

Occurrence of pharmaceuticals and personal care products, and their
associated environmental risks in Guanting Reservoir and its upstream
rivers in north China

Panwei Zhang,^{ab} Huaidong, Zhou,^{ab} Kun Li,^{ab} Xiaohui Zhao,^{ab} Qiaona Liu,^{ab} Dongjiao Li,
^bGaofeng Zhao,^{*ab} Liang Wang^b

^a: State Key Laboratory of Regulation of Water Cycle in River Basin, China Institute of Water
Resource and Hydropower Research, Beijing, 100038, *P.R.* China.

^b: China Institute of Water Resources and Hydropower Research, Beijing 100038, *P.R.* China

*Corresponding Author

Email: zhaogf@iwhr.com

Tel: +86-1068781893

Fax:

+86-1068573618

Table S1 Basic information of eighteen selected PPCPs

Table S2 Sampling site information for samples of Guanting Reservoir

Table S3 Experimental conditions of electrospray tandem mass spectrometry

Table S4 Water quality parameters in surface water samples collected from Guanting Reservoir and its upstream rivers

Table S5 Environmental risk assessment for selected PPCPs in GTR and its upstream rivers

Table S1. Basic information of eighteen selected PPCPs

Classes	Compound	acronym	CAS no.	molecular formula	$\log k_{ow}^a$	pKa ^a	classification
Non-antibiotic pharmaceuticals (N-APs)	Acetaminophen	ACE	103-90-2	C ₈ H ₉ NO ₂	0.46	9.38	Analgesic, antipyretic
	Caffeine	CAF	58-08-2	C ₈ H ₁₀ N ₄ O ₂	-0.07	10.40	Central nervous system stimulant
	Diltiazem	DTZ	42399-41-7	C ₂₂ H ₂₆ N ₂ O ₄ S	2.70	8.90	Calcium channel blocker
	Carbamazepine	CBZ	298-46-4	C ₁₅ H ₁₂ N ₂ O	2.47	7.00	Anticonvulsant, antidepressant
Sulfonamides (SAs)	Fluoxetine	FXT	54910-83-3	C ₁₇ H ₁₈ F ₃ NO	1.80	-	antidepressant
	Sulfadiazine	SDZ	68-35-9	C ₁₀ H ₁₀ N ₄ O ₂ S	-0.34	2.0/6.48	Sulfonamide antibiotic
	Sulfamethoxazole	SMX	723-46-6	C ₁₀ H ₁₁ N ₃ O ₃ S	0.89	1.6/5.7	Sulfonamide antibiotic
	Sulfamethazine	SMZ	57-68-1	C ₁₂ H ₁₄ N ₄ O ₂ S	0.14	2.65/7.65	Sulfonamide antibiotic
Tetracyclines (TCs)	Trimethoprim	TMP	738-70-5	C ₁₄ H ₁₈ N ₄ O ₃	0.91	7.12	antibacterial agent
	Oxytetracycline	OTC	79-57-2	C ₂₂ H ₂₄ N ₂ O ₉	-0.90	9.50	Tetracycline antibiotic
	Tetracycline	TC	60-54-8	C ₂₂ H ₂₄ N ₂ O ₈	-1.37	3.30	Tetracycline antibiotic
	Chlortetracycline	CTC	57-62-5	C ₂₂ H ₂₃ ClN ₂ O ₈	-	3.30/7.55/9.33	Tetracycline antibiotic
Macrolides (MCs)	Doxycycline	DOX	564-25-0	C ₂₂ H ₂₄ N ₂ O ₈	2.37	3.02/7.97/9.15	Tetracycline antibiotic
	Azithromycin	AZM	83905-01-5	C ₃₈ H ₇₂ N ₂ O ₁₂	4.02	8.74	Macrolide antibiotic
	Erythromycin	ERY	114-07-8	C ₃₇ H ₆₇ NO ₁₃	3.06	8.90	Macrolide antibiotic
Quinolones (QNs)	Tylosin	TYL	1401-69-0	C ₄₆ H ₇₇ NO ₁₇	1.05	7.10	Macrolide antibiotic
	Lincomycin	LIN	154-21-2	C ₁₈ H ₃₄ N ₂ O ₆ S	0.56	7.60	Lincosamide antibiotic
	Ofloxacin	OFL	82419-36-1	C ₁₈ H ₂₀ FN ₃ O ₄	-0.02	-	Quinolone antibiotic

a: Stamatis and Konstantinou, 2013; Salgado et al., 2012; Chen et al., 2014; Yang et al., 2011; Marczak et al., 2015

