



Occurrence and distribution of selected antibiotics in the surface waters and ecological risk assessment based on the theory of natural disaster

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Abstract

With increasing population growth and resource depletion, ecological health is a hotspot and urgent topic. Our study investigated the occurrence and distribution of five antibiotics, i.e., metronidazole (MET), sulfamethoxazole (SMZ), ciprofloxacin (CFX), norfloxacin (NFX), and enrofloxacin (EFX), in the surface water from Erlong Lake, China. With the seasonal and spatial variations of antibiotics, this study developed an interdisciplinary approach for the ecological risk of antibiotics considering the natural, human, and socioeconomic elements of watershed based on the risk theory of natural disaster. This approach integrates the geographic information system (GIS) spatial analysis tool, natural disaster theory, “driving force”–“pressure”–“state”–“impact”–“response” (DPSIR) model, and ordered weighted averaging (OWA) operators in terms of various environmental factors, representing a new ecological risk paradigm for environmental managers or decision-makers to identify environmental change. A total of 69 samples were collected in wet, dry, and normal seasons from 2017 to 2018, and laboratory analyses revealed that four antibiotics (MET, SMZ, CFX, and NFX) were widely detected in the lake. The mean concentrations decreased in the order of MET (1041.7 ng L⁻¹) > SMZ (771.4 ng L⁻¹) > CFX (646.4 ng L⁻¹) > NFX (179.0 ng L⁻¹) > EFX (15.3 ng L⁻¹), with their levels in natural surface waters higher than those in other studies. Antibiotic concentrations were higher in dry seasons than in other seasons, and the concentrations were strongly correlated with EC (electrical conductivity), pH, DOC (dissolved organic carbon), and TP (total phosphorus) according to redundancy analysis (RDA). Significant seasonal variations were found in CFX and EFX (ANOVA, $p < 0.001$). For the whole watershed, the ecological extremely and heavily vulnerable levels were concentrated in the central and northwest regions of the watershed, i.e., Changling county and Lishu county. Hence, the ecological distributions of extreme risk and heavy risk posed by the five selected antibiotics were assessed by using the mixture hazard quotient methods and DPSIR model which were also located in these counties in different seasons. The antibiotic results of ecosystem risk assessment can support decision-makers in identifying and prioritizing the necessary taking of specific measures and different risk attitudes to preserve the quality of ecological health for a city or multiple counties.

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Introduction

The extensive use of antibiotics in both humans and veterinary medicine for human diseases, microbial infections, and antibacterial properties, and also as feed additive, promotes animal growth in livestock, poultry, and aquaculture industries for several decades (Henriksson et al. 2018; Kümmerer 2009a, b; Binh et al. 2018). Based on an apparently beneficial treatment effect, the use of antibiotics has led to a growing usage in their consumption. Generally, antibiotics possess poor metabolism properties, and more than half of the chemicals could be excreted as parent compounds or as metabolites (Henriksson et al. 2018; Kümmerer 2009a; Liu et al. 2018a, b; Mirzaei et al. 2018). Most of them were associated with biosolid and livestock manure application onto land, ultimately entering the aquatic environment directly via urine and feces, domestic sewage, agricultural effluent, and surface runoff of soil or via indirect processes (Kümmerer 2009a; Zhou et al. 2011). Nevertheless, wastewater treatment plants (Chen et al. 2014; Yao et al. 2015) poorly remove these soluble antibiotics due to the high expense (Alsager et al. 2018; Henriksson et al. 2018; Hu et al. 2018; Li et al. 2018a, b, c). Owing to continuous inputs into natural waters through numerous pollution sources, in the aquatic environment, antibiotics are regarded as a class of ubiquitous and “pseudo-persistent” pollutions (Yao et al. 2015). Particularly, the reached concentrations of antibiotics in these natural waters were detected from several nanograms per liter to hundreds of micrograms per liter (Kümmerer 2009a; Li et al. 2018a, b, c). Hence, the occurrence and persistence of antibiotics in natural aquatic environments have drawn widespread attention given the close link of antibiotics with antimicrobial resistance and toxicity of aquatic organisms (Fram and Belitz 2011; González-Pleiter et al. 2017, 2019; Hernández et al. 2019; Reardon 2014; Johansson et al. 2014).

