*Highlights (for review)

Elimination of polar micropollutants and anthropogenic markers by wastewater treatment in Beijing, China

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Highlights

- The studied wastewater facilities are representative for large cities in China.
- The occurrence, elimination efficiency, and per-capita loads were assessed.
- Pollutant patterns were similar as in Europe, including caffeine and sucralose.
- Total per capita pollutant loads are currently lower than in Western countries.
- Wastewater used directly for irrigation poses a threat to soils and food safety.

Elimination of polar micropollutants and anthropogenic markers by wastewater treatment in Beijing, China

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Abstract. Anthropogenic contamination of surface waters in Asia is on the increase. While polar organic contaminants are gradually recognized for their impacts on aquatic ecosystems in the Western World, less is known about the situation in Asia. In developing countries like China, water resources are particularly vulnerable. We investigated the occurrence, elimination, and per capita loads of a wide range of pharmaceuticals, household chemicals and pesticides in five Beijing WWTPs representative for megacities in China, and compare the efficiency of different treatment processes. Based on initial screening for 268 micropollutants using high-resolution mass spectrometry, 33 compounds were examined in detail. Pollutant concentrations in raw wastewater ranged from <0.02 µg/L for pesticides to >20 µg/L for caffeine and the contrast agent iopromide. Concentrations in the WWTP effluents were generally <1 µg/L, except for some pharmaceuticals, iopromide (1.2–18 µg/L), caffeine (0.025–2.3 µg/L), and the artificial sweetener sucralose (2.7–3.5 µg/L). Elimination efficiencies varied greatly from <1% to close to 100%, with macrolides, some sulfonamides, metronidazole, iopromide, and 4-acetamidoantipyrine being the most persistent compounds. Total per capita loads of the investigated micropollutants were lower than in communal wastewater of Europe, amounting to 7.9–12.2 and 2.0–6.5 g/d/1000 inhabitants in the influents and effluents, respectively, with an average release of ~100 kg/day by the 11.4 million people and 2.3 million m^3 of wastewater treated per day. Since the wastewater effluents are often used for agricultural irrigation, residual organic pollutants pose a threat to food safety, the development of antibacterial resistance, and combined effects of micropollutants in the aquatic environment.

Keywords. Wastewater; Irrigation; Pharmaceutical; Personal care product; Household chemical; Pesticide

1. Introduction

Increasing contamination of aquatic systems by polar organic micropollutants is a major problem for aquatic life worldwide. These chemicals, which can include pharmaceuticals as well as personal care products (PPCPs), household chemicals, and pesticides, are often not efficiently eliminated by conventional wastewater treatment and are therefore discharged continuously to surface waters. Verlicchi et al. (2012) reviewed the elimination of pharmaceutical compounds after secondary treatment in WWTPs worldwide and discussed factors that influenced elimination efficiency. Parameters of the treatment processes such as sludge retention time (SRT), hydrological retention time (HRT), pH, temperature, and physico-chemical properties of the compounds were important factors that determined removal from wastewater. Generally, an increased SRT, an HRT longer than the half-life time of the compounds, and high temperature help to biodegrade pharmaceuticals during the treatment process. However, compounds such as sulfamethoxazole, carbamazepine, and sucralose show generally low or fluctuating elimination efficiencies, even with high SRT and HRT. Miège et al. (2009) assessed the elimination efficiency of PPCPs in WWTPs by compiling 6641 data for 184 PPCPs, and pointed out a low elimination efficiency (<30%) for atenolol, carbamazepine, metoprolol, trimethoprim, mefenamic acid, and clofibric acid.

The Haihe River Basin is located in the water-scarce area of the North China Plain and is home to several megacities, including Beijing and Tianjin. This area is facing a crisis for water resources due to rapid development and 25 years of drought (<600 mm/yr, average 450 mm/yr) recorded since the 1970s. Consequently, wastewater (WW), both treated and untreated, is the main water source of many rivers in the area. Recently, the occurrence, transport, and bioaccumulation of antibiotics, including tetracycline, sulfonamide, quinolone, and macrolide families, were studied in the Haihe River (Luo et al., 2011; Gao et al., 2012a). Sulfonamides, which have high solubility and chemical stability in water, occurred at the highest concentrations (24-385 ng/L) and detection frequencies (76-100%) (Luo et al., 2011). Ciprofloxacin and erythromycin were found to bio-accumulate in crucian carp in the Haihe River (Gao et al., 2012a). Pharmaceuticals and most household chemicals in rivers downstream of Beijing originate from urban wastewaters, especially from WWTP effluent discharges, as most compounds are poorly eliminated by the conventional treatment processes applied in Beijing's major WWTPs (Heeb et al., 2012).

Several studies have focused on the occurrence and elimination efficiency of pharmaceuticals, caffeine, and DEET in the WWTPs of Beijing (Sui et al., 2010; Zhou et al., 2010; Sui et al., 2011; Li et al., 2013). The pharmaceuticals included antibiotics, lipid regulators, beta-blockers, and antiphlogistics and varied in concentration from several ng/L to thousands of ng/L in the influents and from below detection to hundreds of ng/L in the effluents. The elimination efficiency also varied widely from no or low elimination of carbamazepine to 86% elimination of difloxacin. A membrane bioreactor (MBR) and an oxidation ditch, both with a high HRT (>12 h), were more efficient than a conventional activated sludge process at removing easily biodegradable compounds. According to Ort et al. (2010a; 2010b), uncertainties in the concentrations were probably due to the use of grab sampling for sampling of the inflow.

In 2009, Heeb et al. (2012) studied the rivers downstream of Beijing and screened for 268 organic pollutants including pharmaceuticals, pesticides, biocides, household chemicals, and associated metabolites. Following this initial screening, these authors conducted a comprehensive assessment over a time span of 14 months, focusing on the seasonal occurrence of 62 polar compounds, including pharmaceuticals, pesticides and associated metabolites, and household chemicals. This long-term investigation revealed that pharmaceuticals and the majority of household chemicals in the rivers originated from urban wastewater discharge (Heeb et al., 2012). The present study was conducted to document the occurrence and elimination of these same polar organic micropollutants in five Beijing WWTPs that apply different treatment processes, including conventional activated sludge, oxidation ditches, and MBR. The influence of HRT, SRT, and type of treatment process on the pollutant elimination efficiencies in these WWTPs is discussed, with the aim of extending knowledge on the occurrence and elimination of pharmaceuticals and household chemicals in Beijing’s WWTPs.

2. Materials and methods

2.1 Characteristics of Beijing's WWTPs

This study investigated the five WWTPs with the highest treatment capacities in Beijing (Gaobeidian, Xiaohongmen, Qinghe, Jiuxianqiao, and Beixiaohe) (Figure 1). These WWTPs treat a total of about 2.28 million m^3 of wastewater per day and are responsible for 90% of Beijing's wastewater discharge into the Haihe River system. The WWTP characteristics are summarized in Table 1.

