



Distribution and accumulation of endocrine-disrupting chemicals and pharmaceuticals in wastewater irrigated soils in Hebei, China

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ABSTRACT

This study investigated the occurrence of 43 emerging contaminants including 9 endocrine-disrupting chemicals and 34 pharmaceuticals in three sites in Hebei Province, north China. Each site has a wastewater irrigated plot and a separate groundwater irrigated plot for comparison purpose. The results showed that the concentrations of the target compounds in the wastewater irrigated soils were in most cases higher than those in the groundwater irrigated soils. Among the 43 target compounds, nine compounds bisphenol-A, triclocarban, triclosan, 4-nonylphenol, salicylic acid, oxytetracycline, tetracycline, trimethoprim and primidone were detected at least once in the soils. Preliminary environmental risk assessment showed that triclocarban might pose high risks to terrestrial organisms while the other detected compounds posed minimal risks. Irrigation with wastewater could lead to presence or accumulation of some emerging contaminants to some extent in irrigated soils.

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1. Introduction

Wastewater has increasingly been reclaimed and reused for agricultural irrigation due to scarce water resources, especially in arid and semi-arid regions (Klay et al., 2010; Palese et al., 2009; Rattan et al., 2005; Siemens et al., 2008). China is one of the countries with a severe water shortage problem and uneven water resource distribution. The amount of freshwater resource per capita is approximately 2200 m³, which is only one fourth of the world's average. Thus reclaimed wastewater has become a valuable resource for irrigation of crops in China. However, application of wastewater in agriculture may pose potential risks to the environment and public health because they contain toxic inorganic and organic chemicals and pathogens (Asano and Cotruvo, 2004; Bouri et al., 2008; Chen et al., 2005; Papadopoulos et al., 2009; Ternes, 1998).

Some guidelines have been developed in regard to reclaimed water (treated effluent) for irrigation (Chang et al., 1996; Marcos do Monte et al., 1996; SA EPA, 1999; U.S. EPA, 1992). Most of the irrigation water quality criteria focus on parameters of nutrients, inorganic compounds and pathogens (Chang et al., 1996). This does not adequately address the possible risks to the environment and human health posed by the thousands of potential trace organic pollutants in reclaimed wastewater although these wastewaters (whether

domestic or industrial) have been treated by municipal wastewater treatment plants. Many studies have been undertaken on inorganic compounds (e.g., Klay et al., 2010; Papadopoulos et al., 2009; Rattan et al., 2005; Smith et al., 1996) and pathogens (e.g., Mutengu et al., 2007; Palese et al., 2009; Pedrero and Alarcón, 2009) in wastewater and their possible effects on soil and plants as well as human health. Some studies have investigated some persistent organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in wastewater irrigated soils (e.g., Al Nasir and Batarseh, 2008; Chen et al., 2005; Sun et al., 2009). Few studies have focused on emerging contaminants including endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs). The presence of some EDCs and PPCPs has been reported in wastewater irrigated soils in Colorado, USA (Kinney et al., 2006), Braunschweig, Germany (Ternes et al., 2007) and Tula Valley, Mexico (Durán-Alvarez et al., 2009). Chefetz et al. (2008) reported leaching behavior of three drugs carbamazepine, naproxen and diclofenac in soil columns and found that carbamazepine and diclofenac could be regarded as slow-mobile compounds in organic matter rich soils. Previous studies have showed that some drugs such as antibiotic residues in soils could affect soil microbial activities and terrestrial organisms (Bager et al., 2000; Jensen et al., 2003; Kotzerke et al., 2008; Liu et al., 2009a,b). Nevertheless, our understanding of distribution and potential impacts of these emerging contaminants on soil and food quality is very limited.

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Due to water shortage, reclaimed water has been applied in irrigation of crops in some parts of China for many years. Hebei is a typical province in north China having a water shortage problem and it has used reclaimed wastewater to irrigate crops for more than 50 years. The irrigation area in Hebei is more than 159,800 hm², and the annual reuse of wastewater for agriculture irrigation was approximately 251 million m³ (Wu et al., 2004). Most studies in China have focused on accumulation of heavy metals in soils and plants (e.g., Li et al., 2009; Wang et al., 2003) and a few studies on distribution of persistent organic pollutants such as PAHs and OCPs (Chen et al., 2005; Sun et al., 2009). To the best of our knowledge, there has been no study on the presence and distribution of EDCs and PPCPs in wastewater irrigated soils in China.

The aim of this study was to investigate the presence and distribution of 43 emerging contaminants including 9 endocrine-disrupting chemicals (EDCs) and 34 pharmaceuticals in wastewater irrigated soils from three sites (Cangzhou, Baoding, and Shijiazhuang) in Hebei province, north China by rapid resolution liquid chromatography tandem mass spectrometry. For comparison purpose, each site has a reclaimed wastewater irrigated plot and a groundwater irrigated plot. The results from this study could facilitate better understanding of potential ecological and human health risks of these wastewater-related chemicals in soils, and also help develop better reclaimed water guidelines.

2. Materials and methods

2.1. Chemicals and materials

Standards of 4-nonylphenol, 4-n-nonylphenol, estradiol, ethinylestradiol, triclosan, triclocarban, salicylic acid, clofibrac acid, bentazone, 2, 4-D, MCPA, ibuprofen, fenopropfen, diclofenac, indometacin, mefenamic acid, gemfibrozil, tolfenamic acid, ketoprofen, naproxen, cyclophosphamide, carbamazepine, norfloxacin, ciprofloxacin, trimethoprim, sulfacetamide, sulfapyridine, sulfadiazine, sulfamethazine, sulfamethoxazole, oxytetracycline, tetracycline, erythromycin and oleandomycin were obtained from Dr. Ehrenstorfer GmbH (Germany). 4-tert-octylphenol, bisphenol-A and bisphenol-A-d16 were supplied by Supelco (USA). Estrone, diethylstilbestrol, mecoprop, fenoprop and ofloxacin were obtained from Riedel-de Haën (RDH, Germany). ¹³C₁₂-Triclosan and estrone-d4 were purchased from Cambridge Isotope Laboratories Incorporation (Massachusetts, USA). Meclofenamic acid, primidone, dihydrocarbamazepine, lomefloxacin and roxithromycin were obtained from Sigma-Aldrich (USA), while estradiol-d4 was provided by CDN Isotopes. Ciprofloxacin-d8, sulfamethoxazole-d4, thiabendazole-d4, erythromycin-¹³C-d3 were purchased from TRC (Canada). The physicochemical properties of the target compounds are given in Tables 1 and 2. All the organic solvents were HPLC grade and purchased from Merck Corporation (Shanghai, China). Ultrapure water was supplied by a Milli-Q system from Millipore (Watford, UK). Oasis HLB extraction cartridges (6 mL, 500 mg) from Waters Corporation (Milford, MA, USA) were used for extraction and purification of the target compounds. Sodium sulfate was baked at 400 °C for 4 h and preserved in a desiccator. Silica gel (100–200 mesh) was sequentially Soxhlet extracted with methanol and dichloromethane for 24 h, and then it was baked at 160 °C for 24 h and stored in desiccator.

Individual stock solutions of the target analytes and internal standards were prepared at 100 mg/L in methanol and stored in amber glass bottles at –18 °C.

Composite working solutions at the desired concentrations were made by appropriate dilution of the individual stock solutions.

