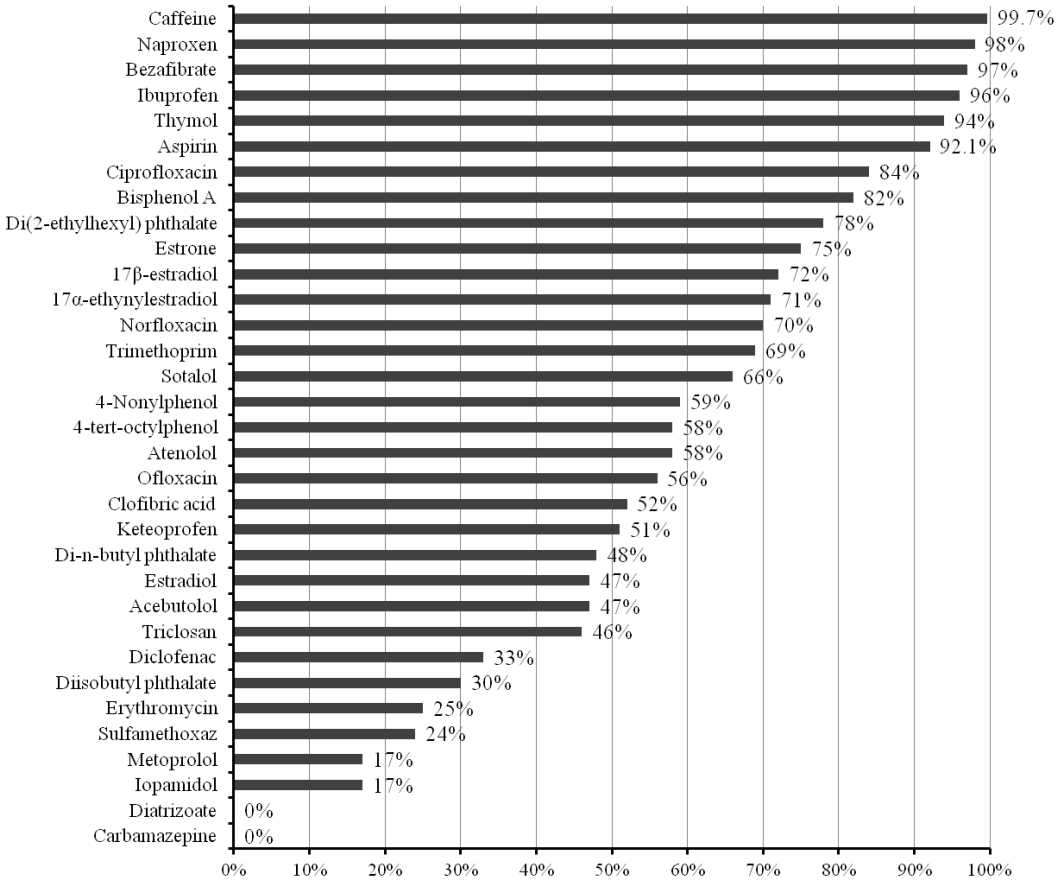


FIGURE 1. Removal rates of PPCPs in municipal sewage treatment plants. Data collected from Sweden, Germany, Japan, Finland and China.[6, 102-105]

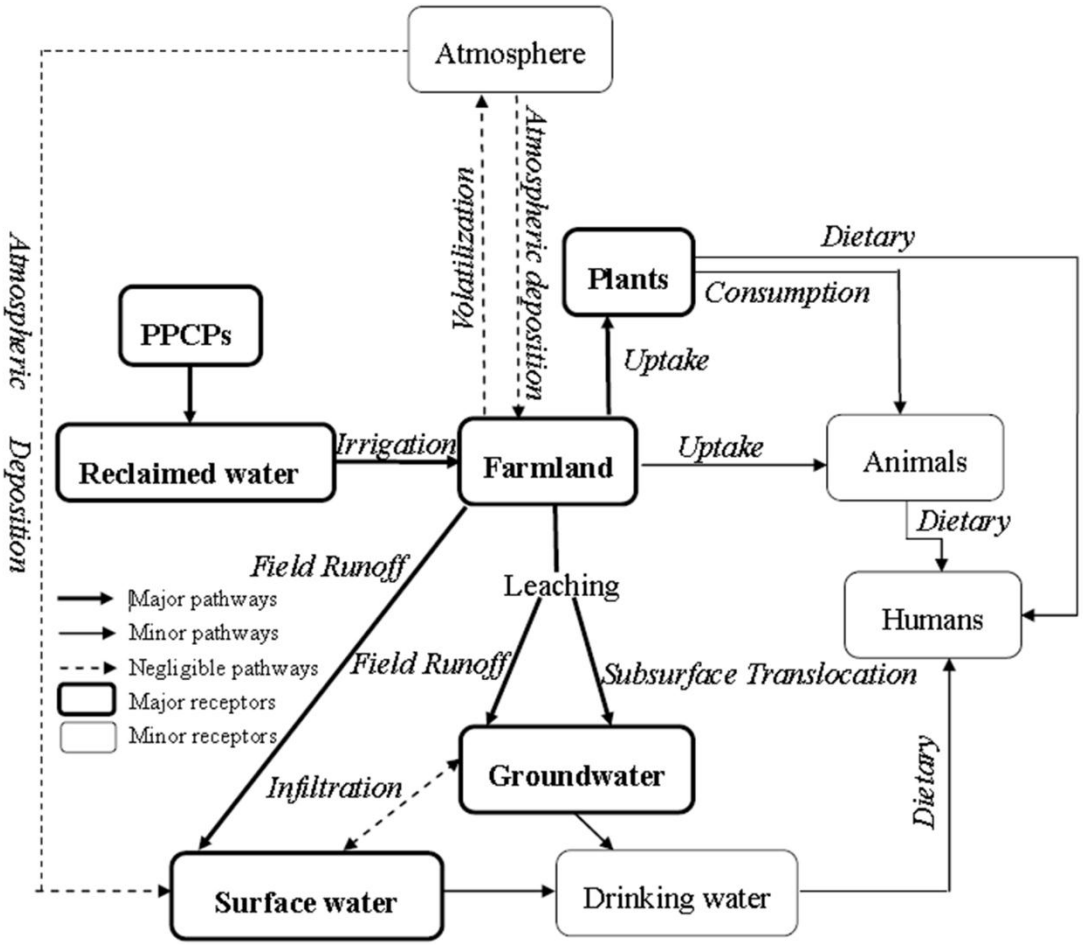


FIGURE 2. Schematic diagram of the potential translocation pathways and behaviors of PPCPs in reclaimed water irrigated farmlands with reference to the literatures.[24, 28, 55, 56, 60, 106]