Under the continual exposure of the bacterial fauna to antibiotics or active metabolites, antibiotic burden in water has direct toxicity to aquatic phytoplankton and animals (González-Pleiter et al. 2013; Rico et al. 2018; Wollenberger et al. 2000; Wang et al. 2014; Yan et al. 2016). Likewise, this process produces resistant bacterial strains or genes, which can be transmitted through food chains (González-Pleiter et al. 2013; Kümmerer 2009a; Rico et al. 2018). Even at low concentrations, antibiotics could also produce biological effects and interact with other pollutants, resulting in potential threat to the ecosystem balance. To date, the global antibiotic consumption has obviously increased due to global economic and population growths (Luo et al. 2011). China, as the largest

producer and consumer of antibiotics worldwide, produced 210,000 t of antibiotics every year, of which 48% were applied in agriculture (Li et al. 2018a, b, c; Liu et al. 2018a, b; Luo et al. 2011). Approximately 54,000 t of antibiotics from feces entered into the receiving environment after treatment processes with low removal efficiencies of wastewater treatment plants (Zhang et al. 2015). The usage of antibiotics may produce toxicity and accelerate the development of antibiotic resistance genes and bacteria, which increase health and ecological risks. Studies (Bai et al. 2014; Binh et al. 2018; Luo et al. 2011; Zhang et al. 2015; Jia et al. 2012; Zhang et al. 2013) have been conducted on the occurrence of antibiotics in different natural waters from various regions in China which have become more frequent after 2005. These studies reported that the potential antibiotic contaminant levels and ecological risk of natural surface waters are due to the high-intensity usage of antibiotics with low treatment rates. The most important parts of inland rivers, lakes, and reservoir ecosystems have a close relation to climate, watershed ecological health, resident health, and economic development. Particularly for watersheds that possess high population density, agriculture activities, livestock, and aquaculture, the antibiotic contamination and ecological risk of lakes are significant for ecological safety and human health (González-Pleiter et al. 2013; Rico et al. 2018). Different environmental factors with different geographical extents contributed varying concentrations of antibiotic residues, signifying different risk levels to the ecological environment (González-Pleiter et al. 2013; Rico et al. 2018). Hence, the occurrence and ecological risks in surface waters in China have been of great concern.

Traditional ecological risks were estimated based on the risk quotient (RQ) for target antibiotics which has been reported in the literature (Kosma et al. 2014; Binh et al. 2018; Verlicchi et al. 2012; Hu et al. 2010; Luo et al. 2011; Wang et al. 2017; Zhang et al. 2015). It is the ratio of the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC) for most aquatic environments referring to technical guidance document on risk assessment by the European Commission in 2003 (González-Pleiter et al. 2013; Wang et al. 2017). However, this method mostly considered the aquatic toxicological properties of pollutants and ignored the ecological affordability. Aquatic ecosystems are under different environmental stresses that have been affected by various types of natural or anthropogenic disturbance, i.e., climate changes, social and economic development, watershed water quality, and environment management, resulting in different ecological vulnerabilities (González-Pleiter et al. 2017, 2019; Liu et al. 2018a, b; Luo et al. 2011; Rico et al.

2018). Particularly, in recent years, economic development and timber harvest operations have exacerbated the imbalance between urban/agricultural development and ecological protection, which brings together a closer examination on vulnerability in terms of “coupled human-environment” or “social-ecological” systems (Eakin and Luers 2006). As such system is susceptible to adverse effects caused by a specific hazard or stressor (Team et al. 2014), identifying the ecological vulnerable areas becomes an integral part of ecological risk and water resource management in fragile regions. Natural disaster theory demonstrated that the risk may be defined simply as the probability of occurrence of an undesired event involving consideration of vulnerability to the hazard (Brooks 2003; Li et al. 2017; Stenchion 1997; Sener and Davraz 2013; Shen et al. 2016; Team et al. 2014; Zhang et al. 2016). For antibiotics targeting pollutants in natural waters, their ecological vulnerability is related to population, livestock, fishery, medical treatment, etc., representing the set of socioeconomic factors that determine people’s ability to cope with stress or change (Allen 2003). Furthermore, due to the mechanism of vulnerability evaluation varying among different ecological regions, developing a local basic set of indicators for antibiotics in natural surface waters is an important and necessary process.

In the present study, we focused on the seasonal occurrence, distribution, and ecological risk of five widely used antibiotics in the surface waters of Lake Erlong, considering the ecological hazard and vulnerability based on the natural disaster theory. Lake Erlong, as the drinking source of Siping city with 320.4 million population, is the largest drinking reservoir in the Northeast plain of China. This is closely related to the ecological safety and the health of residents in the entire watershed. Bain et al. (2014) showed that approximately 1.8 billion people are exposed to fecal contamination through drinking water on a global scale. The specific aims of this study are (1) to discuss the temporal-spatial occurrence, distribution, and sources of the selected antibiotics; (2) to analyze the correlations between the selected antibiotics and water quality parameters; (3) to identify the ecological hazard and vulnerability by multisource data sets in the watershed according to the wide risk formation theory; and (4) to assess the ecological risk of the antibiotics in Lake Erlong.