2.2. Sampling

Three sites (Cangzhou, Baoding and Shijiazhuang) in Hebei province, north China were chosen to conduct the present investigation. Application of wastewaters for irrigation of crops in the three sites started in the early 1960s. The reclaimed water was mainly treated industrial wastewater in Cangzhou, and municipal wastewater (mainly domestic wastewater) in Baoding and Shijiazhuang. At each site, one plot with wastewater irrigation for 50 years and another plot with groundwater irrigation without any history of wastewater irrigation were selected for comparison (Table 3). For both types of plots, no biosolid application was recorded. The two plots at each site were no more than 1 km apart from each other.

Sampling campaign was carried out to collect samples of irrigation waters and soils (five replicates each plot) in July 2008. Irrigation waters were sampled from the bores at the plots with groundwater irrigation system, and from the irrigation channels at the plots with wastewater irrigation system. Water samples were collected in 1 L pre-cleaned amber glass bottles, immediately added with 50 mL of methanol and adjusted to pH 3.0 using 4 M H₂SO₄. Soil samples were sampled in 1 L glass jars at three depths: 0–10 cm, 10–20 cm and 20–30 cm from five points in each plot (100 m by 100 m). The water and soil samples used for controls and recovery tests were collected from Liuxi River reservoir far from human activities and a nearby plot in Guangdong Province, which contained no target compounds (<LOQ) based on repeated analyses in the laboratory. Sample bottles were kept cold during transport to the laboratory. Once in the laboratory, water samples were passed through 0.7 μm glass fiber filters (Whatman GF/F, UK) and further extraction was carried out within a week. Soil samples were freeze-dried and then sieved through a 2 mm mesh standard screen. Before extraction, all the samples were stored in the dark at 4 °C. Field soil samples were characterized and their physicochemical properties are given in Table 4. Soil pH was measured with 0.01 M CaCl₂ (soil to solution ratio of 1:5) using a pH meter. Soil organic matter was determined by a LECO carbon and nitrogen analyzer, while soil particle size distribution was analyzed by using the pipette method (Schinner et al., 1999). The soil properties were similar among the six plots from the three sites (Table 4).

2.3. Extraction

2.3.1. Water samples

The target compounds in water samples were extracted by solid phase extraction (SPE) method using Oasis HLB cartridges. The Oasis HLB extraction cartridges were preconditioned with 10 mL of methanol and 10 mL of Milli-Q water. The internal standards (100 ng/L each) and 0.2 g of Na₂EDTA were spiked into each water sample (1 L) before the water sample was passed through the cartridge at a flow rate of approximately 10 mL/min. Each sample bottle was rinsed twice with Milli-Q water containing 10% methanol (50 mL) and each SPE cartridge rinsed with 10 mL Milli-Q water. The target compounds were eluted from the cartridge sequentially with 4 × 3 mL of methanol and 3 × 2 mL of dichloromethane. The eluate from each cartridge was concentrated under a gentle nitrogen stream and then redissolved in 1 mL methanol. The final extract of each sample was filtered through a nylon syringe filter (13 mm × 0.22 μm, Anpu, Shanghai) into a 2 mL amber glass vial and then stored at –18 °C until further analysis.

2.3.2. Soil samples

Extraction of the EDCs and pharmaceuticals (except antibiotics) in soil samples was conducted at the same time (Chen et al., 2010). An aliquot of 5 g of soil samples spiked with 100 ng/g of each internal standard was extracted three times with 10 mL of ethyl acetate: formic acid (50:1, v/v) mixture by ultrasonication at room temperature (15 min each time). The extracts were combined and concentrated to

Table 1
Physicochemical properties of the endocrine-disrupting chemicals (EDCs) investigated in this study.

Compound	Water solubility (mg/L at 20 °C) ^a	Log K _{ow} ^a	K _{oc} (L/kg) ^b	Half-life (days) in soil	Use
Bisphenol-A	120	3.32	778	5.50 ^d , 7 ^a	Industrial chemical
17-β-Estradiol	13	3.94	4360	3 ^a	Natural estrogen
17α-Ethinylestradiol	4.8	4.15	4840	4.5 ^a	Synthetic estrogen
Estrone	13	3.43	4882		Natural estrogen
Diethylstilbestrol	0.26	5.07	569,200		Synthetic estrogen
Triclocarban	0.6479 ^c	4.9 ^c	50,118 ^c	108 ^c	Antiseptic and disinfectant
Triclosan	4.621 ^c	4.7 ^c	18,408 ^c	18 ^c	Antiseptic and disinfectant
4-tert-Octylphenol	12.6	4.12	18,200	5 ^a	Industrial chemical
4-Nonylphenol	1.57	5.76	38,900	4.6 ^a	Industrial chemical

^a K_{ow}: n-octanol-water partitioning coefficient (Ying and Kookana, 2005).

^b K_{oc}: sorption coefficient (Ying et al., 2003).

^c Water solubility (mg/L at 25 °C) (Ying et al., 2007).

^d Data from Xu et al. (2009).

Table 2
Physicochemical properties of the pharmaceuticals investigated in this study.

Compound	Water solubility (mg/L at 25 °C) ^a	Log K_{ow} ^a	K_{oc} (L/kg)	Half-life (days) in soil	Use
Acidic pharmaceuticals					
Salicylic acid	2240	2.26			Anti-inflammatory
Clofibrac acid	583	2.57	14,125 ^c	11.00 ^c	Blood lipid regulator
2, 4-D	677	2.81			Herbicide
MCPA	630	3.25			Herbicide
Ibuprofen	21	3.97	87 ^c	6.09 ^c	Anti-inflammatory and antipyretic
Bentazone	500	2.34			Herbicide
Fenoprofen	30.13	3.90			Anti-inflammatory and antipyretic
Diclofenac	2.37	4.51	200 ^c	8.47 ^c	Anti-inflammatory
Indometacin	0.937	4.27			Anti-inflammatory and antipyretic
Meclofenamic acid	30	6.02			Anti-inflammatory and antipyretic
Mefenamic acid	20	5.12			Anti-inflammatory and antipyretic
Gemfibrozil	4.964	4.77			Antihyperlipoproteinemic
Tolfenamic acid	0.7823	5.17			Anti-inflammatory and antipyretic
Ketoprofen	51	3.12			Anti-inflammatory and antipyretic
Naproxen	15.9	3.18	490 ^c	14.29 ^c	Anti-inflammatory and antipyretic
Neutral pharmaceuticals					
Paracetamol	14,000	0.46			Antipyretic
Primidone	500	0.91			Anti-epileptic
Cyclophosphamide	40,000	0.63			Immunosuppressant and antitumor
Carbamazepine	112	2.45			Anti-epileptic
Antibiotics					
Norfloxacin	177,900	-1.03			Antibacterial
Ciprofloxacin	30,000	0.28	61,000 ^b		Antibacterial
Lomefloxacin	27,230	-0.30			Antibacterial
Ofloxacin	28,260	-0.39			Antibacterial
Trimethoprim	400	0.91	1680–3990 ^b	4 ^f	Antibacterial
Sulfacetamide	12,500	-0.96			Antibacterial
Sulfapyridine	268	0.35	101–308 ^b		Antibacterial
Sulfadiazine	77	-0.09	37–125 ^b	12–18 ^d	Antibacterial
Sulfamethazine	1500	0.19	82–208 ^b		Antibacterial
Sulfamethoxazole	610	0.89		2 ^f	Antibacterial
Oxytetracycline	313	-0.90	42,506–93,317 ^b	29–56 ^e	Antibacterial
Tetracycline	231	-1.30	40,000 ^b		Antibacterial
Erythromycin-H ₂ O					Antibacterial
Roxithromycin	0.01887	2.75			Antibacterial
Oleandomycin	15.51	1.69			Antibacterial

^a Water solubility and log K_{ow} data from Syracuse Research Corporation.