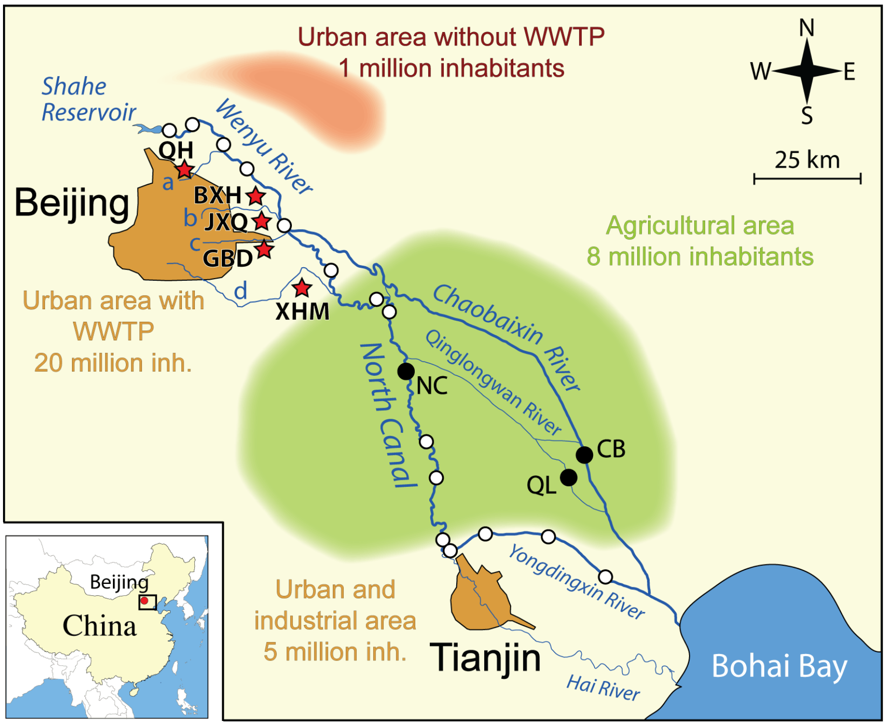

Figure 1. Map of the Beijing region depicting the land use and population. The red stars indicate the locations of the investigated WWTPs, which specifically are the WWTPs of Qinghe (QH), Beixiaohe (BXH), Jiuxianqiao (JXQ), Gaobeidian (GBD), and Xiaohongmen (XHM). Open circles and black dots represent sites along the wastewater-receiving rivers investigated in our earlier study (Heeb et al., 2012). Letters a−d denote urban rivers draining the wastewater effluents of Beijing, which are (a) Qing River; (b) Beixiao River, (c) Tonghui River, and (d) Liangshui River.

Table 1. Characteristics of the five major WWTPs of Beijing and Pharmaceuticals with high or moderate elimination rates in these WWTPs

WWTP	**Inhabitants served (Mio)**	**Capacity (Mio m^3/d)**	**Main treatment process**	**HRT (h)**	**SRT (d)**	**Substances with high or moderate elimination rates in this study (%)**
Jiuxianqiao (JXQ)	1.0	0.2	Oxidation Ditch	15	13	Sulfamethoxazole+ N4-acetylsulfamethoxazole (82%), Atenolol acid (79%), Sulfadiazine (74%), Sulfapyridine (71%), Iopromide (71%)
Qinghe (QH)	2.0	0.4	A/A/O	11	13	Sulfamethoxazole+ N4-acetylsulfamethoxazole (81%), Sulfadiazine (72%), Sulfapyridine (60%), Iopromide (52%)
Gaobeidian (GBD)	4.9	1.0	A/A/O	11	20	Iopromide (90%), Sulfamethoxazole+ N4-acetylsulfamethoxazole (66%)
Beixiaohe (BXH)	0.5	0.1	MBR	17	20	Sulfamethoxazole+ N4-acetylsulfamethoxazole (66%), Sulfadiazine (54%), Sulfapyridine (52%)
Xiaohongmen (XHM)	3.0	0.6	A/A/O	11	15	Sulfadiazine (60%), Sulfapyridine (55%), Sulfamethoxazole+ N4-acetylsulfamethoxazole (52%)

Hydraulic retention time (HRT); Sludge retention time (SRT); A/A/O: Anaerobic/anoxic/aerobic, MBR: Membrane bioreactor

2.2 Sample collection and analysis

Time-proportional 24-hour composite samples of the influents and effluents were collected from the WWTPs in March 2011. This sampling procedure presents a snapshot in time and does not account for short-term fluctuations occurring during the course of one day. It also does not capture monthly or seasonal variations. Elimination rates derived in our study for March 2011 can therefore be seen as approximate values, but may underestimate pesticide loads as March is at the early stage of the application period. Wastewater samples (250 mL) were collected in baked-glass bottles (Schott), packed in cooled containers, and shipped within ≤7 days to Eawag in Switzerland, where the samples were frozen at -20 °C until analysis. Immediately prior to analysis, the thawed samples were filtered through glass fiber filters (GF/F, pore size 0.7 µm, Whatman) and an isotope-labeled internal standard (IS) solution was added. Following an initial screening for 268 micropollutants using high-resolution mass spectrometry, a total of 18 pharmaceuticals, 9 pesticides and associated metabolites, and 6 household chemicals were selected for detailed investigation and analyzed using a fully automated solid phase extraction (SPE) system (Stoob et al., 2005) coupled directly to a liquid chromatography (LC) tandem mass spectrometer. The analytical method has been described in our previous study (Heeb et al., 2012). Briefly, for targets where no structurally identical internal standard (IS) was available, the IS with the most similar retention time was used for quantification. The average relative recoveries were between 85–112 % for all compounds except for imidacloprid (77%) and clindamycin (132%).

3. Results and discussion

3.1 Occurrence and elimination of household chemicals in WWTPs

3.1.1 Caffeine

Caffeine being one of the most abundant household chemicals present in tea, coffee, or analgesics, has the highest concentrations in the influents of the WWTPs (22.1-25.9 µg/L, Table 2) among the six household substances detected in this study. Due to its low persistence during biological treatment process (half lives ~0.8-5 h, Buerge et al., 2006) caffeine was largely eliminated (>90%, Figure 2) by all WWTPs, leaving residual concentrations of 25-2340 ng/L in the effluents. This behavior was in agreement with those of other studies (Buerge et al., 2003; Buerge et al., 2006; Sui et al., 2010). The elimination efficiency for caffeine by WWTPs has been reported to be related to sludge age (Buerge et al., 2003). The sludge residence time of 13-20 days in the Beijing WWTPs (Table 1) was therefore consistent with the high elimination efficiency for caffeine, which had effluent concentrations ranging from 25-350 ng/L if one sample from the XHM WWTP was excluded (Table 2, Figure S1). Therefore, caffeine can be used as an anthropogenic marker for the efficiency of WWTPs (Standley et al., 2000; Buerge et al., 2003).

3.1.2 Sucralose

Sucralose, which has been used in many studies as an indicator of domestic wastewater loads to surface waters, ranged in concentration from 3.21 to 5.04 μg/L in the inflow and from 2.76 to 3.50 μg/L in the outflow (Table 2). The effluent concentrations of sucralose were within the lower range of the world levels, reported at 0.4-11.0 μg/L (Tollefsen et al., 2012), but were significantly lower than those of most WWTPs in the USA where sucralose concentrations in effluents reached as high as 119 μg/L (Mead et al., 2009). Although the sucralose concentration determined in our study was lower than that in most WWTPs in the USA and Europe, the low elimination efficiency (6-31%, Figure 2) was similar in Beijing.

Sucralose is very stable during WW treatment as well as in surface waters, making it a good indicator for wastewater in surface waters. The average sucralose concentrations in WWTP effluents and the actual concentrations in the river can be used to estimate the fraction of wastewater discharged to the river, assuming that seasonal variations of sucralose loads are small due to its steady household use throughout the year. Sucralose concentrations in the rivers of Beijing were reported in our earlier study (Heeb et al., 2012) as 1360 ng/L, 1270 ng/L, and 1040 ng/L at the sites NC, CB, and QL (Figure 1), with water discharge estimates of 18.5 m^3/s, 7.5 m^3/s, and 5.9 m^3/s. We used the average concentration of the three river sections (1.22 μg/L) and the concentration determined in WWTP effluents (3.06 μg/L; Table 2) to estimate that the river water consisted of 44% wastewater, corresponding to a flow of ~1.2 Mio m^3/d.

The estimated WW discharge from all five TPs was ~2.3 Mio m^3/d (Table 1); hence, we find that about half of the WW was not discharged to the river but used as reclaimed water for special purposes. At the GBD WWTP, for example, about one half of the secondary effluents are used as industrial cooling water, landscaping water, and irrigation water in urban green lands, and 10,000 m^3/d are used on the WWTP premises for filter cleaning, truck washing, and gardening.