Materials and methods

Chemicals and standards

Five antibiotics, norfloxacin (NFX), enrofloxacin (EFX), ciprofloxacin (CFX), sulfamethoxazole (SMZ), and metronidazole (MET), were selected for this study based on their high frequency of use in China. All the standard compounds for NFX, EFX, CFX, SMZ, and MET with purities of > 99% were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Separate stock solutions of individual antibiotic standards with concentrations up to 1000 mg L⁻¹ were prepared by diluting an aliquot of the stock solution with methanol (high-performance liquid chromatography grade) before each analytical process. All solvents were of high-performance liquid chromatography grade.

Study area

Lake Erlong is located in the upstream part of the Dongliao River watershed and the east part of Siping City, Jilin Province, northeast of China (124° 46′–124° 58′ E, 43° 7′–43° 20′ N; Fig. 1). It is the largest reservoir in Jilin Province as an essential function in fisheries, agricultural irrigation, and tourism water supply for agriculture and industry in Siping City. Meanwhile, Lake Erlong is an important supply source and pollution source of East Liaohe River which flows through Liaoyuan City and agricultural regions with discharge of domestic and industrial sewage. It is charged with irrigation tasks for Nanwaizi, Lishu, Qinjiatun, and Shuangshan countries with an area of approximately 6700 hm² of cultivated land (Ji et al. 2018). Particularly, with the intensification of human activities, increased population, and intense agricultural production, including soil runoff from fertilizer residues from livestock production, a huge amount of pollutants has been introduced into the lake via adding aquafeed, with about 60% of the lake area being used in aquaculture (silver carp and the fathead minnow, etc.). The main storage capacity of Lake Erlong is 17.6 × 10⁸ m³ with an average flow rate of 15.2 m³ S⁻¹ (Ji et al. 2018). Lake Erlong is located in a transitional zone of humid climate and semi-humid climate, with an annual mean precipitation and air temperature of 650 mm and 5.8 °C, respectively. The rainy season occurs annually from June to August, and the lake freezing period is from November to April the next year.

Sampling procedure

Three sampling campaigns were conducted in Lake Erlong. Surface water samples (0–20 cm) were collected from 25 sites in June 2017 (wet season), 20 sites in October 2017 (dry season), and 25 sites in May 2018 (normal season). In order to compare the seasonal and spatial distributions, all sampling sites covering the north and south sections of the lake were recorded by the global position system (GPS) to ensure the consistent location in every campaign (Fig. 1). Then, all the water samples were collected using a cylinder sampler, and a 2-L water sample at each station was stored in clean amber glass bottles. Before filling, sample containers were first rinsed with local water. Then, these samples were stored in 4 °C coolers, and subsequently transported to the laboratory within 2–3 h (Normal University of Northeast, Changchun, about 110 km far from Lake Erlong). In the laboratory, water

