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Occurrence and ecological potential of pharmaceuticals and personal care products in groundwater and reservoirs in the vicinity of municipal landfills in China

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HIGHLIGHTS

- No groundwater sample was free of contamination of the PPCPs.
- The PPCPs were widely detected in the reservoirs.
- The anti-bacterials in groundwater posed medium risks to sensitive species of algae.
- The PPCPs posed low to high risks to sensitive species of organisms in reservoirs.
- More data are needed to clarify impact of the landfills on the aquatic eco-systems.

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ABSTRACT

Pharmaceutical and personal care products (PPCPs), including antibiotics, azole anti-fungals, non-steroid anti-inflammatory drugs, lipid regulators, parabens, antiseptics, and bisphenol A, were investigated in groundwater and reservoirs in the vicinity of two municipal landfills in the metropolis of Guangzhou, South China. Dehydroerythromycin, sulfamethoxazole, fluconazole, salicylic acid, methylparaben, triclosan, and bisphenol A were the mostly frequently detected PPCPs in the groundwater at low ng L^{-1} levels. In the reservoirs, the PPCPs were widely detected at higher frequencies and concentrations, especially sulfamethoxazole, propiconazole, and ibuprofen, with maximal concentrations above 1 μg L^{-1}. The PPCPs in the groundwater did not show significant seasonal differences or spatial trends. However, in the reservoirs, higher PPCP concentrations were observed in spring than in other seasons. The anti-bacterials in the groundwater posed medium risks to algae. In the reservoirs, the sulfonamides and macrolides posed low to high risks, while ibuprofen, salicylic acid, and clofibric acid presented low to medium risks to aquatic organisms. Overall, the results showed that the PPCP contaminants and subsequent ecological risks in the groundwater and surface water in the vicinity of the landfills may be of serious concern. More research is needed to better correlate the landfill leachates and PPCP contamination in the nearby aquatic environments.

1. Introduction

Groundwater contamination is attracting increasing concerns as chemicals may be more persistent and much more difficult to eliminate due to relatively reduced redox conditions and lack of photodegradation than in surface waters. Additionally, microbial degradation in groundwater systems is much less efficient. Therefore, chemicals in groundwater systems may pose hazards for a much longer period of time compared to chemicals in surface waters (Barber et al., 2009; Greskowiak et al., 2006; Lapworth et al., 2012). Previous research has revealed the presence of various contaminants in groundwater. Several antibiotic compounds (e.g., sulfamethoxazole, lincomycin, and erythromycin) have been detected in groundwater in Europe and North America, with maximum concentrations in the range of 5.7–103 ng L^{-1} (Barnes et al., 2008; Garcia-Galan et al., 2010). Moreover, a variety of industrial chemicals (e.g., detergents, fire retardants, and plasticizers), PPCPs (e.g., anti-inflammatories, β-blockers, drugs of abuse, antiseptics, preservatives, and sweeteners) and their metabolites have been observed in groundwater (Buerge et al., 2009; Grujic et al., 2009; Hohenblum et al.,

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2004; Houtz et al., 2013; Jurado et al., 2012a,b; Kahle et al., 2009; Kuroda et al., 2012; Lopez-Serna et al., 2013; Loos et al., 2010; Osenbruck et al., 2007; Schaider et al., 2014; Teijon et al., 2010; Vulliet and Cren-Olive, 2011; Wolf et al., 2012). The presence of some antibiotics has also been reported in groundwater in North China due to soil manure applications (Hu et al., 2010). Ma et al. (2012) detected eight nitrosamines in shallow groundwater in the Jialu River basin, China. It has been reported that subtherapeutic levels of sulfamethoxazole likely change composition of nitrate-reducing microcosms in groundwater and subsequently inhibit nitrate reduction capabilities (Underwood et al., 2011; Haack et al., 2012). However, information about potential risks of chemicals in groundwater is still very limited.

Landfilling is so far the most common practice for the disposal of municipal solid waste (MSW) worldwide (Buszka et al., 2009; Eggen et al., 2010). Some solid wastes, such as discarded pharmaceuticals and personal care products (PPCPs), plastic products, and electrical products, may release hazardous substances into landfill leachate and subsequently into recipient environments, threatening the health of ecosystems and even human beings (Eggen et al., 2010). A variety of chemicals, including high concentrations of dissolved organic/inorganic carbon, ammonium, methane, and heavy metals, have been detected in landfill leachate (Befenati et al., 2003; Li et al., 2014; Peng et al., 2014; Roy et al., 2014; Yamamoto et al., 2001). In addition, research has also revealed persistence of various chemicals, such as plasticizers and PPCPs, in the groundwater down gradient of landfills (Barnes et al., 2008; Buszka et al., 2009). Holm et al. (1995) detected sulfonamides in the groundwater down gradient of a landfill site in Denmark at concentrations up to 10^4–10^6 ng/L. It was found that landfill leachate-contaminated groundwater had the highest median concentrations of emerging organic contaminants (Lapworth et al., 2012). As a result, landfills have been recognized as one of the primary sources of contamination in groundwater and surface water (Barnes et al., 2008; Befenati et al., 2003; Buszka et al., 2009; Holm et al., 1995; Stuart et al., 2012). Furthermore, Norman Landfill, located in the USA, was observed to influence the functional structure of aquifer microbial communities in the surrounding groundwater (Lu et al., 2012).

China has the largest MSW production in the world, with an increasing rate of 8–10% annually for MSW generation. According to the National Bureau of Statistics of China (2012), the nationwide MSW production was 164 million tons in 2011, 76.9% of which ended up in landfills (including sanitary landfills, incineration, and compost). Moreover, solid waste sorting has only recently been implemented in some large cities in China, meaning that MSW containing various toxic chemicals may have been introduced into landfills without pretreatment and released into landfill leachate, posing potential contamination of the surrounding environment. Li et al. (2014) reported the presence of polybrominated diphenyl ethers at 4.0–351.2 ng/L in landfill leachate in a city in North China. In a previous study, we detected high levels of anti-virals (i.e., acyclovir and ganciclovir) in the landfill leachate of Guangzhou, China (Peng et al., 2014). However, the impact of municipal landfills on the contamination of the aquatic environment, especially groundwater, is still poorly understood compared with those of municipal wastewater. Moreover, very few data have been available revealing contamination of organic chemicals in groundwater in China.

This work aimed to reveal the occurrence of typical PPCPs and to preliminarily assess the potential risks of the PPCPs in groundwater and surface water in the vicinity of municipal landfills. The PPCPs in this study included anti-bacterials (sulfonamides, macrolides, and fluoroquinolones), azole anti-fungals and pesticides, non-steroidal anti-inflammatory drugs (NSAIDs), lipid regulators, and several estrogen-like personal care products (i.e., parabens, triclosan, triclocarban and its metabolite non-chlorinated carbanilide, 2-phenylphenol, and bisphenol A). Organic contaminants in the groundwater of China have received less attention relative to surface waters. This work would therefore provide insight into the impact of landfills on the nearby aquatic environment as well as bridge the knowledge gap of organic contaminants in the groundwater of China.

