Chemosphere 111 (2014) 327–335

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence, seasonal variation and risk assessment of antibiotics in the reservoirs in North China

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HIGHLIGHTS

- 29 Selected antibiotics were found to be prevalent in four reservoirs.
- Seasonal variations of most antibiotics were significant.
- Antibiotics occurrence at the reservoir was related to cage culture of fish.
- Alage, daphnid and fish might be at low short-term risk in the reservoir.

ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 7 March 2014
Accepted 24 March 2014
Available online 13 May 2014

Handling Editor: X. Cao

Keywords:
Antibiotic
Reservoir
Seasonal variation
Risk assessment

ABSTRACT

The occurrence and seasonal variability of five groups (tetracycline, quinolone, chloramphenicol, macrolide and sulfonamide) of antibiotics were investigated in the surface water of four reservoirs. The dissolved concentrations of 29 antibiotics were in the $ng\,L^{-1}$ level. Trace levels of all target antibiotics were analyzed using solid-phase extraction followed by liquid chromatography electrospray tandem mass spectrometry. All of the antibiotics were detected at all sampling sites, indicating widespread occurrence of antibiotics in the study area. The detection of florfenicol, josamycin, kitasamycin, spiramycin and sulfameter is the first report of these compounds in reservoir samples. The results showed an association between the presence of some antibiotics at Panjiakou reservoir and cage culture of fish. Twenty-three types of antibiotics showed significant seasonal variations ($p < 0.001$) due to human activities and flow conditions. A risk assessment showed that all antibiotics detected could cause very low risk to algae, daphnid and fish. Further health risk need to be investigated because these reservoirs are drinking water sources.

1. Introduction

In recent years, the occurrence and fate of antibiotics in the aquatic environment has been an emerging issue because of increasing concern over the potential adverse effects of these compounds on the ecosystem and on the health of humans and animals (Pruden et al., 2006; Sapkota et al., 2008; Luo et al., 2010). Antibiotics are commonly used to treat or prevent infective diseases in human and veterinary medicine worldwide. Large amounts are also used in agriculture, bee-keeping, livestock and aquaculture as growth promoters (Kümmerer, 2009). Therefore, antibiotics in the aquatic environment could originate from a variety of sources, such as municipal and pharmaceutical wastewater, improper disposal of unused/expired antibiotics and agricultural runoff or leaching (Brown et al., 2006; Sapkota et al., 2008). Antibiotics have been detected worldwide at nanogram to low-microgram per liter levels in natural waters (Sacher et al., 2001; McArdell et al., 2003; Constanzo et al., 2005; Ferding et al., 2005; Batt et al., 2006; Xu et al., 2007; Watkinson et al., 2009; Wang et al., 2010). Therefore, it is important to investigate the occurrence and distribution of antibiotics in the aquatic environment.

In the 1980s, Watts et al. reported the presence of several antibiotics, including erythromycin, sulfamethoxazole, and tetracycline in a river at concentrations of $1\,\mu g\,L^{-1}$ for the first time (Watts et al., 1983). However, it was in the middle of the 1990s, when antibiotics were widely used and new analytical technologies were developed, that their presence raised increasing concern

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http://dx.doi.org/10.1016/j.chemosphere.2014.03.129
0045-6535/

(Homem and Santos, 2011). The United Stated Geological Survey (USGS) reported the occurrence of 21 antibiotic compounds in 139 streams around the United States in a national reconnaissance conducted during 1999–2000. The antibiotics included tetracyclines, sulfonamides, macrolides and tylosin (Kolpin et al., 2002). Since this study, a variety of antibiotics have been detected in different aquatic environments, such as wastewater (McArdell et al., 2003; Ferding et al., 2005), surface water (Constanzo et al., 2005; Xu et al., 2007), groundwater (Sacher et al., 2001; Batt et al., 2006), and even drinking water (Watkinson et al., 2009; Wang et al., 2010), throughout the world. The types and concentrations of antibiotics in the aquatic environment vary according to countries and usage patterns (Kolpin et al., 2002). The annual usage of antibiotics has been estimated to be between 100000 and 200000 tons globally, with more than 25000 tons used each year in China (Gao et al., 2012). And antibiotic pollution could be serious on the basis of the investigations on antibiotics in the surface water of the Pearl River Delta, Yellow River, Haihe River, Baiyangdian Lake and Bohai Bay (Xu et al., 2007, 2009; Luo et al., 2011; Zou et al., 2011; Li et al., 2012). The frequent occurrence of antibiotics in surface water and groundwater, some of which are used as sources of drinking water, gives rise to concern over the potential for antibiotics to occur in drinking water and, thus, to affect human health through chronic exposure (Ye et al., 2006). The U.S.A. has already examined the presence of antibiotics in untreated drinking water sources (Focazio et al., 2008). However, limited information is available about the occurrence and distribution of antibiotics in natural water reservoirs supplying raw water for drinking water.

This study focused on the occurrence and distribution of five classes of antibiotics in four water reservoirs in North China, including seasonal variations and risk assessment, in an attempt to fill in a gap in the literature. In this study, 29 antibiotics including four tetracylines (TCs), three quinolones (QNs), four chloramphenicols (CPs), five macrolides (MCs), and thirteen sulfonamides (SAs) were examined. To determine low levels of antibiotics in water sources, a trace analysis method was developed for the 29 antibiotics using a single solid-phase extraction and liquid chromatography electrospray tandem mass spectrometry.