^b Data from Sarmah et al. (2006).

^c Data from Xu et al. (2009).

^d Data from Yang et al. (2009a).

^e Data from Yang et al. (2009b).

^f Data from Liu et al. (2010).

nearly dryness under a gentle nitrogen stream. The extracts were redissolved in 1 mL of n-hexane, and then purified by silica gel column (18 cm × 1 cm i.d.), which consisted of anhydrous sodium sulfate (about 0.5 cm, on top) and silica gel (1 g). The silica gel sorbent was conditioned sequentially with methanol (4 mL), ethyl acetate (4 mL) and n-hexane (6 mL). The extracts were loaded onto the silica gel column (18 cm × 1 cm i.d.), and sequentially eluted by 6 mL each of n-hexane, ethyl acetate and methanol. The last two eluates were collected and dried under a gentle stream of nitrogen gas. The final extracts were redissolved in 1 mL of the initial mobile phase, passed through a nylon filter (13 mm × 0.22 μm, Anpu, Shanghai) into 2 mL amber glass vials, and stored at -18 °C until analysis.

For antibiotics, 2 g of each soil sample was accurately weighed and spiked with 100 ng/g of each internal standard. The prepared soil samples were extracted three times with 10 mL 0.2 M citric acid buffer (pH 4.4) and 10 mL acetonitrile by

ultrasonication at room temperature (15 min each time) (Yang et al., 2010). The extracts were combined and evaporated to an appropriate volume (30–40 mL) to remove organic solvent. Na₂EDTA (0.2 g) was added into each extract, which was diluted to 200 mL with Milli-Q water. Subsequently, the extracts were purified using Oasis HLB extraction cartridges with the same method as used for water samples. But the target antibiotics were eluted from the cartridges with 10 mL of methanol. The final extracts were dried under a gentle nitrogen stream and redissolved in 1 mL of the initial mobile phase.

2.4. LC-MS/MS

The target compounds in the water and soil samples were separated into four groups (EDCs, acidic and neutral pharmaceuticals, and antibiotics) and determined

Table 3
Information of the sampling sites in Hebei, China.

Water sample	Soil sample	Plot type	Location	Coordinates
GWC	GSC	Irrigation with groundwater	Cangzhou	38°01'N 116°12'E
WWC	WSC	Irrigation with industrial effluent		
GWB	GSB	Irrigation with groundwater	Baoding	38°52'N 115°33'E
WWB	WSB	Irrigation with municipal effluent		
GWS	GSS	Irrigation with groundwater	Shijiazhuang	37°54'N 114°32'E
WWS	WSS	Irrigation with municipal effluent		

Note: Three letter coding system used for water and soil samples. First letter (reclaimed water type), G - groundwater, W - wastewater; second letter (sample type), W - water, S - soil; third letter (location), C - Cangzhou, B - Baoding, and S - Shijiazhuang.

Table 4
Properties of soils from the study sites in Hebei, China.

Site	Depth (cm)	pH	Organic matter (g/kg)	Sand (0.05–2 mm) (%)	Silt (0.002–0.05 mm) (%)	Clay (<0.002 mm) (%)
GSC	0–10	7.9 ± 0.1	3.7 ± 1.8	11.5 ± 3.4	57.8 ± 2.3	30.7 ± 2.4
	10–20	7.9 ± 0.1	3.0 ± 1.0	8.5 ± 3.3	61.9 ± 2.5	29.6 ± 2.0
	20–30	8.0 ± 0.1	2.2 ± 0.9	11.7 ± 3.6	58.4 ± 2.9	30.0 ± 3.4
WSC	0–10	7.8 ± 0.1	2.5 ± 0.8	11.3 ± 1.1	64.3 ± 2.0	24.4 ± 1.1
	10–20	7.9 ± 0.1	2.2 ± 0.5	9.2 ± 1.4	63.4 ± 2.1	27.4 ± 0.9
	20–30	8.0 ± 0.1	1.1 ± 0.3	9.6 ± 2.3	62.3 ± 2.7	28.1 ± 0.8
GSB	0–10	7.8 ± 0.0	3.0 ± 0.5	12.8 ± 1.2	58.0 ± 2.3	29.2 ± 1.3
	10–20	7.9 ± 0.0	2.2 ± 0.3	15.7 ± 2.3	54.9 ± 1.9	29.4 ± 0.9
	20–30	7.9 ± 0.0	0.8 ± 0.2	12.3 ± 1.4	58.5 ± 2.5	29.2 ± 1.2
WSB	0–10	7.2 ± 0.2	4.3 ± 0.5	18.5 ± 1.6	56.6 ± 1.6	25.0 ± 1.2
	10–20	7.5 ± 0.2	4.2 ± 1.7	12.8 ± 3.2	55.6 ± 1.1	31.6 ± 2.1
	20–30	7.7 ± 0.1	1.2 ± 0.8	16.1 ± 4.4	51.4 ± 6.2	32.5 ± 1.9
GSS	0–10	7.6 ± 0.1	2.4 ± 0.3	9.3 ± 1.2	60.4 ± 1.0	30.3 ± 1.1
	10–20	7.7 ± 0.0	2.1 ± 0.7	11.8 ± 1.2	59.8 ± 0.9	28.4 ± 0.6
	20–30	7.8 ± 0.0	1.9 ± 0.8	10.7 ± 1.6	60.8 ± 1.5	28.5 ± 1.8
WSS	0–10	7.4 ± 0.1	3.0 ± 1.0	13.5 ± 2.7	60.5 ± 0.9	26.0 ± 2.7
	10–20	7.6 ± 0.0	2.9 ± 0.4	6.9 ± 4.1	59.1 ± 1.1	34.1 ± 4.3
	20–30	7.7 ± 0.1	2.0 ± 0.9	7.0 ± 1.8	59.4 ± 1.8	33.6 ± 0.4

using Agilent 1200 rapid resolution liquid chromatograph coupled to Agilent G6460A triple quadrupole mass spectrometer (RRLC-MS/MS). The chromatographic column was an Agilent SB-C18 (3.0 mm × 100 mm ID, 1.8 μm particle size) for the EDCs and acidic and neutral pharmaceuticals, and an Agilent Zorbax XDB-C18 (2.1 mm × 50 mm ID, 1.8 μm particle size) for the antibiotics. A precolumn filter, a RRLC in-line filter kit (4.6 mm, 0.2 μm filter), was used in front of the analytical column. The column temperature was maintained at 40 °C for analysis of the EDCs, acid and neutral pharmaceuticals, and 45 °C for analysis of the antibiotics. The injection volume was 10 μL. The flow rate of the mobile phases was all set at 0.3 mL/min.