1.1. Study area and sampling

The Pearl River Delta (PRD) is one of the most developed and densely populated areas of China. Located in the south end of the subtropical belt (Fig. 1), the PRD has a warm and humid climate with an annual precipitation of 1600–2000 mm. Moreover, the PRD plain is abundant with groundwater, including phreatic water and underlying confined groundwater (generally with a depth of 10–20 m, the shallowest being 2-m underground). The aquifers of both phreatic and confined groundwater consist mainly of fine-, silt-, and clay–sandstones from the Holocene and Quaternary. Precipitation is the primary recharge source for groundwater, followed by river water, bedrock crack water, intruding seawater and, sometimes, irrigation water. The groundwater level varies seasonally, reaching its peak in June to September and decreasing gradually from September on, until it reaches its lowest point in January, with an annual variation of 1–3 m. The groundwater temperature averages 22–23.6 °C with an annual variation amplitude of 5.3–9.4 °C, the lowest temperature being in March and the highest from September to November. The groundwater flows slowly southward and finally discharges into Lingding Bay via the mouth of the Pearl River.

As a metropolis of the PRD, Guangzhou has a population of approximately 13 million and an estimated daily MSW production of 18,000 tons, 90% of which was disposed through landfilling (Statistics Bureau of Guangzhou Municipality, 2012). The huge volume of MSW and its treatment have become serious issues, attracting concerns of the government, public, and academic societies. In recent years, the Government of Guangzhou Municipality has made efforts to implement separated collection of garbage, however, MSW had been mostly dumped unsorted in landfills for years prior.

The two municipal landfills in this study, located in the outskirt of Guangzhou, were described previously (Peng et al., 2014). LF1 (small and old) opened in 1989 and closed in 2002, with a total filled MSW of approximately 5 million tons. LF2 (large and new), opened in 2002, is the largest landfill currently operating in Guangzhou, accepting MSW of 7000–9000 tons per day.

There are villages in the vicinity of the two landfills. Most villagers have wells at home which are supplied by the phreatic aquifer with depths of less than 10 m that were supposed to provide a water supply for the family. However, the well water is rarely used for drinking and cooking and is now only used for washing due to concerns of contamination by leachates from the landfills and nearby chemical factories. Additionally, there are no intensive agricultural activities, only small and scarce aquaculture and vegetable fields due to progressing urbanization.

Fourteen and thirteen domestic wells were sampled in the villages in the vicinity of LF1 and LF2, respectively, with a distance of 582–3178 m from the landfills. The wells are covered and/or indoors and are therefore not significantly impacted by rain, sunlight, or surface runoff. A spring water sample was also collected in a potentially affected area of each landfill (Fig. 1). In addition, groundwater samples were collected from four wells that were not impacted by landfills.

There are two reservoirs south of LF2. Water samples were collected upstream (R1a) and downstream (R1b) of R1 at 943 m and 2846 m from LF2, respectively. R2 was also sampled at a distance of 4683 m from LF2 (Fig. 1).

Samplings were conducted seasonally in April (spring), June (summer), October (fall) 2012 and January 2013 (winter). Water samples were collected in amber glass bottles and surrounded with ice during transport to the laboratory where they were stored in the dark at 4 °C until treatment within 48 h.

To assess the presence of PPCPs in landfill leachates, untreated leachates were sampled from both landfills. Moreover, aged and fresh

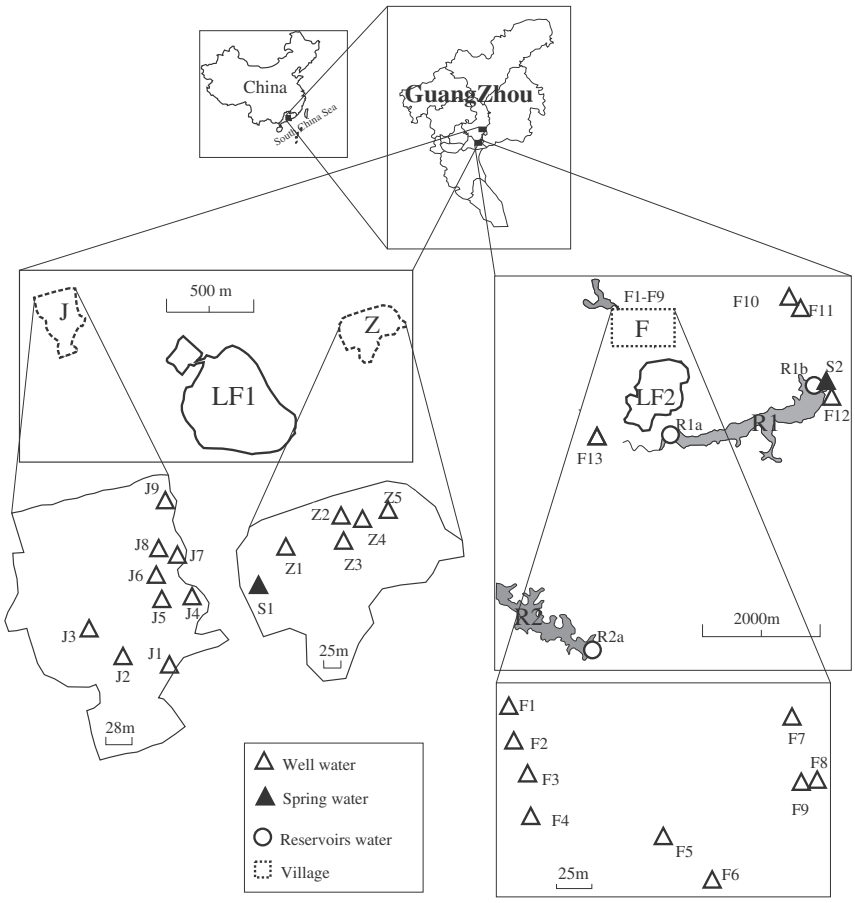

Fig. 1. Sketch map of the municipal landfills and sampled wells and reservoirs.

leachates were collected from both the leachate tank and from the fresh solid waste storage area in LF2.