Table S2. Sampling site information for samples of Guanting Reservoir

Sites	Coordinates	Date	Location
L01	115°46'36.84"E 40°22'16.752"N	August, 01 2017	Guanting Reservoir
L02	115°45'43.56"E 40°21'43.344"N	August, 01 2017	Guanting Reservoir
L03	115°45'48.24"E 40°21'38.592"N	August, 01 2017	Guanting Reservoir
L04	115°45'54.72"E 40°21'27.072"N	August, 01 2017	Guanting Reservoir
L05	115°44'30.12"E 40°20'52.26"N	August, 01 2017	Guanting Reservoir
L06	115°44'13.56"E 40°21'5.04"N	August, 01 2017	Guanting Reservoir
L07	115°43'54.48"E 40°21'13.32"N	August, 01 2017	Guanting Reservoir
L08	115°43'11.99"E 40°20'55.788"N	August, 01 2017	Guanting Reservoir
L09	115°41'25.08"E 40°20'20.04"N	August, 01 2017	Guanting Reservoir
L10	115°37'35.40"E 40°18'25.668"N	August, 01 2017	Guanting Reservoir
L11	115°37'9.12"E 40°17'29.076"N	August, 01 2017	Guanting Reservoir
L12	115°36'59.04"E 40°16'56.279"N	August, 01 2017	Guanting Reservoir
L13	115°36'26.48"E 40°16'18.336"N	August, 01 2017	Guanting Reservoir
L14	115°36'9.72"E 40°14'7.799"N	August, 01 2017	Guanting Reservoir
R01	115°52'28.20"E 40°26'47.868"N	August, 04 2017	Guishui River
R02	114°30'20.52"E 40°37'1.235"N	August, 02 2017	Yongding River
R03	115°28'1.20"E 40°21'25.128"N	August, 02 2017	Yongding River
R04	115°21'18.72"E 40°21'15.696"N	August, 02 2017	Sanggan River
R05	115°12'40.32"E 40°21'30.96"N	August, 02 2017	Sanggan River
R06	115°18'20.88"E 40°24'52.344"N	August, 02 2017	Yanghe River
R07	115°7'9.84"E 40°31'4.295"N	August, 02 2017	Yanghe River
R08	114°58'19.91"E 40°37'10.488"N	August, 02 2017	Yanghe River

R09	114°49'3.36"E	40°40'49.656"N	August, 02 2017	Yanghe River
R10	114°50'25.44"E	40°42'47.268"N	August, 03 2017	Qingshui River
R11	114°45'38.16"E	40°42'55.44"N	August, 03 2017	Yanghe River
R12	114°30'20.52"E	40°40'29.136"N	August, 03 2017	Yanghe River
R13	114°25'39.36"E	40°37'1.236"N	August, 03 2017	Nanyanghe River
R14	114°28'33.96"E	40°41'3.48"N	August, 03 2017	Dongyanghe River

Table S3. Experimental conditions of electrospray tandem mass spectrometry

Analytes	Parent ion (m/z)	Daughter ion (m/z)	Fragmentor/ V	Collision energy/ eV
ACE	152	110	90	15
		65	90	35
CAF	195	138	110	15
		110	110	25
DTZ	415	178	130	25
		150	130	25
CBZ	237	194	110	15
		179	110	35
FXT	310	148	110	5
		156	110	15
SDZ	251.2	92	110	25
		156	110	15
SMX	254	92	110	25
		186	90	25
SMZ	279	156	90	25
		261	110	25
TMP	291	230	110	25
		444	130	13
OTC	461	426	130	17
		427	110	5
TC	445.2	410	110	15
		462	110	15
CTC	479	197	110	35
		428	110	15
DOX	445..2	154	110	35
		591.2	130	30
AZM	749.5	158	130	35
		576	90	15
ERY	734.5	158	90	35
		772	110	35
TYL	916.3	174	110	35