For the analysis of EDCs, the mobile phase was (A) Milli-Q water and (B) acetonitrile. The gradient elution started with 40% B, increased to 70% B at 15 min, and to 95% B at 20 min and kept at 95% B for 2 min. For acidic pharmaceuticals, the mobile phase was (A) Milli-Q water containing 0.01% acetic acid (v/v) and (B) acetonitrile: methanol (1:1, v/v). The gradient elution started with 40% B, increased to 50% B at 15 min, to 75% B at 20 min, and kept at 75% B for 5 min. For neutral pharmaceuticals, the mobile phase was (A) Milli-Q water and (B) acetonitrile. The gradient elution started with 20% B, increased to 60% B at 10 min, to 90% B at 13 min, and kept at 90% B for 2 min. For antibiotics, the mobile phase was (A) 5 mM oxalic acid buffer and (B) acetonitrile. The gradient elution started with 5% B, increased to 10% B at 5 min, and to 30% B at 6 min, kept at 30% B for 2 min, reached 80% B at 9 min and then kept at 80% B for 3 min.

Mass spectrometric conditions were optimized using Optimizer (Agilent, Palo Alto, USA) for collision energy (CE), fragmentor voltage, and multiple reaction monitoring mode (MRM) transitions for each compound. More detailed mass spectrometric operating conditions could be referred to Chen et al. (2010) and Yang et al. (2010). Analysis was carried out in ESI (+) mode for the neutral pharmaceuticals and antibiotics and ESI (–) mode for the EDCs and acidic pharmaceuticals. The following optimized parameters were selected: drying gas temperature 350 °C, drying gas flow rate 6 mL/min, capillary voltage 3500 V, nebulizing gas pressure 50 psi, sheath gas temperature 350 °C and sheath gas flow rate 12 mL/min. N₂ was used as the nebulizer, drying, curtain and collision gas. The system was re-equilibrated for 8 min between runs. Quantification of each target compound in the samples was performed in the MRM mode.

2.5. Quality assurance and quality control

During each set of samples analyzed, a reagent blank, method blank and spiked matrix were analyzed together with the water and soil samples. None of the analytes were detected in the blank controls for both water and soil samples. The analytical methods developed for the EDCs and pharmaceuticals showed satisfactory performance in respect of recovery and limit of detection (LOD) and quantitation (LOQ), as shown in Tables 5 and 6. The recovery experiments were carried out by spiking a known concentration of the target analytes (100 ng/L each for water and 100 ng/g each for soil) into clean water and soil samples. The recoveries of the most target analytes ranged between 70% and 120% (Tables 5 and 6). The LOD and LOQ were defined as a signal-to-noise (S/N) ratios of 3 and 10, respectively, which were determined in analysis of those water and soil samples spiked at low concentrations close to the corresponding instrumental LOQ. The LOQ of the target analytes ranged from 0.028 to 14.08 ng/L for water samples, and 0.06 to 14.01 μg/kg for soil samples (Tables 5 and 6).

3. Results

3.1. Concentrations of the EDCs and pharmaceuticals in the irrigation waters

Except for ethynylestradiol (<LOQ, data not shown), the target EDCs (4-t-octylphenol, 4-nonylphenol, bisphenol-A, estrone, diethylstilbestrol, estradiol, triclocarban and triclosan) were detected in at least one reclaimed wastewater sample collected in July 2008 (Table 7). We only listed those compounds detected in the water or soil samples in Tables 7–10. Only four target EDCs 4-t-octylphenol, 4-nonylphenol, bisphenol-A and triclosan were detected at similar concentrations between the groundwater samples (GWC, GWB and GWS) from the three sites, which suggests similar groundwater quality in the three sites (Cangzhou, Baoding and Shijiazhuang). In Cangzhou, the two types of irrigation waters (GWC: groundwater; and WWC: wastewater) contained similar concentrations of the target EDCs. However, the reclaimed wastewaters used for irrigation of crops in Baoding (WWB) and Shijiazhuang (WWS) had much higher concentrations of the detected EDCs than their corresponding groundwaters (GWB and GWS). Up to 4879 ng/L and 390 ng/L were found for 4-nonylphenol and triclocarban in reclaimed wastewaters, respectively; whereas the concentrations of 4-nonylphenol were only up to 396 ng/L and triclocarban was not detected in the groundwater from Baoding and Shijiazhuang.

Table 5

Recoveries (%) and method precision (RSD % for $n = 4$), limits of detection (LOD) and quantitation (LOQ) for the endocrine-disrupting chemicals (EDCs).

Compound	Water			Soil		
	Recovery % ± RSD	LOD (ng/L)	LOQ (ng/L)	Recovery % ± RSD	LOD (μg/kg)	LOQ (μg/kg)
Bisphenol-A	78 ± 4	0.11	0.37	111 ± 2	1.02	3.40
17-β-Estradiol	104 ± 5	1.18	3.92	106 ± 2	0.49	1.63
17α-Ethinylestradiol	65 ± 14	0.60	2.01	115 ± 7	0.83	2.77
Estrone	98 ± 2	0.42	1.41	97 ± 5	0.60	1.99
Diethylstilbestrol	119 ± 16	0.53	1.75	56 ± 20	1.62	5.41
Triclocarban	128 ± 3	0.24	0.79	108 ± 1	0.12	0.39
Triclosan	97 ± 1	0.21	0.70	95 ± 3	0.47	1.58
4-tert-Octylphenol	62 ± 14	0.40	1.33	94 ± 15	1.29	4.29
4-Nonylphenol	135 ± 2	0.09	0.31	124 ± 3	0.49	1.63

Note: Bold letters in the table represent those recoveries outside the range of 70–120%.

Table 6
Recoveries (%) and method precision (RSD % for $n = 4$), limits of detection (LOD) and quantitation (LOQ) for the pharmaceuticals.