1.2. Analysis

Sample treatment and chemical analysis were performed by employing protocols described previously (Huang et al., 2011; Tang et al., 2009; Yu et al., 2011). In short, groundwater and reservoir water samples (500 mL each) were spiked with isotope-labeled internal standards and concentrated by solid phase extraction (SPE) on HLB cartridges (200 mg, Waters, Massachusetts, USA) at pH 4.2, pH 4.0, and pH 7.0 for the anti-bacterials, the acid pharmaceuticals and azole anti-fungals, and the endocrine disruption personal care products (PCPs), respectively. Landfill leachates (100 mL each) were filtered with 0.7-μm glass fiber filter (GFF, Whatman, Maidstone, England) prior to the addition of internal standards and SPE concentration as mentioned above. The extracts were concentrated to approximately 0.1 mL by a gentle flow of high purity nitrogen and filtered through a 0.22-μm nylon syringe filter (Anpel, Shanghai, China) followed by LC–MS/MS analysis.

The anti-bacterials, azole anti-fungals, pharmaceuticals, triclocarban, and non-chlorinated carbanilide were determined directly on an Agilent Liquid Chromatography 1200 system coupled with an Agilent 6410 triple quadrupole mass spectrometry with electrospray ionization (Agilent, Palo Alto, CA, USA). For the analysis of the other PCPs, the extract was further treated with derivatization by dansyl chloride prior to HPLC–MS/MS analysis. The chromatographic conditions were provided in Table S1 in the Supporting information. Quantification of the PPCPs was performed in the selected multiple reaction mode (MRM) using an internal standard method as detailed in the Supporting information (Table S2).

1.3. Quality assurance and quality control

Recoveries obtained by spiking the analytes into groundwater ranged from 63 to 124% except for non-chlorinated carbanilide (51%). The limits of quantification (LOQs) were 0.2–5, 0.1–0.4, 0.2–6, 0.1–0.2 ng L^{-1} and 3–51, 1–6, 3–61, 1–4 ng L^{-1} for anti-bacterials, azole anti-fungals, pharmaceuticals, and PCPs in groundwater and landfill leachate, respectively. Procedural blanks and instrumental blanks were set to monitor laboratory contamination and instrumental performance. Trace amounts of clotrimazole and miconazole were detected in the procedural blanks and were appropriately subtracted from the reported concentrations of the samples. Detailed information about the QA/QC procedure was provided elsewhere (Huang et al., 2010; Tang et al., 2009; Yu et al., 2011).

1.4. Statistical analysis

Data processing was performed by Origin 8.0 (OriginLab, Northampton, MA, USA) and SPSS 11.5 (SPSS, Chicago, IL, USA). When the detected concentrations were below limits of detection and quantification, 0 and half of the LOQs were used respectively in the statistical analysis. The level of significance was set at 0.05.

2. Results and discussions

2.1. Occurrence of PPCPs in groundwater

2.1.1. Anti-bacterial

The most frequently detected anti-bacterial was dehydroerythromycin (detection frequency of 68.9%), followed by sulfamethoxazole

Table 1
Comparison of the PPCPs concentrations in the groundwater of Guanzgou, China and other regions in the world.

Compound (abbreviation)	CAS no.	Region/country	Detection frequency	Concentration (ng L^{-1})[a]	Reference
Anti-bacterial					
Sulfadiazine (SDZ)	68-35-9	Guangzhou, China	0	ND	This work
		Barcelona, Spain	0–100%	ND – 65/208	Lopez-Serna et al. (2013)
Sulfapyridine (SPD)	144-83-2	Guangzhou, China	0	ND	This work
		Spain	24.1%	43.21/104	Teijon et al. (2010)
Sulfamethazine (SMZ)	57-68-1	Guangzhou, China	0	ND	This work
		Tianjin North China	–[b]	/9.5	Hu et al. (2010)
		USA	2.7%	/360	Barnes et al. (2008)
		Barcelona, Spain	0–100%	ND – 21.8/29.2	Lopez-Serna et al. (2013)
		Spain	34.5%	74.45/446	Teijon et al. (2010)
Sulfamethoxazole (SMX)	723-46-6	Guangzhou, China	23.6%	28.7/124.5	This work
		USA	23.4%	/1110	Barnes et al. (2008)
		Massachusetts, USA	60%	/113	Schaider et al. (2014)
		California, USA	0.41%	160[c]/170	Fram and Belitz (2011)
		Pan-Europe	4.4%	2/38	Loos et al. (2010)
		France	66%	11/	Vulliet and Cren-Olive (2011)
		Barcelona, Spain	80–100%	9.66–22.9/65	Lopez-Serna et al. (2013)
		Spain	15.1%	47.57/117	Teijon et al. (2010)
Trimethoprim (TMP)	738-70-5	Guangzhou, China	3.8%	3.3/10.5	This work
		USA	0	ND	Barnes et al. (2008)
		Massachusetts, USA	5%	/0.7	Schaider et al. (2014)
		California, USA	0.08%	18[c]/18	Fram and Belitz (2011)
		France	1%	1.4/	Vulliet and Cren-Olive (2011)
		Barcelona, Spain	20–100%	ND-3.04/9.41	Lopez-Serna et al. (2013)
Ofloxacin (OFX)	82419-36-1	Guangzhou, South China	9.4%	9.1/44.2	This work
		Tianjin, China	0	ND	Hu et al. (2010)
		France	0	0	Vulliet and Cren-Olive (2011)
		Barcelona, Spain	100%	24.1–79.5/367	Lopez-Serna et al. (2013)
		Spain	15.1%	23.01/48	Teijon et al. (2010)
Norfloxacin (NFX)	70458-96-7	Guangzhou, China	0	ND	This work
		USA	0	ND	Barnes et al. (2008)
		Barcelona, Spain	69–100%	33–123/462	Lopez-Serna et al. (2013)
Enrofloxacin (EFX)	93106-60-6	Guangzhou, China	0	ND	This work
		USA	0	ND	Barnes et al. (2008)
		Barcelona, Spain	100%	19.2–74.8/264	Lopez-Serna et al. (2013)
Ciprofloxacin (CFX)	85721-33-1	Guangzhou, China	0	ND	This work
		Tianjin, China	–[b]	/42.5	Hu et al. (2010)
		USA	0	ND	Barnes et al., 2008
		Barcelona, Spain	80–100%	12.3–87.9/443	Lopez-Serna et al. (2013)
Lomefloxacin (LFX)		Guangzhou, China	0	ND	This work
Clarithromycin (CTM)	81103-11-9	Guangzhou, China	0	ND	This work
Erythromycin- H_2O (ETM-H_2O)	114-07-8	Guangzhou, China	68.9%	5.6/12.4	This work
		USA	0	ND	Barnes et al. (2008)
		Barcelona, Spain	54–92%	0.31–4.2/8.51	Lopez-Serna et al. (2013)
Roxithromycin (RTM)	80214-83-1	Guangzhou, China	0	ND	This work
		USA	0	ND	Barnes et al. (2008)
		France	7%	1.3/	Vulliet and Cren-Olive (2011)
		Barcelona, Spain	0–54%	ND – 7.95/23.8	Lopez-Serna et al. (2013)
Azole anti-fungal drugs and pesticides					
Clotrimazole (CTZ)	23593-75-1	Guangzhou, China	4%	1.0/1.5	This work
Econazole (ECZ)	24169-02-6		0	<LOQ	
Fluconazole (FCZ)	86386-73-4		23%	21.7/56.2	
Ketoconazole (KCZ)	65277-42-1		2%	1.5/3.3	
Miconazole (MCZ)	22916-47-8		8%	2.8/6.7	
Propiconazole (PCZ)	60207-90-1		6%	0.3/0.8	
Tebuconazole (TCZ)	107534-96-3		14%	0.3/0.8	
Non-steroid anti-inflammatory drugs (NSAIDs)					
Diclofenac (DCF)	15307-79-6	Guangzhou, China	0	<LOQ	This work
		Pan-Europe	4.9%	0/24	Loos et al. (2010)
		Spain	3.7%	256/477	Teijon et al. (2010)
		Barcelona, Spain	40–100%	0.184–225/380	Lopez-Serna et al. (2013)
		France	20%	9.7/	Vulliet and Cren-Olive (2011)
Ibuprofen (IPF)	15687-27-1	Guangzhou, China	11%	19.7/57.9	This work
		USA	2.1%	/3110	Barnes et al. (2008)
		Pan-Europe	6.7%	3/395	Loos et al. (2010)
		France	0	0	Vulliet and Cren-Olive (2011)
		Barcelona, Spain	46–92%	0.16–200/988	Lopez-Serna et al. (2013)
		Spain	1.9%	185/185	Teijon et al. (2010)
Indomethacin (IMC)		Guangzhou, China	6%	3.5/11.7	This work
		Barcelona, Spain	0	ND	Lopez-Serna et al. (2013)
Naproxen (NPX)	23979-41-1	Guangzhou, China	3%	67.0/86.9	This work
		France	3%	1.2/	Vulliet and Cren-Olive (2011)
		Barcelona, Spain	8-40%	ND – 0.43/5.59	Lopez-Serna et al. (2013)
		Spain	–[b]	/263	Teijon et al. (2010)