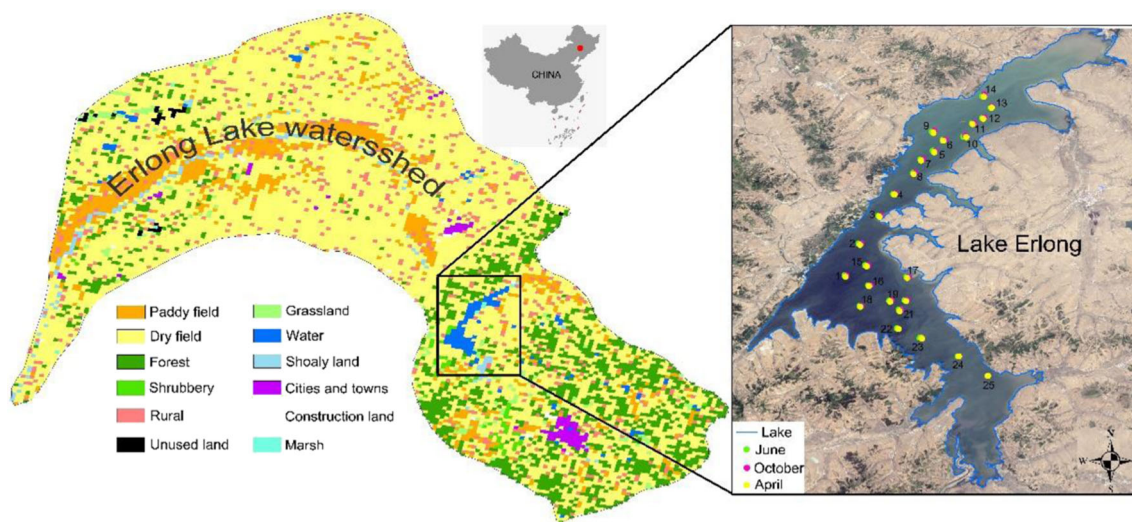


Fig. 1 The watershed of Lake Erlong with various cover types and the map of sampling locations. The land cover raster data was from the Geospatial Data Cloud (<http://www.gscloud.cn/>)

samples were processed as required within 48 h, and remaining samples were kept at $-20\text{ }^{\circ}\text{C}$ for further analysis within 2 days.

Environmental parameter determination

Electrical conductivity (EC) and pH were determined by a portable multiparameter water quality analyzer (Hach, Loveland, CO, USA). The transparency (cm) was measured by a Secchi disk depth (SDD). According to the Environmental Quality Standards for Surface Water (GB3838-2002, China) (<http://kjs.mep.gov.cn/>), chemical oxygen demand (COD) was determined using dichromate, ammonia nitrogen ($\text{NH}_3\text{-N}$) via Nessler's reagent colorimetry, and total phosphorus (TP) using the molybdenum blue method after the lake samples were digested with potassium peroxydisulfate. All the lake samples need to be filtered through a pre-combusted Whatman GF/F (1825-047) filter (pore size $0.45\text{ }\mu\text{m}$) under low vacuum, and DOC (dissolved organic carbon) concentrations were determined by a Shimadzu TOC-VCPH analyzer. Chlorophyll a (Chl-a) was extracted from the filtered ($0.45\text{ }\mu\text{m}$ Whatman GF/F) samples using a 90% acetone solution, and subsequently determined by a UV-Vis spectrophotometer (UV-2006 PC, Shimadzu, Kyoto, Japan). Total suspended matter (TSM), inorganic suspended matter (ISM), and organic suspended matter (OSM) were determined by gravimetric analysis (Song et al. 2013).

Antibiotic extraction procedure and quality control

Extraction procedures for the five antibiotics, e.g., SMZ of sulfonamides (SAs), MET of nitroimidazoles (NIs), and NFX, CFX, and EFX of quinolones (QAs) (Table S1) in water

samples, were optimized according to Hu et al. (2010). Briefly, 1-L water samples were filtered with a muffle furnace-burned glass filter ($\Phi\text{ }47\text{ mm}$, pore size $0.45\text{ }\mu\text{m}$). The filtered samples were added to 50 mL of 0.1 M EDTA–McIlvaine buffer and then 0.4 mL of HCl ($\text{pH} = 4.2$), and then the mixtures were put to a vortex agitator and agitated for 30 s. The antibiotics were extracted using a classical soil-phase extraction method (SPE). Disposable Oasis hydrophilic–lipophilic balance (HLB) cartridges ($0.2\text{ g}/6\text{ mL}$, Waters Corp., Milford, MA) were used to gather antibiotics. Before sample loading, the cartridges were pre-treated with 6 mL methanol and ethyl acetate (v/v), followed by 6 mL methanol and 6 mL pH 4.2 ultrapure water. Sequentially, the samples were passed through at a loading rate of $2\text{--}3\text{ mL min}^{-1}$. After all samples were loaded, the HLB cartridges were washed with $>6\text{ mL}$ of 5% methanol. The analytes were eluted from the HLB cartridges which were reduced to 1 mL under a gentle stream of high-purity nitrogen gas to dryness depending on the loading volume of the sample. The residue was diluted by adding 1 mL methanol and transferred into a 2-mL polypropylene vial for further analysis. Instrumental determinations of antibiotics were performed using high-performance liquid chromatography (HPLC). Descriptions of excitation and emission wavelengths and the mobile phase is found in Table S2.

Analysis of antibiotics was subject to strict quality control procedures. (1) First, individual standards for antibiotics were analyzed using HPLC operating conditions to form the calibration. Linear curve fits (each antibiotic concentration ranged from 0.1 to 5 mg L^{-1}) were used with calibration points, e.g., 1, 2, 5, 10, 20, 50, 100, 200, 500, $1000\text{ }\mu\text{g L}^{-1}$, according to the peak area and concentrations to fit the standard curve with the correlation coefficients exceeding 0.995. Standard solutions were inserted into the sample sequence every 10 samples

to verify sensitivity and repeatability. When the peak area changed by more than 15%, standards were re-analyzed, also for the calibration curve. The external standard method was used in this process. The qualitative analysis of antibiotics was based on the comparison of the retention time and three-dimensional fingerprint between unknown substances and standard products, which are described in Fig. S1. The quantitative analysis was performed according to the standard curve of each antibiotic.