3.1.3 Benzotriazole

The corrosion inhibitors benzotriazole and 4-/5-methyl-benzotriazole occurred in the WWTP influents at concentrations of 550-1380 ng/L and 310-630 ng/L, respectively. These levels were much lower than those reported for WWTPs in Berlin (Germany) with samples collected between June and December of 2006, where concentrations were 17-44 µg/L for benzotriazole and 1.1-4.9 µg/L for the sum of 4-methyl-benzotriazole and 5-methyl-benzotriazole (Reemtsma et al., 2010). The sampling time (March) in this study was probably one of the reasons for the low concentration of these corrosion inhibitors included in aircraft de-icing fluid and motor vehicle antifreeze. In Beijing, benzotriazole was moderately eliminated (56-74 %), whereas 4-/5-methyl-benzotriazole elimination was limited (2-37 %) (Figure 2). These elimination efficiencies are comparable to those observed for WWTPs in Berlin (Germany), which were 30-55% for benzotriazole, 20-70% for 5-methyl-benzotriazole and insignificant for 4-methyl-benzotriazole (Reemtsma et al., 2010).

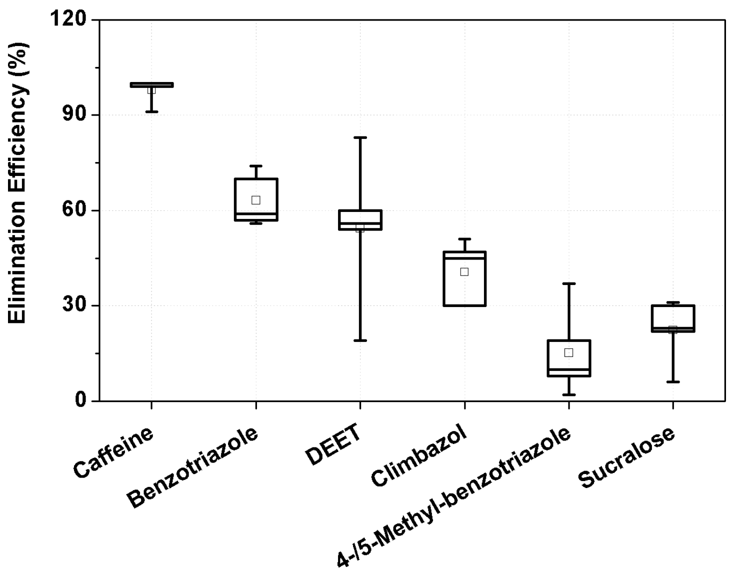

Figure 2. Elimination efficiencies of household chemicals in WWTPs of Beijing. (DEET: N,N-Diethyl-3-methylbenzamide). Boxes illustrate the concentration ranges between the 25th and 75th percentiles. The whiskers extend to the minimum and maximum concentration values. The horizontal lines and squares inside the box indicate the median and average values, respectively.

Table 2. Concentrations and eliminations of pharmaceuticals, household chemicals, and pesticides in influents and effluents of WWTPs in Beijing

Substances			**LOQ**[1] (ng/L)	**Recovery**[2] (%)	**Concentration** (ng/L) Influent (n=5)	Effluent (n=5)	**Elimination**[6] (%)
Pharmaceuticals							
Antibiotics	Sulfonamides	Sulfamethoxazole*	33	94	300-460	100-250	33-72
		*N4-Acetylsulfamethoxazole**	2	90	460-640	40-320	50-92
		SMX + N_4-AcSMX[3]			810-1100	150-530	52-82
		Sulfadiazine*	30	91	190-320	70-130	44-74
		Sulfapyridine*	15	90	130-220	50-100	29-71
		Trimethoprim*	15	110	300-370	200-370	<1-35
		Sulfamethazine*	3	90	10-20	3-6	63-100
	Macrolides	Erythromycin (and -H_2O)*	22	86	330-390	270-290	19-28
		Clarithromycin*	14	89	130-260	130-260	-22-41
	Nitroimidazoles	Metronidazole	11	99	140-380	250-900	-320-33[5]
Antifungal	Pyrrolic	Fluconazole*	6	92	110-170	110-170	<10
Analgesics/anti-inflammatories		*4-Acetamidoantipyrine*	31	72	1520-2520	1300-2240	-22-27
		Diclofenac*	17	88	180-280	140-300	-7-25
Antiepileptics		Carbamazepine*	16	92	60-100	70-110	-13-4
		Carbamazepine-10,11-dihydro-10,11-dihydroxy	2	93	650-1020	450-560	29-45
ß-Blocker		*Atenolol acid**	5	86	940-1380	280-1240	10-79
Contrast agent		Iopromide*	18	101	2510-21,300	1160-17,800	9-91
Anesthetic		Lidocaine*	89	92	137-180	120-180	<15
Pesticides							[4]
Herbicides		Atrazine*	29	87	10-20	8-19	
		*Atrazine-desethyl**	9	91	17-64	14-63	
		Diuron*	7	101	14-31	14-25	
		Metolachlor*	9	91	9-30	9-19	

	Prometryn	3	109	3-4	<LOQ-3	
	Propazin-hydroxy	2	114	4-10	2-4	
Insecticides	Imidacloprid	15	71	45-100	45-106	
Fungicides	Carbendazim*	3	84	360-580	370-610	
	Metalaxyl	6	88	6-17	6-14	
Household chemicals						
	Caffeine*	12	97	22,100-25,900	25-2340	91-100
	DEET*	58	99	115-270	77-170	19-83
	Benzotriazole*	16	86	550-1380	226-520	56-74
	Climbazol	6	94	610-940	300-615	30-51
	4-/5-Methyl-benzotriazole	8	98	310-630	260-580	2-37
	Sucralose*	113	100	3210-5040	2760-3500	6-31

* Structurally identical isotope labeled internal standard used for quantification; for all other compounds, the isotope labeled standard with the nearest retention time was used.

(1) Limit of quantification was determined from the analyte concentration producing at least a signal-to-noise ratio of 10:1 in the sample matrix.

(2) Recoveries were calculated from influent and effluent samples (N=8) spiked with analyte concentration of 500 ng/L considering the analyte background of the unspiked sample.

(3) Sum of sulfamethoxazole and N4-acetylsulfamethoxazole was calculated due to the deconjugation during the biological treatment step.

(4) Elimination of pesticides was not calculated as peak concentrations caused by disposal because application events would dramatically affect the calculation with the time-proportional 24-hour composite sampling scheme.

(5) Negative elimination efficiencies can be observed for pharmaceuticals that are reconverted from their conjugates during biological wastewater treatment. See chapter 3.2.1 for a more detailed discussion.

(6) The relative uncertainty of the calculated elimination is 14% for compounds calibrated with structurally identical isotope labeled internal standards (marked by *), and 28% for compounds for the other compounds.

Compounds in italics are transformation products.

3.2 Occurrence and elimination of pharmaceuticals by WWTPs

3.2.1 Antibiotics

The inflows and outflows of the WWTPs included 10 antibiotics and one antifungal: sulfadiazine (SFDZ), sulfapyridine (SFPD), sulfamethoxazole (SMX) and its metabolite N4-Acetylsulfamethoxazole (N_4-AcSMX), erythromycin (and $-H_2O$) (ERT), clarithromycin (CTM), metronidazole (MTNZ), trimethoprim (TMTP), sulfamethazine (SFMT) and fluconazole (FCNZ), which ranged in concentrations from 110 to 640 ng/L in the influents and from 40 to 900 ng/L in the effluents (except for sulfamethazine, which was always below 20 ng/L). These concentrations were similar to the values reported in an international database compiled from 117 publications of PPCPs in wastewater treatment plants around the globe (Miège et al., 2009); for example, erythromycin (and $-H_2O$) was present at 270-290 ng/L in the effluents of Beijing vs. 145-290 ng/L in the database and sulfamethoxazole was present at 100-250 ng/L in Beijing vs.18-320 ng/L in the database. Gao et al. (2012b) recently reported the occurrence and elimination efficiencies of 22 antibiotics in eight WWTPs in Beijing in May 2010, where sulfadiazine ranged between 380-2000 ng/L and 120-560 ng/L in the influents and effluents, respectively. These levels were 2-4 times higher than those found in our study although the elimination efficiencies were similar. Both studies used 24h composite samples, so the differences observed for this compound could possibly be explained by seasonal variations in the raw wastewater (Gao et al., 2012b; Sui et al., 2011).