Table 1 (*continued*)

Compound (abbreviation)	CAS no.	Region/country	Detection frequency	Concentration (ng L^{-1})[a]	Reference
Salicylic acid (SA)	69-72-7	Guangzhou, China	98%	47.3/2014.7	This work
		Barcelona, Spain	100%	58.9–110/620	Lopez-Serna et al. (2013)
		France	53%	6.5/	Vulliet and Cren-Olive (2011)
Lipid regulator					
Clofibric acid (CFA)	882-09-7	Guangzhou China	3%	51.6/73.9	This work
		Barcelona, Spain	0–31%	ND – 1.26/7.57	Lopez-Serna et al. (2013)
Bezafibrate (BZF)	41859-67-0	Guangzhou China	0	ND	This work
		Barcelona, Spain	20–100%	ND – 6.64/25.8	Lopez-Serna et al. (2013)
		France	0	0	Vulliet and Cren-Olive (2011)
Gemfibrozil (GFZ)	25812-30-0	Guangzhou China	0	ND	This work
		USA	0	ND	Barnes et al. (2008)
		Massachusetts, USA	5%	/1.2	Schaider et al. (2014)
		Barcelona, Spain	20–100%	ND – 6.64/25.8	Lopez-Serna et al. (2013)
		Spain	11.3%	163.5/574	Teijon et al. (2010)
Endocrine-disrupting personal care products					
Methyparaben (MP)	99-76-3	UK	–[b]	/5000	Stuart et al. (2012)
		Guangzhou China	97.2%	6.7/83.2	This work
Ethylparaben (EP)	120-47-8		22.2%	1.6/12.5	
Propylparaben (PP)	94-13-3		97.2%	0.9/22.5	
		UK	–[b]	/5500	Stuart et al. (2012)
Butylparaben (BP)	94-26-8	Guangzhou, China	0	ND	This work
2-Phenylphenol (PHP)	90-43-7		100%	0.6/8.8	
Triclosan (TCS)	3380-34-5		100%	8.7/39.9	
		USA	14.9%	<LOQ	Barnes et al. (2008)
		Pan-Europe	1.8%	0/9	Loos et al. (2010)
		UK	–[b]	/2011	Stuart et al. (2012)
Triclocarban (TCC)	101-20-2	Guangzhou, China	79.6%	3.3/36.2	This work
Non-chlorinated carbanilide (NCC)	85-98-3		1.9%	6.7/4.8	
Bisphenol A (BPA)	80-05-7		100%	6.6/160.3	
		USA	29.8%	/2550	Barnes et al. (2008)
		Pan-Europe	39.6%	79/2299	Loos et al. (2010)
		UK	–[b]	/9300	Stuart et al. (2012)
		Germany	100%	/1136	Osenbruck et al. (2007)

[a] Mean/max.
[b] Not reported.
[c] Median concentration ND: not detected, <LOQ: below limit of quantification.

(detection frequency of 23.6%). Ofloxacin and trimethoprim were occasionally detected, whereas the other anti-bacterials were generally below LOQs or not detected. Sulfamethoxazole had the highest median and maximum concentrations (15.9 and 124.5 ng L^{-1}, respectively). Barnes et al. (2008) also found that in USA groundwater, organic wastewater contaminants with the highest concentrations did not necessarily have the highest detection frequencies. The detection frequencies and concentrations of the anti-bacterials fell in the range of those reported in European countries and the USA (Table 1). Spatially, high sulfamethoxazole concentration was generally observed in wells located in village J, in proximity to LF1, especially at sites J4–J9 (Fig. 1), whereas dehydroerythromycin showed no obvious spatial trends. In addition, both detection frequencies and concentrations of anti-bacterials did not show significant seasonal variations despite seasonal variations in groundwater level as mentioned above. This result was quite different from that obtained for the groundwater from organic vegetable bases in Northern China where antibiotic concentrations were higher in winter than in summer, which was ascribed to elevated usage of antibiotics applied to organic vegetable bases in winter through application of manure (Hu et al., 2010). However, there are no intensive agricultural activities in the vicinity of the wells investigated in this work, suggesting that agriculture was not an important contributor to the anti-bacterial levels in the well water. This finding suggests different sources of the antibiotics in the groundwater investigated in this study.