LIN	407	359.1	110	15
		126	110	25
OFX	362.2	318	90	15
		261	90	25
SMZ- ¹³ C ₆	285	186	90	25
		162	90	25
ERY- ¹³ C, d ₃	738.5	587	90	15
		160	90	35
ATZ-d ₅	221	179	110	15
		137	110	15

Table S4. Water quality parameters in surface water samples collected from Guanting Reservoir and its upstream rivers

Sites	DOC (mg·L ⁻¹)	TN (mg·L ⁻¹)	TP (mg·L ⁻¹)	NH ₃ -N (mg·L ⁻¹)
L01	13.17	0.326	0.013	0.27
L02	10.11	0.280	0.022	0.16
L03	10.75	0.234	0.026	0.14
L04	11.52	0.222	0.023	0.16
L05	11.65	0.230	0.016	0.30
L06	11.47	0.329	0.016	0.11
L07	12.52	0.322	0.020	0.11
L08	10.58	0.249	0.025	0.10
L09	11.24	0.276	0.012	0.25
L10	10.48	0.234	0.030	0.16
L11	7.98	0.257	0.027	0.18
L12	9.58	0.268	0.023	0.12
L13	10.89	0.130	0.026	0.19
L14	7.83	0.283	0.039	0.22
R01	14.65	1.261	0.140	0.26
R02	6.33	2.024	0.325	0.16
R03	8.74	0.188	0.075	0.12
R04	17.19	0.479	0.037	0.59
R05	3.20	1.775	0.025	0.23
R06	4.64	1.073	0.104	0.16
R07	11.67	2.116	0.467	0.77
R08	21.98	1.100	1.639	0.87
R09	14.47	0.855	0.143	19.70
R10	13.55	1.146	0.206	1.02
R11	6.45	0.164	0.083	0.45
R12	2.33	0.617	0.089	0.04
R13	0.61	0.398	0.080	0.06
R14	1.91	0.797	0.007	0.07

Table S5. Environmental risk assessment for selected PPCPs in GTR and its upstream rivers

Analytes	EC50 (mg/L)	PNEC ($\mu\text{g}\cdot\text{L}^{-1}$)	Maxium MEC ($\text{ng}\cdot\text{L}^{-1}$)		RQ	
			GTR	Upstream rivers	GTR	Upstream rivers
ACE	9.2	9.2 ^a	506.47	901.73	5.51E-02	9.80E-02
CAF	69	69 ^b	620.39	707.51	0.009	0.010
DTZ	8.2	8.2 ^c	17.37	8.64	2.12E-03	1.05E-03
CBZ	31.6	31.6 ^c	5.90	11.47	0.000	0.000
FXT	41	41 ^d	3.40	4.45	8.29E-05	1.09E-04
SDZ	10	10 ^e	23.51	20.58	0.002	2.06E-03
SMX	20	20 ^a	44.39	42.59	0.002	0.002
SMZ	15.6	15.63 ^e	25.68	14.11	0.002	9.03E-04
TMP	1.0	1 ^a	15.26	20.23	0.015	0.020
OTC	2.0	2 ^e	30.45	36.26	0.015	0.018
TC	3400	3400 ^e	14.86	18.86	4.37E-06	5.55E-06
CTC	5.0	5 ^f	15.38	19.68	0.003	3.94E-03
DOX	430	430 ^d	10.11	12.76	2.35E-05	2.97E-05
AZM	0.45	0.454 ^g	16.72	25.71	0.037	0.057
ERY	0.04	0.04 ^a	27.56	63.69	0.689	1.592
TYL	0.34	0.34 ^g	1.49	0.00	0.004	0.000
LIN	14.0	13.98 ^h	10.53	59.19	0.001	0.004
OFL	100	100 ^e	26.37	36.73	2.64E-04	3.67E-04