Sulfamethoxazole, its metabolite N_4-acetylsulfamethoxazole, erythromycin (and $-H_2O$), and trimethoprim were the antibiotic compounds with the highest inflow concentrations, with average concentrations of 366, 516, 365, and 318 ng/L, respectively. The elimination efficiencies for sulfamethoxazole and N4-acetylsulfamethoxazole were calculated based on the sum of both compounds because deconjugation occurred during biological treatment (Kovalova et al., 2012) and was only moderate (>50%, Table 2), leaving residual concentrations of 150-290 ng/L in the effluents (except for those from the XHM WWTP, at 530 ng/L). Two other sulfonamides, sulfadiazine and sulfapyridine, were also moderately eliminated (29-74 %) (Figure 3), with effluent concentrations being 70-130 ng/L and 50-100 ng/L, respectively (Table 2). Minimal elimination was observed for erythromycin (and $-H_2O$) (19-28 %) and trimethoprim (<1-35 %) by all five WWTPs (Figure 3).

Elimination of the antifungal drug fluconazole was negligible (<10%), with residual concentrations of 110-170 ng/L in the effluents (Figure 3, Table 2).

Metronidazole showed higher effluent concentrations (250-900 ng/L) than influent concentrations (140-380 ng/L) in four WWTPs. A slight formation during biological treatment was also found for clarithromycin in the XHM WWTP. The same finding was reported for erythromycin (and –H2O) and clarithromycin in WWTPs in Taiwan and South China and was explained by the presence of antibiotic conjugates (García-Galán et al., 2008; Zhou et al., 2013) that are retransformed to the parent compounds during biological wastewater treatment.

3.2.2 Analgesics

Among the three analgesics/anti-inflammatory drugs detected in this study, 4-acetamidoantipyrine (AAA), a human metabolite of the analgesic metamizole, was the most abundant pharmaceutical in both influents and effluents indicating the common use of metamizole in Beijing. The similar concentrations of 1520-2520 ng/L and 1300-2240 ng/L for influents and effluents, respectively (Table 2), indicated limited elimination (-22-27 %) of this substance by the WWTPs (Figure 3). Concentrations reported for AAA in European WWTPs were much higher, ranging from 1100 to 15000 ng/L in influents and from 950 to 6000 ng/L in effluents (Zühlke, 2004; Kahle et al., 2009).

The anti-inflammatory drug diclofenac was present in Beijing's WWTPs at concentrations of 180-280 ng/L in the influents and similar concentrations of 140-300 ng/L in the effluents, again indicating little or negligible elimination (-7% to 25 %). Effluent concentrations in Beijing were lower than those reported for e.g. Switzerland (200-990 ng/L, Tixier et al., 2003), whereas the limited elimination was similar to observations in Germany and Spain that spanned from 0% to 40% elimination in conventional activated sludge treatment (Joss et al., 2005; Radjenović et al., 2009).

3.2.3 Antiepileptics

The antiepileptic agent carbamazepine (CBMZ) and its metabolites, carbamazepine-10,11-dihydro-10,11-dihydroxy (CBMZDI) and carbamazepine epoxide, were analyzed in the wastewater samples. CBMZDI was the major metabolite present, ranging from 650 to 1020 ng/L in the influents, which was one order of magnitude higher than the concentration of its parent compound carbamazepine (60-100 ng/L) (Table 2). Higher aqueous concentrations of CBMZDI were also reported in other studies

(Miao et al., 2003; 2005). This observation might be explained by the hydrophilicity of CBMZDI and that this compound is also being a metabolite of oxcarbazepine (Zhang et al., 2008). Carbamazepine epoxide concentrations were below the LOQ (3 ng/L) in all samples. The elimination of both CBMZDI and carbamazepine was limited (-13-45 %) in the WWTPs, as found in other studies, due to the chemical inertness and weak adsorption of these compounds on sludge (Lin et al., 2009; Zhou et al., 2010; Sui et al., 2011; Bueno et al., 2012), as well as by the reformation from the conjugated forms by microbial activity during treatment (Miao et al., 2005).

3.2.4 Contrast agents (iopromide)

The concentrations of iopromide (IPM, contrast agent) in the influents (2.5-21.3 μg/L) and effluents (1.2-17.9 μg/L) were the highest among all pharmaceuticals detected. These levels were even higher than those reported in a compilation as a world average (0.03-7.5 and 0.25-9.3 μg/L in the in- and outflow, respectively, Miège et al., 2009). A range of 9-91 % for the elimination efficiency of iopromide was observed in the five WWTPs (Figure 3). Similar variations were also found in Swiss WWTPs, where no correlation between elimination efficiency and sludge age or treatment processes was found. The concentrations of iopromide also varied in the inflow of the five Beijing WWTPs, as they were higher in JXQ (21.3 μg/L) and XHM (19.7 μg/L) but clearly lower in QH (4.5 μg/L) and BXH (2.5 μg/L) (Figure S2). Joss et al. (2005) suggested that these high variations of the inflow concentrations were caused by irregular emission of the compound.

3.2.5 Other Pharmaceuticals

Other pharmaceuticals, such as atenolol acid (metabolite of β-blocker metoprolol), ranged in concentration from 940 to 1380 ng/L in the influents. Considerable variation in efficiency of elimination was observed for atenolol acid (10-79 %) among the five WWTPs, probably because this compound may also be formed from atenolol during wastewater treatment (Radjenović et al., 2008). The anesthetic lidocaine was detected in all samples (137-180 ng/L in influents, 120-180 ng/L in effluents), and was poorly eliminated (less than 15 %) in all five Beijing WWTPs.

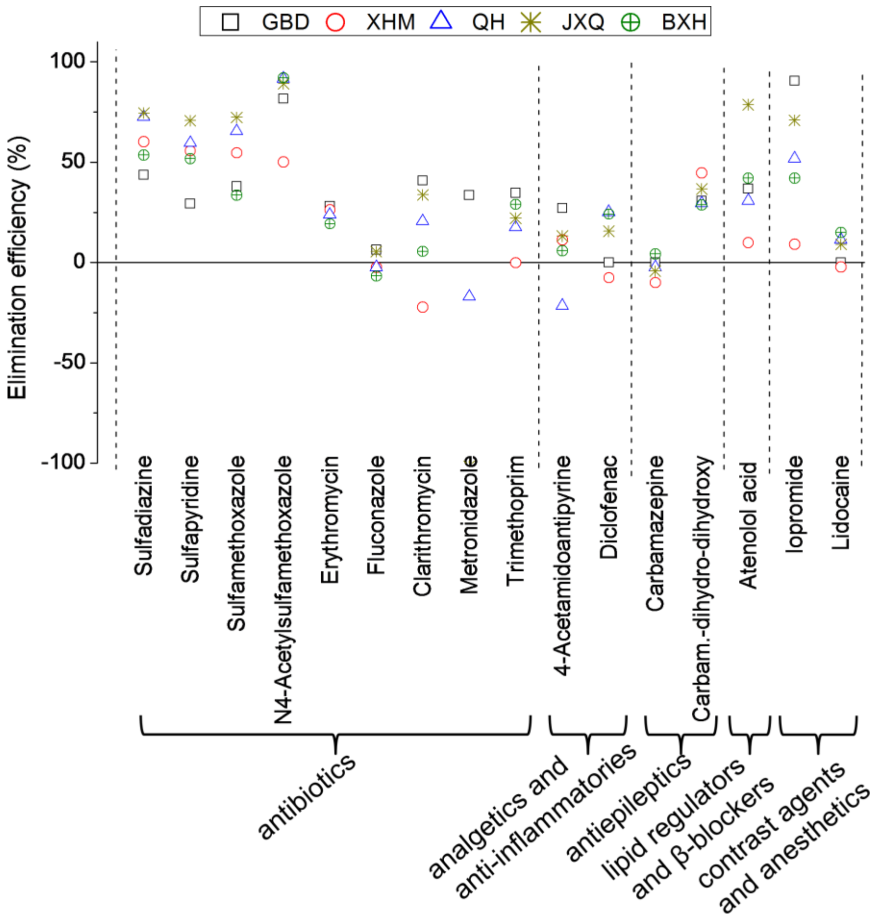

Figure 3. Elimination efficiencies of Beijing's WWTPs for antibiotics, analgesics and anti-inflammatories, antiepileptics, lipid regulators and β-blockers, contrast agents and anesthetics.