Compound	Water			Soil		
	Recovery % ± RSD	LOD (ng/L)	LOQ (ng/L)	Recovery % ± RSD	LOD (μg/kg)	LOQ (μg/kg)
Acidic pharmaceuticals						
Salicylic acid	64 ± 7	0.34	1.15	108 ± 8	0.33	1.11
Bentazone	86 ± 4	0.13	0.43	95 ± 4	0.06	0.20
2, 4-D	90 ± 3	0.24	0.79	85 ± 4	0.53	1.78
MCPA	90 ± 2	0.37	1.23	97 ± 3	0.19	0.63
Clofibrac acid	97 ± 6	0.22	0.74	96 ± 1	0.15	0.49
Ketoprofen	103 ± 6	1.25	4.17	123 ± 1	3.19	10.64
Naproxen	77 ± 3	0.06	0.20	98 ± 2	1.06	3.55
Fenoprofen	99 ± 7	0.20	0.66	127 ± 4	2.34	7.81
Diclofenac	93 ± 6	0.43	1.43	129 ± 6	0.35	1.16
Indometacin	68 ± 7	0.65	2.17	91 ± 7	1.88	6.25
Ibuprofen	82 ± 11	1.25	4.17	160 ± 10	1.51	5.03
Meclofenamic acid	108 ± 3	4.23	14.08	113 ± 14	1.36	4.52
Mefenamic acid	102 ± 10	2.70	9.01	111 ± 5	0.63	2.11
Gemfibrozil	89 ± 7	0.16	0.53	77 ± 11	0.08	0.26
Tolfenamic acid	109 ± 4	0.14	0.46	177 ± 14	0.26	0.87
Neutral pharmaceuticals						
Paracetamol	208 ± 10	0.15	0.49	72 ± 6	2.94	9.80
Primidone	70 ± 14	0.18	0.59	69 ± 4	0.33	1.11
Cyclophosphamide	103 ± 18	0.06	0.21	43 ± 4	0.03	0.09
Carbamazepine	103 ± 1	0.05	0.15	123 ± 21	0.02	0.06
Antibiotics						
Sulfacetamide	68 ± 2	0.67	2.22	108 ± 5	1.01	3.37
Sulfadiazine	72 ± 2	0.072	0.24	123 ± 2	1.15	3.82
Sulfapyridine	88 ± 2	0.11	0.36	85 ± 5	1.90	6.33
Sulfamethazine	92 ± 3	0.023	0.077	84 ± 6	0.51	1.69
Sulfamethoxazole	86 ± 2	0.31	1.01	77 ± 2	0.58	1.94
Trimethoprim	133 ± 2	0.10	0.33	245 ± 1	0.64	2.15
Oxytetracycline	300 ± 3	0.20	0.67	64 ± 15	0.19	0.64
Tetracycline	127 ± 5	0.24	0.79	68 ± 2	0.80	2.67
Norfloxacin	66 ± 4	0.036	0.12	108 ± 5	4.20	14.01
Ofloxacin	155 ± 6	0.15	0.5	75 ± 3	1.56	5.20
Ciprofloxacin	70 ± 3	1.32	4.35	160 ± 6	2.01	6.70
Lomefloxacin	113 ± 7	1.61	5.3	92 ± 16	2.15	7.17
Erythromycin-H ₂ O	85 ± 4	0.16	0.53	86 ± 2	0.08	0.26
Roxithromycin	83 ± 1	0.036	0.12	148 ± 3	0.18	0.59
Oleandomycin	158 ± 4	0.0085	0.028	83 ± 2	0.22	0.73

Note: Bold letters in the table represent those recoveries outside the range of 70–120%.

Among all 34 target pharmaceuticals, 13 acidic pharmaceuticals (except for meclufenamic acid and tolfenamic acid), 2 neutral pharmaceuticals (except for paracetamol and cyclophosphamide) and 12 antibiotics (except for ciprofloxacin, lomefloxacin and oleandomycin) were detected at concentrations above the LOQ in at least one of the irrigation water samples (Table 8). In the groundwaters (GWC, GWB and GWS) from the three sites without previous irrigation of reclaimed wastewaters, salicylic acid and five antibiotics (sulfadiazine, sulfamethazine, trimethoprim, oxytetracycline and tetracycline) were detected unexpectedly at similar concentrations between

the three sites. These wastewater-related compounds are not expected to occur in groundwater. This suggests that the groundwater has been contaminated due to leaching of these compounds from other wastewater irrigated sites. The rest of the detected target compounds were only found in the reclaimed wastewaters (WWC, WWB and WWS) used for irrigation. Six more pharmaceuticals were detected in the reclaimed wastewater from Cangzhou (WWC) than the corresponding groundwater (GWC). More pharmaceuticals (≥ 24 compounds) were detected at higher concentrations in the other two reclaimed wastewaters (WWB and WWS) than the corresponding groundwater samples (GWB and GWS). The highest mean concentrations were found for oxytetracycline (1600 ng/L) and tetracycline (1504 ng/L) in the reclaimed wastewater from Shijiazhuang (WWS).

3.2. Concentrations of the EDCs and pharmaceuticals in the soils

Only 9 out of 43 target compounds were detected in the irrigated soil samples from the three sites (Tables 9 and 10). The nine detected compounds include bisphenol-A, triclocarban, triclosan, 4-nonylphenol, salicylic acid, oxytetracycline, tetracycline, trimethoprim and primidone. Many target compounds found in the irrigation water samples were not detected in the corresponding irrigated soil samples. On the contrary, those detected in the irrigated soil samples were all detected in the irrigation water samples. Among the nine compounds detected in the irrigated soils, three compounds 4-nonylphenol, salicylic acid and oxytetracycline were found in all six plots from three locations (Tables 9 and 10). Similar concentrations in the soils were determined for salicylic acid and 4-nonylphenol in both groundwater and wastewater irrigated plots except for salicylic acid ($< \text{LOQ}$) in the depths (10–20 cm and 20–30 cm) of plot GSC (Tables 9 and 10). Among the nine detected compounds, three compounds triclocarban, oxytetracycline and tetracycline in most cases had significantly higher concentrations in the wastewater irrigated plots than in the groundwater irrigated plots ($p < 0.05$, Tables 9 and 10). Concentrations up to 212 μg/kg was found for oxytetracycline in the wastewater irrigated soils. However, bisphenol-A, triclosan, trimethoprim and primidone were found only in one plot with low concentrations ranging from 1.6 to 4.3 μg/kg. For most compounds detected in the soils, they were found in all the three soil layers.

4. Discussion

The present study found the presence of nine target compounds bisphenol-A, triclocarban, triclosan, 4-nonylphenol, salicylic acid, oxytetracycline, tetracycline, trimethoprim and primidone in the wastewater irrigated soils from the three locations in Hebei, China. The most interesting compounds were triclocarban, oxytetracycline and tetracycline, which in most cases had significantly higher concentrations in the wastewater irrigated soils than in the

Table 7
Concentrations (ng/L) of the endocrine-disrupting chemicals (EDCs) detected in the irrigation waters in Hebei, China (mean ± SD, $n = 5$).

Compounds	GWC	WWC	GWB	WWB	GWS	WWS
4-tert-Octylphenol	6.8 ± 2.1	7.4 ± 1.6	5.2 ± 0.66	126 ± 3.6	9.0 ± 1.4	168 ± 15.3
4-Nonylphenol	350 ± 37.2	460 ± 18.8	202 ± 69.6	3167 ± 233	396 ± 51.2	4879 ± 161
Bisphenol-A	61.2 ± 5.2	91.8 ± 3.8	44.8 ± 2.8	148 ± 20.0	51.7 ± 2.9	265 ± 10.6
Estrone	ND	ND	ND	<LOQ	ND	6.0 ± 0.37
Diethylstilbestrol	ND	ND	ND	12.1 ± 0.09	ND	5.6 ± 1.1
Estradiol	ND	ND	ND	ND	ND	4.5 ± 0.28
Triclocarban	ND	ND	ND	390 ± 2.4	ND	183 ± 1.1
Triclosan	1.6 ± 0.06	1.8 ± 0.1	1.2 ± 0.23	108 ± 2.8	10.8 ± 2.0	66.2 ± 8.2

<LOQ: below the limit of quantification; ND: not detected; SD: standard deviation.

GWC, GWS and GWS are groundwaters from Cangzhou, Baoding and Shijiazhuang, respectively. WWC, WWB and WWS are reclaimed wastewaters from Cangzhou, Baoding and Shijiazhuang, respectively.

Table 8
Concentrations (ng/L) of the pharmaceuticals detected in the irrigation waters in Hebei, China (mean \pm SD, $n = 5$).