^a: Lin et al., 2008; ^b: Muñoz et al., 2008; ^c: Kim et al., 2007; ^d: Schwab et al., 2005; ^e: Bu et al., 2013; ^f: Ji et al., 2012; ^g: Verlicchi et al., 2014; ^h: Isidori et al., 2005

References:

- Bu, Q., Wang, B., Huang, J., Deng, S., Yu, G., 2013. Pharmaceuticals and personal care products in the aquatic environment in China: a review. *Journal of Hazardous Materials.* 262,189-211.
- Isidori, M., Lavorgna, M., Nardelli A, Pascarella, L., Parrella, A., 2005. Toxic and genotoxic evaluation of six antibiotics on non-target organisms. *Science of the Total Environment.* 346, 87-98.
- Ji K, Kim S, Han S, Seo, J., Lee, S., Park, Y., Choi, K., Kho, Y.L., Kim, P.G., Park, J., Chio, K., 2012. Risk assessment of chlortetracycline, oxytetracycline, sulfamethazine, sulfathiazole, and erythromycin in aquatic environment: are the current environmental concentrations safe?. *Ecotoxicology.* 21, 2031-2050.
- Kim, Y., Choi, K., Jung, J., Jung, J.Y. Park, S.J., Kim, P.G., Park, J., 2007. Aquatic toxicity of acetaminophen, carbamazepine, cimetidine, diltiazem and six major sulfonamides, and their potential ecological risks in Korea. *Environment International,* 33, 370-375.
- Lin A Y, Yu T H, Lin C F. 2008. Pharmaceutical Contamination in Residential, Industrial, and Agricultural Waste Streams: Risk to Aqueous Environments in Taiwan. *Chemosphere.* 74, 131-141.
- Marczak, M., Okoniewska, K. M., Okoniewski, J., Grabowski, T., Jaroszewski, J. J. (2015). Indirect relationship between lipophilicity and maximum residue limit of drugs determined for fatty tissue. *Bulletin of the Veterinary Institute in Pulawy,* 59, 383-391.
- Muñoz, I., Gómez, M.J., Molina-Díaz, A., Mark, A.J., Fernández-Alba, A.R., García-Calvo, E., 2008. Ranking potential impacts of priority and emerging pollutants in urban wastewater through life cycle impact assessment. *Chemosphere,* 74, 37-44.
- Salgado, R., Marques, R., Noronha, J. P., Carvalho, G., Oehmen, A., Reis, M. A. (2012). Assessing the removal of pharmaceuticals and personal care products in a full-scale activated sludge plant. *Environmental Science and Pollution Research,* 19, 1818-1827.
- Schwab, B.W., Hayes, E.P., Fiori, J.M., Roden, N.M., Cragin, D., Meyerhoff, R.D., Vincent, J.D., Anderson, P.D., 2005. Human pharmaceuticals in US surface waters: a human health risk assessment. *Regulatory Toxicology and Pharmacology,* 42, 296-312
- Stamatis, N. K., Konstantinou, I. K. (2013). Occurrence and removal of emerging pharmaceutical, personal care compounds and caffeine tracer in municipal sewage treatment plant in Western Greece. *Journal of Environmental Science and Health. part. b: Pesticides Food Contaminants and Agricultural Wastes,* 48, 800-813.
- Verlicchi, P., Al, A.M., Jelic, A., Petrović, M., Barceló, D., 2014. Comparison of measured and predicted concentrations of selected pharmaceuticals in wastewater and surface water: a case study of a catchment area in the Po Valley (Italy). *Science of the Total Environment.* 470-471, 844-854.
- Yang, X., Flowers, R. C., Weinberg, H. S., Singer, P. C. (2011). Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. *Water Research,* 45, 5218–5228.