3.2.6 Elimination efficiency of pharmaceuticals by different WWTPs

This study found high concentrations and low elimination efficiencies for several pollutants, including contrast agents, macrolides, some sulfonamides, metronidazole, and 4-acetamidoantipyrine in the Beijing WWTPs (Table 2, Figure 3). Elimination of some pharmaceuticals, such as beta blockers and psycho-active drugs, during wastewater treatment could be predicted with a model using the transformation constants (Wick et al., 2009), but no general trend for the elimination of pharmaceuticals has been reported in the literature (Gulkowska et al., 2008; Zhou et al., 2010, Gao et al., 2012b, Verlicchi et al., 2012).

As mentioned in section 3.2.1, Miège et al. (2009) assessed the elimination efficiencies of PPCPs in wastewater treatment around the globe and pointed out that activated sludge with nitrogen treatment (a low loaded activated sludge process) and membrane bioreactors showed the best efficiency. In our study, the WWTP with the oxidation ditch treatment (JXQ) was more efficient than A/A/O or MBR in removing sulfamethoxazole+N4-acetylsulfamethoxazole, atenolol acid, sulfadiazine, sulfapyridine and iopromide and showed elimination rates >70 % (Table 1). The sludge retention time (SRT) did not seem to be a decisive factor for the elimination efficiency of pharmaceuticals, since no trend in elimination efficiency was evident for the QH, GBD, and XHM treatment plants that used the same treatment technology (i.e., A/A/O treatment), despite their variations in SRT (Table 1). However, QH and XHM, with lower sludge retention times (13-15 days), showed a more efficient elimination of sulfadiazine and sulfapyridine when compared with GBD with a SRT of 20 days, where the elimination of the sulfonamides was below 45 %. Finally, the membrane bioreactor (MBR) at BXH was no more efficient than the treatment processes used at the other WWTPs.

Sui et al. (2011) compared the elimination of pharmaceuticals over the course of one year in Beijing in two WWTPs that apply MBR and conventional activated sludge with biological nutrient elimination. They found a significantly better elimination of diclofenac and trimethoprim for the MBR (60% in summer/autumn and 40% in winter/spring), while elimination was much lower or even negligible using the conventional treatment. The authors attributed the higher elimination of diclofenac and trimethoprim by MBR in summer/autumn to the higher biomass and longer sludge retention time 'which are often used to explain the variation of PPCPs elimination efficiency for WWTPs' (Miège et al. 2009).

3.3 Occurrence of Pesticides in WWTPs

In general, concentrations of 20 pesticides and their transformation products analyzed in this study did not exceed 1000 ng/L in the five Beijing WWTPs (Table 2). Carbendazim (CBD) had highest concentrations in influents (360-580 ng/L) and effluents (370-610 ng/L), which is in accordance with its widespread use as fungicide for the production of fruit and vegetables and in lawn maintenance in Beijing. The occurrence of different pesticides was quite similar in the studied WWTPs (Figure 4a). Calculating the elimination of pesticides is not very meaningful because peak concentrations, commonly caused by disposal or application events, cause unreliable results with the time-proportional 24-hour composite sampling scheme. Notably, however, no significant elimination was observed for any of the pesticides. In addition, March is at the early stage of the pesticides application period. Our sampling in this period may underestimate the concentrations and loads of pesticides in the wastewater systems.

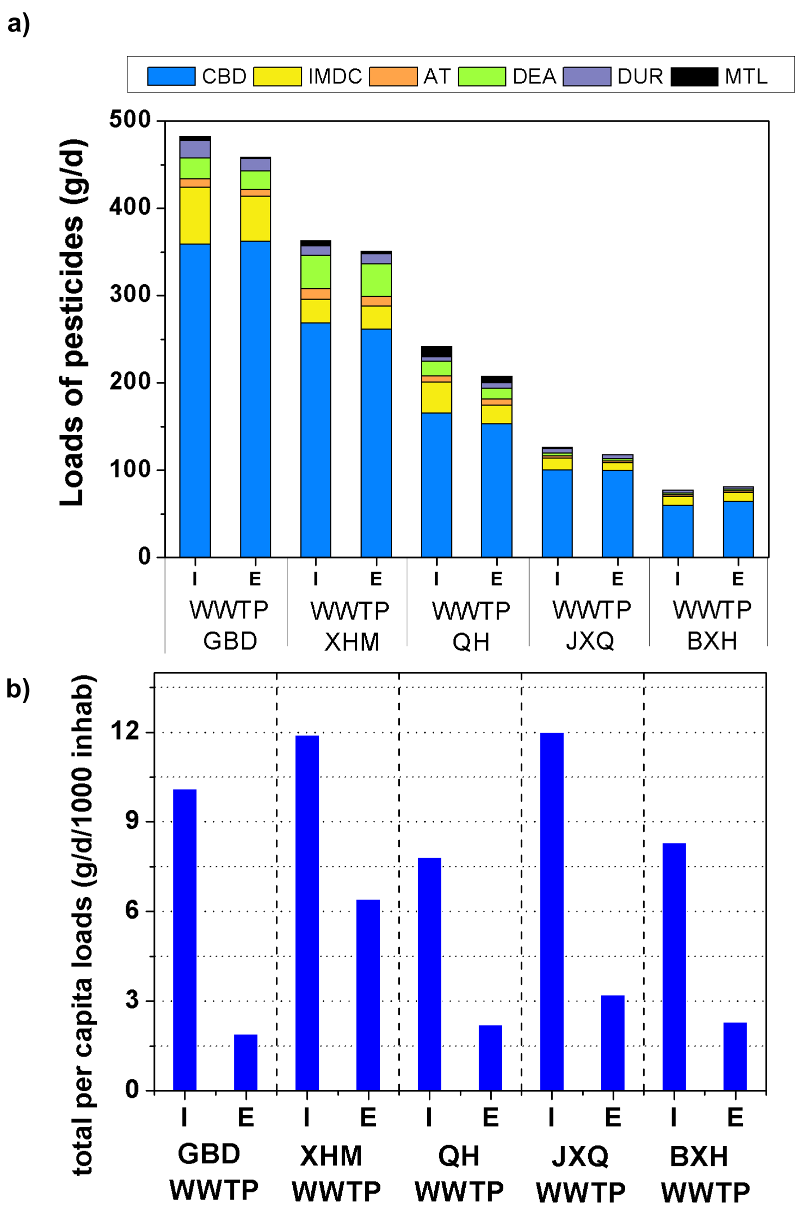

Figure 4. a) Cumulative loads (g/d of pesticides in Beijing WWTPs in March 2011. (CBD: Carbendazim; IMDC: Imidacloprid ; AT: Atrazine; DEA: Atrazine-desethyl; DUR: Diuron; MTL: Metolachlor). **b)** Total per capita loads of 27 detected polar micropollutants (including pharmaceuticals and household chemicals) in the influents (I) and effluents (E) of the Beijing WWTPs.

3.4 Pollutant loads in Beijing's WWTPs

As can be seen in Table 3, the per capita loads of the pharmaceuticals bezafibrate, carbamazepine, diclofenac, mefenamic acid, and the household chemicals benzotriazole and methylbenzotriazole, were

6−100 times lower in influents in Beijing than in those reported for Switzerland and Italy (Castiglioni et al., 2006; Hollender et al., 2009). The opposite was the case for erythromycin (and -H_2O) and sulfadiazine, where per capita loads were higher in Beijing than in Switzerland and Italy (Table 3). Some Beijing WWTPs also exhibited higher loads of Iopromide and sulfamethoxazole.