Compounds	GWC	WWC	GWB	WWB	GWS	WWS
Acidic pharmaceuticals						
Salicylic acid	3.5 \pm 141	7.8 \pm 13.0	2.9 \pm 11.3	6.4 \pm 11.7	1.2 \pm 2.7	41.4 \pm 39.4
Clofibrac acid	ND	ND	ND	43.6 \pm 6.7	ND	ND
Ibuprofen	ND	ND	ND	204 \pm 28.9	ND	476 \pm 14.3
MCPA	ND	ND	ND	ND	ND	183 \pm 0.44
2,4-D	ND	6.7 \pm 4.6	ND	29.5 \pm 15.0	ND	4.3 \pm 40.2
Gemfibrozil	ND	ND	ND	51.0 \pm 2.1	ND	64.1 \pm 1.3
Bentazone	ND	ND	ND	15.6 \pm 1.4	ND	48.0 \pm 7.9
Fenoprofen	ND	10.9 \pm 0.05	ND	7.8 \pm 0.15	ND	189 \pm 13.2
Naproxen	ND	13.0 \pm 0.88	ND	14.2 \pm 0.30	ND	109 \pm 1.1
Ketoprofen	ND	26.7 \pm 3.3	ND	31.2 \pm 1.1	ND	66.4 \pm 1.1
Mefenamic acid	ND	ND	ND	15.9 \pm 1.7	ND	15.9 \pm 0.86
Diclofenac	ND	ND	ND	64.0 \pm 0.01	ND	269 \pm 28.1
Indomethacin	ND	ND	ND	66.7 \pm 1.2	ND	238 \pm 12.8
Neutral pharmaceuticals						
Primidone	ND	ND	ND	17.4 \pm 29.7	ND	ND
Carbamazepine	ND	ND	ND	46.9 \pm 24.9	ND	2.2 \pm 20.2
Antibiotics						
Sulfacetamide	ND	14.0 \pm 6.7	ND	18.8 \pm 23.8	ND	29.1 \pm 4.8
Sulfadiazine	3.5 \pm 0.14	3.7 \pm 0.70	3.6 \pm 0.30	14.5 \pm 17.0	3.5 \pm 0.01	15.7 \pm 32.6
Sulfapyridine	ND	ND	ND	12.1 \pm 3.4	ND	20.9 \pm 1.6
Sulfamethazine	3.5 \pm 3.3	3.6 \pm 0.00	3.4 \pm 0.21	6.7 \pm 0.40	3.4 \pm 0.43	33.8 \pm 0.02
Trimethoprim	2.6 \pm 0.37	3.3 \pm 8.8	2.6 \pm 0.27	30.4 \pm 2.0	4.2 \pm 2.4	49.9 \pm 2.7
Oxytetracycline	12.9 \pm 0.40	13.0 \pm 1.5	12.8 \pm 0.00	12.9 \pm 0.00	12.9 \pm 0.80	1600 \pm 2.5
Tetracycline	12.4 \pm 1.8	12.6 \pm 1.1	12.3 \pm 0.15	12.2 \pm 0.27	12.3 \pm 0.19	1504 \pm 3.9
Compounds						
Norfloxacin	WCA	WCB	WBA	WBB	WSA	WSB
Ofloxacin	ND	23.5 \pm 6.1	ND	9.0 \pm 28.2	ND	ND
Sulfamethoxazole	ND	ND	ND	6.6 \pm 9.1	ND	38.1 \pm 6.0
Erythromycin-H ₂ O	ND	2.6 \pm 15.7	ND	21.8 \pm 4.6	ND	15.6 \pm 27.5
Roxithromycin	ND	ND	ND	14.5 \pm 0.86	ND	253 \pm 2.2
				1.0 \pm 15.0	ND	3.0 \pm 4.0

<LOQ: below the limit of quantification; ND: not detected; SD: standard deviation.

GWC, GWC and GWS are groundwaters from Cangzhou, Baoding and Shijiazhuang; WWC, WWB and WWS are reclaimed wastewaters from Cangzhou, Baoding and Shijiazhuang, respectively.

groundwater irrigated soils. These nine compounds were also found in the corresponding irrigation waters, suggesting irrigation waters (groundwater and reclaimed wastewater) were a contribution source.

Among the nine detected compounds, 4-nonylphenol and salicylic acid were detected in all six plots with wastewater irrigation or with groundwater irrigation. 4-Nonylphenol has been reported ubiquitously in various environmental media including air, water and sediment (Dachs et al., 1999; Isobe et al., 2001; Van Ry et al., 2000; Ying et al., 2002). Thus, in addition to application of irrigation water, atmospheric deposition might also contribute to the presence of 4-nonylphenol in the soils (Dachs et al., 1999; Van Ry et al., 2000). For salicylic acid, it was one of the most frequently detected acidic pharmaceuticals in surface waters and sewage effluents (Kasprzyk-Hordern et al., 2008; Matamoros and Bayona, 2006; Peng et al., 2008; Ternes, 1998; Zhao et al., 2010), which could be attributed to the extensive use in human and animals to reduce inflammation. The compound is very mobile as indicated by its physicochemical properties with a high water solubility and low log K_{ow} value (Table 2). Therefore, it is not surprising to have detected salicylic acid in the groundwater of the three sites. Due to repeated application of irrigation waters, this compound was also detected in the soils of the study plots irrigated by both wastewater and groundwater.

Triclocarban, oxytetracycline and tetracycline in the wastewater irrigated soils were found to be consistent with their concentrations in the corresponding wastewaters. These three compounds have a strong tendency to sorb onto soils with very high K_{oc} values (Tables 1 and 2). Triclocarban is widely used in toothpaste, deodorant and soap. The compound was found to degrade slower in soils under

Table 9

Concentrations ($\mu\text{g}/\text{kg dw}$) of the endocrine-disrupting chemicals (EDCs) detected in the irrigated soils in Hebei, China (mean \pm SD, $n = 5$).

Site	Depth (cm)	Bisphenol-A	Triclocarban	Triclosan	4-Nonylphenol
GSC	0–10	<LOQ	<LOQ	<LOQ	32.8 \pm 13.4
	10–20	<LOQ	<LOQ	<LOQ	58.2 \pm 10.3
	20–30	<LOQ	<LOQ	<LOQ	36.3 \pm 21.1
WSC	0–10	<LOQ	<LOQ	<LOQ	34.8 \pm 10.8
	10–20	<LOQ	<LOQ	<LOQ	36.9 \pm 14.8 ^a
	20–30	<LOQ	<LOQ	<LOQ	33.6 \pm 21.5
GSB	0–10	<LOQ	<LOQ	<LOQ	43.7 \pm 11.2
	10–20	<LOQ	<LOQ	<LOQ	31.2 \pm 8.8
	20–30	<LOQ	<LOQ	<LOQ	57.4 \pm 10.6
WSB	0–10	<LOQ	105 \pm 38.9	1.8 \pm 1.7	14.2 \pm 9.0 ^a
	10–20	<LOQ	39.7 \pm 18.3	<LOQ	25.8 \pm 5.4
	20–30	<LOQ	10.6 \pm 6.1	<LOQ	24.2 \pm 3.8 ^a
GSS	0–10	<LOQ	<LOQ	<LOQ	60.3 \pm 23.3
	10–20	4.3 \pm 5.9	<LOQ	<LOQ	22.1 \pm 4.6
	20–30	<LOQ	<LOQ	<LOQ	25.9 \pm 3.6
WSS	0–10	<LOQ	41.1 \pm 21.5	<LOQ	21.5 \pm 8.7 ^a
	10–20	<LOQ	26.6 \pm 15.0	<LOQ	19.2 \pm 5.1
	20–30	<LOQ	8.5 \pm 11.9	<LOQ	55.4 \pm 53.4

<LOQ: below the limit of quantification; ND: not detected; SD: standard deviation. GSC, GSB and GSS are plots irrigated with groundwater from Cangzhou, Baoding and Shijiazhuang; WSC, WSB and WSS are plots irrigated with reclaimed wastewater from Cangzhou, Baoding and Shijiazhuang, respectively.