2.1.2. Azole anti-fungals

Among the 7 investigated azole anti-fungals, fluconazole had both the highest detection frequency (21.5%) and concentration (median and maximal of 16.3 and 56.2 ng L^{-1}, respectively). The other azole anti-fungals were all only occasionally detected and at very low concentrations (Table 1). This pattern was similar to that in the water of the Pearl River (Huang et al., 2013). However, the presence of the azole anti-fungals in groundwater has rarely been reported worldwide, precluding further discussion or comparison (Table 1). Significant spatial or seasonal differences were not observed for the distribution of the azole anti-fungals.

2.1.3. Pharmaceuticals

Salicylic acid was found in all groundwater samples, ranging from 6.8 to 2014.4 ng L^{-1}, comparable with that reported in the groundwater of Barcelona, Spain (Lopez-Serna et al., 2013) but higher than those in the groundwater of France (Vulliet and Cren-Olive, 2011). Diclofenac, bezafibrate, and gemfibrozil were not detected above LOQs, although they were detected in European groundwater up to 477, 25.8, and 574 ng L^{-1}, respectively (Lopez-Serna et al., 2013; Vulliet and Cren-Olive, 2011). The other pharmaceuticals (i.e., ibuprofen, indomethacin, naproxen, and clofibric acid) were sparsely detected (detection frequency ≦ 10%), with levels falling within the range reported for European groundwater (Table 1). The distribution pattern of the pharmaceuticals in the groundwater was basically consistent with the distribution pattern observed in the water of the Pearl River (Huang et al., 2011), while the concentrations were much lower in the groundwater. Spatially, all pharmaceuticals, except salicylic acid, were only observed in the wells of village J in the vicinity of LF1. The pharmaceutical concentrations in the groundwater did not show significant seasonal differences.

2.1.4. Endocrine-disrupting PCPs

The PCPs, except butylparaben, were widely detected in the groundwater, with median and maximum concentrations of 0.3–3.2 and 12.5–160.3 ng L^{-1}, respectively. Although the detection frequencies of the PCPs were comparatively high, the maximum concentrations were

generally much lower than those reported for groundwater in Europe and the USA (Table 1). As a dechlorination metabolite of triclocarban (Miller et al., 2008), non-chlorinated carbanilide was detected in two groundwater samples, suggesting a possible occurrence of metabolism for triclocarban. However, due to limited data, it cannot be determined if this metabolic process occurred before or after triclocarban entered the groundwater. Additionally, the distribution of the PCPs in the groundwater showed no significant spatial or seasonal differences.

2.2. PPCPs in the reservoirs

More anti-bacterials were observed in the reservoir than in the groundwater, with sulfamethoxazole having the highest concentration. Dehydroerythromycin, clarithromycin, and sulfamethazine were ubiquitous in the reservoirs. On the contrary, ofloxacin was the only fluoroquinolone detected, with both low detection frequency and low concentration (Fig. 2a). This result was consistent with observations in the reservoirs and lakes of Europe and North America. For example, Huerta et al. (2013) reported the wide presence of erythromycin and sulfamethoxazole and found that the macrolides were correlated with the presence of anti-resistance genes and, consequently, the composition of bacterial communities in two reservoirs in Spain. Similarly, in Lake Michigan, USA, sulfamethoxazole was among the most frequently detected PPCPs, while the other antibiotics were only either occasionally detected or not quantifiable (Blair et al., 2013).

For the azole anti-fungals, the two pesticides, propiconazole and tebuconazole, were ubiquitous, with median concentrations of 58.1 and 38.2 ng L^{-1}, respectively. As in the groundwater, fluconazole had the highest level among the five azole pharmaceuticals, with median and maximum concentrations of 19.6 and 36.2 ng L^{-1}, whereas the other four azole anti-fungal pharmaceuticals were less frequently detected and at much lower concentrations (Fig. 2b).

All the pharmaceuticals were detected at least once in the reservoir water (Fig. 2c). Surprisingly, ibuprofen was ubiquitous and had the highest concentration (median and maximum concentrations of 131.9 and 1416.9 ng L^{-1}, respectively), higher than the levels found in the Pearl River, which receives the treated wastewater of several sewage treatment plants in the metropolis of Guangzhou (Huang et al., 2011). This finding was unexpected, as no direct discharge of domestic wastewater to the reservoirs was observed. Salicylic acid was the second most abundant pharmaceutical, although it had the highest concentration in the groundwater and in the Pearl River (Huang et al., 2011). Diclofenac and indomethacin were also widely detected with median concentrations of 32.5 and 15.5 ng L^{-1}, respectively. These detected pharmaceutical concentrations were higher than those reported for lakes in Switzerland, Sweden, and the USA (Blair et al., 2013; Daneshvar et al., 2010).

The personal care products were widely detected in the reservoirs with median concentrations of 0.7–17.6 ng L^{-1}, among which triclosan and BPA were the most abundant (Fig. 2d). Triclosan was also one of the most frequently detected PPCPs in Lake Michigan, USA (Blair et al., 2013).

PPCPs in the reservoirs generally showed higher levels in spring than in other seasons (Fig. 3). Daneshvar et al. (2010) observed a winter accumulation of NSAIDs in a lake in Sweden, which was ascribed to high water flow rate, low degree of phototransformation and biotransformation during winter in both sewage treatment plants and lakes. Our previous work