The total loads of 27 pharmaceuticals and household chemicals ranged from 7.8-12.0 g/d/1000 inhabitants in the WWTP influents and were eliminated by 70-80 % during the treatment processes, except at the XHM WWTP (46%) (Figure 4b). The lower total elimination at the XHM WWTP was mainly due to the low elimination efficiency for iopromide, which is among the most abundant and persistent contaminants (Figure 3). Pesticides loads discharged by the individual WWTPs to the rivers were 80-460 g/d (Figure 4a). Per capita loads of the pharmaceuticals and household chemicals discharged from each WWTP to the Haihe river system were 1.9-6.4 g/d/1000 inhabitants (Figure 4b). Therefore, about 96 kg of polar micropollutants reach the surface waters this way every day from the five WWTPs in Beijing.

Table 3. Per capita loads of selected micropollutants in the influent of Beijing WWTPs compared to values from Switzerland (Hollender et al., 2009) and Italy (Castiglioni et al., 2006).

	Per capita loads(g/day/1000 inhab)		
	Beijing (5 WWTPs)	Switzerland (1 WWTP)	Italy (6 WWTPs)
Household chemicals			
benzotriazole	0.11-0.27	1.94	
Methylbenzotriazole	0.06-0.13	0.39	
Pharmaceuticals			
Iopromide	0.52-4.24	1.04	
SMX+N4-AcSMX	0.10-0.99	0.20	nd-0.21
Diclofenac	0.04-0.05	0.32	
Mefenamic acid	0.002-0.006	0.55	
Erythromycin	0.07-0.08	0.01	nd-0.001
Sulfadiazine	0.04-0.06	0.03	
Carbamazepine	0.01-0.02	0.11	nd-0.39
Clarithromycin	0.03-0.05	0.09	nd-0.05
Bezafibrate	0.01-0.03	0.09	0.02-0.68

4. Conclusions

Effluents from WWTPs are the main water source for rivers in the Beijing region and other cities located in the water-scarce region of Northern China (Pernet-Coudrier et al., 2012). Therefore, the polar micropollutants investigated in this study, as well as thousands of other organic chemicals that can be present today in wastewater effluents, significantly contribute to the organic pollutant loads in the receiving surface waters. Improvement and monitoring of the quality of WWTP effluents is even more pressing because precious water is pumped for irrigation and other uses in the agricultural areas downstream of Beijing. Consequently, accumulation of persistent chemicals in soils jeopardizing food quality and bearing health risks of the population are pressing problems demanding highest priority for political action (Liu, 2010). Additionally, the potential risks to ecosystems due to sewage irrigation extend to spreading antibiotic-resistance genes, which are currently discussed as emerging environmental contaminants (Czekalski et al., 2014). Studies on elimination of pharmaceuticals during wastewater treatment suggest that activated carbon and ozonation are the most promising processes for improving the efficiency of pollutant removal by WWTPs (Larsen et al., 2004, Hollender et al., 2009).

This study serves as a baseline and point of reference for further assessing per-capita loads and the ecological impact of wastewater-borne pollutants. The consumption of pharmaceuticals and household chemicals are expected to increase with the rapid development of China. This will lead to higher pollutant concentrations in wastewater, and, without more efficient wastewater treatment, cause higher loads to irrigated cropland and the aquatic environment.

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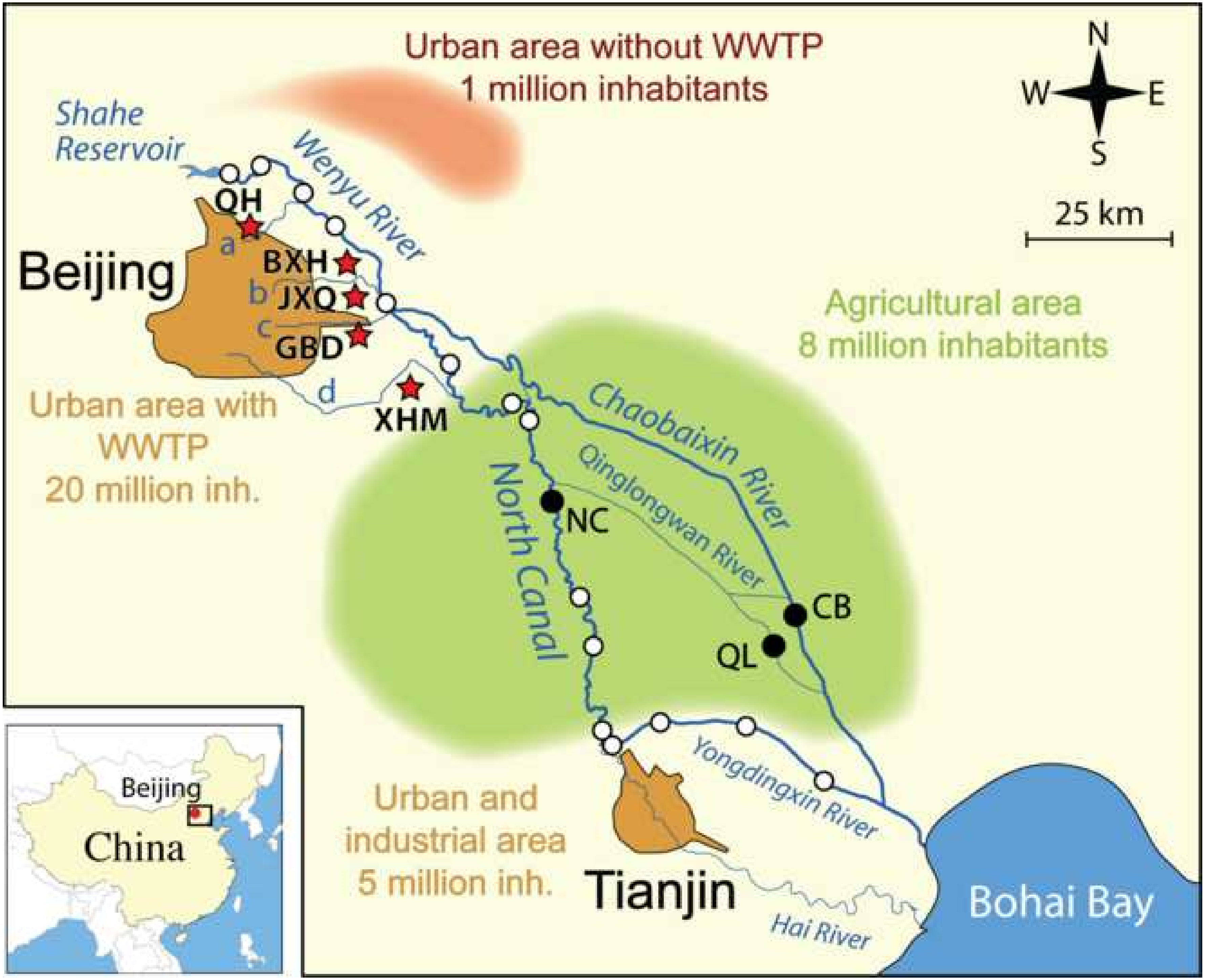
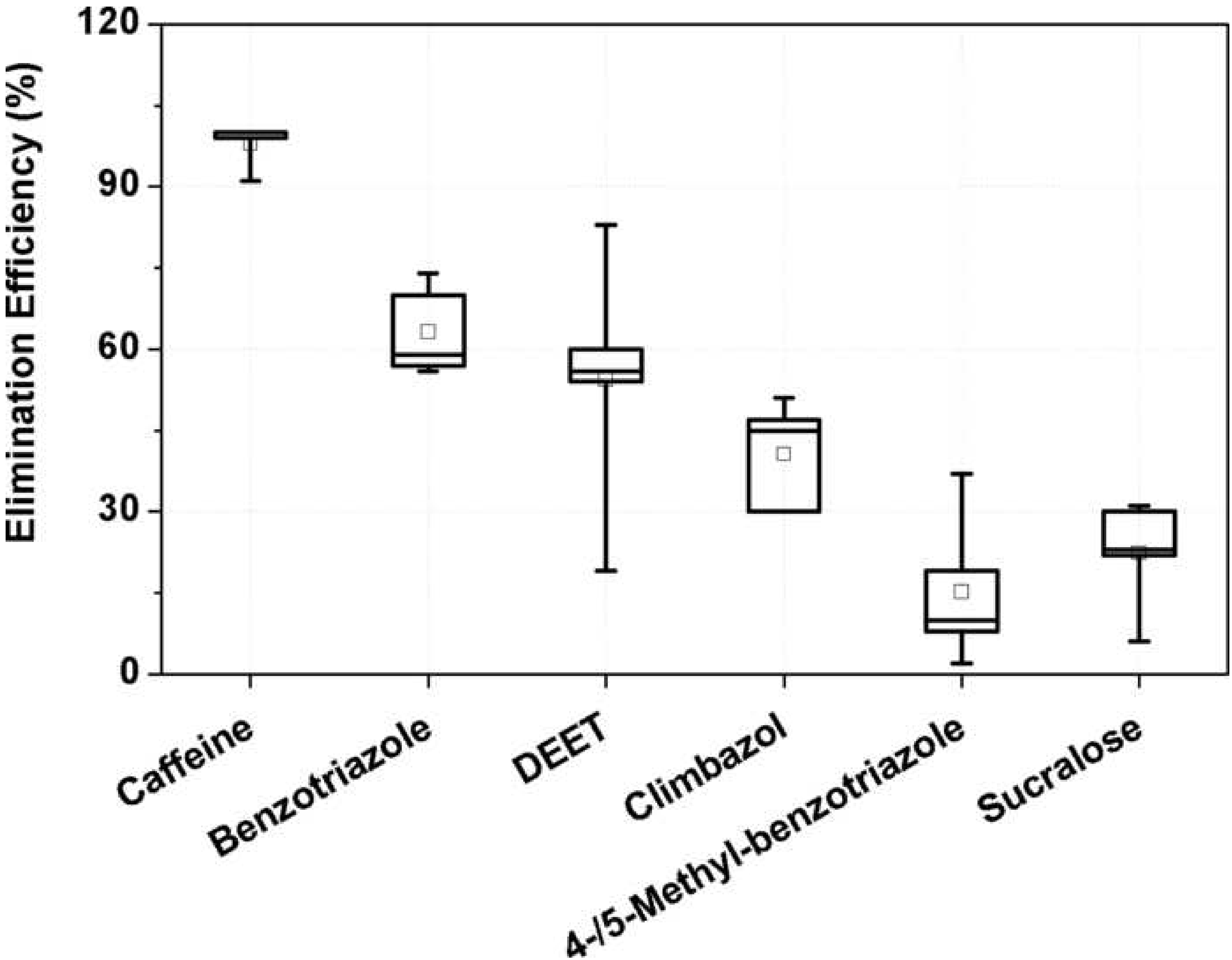
Figure1