^a Data were statistically analyzed by using ANOVA at the significant level of $p < 0.05$.

Table 10
Concentrations ($\mu\text{g}/\text{kg}$ dw) of the pharmaceuticals detected in the irrigated soils in Hebei, China (mean \pm SD, $n = 5$).

Site	Depth (cm)	Salicylic acid	Oxytetracycline	Tetracycline	Trimethoprim	Primidone
GSC	0–10	1.4 \pm 1.0	4.4 \pm 2.5	<LOQ	<LOQ	<LOQ
	10–20	<LOQ	4.4 \pm 2.5	<LOQ	<LOQ	<LOQ
	20–30	<LOQ	2.3 \pm 3.1	<LOQ	<LOQ	<LOQ
WSC	0–10	4.5 \pm 0.8	6.2 \pm 0.2	<LOQ	<LOQ	<LOQ
	10–20	2.0 \pm 0.6	6.1 \pm 0.4	<LOQ	<LOQ	<LOQ
	20–30	1.6 \pm 0.3	5.8 \pm 0.3 ^a	<LOQ	<LOQ	<LOQ
GSB	0–10	6.6 \pm 0.9	3.3 \pm 3.0	<LOQ	<LOQ	ND
	10–20	4.9 \pm 0.9	1.1 \pm 2.5	<LOQ	<LOQ	ND
	20–30	3.3 \pm 0.7	2.2 \pm 3.0	<LOQ	<LOQ	ND
WSB	0–10	9.1 \pm 0.9 ^a	7.5 \pm 0.7 ^a	6.9 \pm 0.5	2.6 \pm 0.6	ND
	10–20	8.3 \pm 1.2 ^a	6.3 \pm 0.3 ^a	6.8 \pm 0.9	<LOQ	3.3 \pm 5.6
	20–30	4.6 \pm 1.2	5.8 \pm 0.2 ^a	2.8 \pm 3.9	<LOQ	1.6 \pm 2.3
GSS	0–10	8.4 \pm 1.6	16.0 \pm 13.0	8.9 \pm 3.2	<LOQ	ND
	10–20	6.3 \pm 1.5	9.1 \pm 4.3	7.2 \pm 1.1	<LOQ	ND
	20–30	4.6 \pm 2.2	6.7 \pm 1.5	8.9 \pm 5.3	<LOQ	<LOQ
WSS	0–10	10.7 \pm 4.6	212 \pm 122 ^a	19.6 \pm 6.1 ^a	<LOQ	ND
	10–20	5.3 \pm 1.0	150 \pm 58.1 ^a	19.9 \pm 1.7 ^a	<LOQ	ND
	20–30	4.7 \pm 2.0	54.5 \pm 39.4 ^a	12.8 \pm 3.5	<LOQ	ND

<LOQ: below the limit of quantification; ND: not detected; SD: standard deviation.

GSC, GSB and GSS are plots irrigated with groundwater from Cangzhou, Baoding and Shijiazhuang; WSC, WSB and WSS are plots irrigated with reclaimed wastewater from Cangzhou, Baoding and Shijiazhuang, respectively.

^a Data were statistically analyzed by using ANOVA at the significant level of $p < 0.05$.

aerobic conditions, with a half-life of 108 days when comparing with another antiseptic triclosan with a half-life of 18 days (Ying et al., 2007). Tetracycline and oxytetracycline are broad-spectrum antibiotics used to treat human and animals. Highest concentrations of oxytetracycline and tetracycline were also found in the reclaimed wastewater (WWS) of Shijiazhuang (Table 8), which is consistent with the highest concentrations in the wastewater irrigated soils (WSS) of the site. Therefore, it is clear that application of reclaimed wastewaters led to accumulation of these three compounds in the irrigated soils.

Reclaimed wastewaters have also been applied to irrigate crops in other countries, but few previous studies reported on the presence and accumulation of these emerging contaminants such as EDCs and pharmaceuticals in irrigated soils (Durán-Alvarez et al., 2009; Kinney et al., 2006). Kinney et al. (2006) detected some pharmaceuticals including erythromycin, carbamazepine, fluoxetine and diphenhydramine in the wastewater irrigated soils of Colorado, USA at typical concentrations of 0.02–15 $\mu\text{g}/\text{kg}$ Durán-Alvarez et al. (2009) measured low concentrations of various EDCs and pharmaceuticals in the soils of the Tula Valley, Mexico, under irrigation of wastewater for approximately 90 years. The list of detected analytes includes a few drugs (ibuprofen, naproxen, and carbamazepine), 4-nonylphenol, triclosan, and bisphenol-A; but no estrogens were detected in the investigation (Durán-Alvarez et al., 2009). Ternes

et al. (2007) screened 52 pharmaceuticals in the groundwater and lysimeter samples of Braunschweig, Germany with irrigation of wastewater for more than 45 years, and found diatrizoate and iopamidol, carbamazepine and sulfamethoxazole at concentrations up to $\mu\text{g}/\text{L}$, but no acidic pharmaceuticals and estrogens. The present study also found trace levels of some pharmaceuticals in the groundwater samples from the three sites in Hebei province, north China. Distribution of some target compounds in the soil profiles were also observed in the present study and previous studies (Chefetz et al., 2008; Kinney et al., 2006). This indicates that irrigation of wastewater may lead to a contamination of groundwater with some pharmaceuticals. Fortunately, some pharmaceuticals and EDCs in reclaimed wastewater could be retained by soil, and/or degraded during passage through the soil layers (Tables 1 and 2). Some compounds such as tetracyclines and triclocarban have high sorption coefficients in soils as shown in Tables 1 and 2. Previous laboratory degradation studies showed that phenolic EDCs bisphenol-A, octylphenol, nonylphenol, estrone, estradiol and ethynylestradiol were degraded rapidly in aerobic soils with half-lives of less than 7 days (Ying and Kookana, 2005). The half-life for triclosan in aerobic soils was 14–18 days (Xu et al., 2009; Ying et al., 2007), while those for acidic pharmaceuticals (clofibric acid, ibuprofen, naproxen and diclofenac) ranged from 1 to 19 days (Xu et al., 2009). The reported half-lives for sulfamethoxazole and sulfadiazine were 2 days

Table 11
Comparison of the measured and calculated concentrations ($\mu\text{g}/\text{kg}$) for five frequently detected compounds in the soils.^a

Sites	Triclocarban		4-Nonylphenol		Salicylic acid		Oxytetracycline		Tetracycline	
	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated
GSC	0.3	–	42.4	47.1	1.0	0.5	3.7	1.7	1.9	1.7
WSC	0.3	–	35.1	61.9	2.7	1.0	6.0	1.7	1.9	1.7
GSB	0.3	–	44.1	27.2	4.9	0.4	3.3	1.7	1.9	1.7
WSB	51.8	52.5	21.4	426	7.3	0.9	6.5	1.7	5.5	1.6
GSS	0.3	–	36.1	53.3	6.4	0.2	10.6	1.7	8.3	1.7
WSS	25.4	24.6	32.0	657	6.9	5.6	139	215	17.4	202

^a The calculated concentrations were calculated using the measured concentrations of corresponding compounds in the irrigation waters. We assume that the water application rate is 10,500 m^3/hm^2 per year, the plough depth is 30 cm and the soil bulk density is 1.3 g/cm^3 . We also assume that the compounds did not degrade within 50 years, which is used in calculation. The measured concentrations are the mean concentrations of each compound in the soil depth of 0–30 cm. For those compounds detected below the LOQ in soil, a value equal to the LOQ divided by square root of 2 was used.