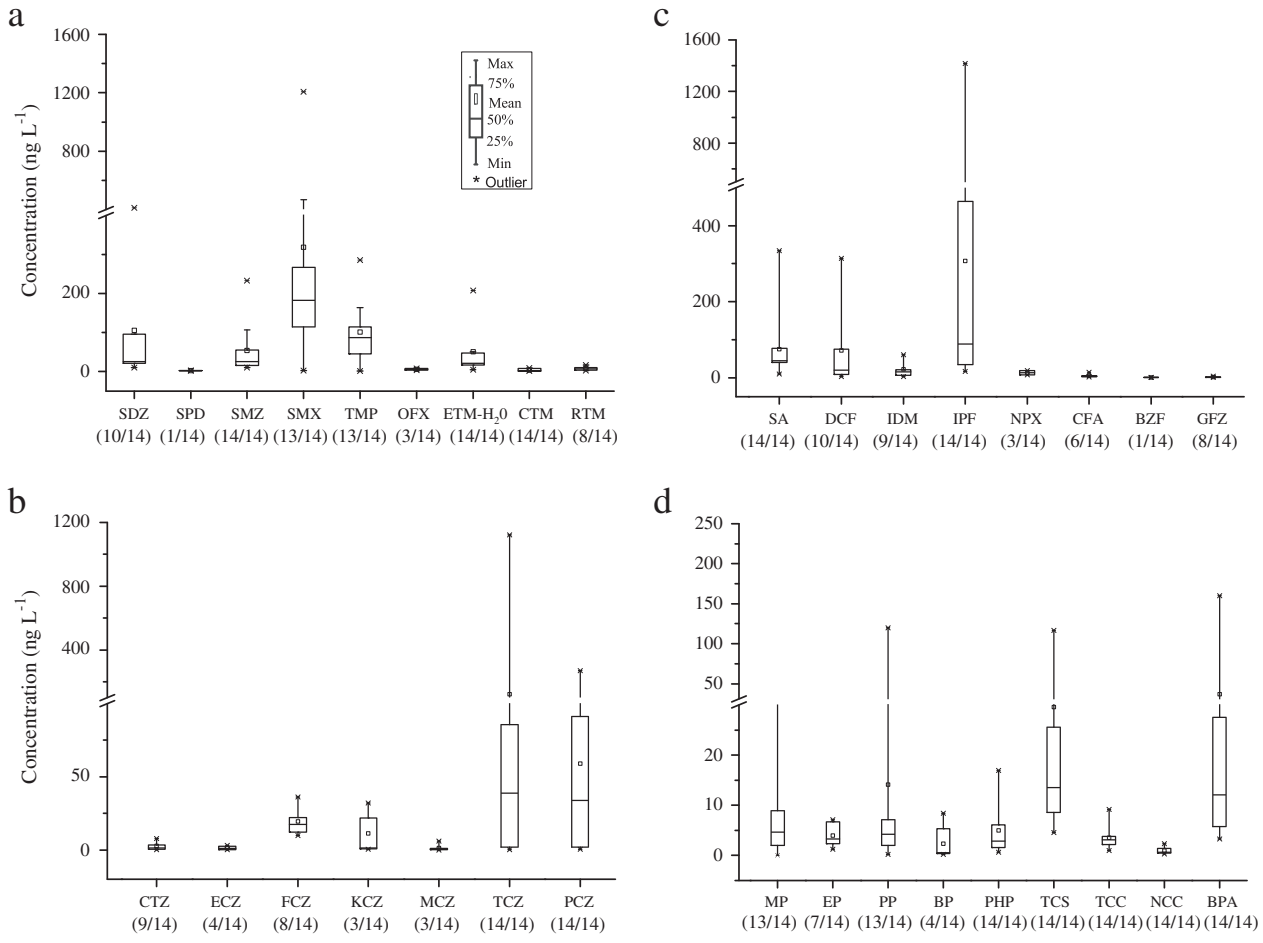

Fig. 2. Box-and-whisker plots of the PPCPs in the reservoirs in the vicinity of the landfills. See Table 1 for abbreviations of the compound names. (a) Anti-bacterials, (b) azole anti-fungals, (c) pharmaceuticals, (d) personal care products.

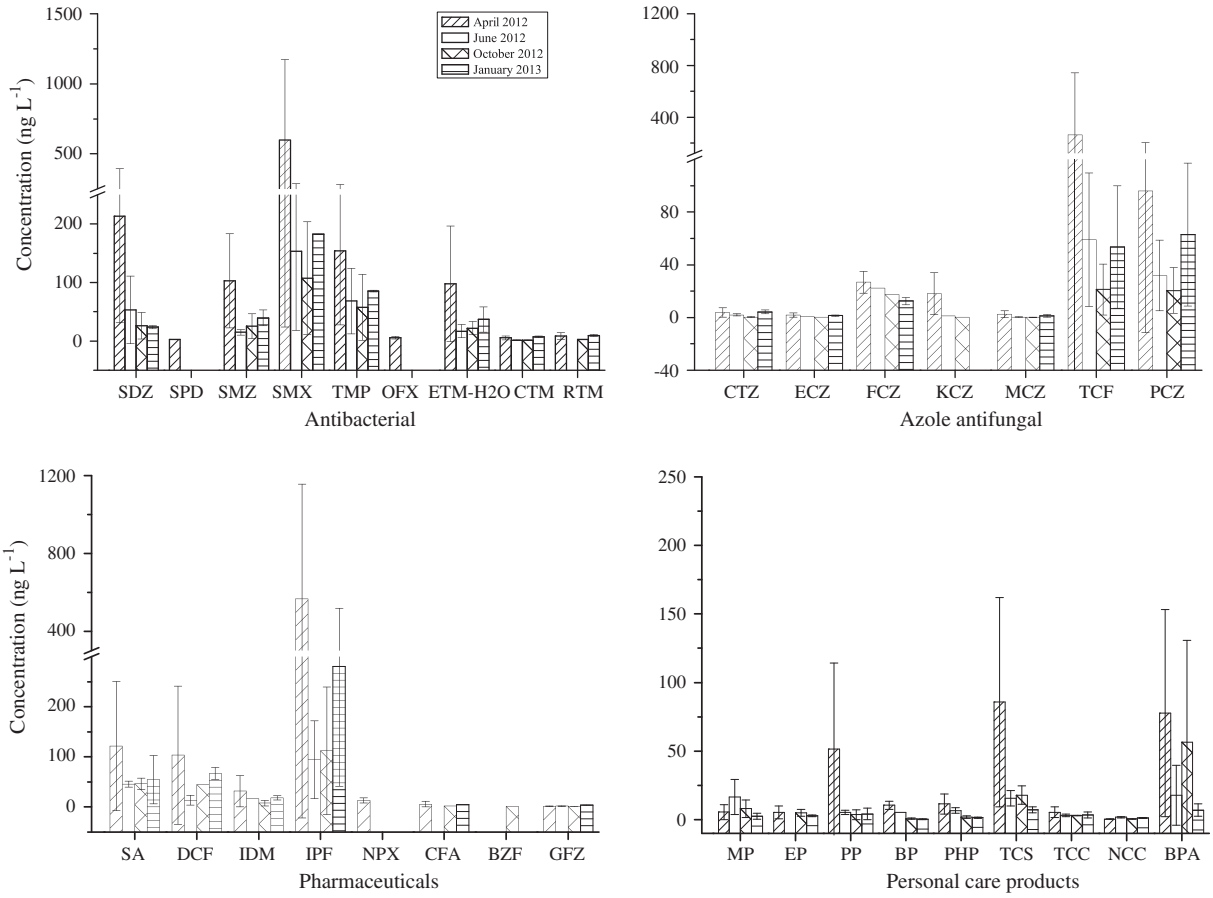

Fig. 3. Seasonal distribution of the PPCPs in the reservoirs. See Table 1 for abbreviations of the compound names.

also revealed higher PPCP concentrations in wintertime in the Pearl River and suggested that dilution effects play a predominant role in seasonal PPCP patterns in river water (Huang et al., 2011, 2013; Peng et al., 2011). However, limited sampling sites in the reservoirs precluded in-depth analysis of seasonal effects on the distribution of PPCPs in the reservoirs. More research is warranted to reveal in-depth sources and fate of the PPCPs in the reservoirs potentially impacted by the municipal landfills.