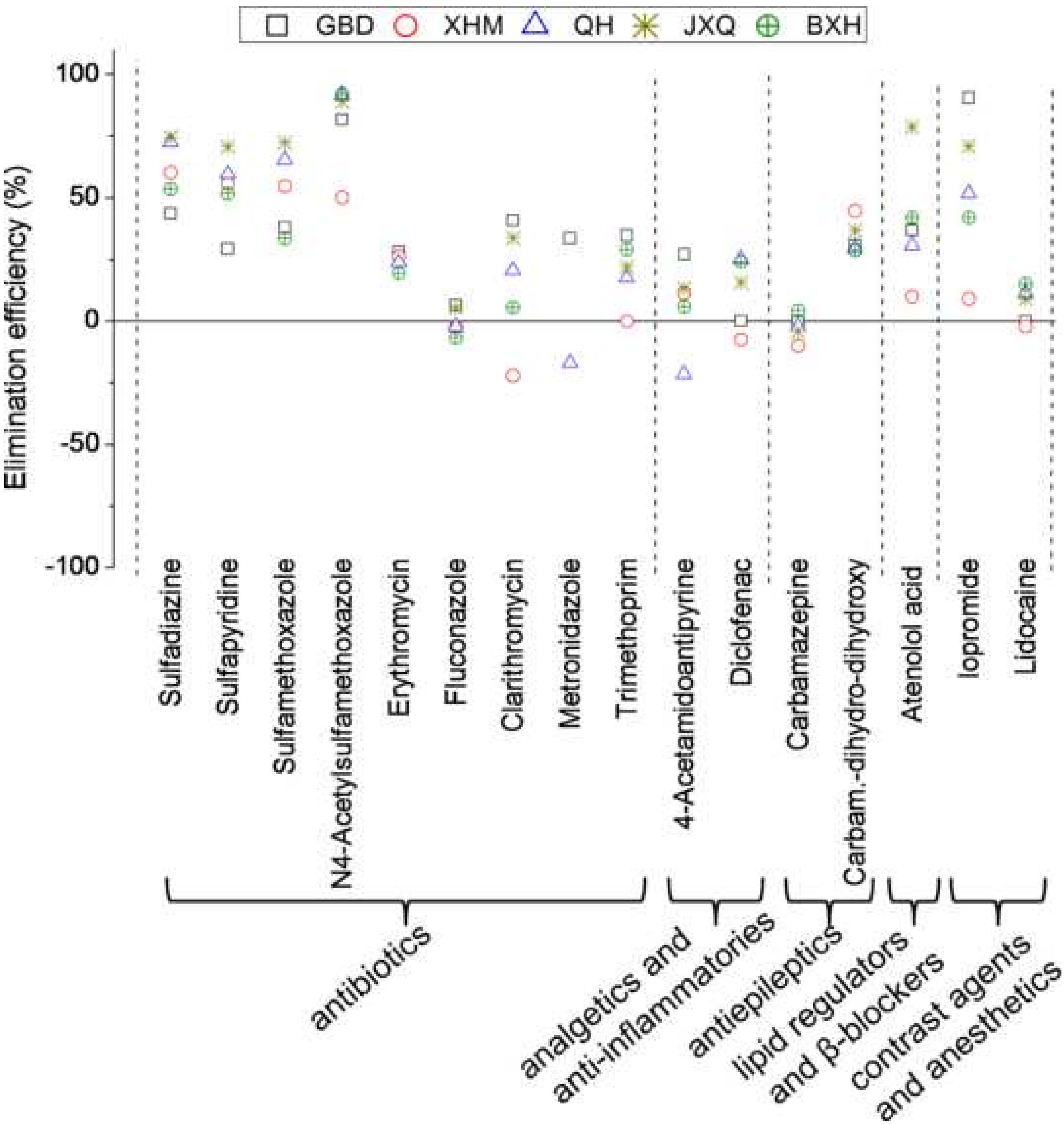
Urban area without WWTP
1 million inhabitants
N
W
E
S
25 km
Shahe Reservoir
Wenyu River
QH
a
Beijing
BXH
b
JXQ
c
GBD
d
XHM
Urban area with WWTP
20 million inh.
Agricultural area
8 million inhabitants
Chaobaixin River
Qinglongwan River
North Canal
NC
CB
QL
Yongdingxin River
Urban and industrial area
5 million inh.
Tianjin
Hai River
Bohai Bay
Beijing
China