(Liu et al., 2010) and 12–18 days (Yang et al., 2009a), respectively. Trimethoprim could also be degraded easily in aerobic soils with a half-life of 4 days (Liu et al., 2010). Those previous studies (Table 1) clearly showed that some pharmaceuticals and EDCs could be easily degraded in aerobic soils.

Based on the use of wastewater irrigation for 50 years, the theoretical concentrations were calculated by assuming no dissipation, and compared with the mean measured concentrations for five frequently detected compounds (Table 11). From the data shown in the table, triclocarban was persistent in the wastewater irrigated soils, which is consistent with the soil degradation data from Ying et al. (2007). The measured concentrations for 4-nonylphenol in the wastewater irrigated soils from the three sites were all lower than the calculated concentrations, probably suggesting dissipation of this compound in the soils. For the other three compounds (salicylic acid, oxytetracycline and tetracycline), the calculated concentrations were even lower than the measured concentrations in the wastewater irrigated soils from some plots. This suggests that uncertainties might be associated with the calculation, such as varying concentrations in reclaimed waters and application rate.

It is not known whether the presence of these detected pharmaceuticals and EDCs at the concentrations (<1 mg/kg) found in the present study pose any risk to the soil ecosystem and human health; therefore, a simple risk assessment was performed for those compounds detected in the soils through calculation of risk quotients (RQ). RQ values for soil terrestrial organisms were calculated from the measured environmental concentration (MEC) and the predicted no effect concentration (PNEC) of each compound (European Commission, 2003). It has been reported that 4-nonylphenol in soil did not adversely affect soil respiration or plant growth until its concentration reached 10,000 mg/kg, and the uptake by plants was very low (Roberts et al., 2006). The RQ values for 4-nonylphenol was all less than 1 based on the measured soil concentrations in the present study and the PNEC value of 0.3 mg/kg (European Commission, 2002). This suggests 4-nonylphenol in the soils most probably poses very low risks to the soil terrestrial organisms. Triclocarban and triclosan are both antimicrobial agents and had similar physicochemical properties. Triclosan inhibited plant growth in soil with EC10 values (10% effective concentration for root elongation) of 17 mg/kg to cucumber and 27 mg/kg to rice (Liu et al., 2009b). Soil respiration was significantly inhibited by triclosan at concentrations more than 10 mg/kg during the first 4 days of incubation, but recovered later on after longer incubation (Liu et al., 2009b). The only terrestrial toxicity data for triclocarban was LC50 value (40 mg/kg) for *Eisenia fetida* earthworms (Snyder et al., 2011), so the PNEC value for triclocarban was 40 µg/kg. Based on this toxicity data, the calculated RQ values for triclocarban in the wastewater irrigated soils from Baoding (WSB: 0–10 and 10–20 cm) and Shijiazhuang (WSS: 0–10 cm) were more than 1, indicating potential high risks to earthworms.

If we use the calculated concentrations in Table 11 for risk assessment, high risks are expected for triclocarban in the wastewater irrigated soils in Baoding (WSB) and for 4-nonylphenol in the wastewater irrigated soils in Baoding and Shijiazhuang (WSB and WSS) after 50 years' irrigation. It is estimated to take 23–35 years for 4-nonylphenol to reach the threshold concentration (0.3 mg/kg); but due to degradation of 4-nonylphenol in soil (Ying and Kookana, 2005), it will take longer time to reach the toxic effect level. But minimal risks are expected for the other compounds salicylic acid, oxytetracycline and tetracycline. It will take more than 70 years for tetracyclines to reach the threshold concentrations. Improvement in wastewater treatment will also further reduce or remove these compounds in the reclaimed water used for irrigation.

Liu et al. (2009a) measured toxicity of six antibiotics (chlortetracycline, tetracycline, tylosin, sulfamethoxazole, sulfamethazine and trimethoprim) to plant growth in soil with root elongation as the endpoint. The EC10 values ranged from 1 mg/kg for sulfamethazine to >300 mg/kg for the two tetracyclines. In comparison with the controls, all six antibiotics tested inhibited soil phosphatase activity at the concentration range used (1–300 mg/kg). Sulfamethoxazole, sulfamethazine and trimethoprim had temporal effects on soil respiration whereas tetracycline, chlortetracycline and tylosin had little effects on soil respiration (Liu et al., 2009a). Thiele-Bruhn and Beck (2005) also observed no effects of oxytetracycline on soil respiration and dehydrogenase activity at the concentration of 1000 mg/kg. However, the Fe(III) reduction test with a 7-day incubation showed EC10 values of approximately 4 µg/kg for oxytetracycline (Thiele-Bruhn and Beck, 2005). It has been reported that pharmaceuticals could be uptaken by plants under hydroponic conditions (Herklotz et al., 2010) and under soil conditions (Boxall et al., 2006). Boxall et al. (2006) found uptake of some veterinary drugs (amoxicillin, diazinon, enrofloxacin, florfenicol, levamisole, oxytetracycline, phenylbutazone, sulfadiazine, trimethoprim and tylosin) from soils into plants, but the exposure of humans via plant-derived foodstuffs was predicted to be generally low and the effects on human health were unlikely. Based on the terrestrial toxicity data for plants, springtails, enchytraeids and earthworms from Liu et al. (2009a) and Bagger et al. (2000), the calculated RQ values for tetracycline and oxytetracycline in the soils from the present study were all less than 1. From the above analysis, the potential risks posed by the two antibiotic residues in the soils would be very low. So far there has been no terrestrial toxicity data for salicylic acid, so risk assessment could not be performed at this stage. However, a further study is needed to investigate actual concentrations of these contaminants in the crops grown in the wastewater irrigated plots in order to have a realistic risk assessment.

5. Conclusion

The present study clearly showed that irrigation of wastewater could lead to existence of some pharmaceuticals and EDCs in the irrigated soils. The concentrations and compositions of the contaminants present in the irrigated soils depend on the type of source water used for irrigation. Nine compounds (bisphenol-A, triclocarban, triclosan, 4-nonylphenol, salicylic acid, oxytetracycline, tetracycline, trimethoprim and primidone) were detected in the irrigated soils of three sites in Hebei, China; and in most cases three of them (triclocarban, oxytetracycline and tetracycline) showed significantly higher concentrations in the wastewater irrigated soils than in the groundwater irrigated soils. These contaminants in the wastewater irrigated soils were found to have very low concentrations (<1 mg/kg) and would pose low risks to the environment and human health based on the existing data except for triclocarban showing high risks to soil organisms. However, more studies are needed to investigate uptake of these emerging contaminants by plants and potential long-term impacts on the soil and food quality.

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