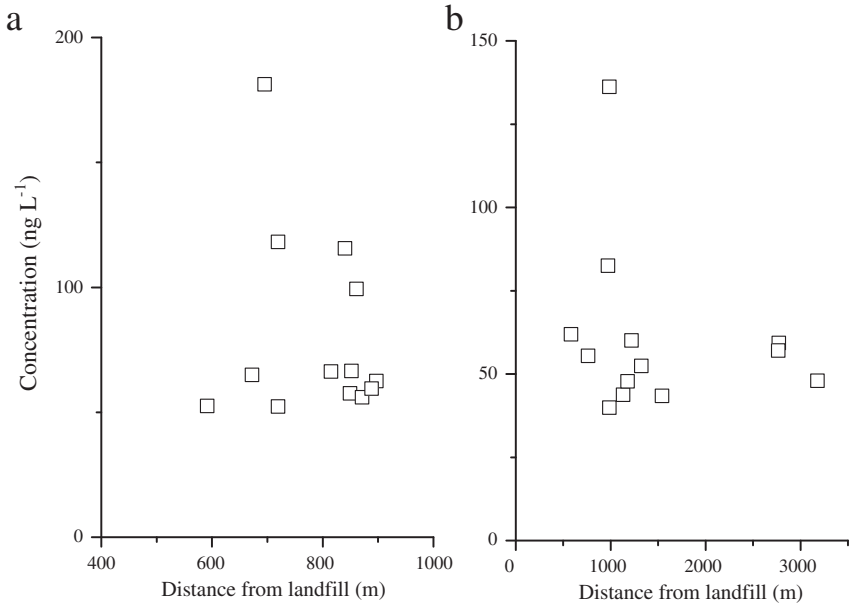

Fig. 4. The PPCP concentrations in the groundwater with distance from LF1 (a) and LF2 (b). See Table 1 for abbreviations of the compound names.

2.3. Potential impact of the landfills on PPCP pollution in groundwater and reservoirs

Some of the investigated PPCPs were detected at high levels in the landfill leachates, with the highest concentration up to nearly 4.5 mg L^{-1} (BPA), as shown in the Supporting information (Table S3). The PPCP concentrations in leachate from LF1 were generally lower than those from LF2, while no obvious difference was observed between the occurrence of the PPCPs in the aged and fresh leachates from LF2. Unfortunately, no seasonal pattern could be determined for the PPCPs in the leachates, as we were only allowed to sample the leachates twice in LF1 and once in LF2. The distribution of PPCPs in the landfill leachates are summarized in Table S3 of the Supporting information.

However, no obvious decrease in PPCP concentration in groundwater was observed in correlation to distance from the landfills (Fig. 4). As salicylic acid was the main pharmaceutical detected and can originate naturally from some plants (Verenitch et al., 2006), it is understandable that its correlation with landfill leachate ($R = -0.06$) was poor. Furthermore because the frequently detected antibiotics (i.e., sulfamethaxazole, dehydroerythromycin, and fluconazole) are readily water-soluble, they may be mobile in the groundwater, and subsequently, dilution could be very important in decrease of their concentrations as dilution, sorption, and degradation are considered to be dominant natural attenuation processes of contaminants in groundwater (Lapworth et al., 2012). Nonetheless, their concentrations showed only a weak negative relationship with the distance from the landfills ($R = -0.17$). The investigated personal care products are moderately hydrophobic (LogKow 2.0–4.9), while their concentrations in the groundwater were slightly negatively correlated with the distance from the landfills ($R = -0.30$). Factor analysis also demonstrated no difference among groundwaters from wells in the vicinity of the two landfills compared with wells free from impact of landfilling (Fig. 5). These results suggest that there might be other PPCP sources in the groundwater besides the landfill leachates. In fact, there are some home-built septic tanks in the villages with depths usually equal to or higher than the water levels of the wells (via personal communication with the villagers) that may possibly introduce the PPCPs to the groundwater. Septic tanks in the USA and Canada have been reported to contribute a variety of PPCPs to the groundwater (Barber et al., 2009; Carrara et al., 2007; Swartz et al., 2006). Septic tank samples will be included in our future work to better illustrate sources of PPCPs in the groundwater. Moreover, principal components analysis revealed that PCPs and pharmaceuticals most likely experienced different fate or had different sources from the antibiotics (Fig. 5).

The PPCP concentrations in the reservoirs, on the other hand, decreased significantly with distance from the landfills (Fig. 6). However, the two azole pesticides were ubiquitous, with a maximal concentration up to 1122 ng L^{-1}, although they were generally at trace levels and below LOQs in the landfill leachates. It is most likely that the azole pesticides were at least partially sourced from agricultural runoff, considering the scattered and small vegetable plots around the reservoirs. In addition, only three sampling sites were set in the reservoirs, limiting extensive discussion about sources of the PPCPs in the reservoirs.

Overall, more work is needed to properly determine the impact of the landfills on PPCP contamination in the groundwater and surface water systems.

2.4. Environmental risks

Risk assessment was performed by calculation of risk quotients (RQ) for the detected PPCPs according to the protocol in literature (Hernando et al., 2006):

$$RQ = \frac{C}{PNEC} \quad (1)$$

where C and PNEC were measured and predicted no-effect concentrations for a contaminant, respectively. PNEC values of the PPCPs were estimated based on toxicity data reported in the literature (Hernando et al., 2006; Verlicchi et al., 2012), as summarized in the Supporting information (Table S4). Risks were subsequently classified into three levels: RQ 0.01–0.1, low risk; RQ 0.1–1, medium risk; and RQ > 1, high risk (Hernando et al., 2006).

Sulfamethoxazole and dehydroerythromycin posed medium risks to sensitive species of algae in the groundwater in the vicinity of both landfills. While in the reservoirs, sulfamethazine, sulfamethoxazole, dehydroerythromycin, and clarithromycin posed high to medium risks to sensitive species of algae, and sulfadiazine, trimethoprim, and roxithromycin posed low risks to sensitive species of algae and daphnia. Sulfamethoxazole may also present medium risks to daphnia. In addition, ibuprofen, salicylic acid, and clofibric acid may slightly to moderately threaten the health of aquatic organisms, from bacteria to fish, especially in R1 (Fig. 7). The ecological risk of the investigated anti-bacterials in the groundwater and reservoirs were higher than the risk estimated in Bohai Sea (Zhang et al., 2013) and comparable to observations from Lake Michigan (Blair et al., 2013). However, limited toxicity information about the PPCPs increased uncertainty in this assessment. Moreover, it has been found that risk assessment based on individual chemicals is often greatly lower than assessments based on chemical mixture (Ferrari et al., 2004; Backhaus and Karlsson, 2014). Therefore, the presence of the PPCPs and the potential ecological risks posed to the groundwater and reservoirs could be a serious issue.