2. Materials and methods

2.1. Chemicals and standards

Oxytetracycline, thiamphenicol, josamycin, and kitasamycin were obtained from the Institute of Biomedical Research (China) and chloramphenicol and sulfapyridine were obtained from the Institute of Metrology (China). Other standards were purchased from J&K Scientific. The physicochemical properties of these 29 compounds are shown Table 1. Methanol and acetonitrile (HPLC grade) were obtained from J.T. Baker (Deventer, The Netherlands). Formic acid (8%) was purchased from Sigma (St. Louis, MO). Ultrapure water, with a resistivity of at least 18.2 MΩ, was prepared with a Milli-Q purification system (Millipore, USA). Unless otherwise indicated, chemicals were at least reagent grade.

2.2. Sampling and sample preparation

Sampling was performed eight times in the Luan River to the Tianjin Diversion from 2010 to 2011 at 20 different sites (D1–D20) (Fig. 1). The Luan River to the Tianjin Diversion across the Luan River Basin stretches over 234 km. It supplies 0.1 billion m^3 water each year to Tianjin (approximately 12 million inhabitants) and 0.03 billion m^3 water to Tangshan (approximately 7.6 million

Table 1
Physico-chemical properties of antibiotics investigated in this study.

Group	Compound	Acronym	CASRN[a]	Molecular mass	Log K_{ow}[b]	pKa[b]	Molecular formula
Tetracyclines (TCs)	Oxytetracycline	OTC	79-57-2	460.45	−0.9	3.27	$C_{22}H_{24}N_2O_9$
	Chlortetracyclin	CTC	57-62-5	478.88	−0.62	3.3	$C_{22}H_{23}ClN_2O_8$
	Tetracycline	TC	60-54-8	444.43	−1.30	3.3	$C_{22}H_{24}N_2O_8$
	Doxycycline	DXC	564-25-0	444.44	−0.02	n/a[c]	$C_{22}H_{24}N_2O_8$
Quinolones (QNs)	Nalidixic acid	NDA	389-08-2	232.23	1.59	8.6	$C_{12}H_{12}N_2O_3$
	Oxolinic acid	OLA	14698-29-4	261.23	0.94	6.87	$C_{13}H_{11}NO_5$
	Flumequine	FMQ	42835-25-6	261.25	1.6	n/a	$C_{13}H_{11}NO_5$
Chloramphenicols (CPs)	Chloramphenicol	CAP	56-75-7	323.13	1.14	n/a	$C_{11}H_{12}Cl_2N_2O_5$
	Thiamphenicol	TAP	15318-45-3	356.22	−0.33	n/a	$C_{12}H_{15}Cl_2NO_5S$
	Florfenicol	FF	76639-94-6	358.21	n/a	n/a	$C_{12}H_{14}Cl_2FNO_4S$
	Penicillin G	PENG	61-33-6	373.49	1.83	n/a	$C_{16}H_{18}KN_2O_4S$
Macrolides (MCs)	Erythromycin	ERY	114-07-8	733.92	3.06	8.88	$C_{37}H_{67}NO_{13}$
	Roxithromycin	ROX	80214-83-1	837.05	2.75	n/a	$C_{41}H_{76}N_2O_{15}$
	Josamycin	JOS	16846-24-5	827.99	3.16	n/a	$C_{42}H_{69}NO_{15}$
	Kitasamycin	KIT	1392-21-8	785.98	3.077	n/a	$C_{40}H_{67}NO_{14}$
	Spiramycin	SPI	8025-81-8	843.05	1.456	n/a	$C_{43}H_{74}N_2O_{14}$
Sulfonamides (SAs)	Sulfaguanidine	SPGD	57-67-0	214.24	−1.22	11.25	$C_7H_{10}N_4O_2S$
	Sulfacetamide	STM	144-80-9	214.24	−0.96	7.59	$C_8H_{10}N_2O_3S$
	Sulfamethazine	STZ	57-68-1	278.33	0.89	8.43	$C_{12}H_{14}N_4O_2S$
	Sulfapyridine	SPD	144-83-2	249.29	0.35	6.36	$C_{11}H_{11}N_3O_2S$
	Sulfadiazine	SDZ	68-35-9	250.28	−0.09	6.5[d]	$C_{10}H_{10}N_4O_2S$
	Sulfadimethoxine	SDMX	122-11-2	310.33	1.63	5.9[d]	$C_{12}H_{14}N_4O_4S$
	Sulfachlorpyridazine	SCPD	80-32-0	284.73	0.31	5.5[d]	$C_{10}H_9ClN_4O_2S$
	Sulfamethizole	STL	144-82-1	270.33	0.54	5.5 [d]	$C_9H_{10}N_4O_2S_2$
	Sulfamonomethoxine	SMMX	1220-83-3	280.30	0.7	7.2[d]	$C_{11}H_{12}N_4O_3S$
	Sulfamethoxypyridazine	STPD	2577-32-4	302.28	n/a	n/a	$C_{11}H_{11}N_4NaO_3S$
	Sulfameter	ST	651-06-9	280.30	0.41	n/a	$C_{11}H_{12}N_4O_3S$
	Sulfamethoxazole	STX	723-46-6	253.27	0.89	8.8[d]	$C_{10}H_{11}N_3O_3S$
	Sulfamerazine	SMR	127-79-7	264.30	0.14	8.0[d]	$C_{11}H_{12}N_4O_2S$

[a] Chemical Abstracts Service Registry Number.
[b] Values obtained from U.S. National Library of Medicine: http://toxnet.nlm.nih.gov/.
[c] Not available.
[d] Values from Białk-Bielińska A, 2011.