Figure2



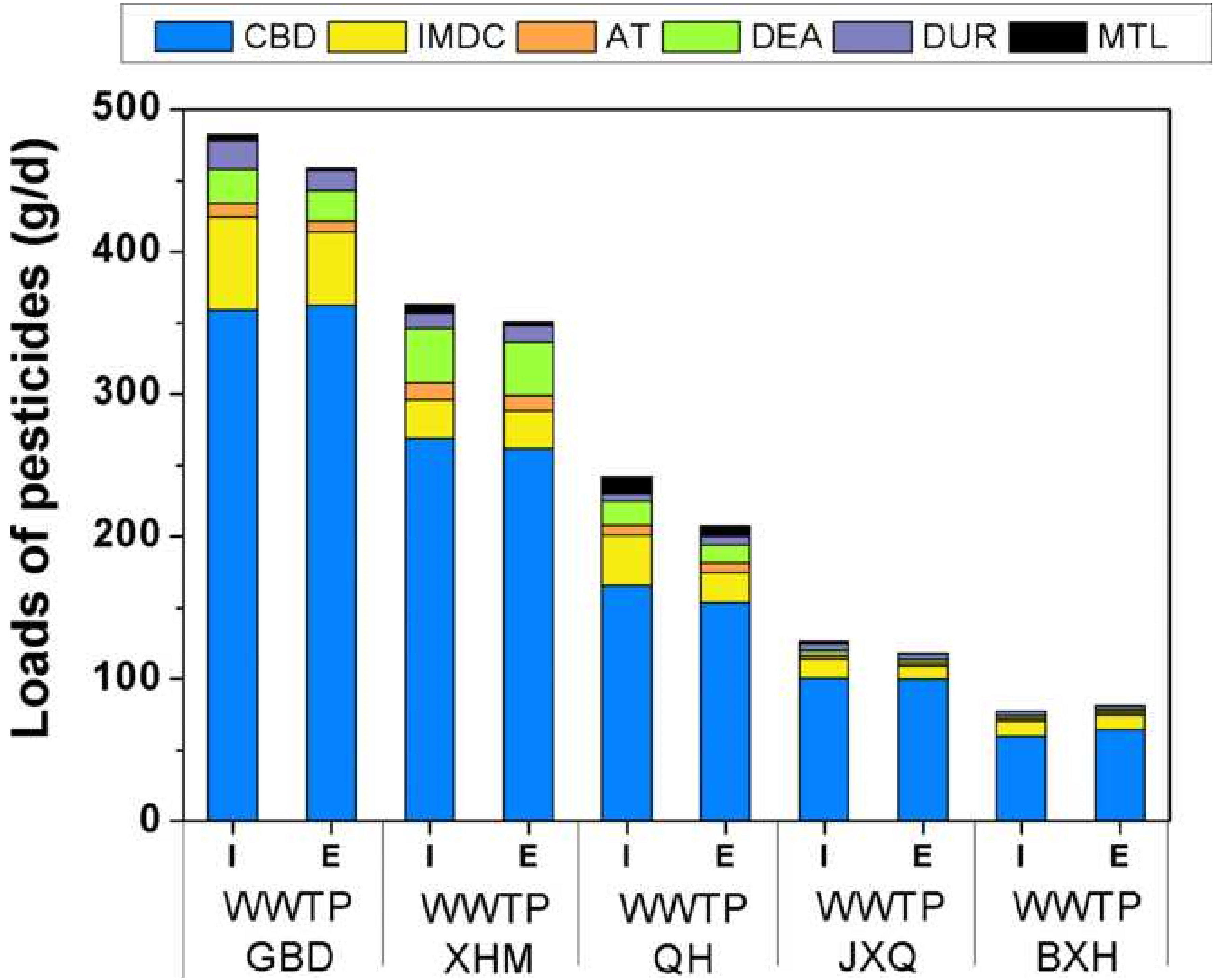
Elimination Efficiency (%)
120
90
60
30
0
Caffeine
Benzotriazole
DEET
Climbazol
4-/5-Methyl-benzotriazole
Sucralose

Figure3



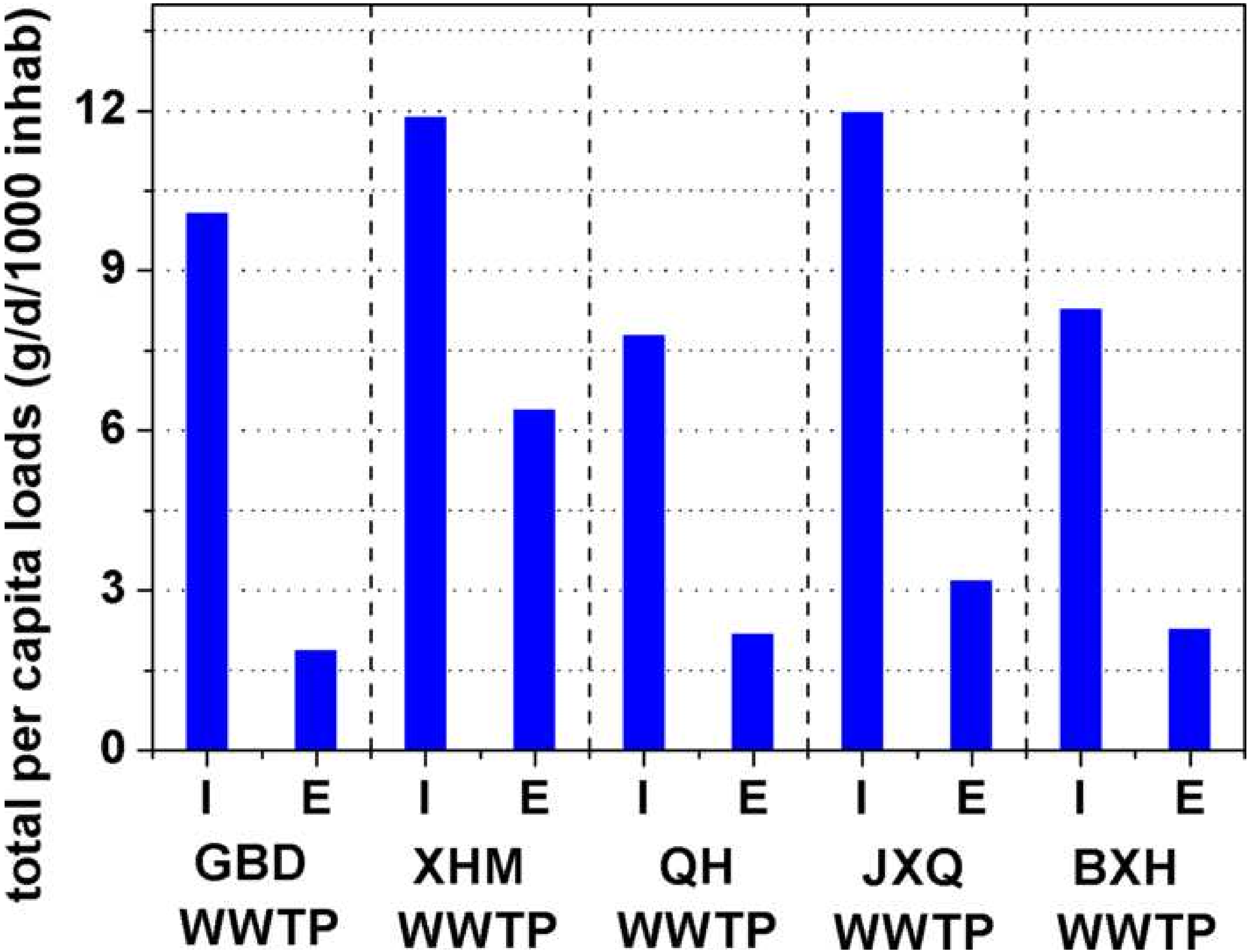
GBD
XHM
QH
JXQ
BXH
Elimination efficiency (%)
100
50
0
-50
-100
Sulfadiazine
Sulfapyridine
Sulfamethoxazole
N4-Acetylsulfamethoxazole
Erythromycin
Fluconazole
Clarithromycin
Metronidazole
Trimethoprim
4-Acetamidoantipyrine
Diclofenac
Carbamazepine
Carbam.-dihydro-dihydroxy
Atenolol acid
Iopromide
Lidocaine
antibiotics
analgetics and anti-inflammatories
antiepileptics
lipid regulators and β-blockers
contrast agents and anesthetics

Figure4a



CBD
IMDC
AT
DEA
DUR
MTL
Loads of pesticides (g/d)
500
400
300
200
100
0
I
E
I
E
I
E
I
E
I
E
WWTP GBD
WWTP XHM
WWTP QH
WWTP JXQ
WWTP BXH

Figure4b



total per capita loads (g/d/1000 inhab)
0
3
6
9
12
I
E
I
E
I
E
I
E
I
E
GBD WWTP
XHM WWTP
QH WWTP
JXQ WWTP
BXH WWTP