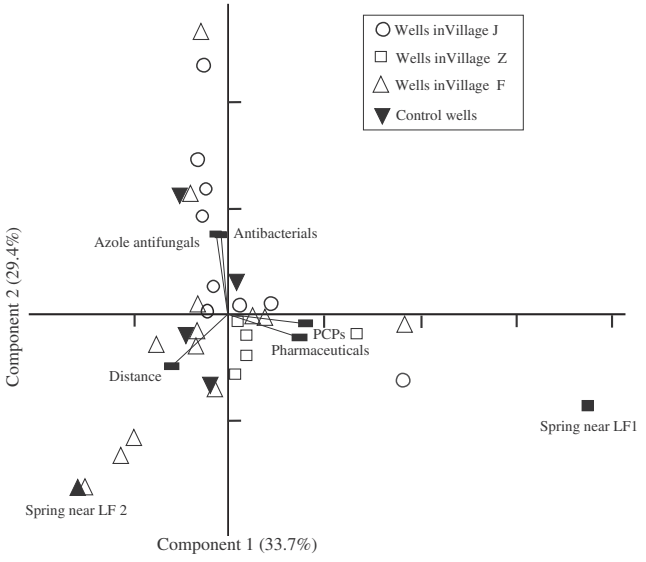

Fig. 5. Principal component analysis of the PPCPs in the groundwater. See Table 1 for abbreviations of the compound names.

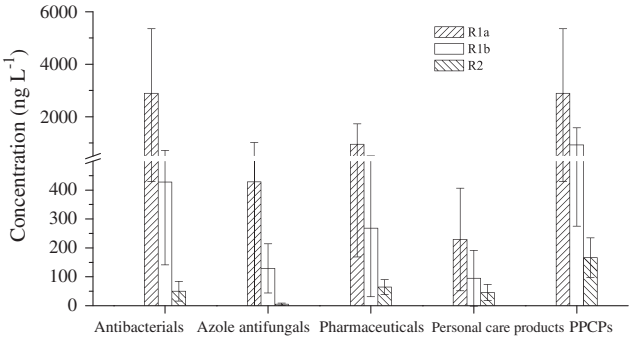

Fig. 6. PPCP concentrations in the reservoirs with distance from the landfills. See Table 1 for abbreviations of the compound names. Sampling sites in the reservoirs are shown in Fig. 1.

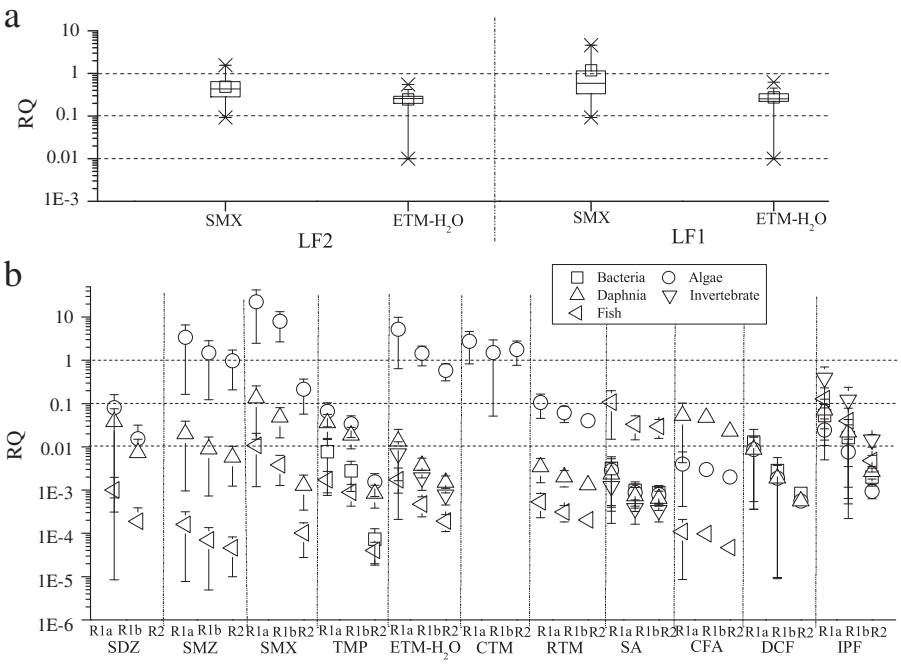

Fig. 7. Risk quotients of the PPCPs in the groundwater (a) and reservoirs (b). See Table 1 for abbreviations of the compound names. Sampling sites in the reservoirs are shown in Fig. 1.

3. Conclusions

A variety of PPCPs belonging to different groups, including anti-bacterials, azole anti-fungals and pesticides, NSAIDs, lipid regulators, and endocrine-disrupting PCPs (i.e., parabens, antiseptics, and bisphenol A), were investigated in typical aquatic environments in the vicinity of two municipal landfills in a metropolitan area of South China. No groundwater sample was free of PPCPs, although the concentrations were generally at low ng L^{-1}. Dehydroerythromycin, sulfamethoxazole, fluconazole, salicylic acid, methylparaben, triclosan, and BPA were the most frequently detected PPCPs in the groundwater. By contrast, the reservoirs were much more contaminated with both higher detection frequencies and concentrations. The sulfonamides (sulfamethoxazole, sulfamethazine, and sulfadiazine), trimethoprim, macrolides (dehydroerythromycin and clarithromycin), azole pesticides (propiconazole and tebuconazole), NSAIDs (ibuprofen, salicylic acid, diclofenac and indomethacin), and most PCPs were widely present. PPCPs in the groundwater did not show significant seasonal differences or spatial trends. However, in the reservoirs, PPCP concentrations were generally higher in spring than in other seasons and decreased with distance from the landfill.

The anti-bacterials in the groundwater posed medium risks to sensitive species of algae. In the reservoirs, the sulfonamides and macrolides posed low to high risks to sensitive species of algae and daphnia, while the 3 pharmaceuticals (ibuprofen, salicylic acid, and clofibric acid) presented low to medium risks to aquatic organisms. Overall, the PPCP contamination and subsequent ecological risks in the groundwater and reservoirs could be of serious concerns, warranting further research about impact of landfills on PPCP contamination in the aquatic environment. To the best of our knowledge, this was the first work investigating the impact of municipal landfilling on PPCP contamination in the groundwater in China. In addition, this work provided preliminary information about environmental risks of PPCPs in groundwater, which has been rarely reported.

Conflict of interest

The authors declare that there is not any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within the three years of beginning the submitted work that could inappropriately influence, or be perceived to influence this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.05.068.

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