(2) Each of the seven pure water samples (1 L) were spiked with the test compounds to a final concentration of 10 ng L^{-1} per compound. The extracted process is similar to the field samples (soil-phase extraction method). The external standard method was calculated using the standard deviation of the measured concentrations multiplied by the Student *t* test value at *n* degrees of freedom at a 99% confidence level. Recovery experiments were performed by spiking the field water samples with the standard solution. The detection limits of the fluorescence and UV detectors were 10^3 ng L^{-1} and 1 ng L^{-1} , respectively. Information about the recoveries, limits of detection (LODs), and limits of quantifications (LOQs) is provided in Table S3.

Natural and socioeconomic data

Natural data include digital elevation model data with a 30-m resolution from the Computer Network Information Center, Chinese Academy of Sciences (<http://datanirror.csdb.cn>), and meteorological data (National Climate Data Center, <https://gis.ncdc.noaa.gov>; National Meteorological Information Center, China, <http://data.cma.cn/>). Socioeconomic data include meat production, egg production, milk production, aquatic production, medical treatment expenditure, discharged amounts of wastewater, discharged amounts of waste gas, consumption of chemical pesticides, pollutant discharge coefficient of dairy cow, pollutant discharge coefficient of beef, pollutant discharge coefficient of pig, rural household income, town household income, sowing area of the crop, beds of medical organization, population of medical technicians, city's ability to treat wastewater, centralized processing rate of wastewater, education expenditure, population of high school graduates, and science and technology expenditure obtained from the Jilin Statistics Yearbook of 2016, China. Detailed acquisitions and data processing are found in Table S4 and Fig. S2.

Ecological risk assessment

Stenchion (1997) and UNDHA (1992) defined risk as a function of hazard and social vulnerability, of which the outcome depended on the probability of occurrence of a hazard and on the social vulnerability of the exposed

system. The United Nations Office for Disaster Risk Reduction (UNISDR) proposed the wide risk formation theory of natural disaster in a region which is related to an integration of hazard and vulnerability (Zhang 2004). In the work presented here, we provided an ecological risk assessment method with a consideration of the likely consequences of the regional ecological hazard and vulnerability based on the natural disaster theory (Fig. 2). This vulnerability pertains to the inherent characteristics of the ecological system that create the potential for hazard, and also represent the set of socioeconomic factors that determine people's ability to produce and cope with environmental stress (Sener and Davraz 2013; Shen et al. 2016; Li et al. 2017; Zhang et al. 2016). The UNISDR expression was applied to build a dynamic risk assessment model of antibiotics as follows:

$$\text{risk} = \text{hazard} \times \text{vulnerability} = \text{HI} \times \text{VI} \quad (1)$$

where *H* represents the hazard evaluation (HI is hazard index) and *V* represent the water disaster vulnerability evaluation (VI is vulnerability index).

Hazard index

According to the natural disaster theory, hazard index (HI) is equivalent to the potential risk of a certain pollutant or complex pollutants to the aquatic ecosystem (Li et al. 2017). The European Commission Technical Guidance Document (EC, 2003) and European Chemicals Agency (ECHA (European Chemicals Agency) 2008) guideline defined the hazard quotient (HQ) considering the different trophic levels (algae, daphnids, and fish) for hazard evaluation. Because the conditions of the laboratory test methods differ from natural conditions, it is considered most likely that ecosystems will be more sensitive to the chemicals than individual organisms in the laboratory. Therefore, in this study, the measured results are not used directly for hazard assessment but are used as a basis for extrapolation of the predicted no-effect concentration (PNEC). Then, for an individual antibiotic *i*, the HI_i between the measured environmental measured environmental concentration (MEC) and the PNEC is shown in Eq. (2):

$$\text{HI}_i = \frac{\text{MEC}_i}{\text{PNEC}_i} \quad (2)$$

where *i* is the individual antibiotics, and PNEC is the quotient of the lowest no observed effect concentration (NOEC) for the most sensitive species (algae, daphnids, and fish). An assessment factor (AF) was developed for estimating PNEC values for chemicals in this study. Given the insufficient NOEC data for most compounds, PNEC was extrapolated from acute toxicity data or chronic toxicity data of compounds through the division of appropriate AF values. According to ECHA

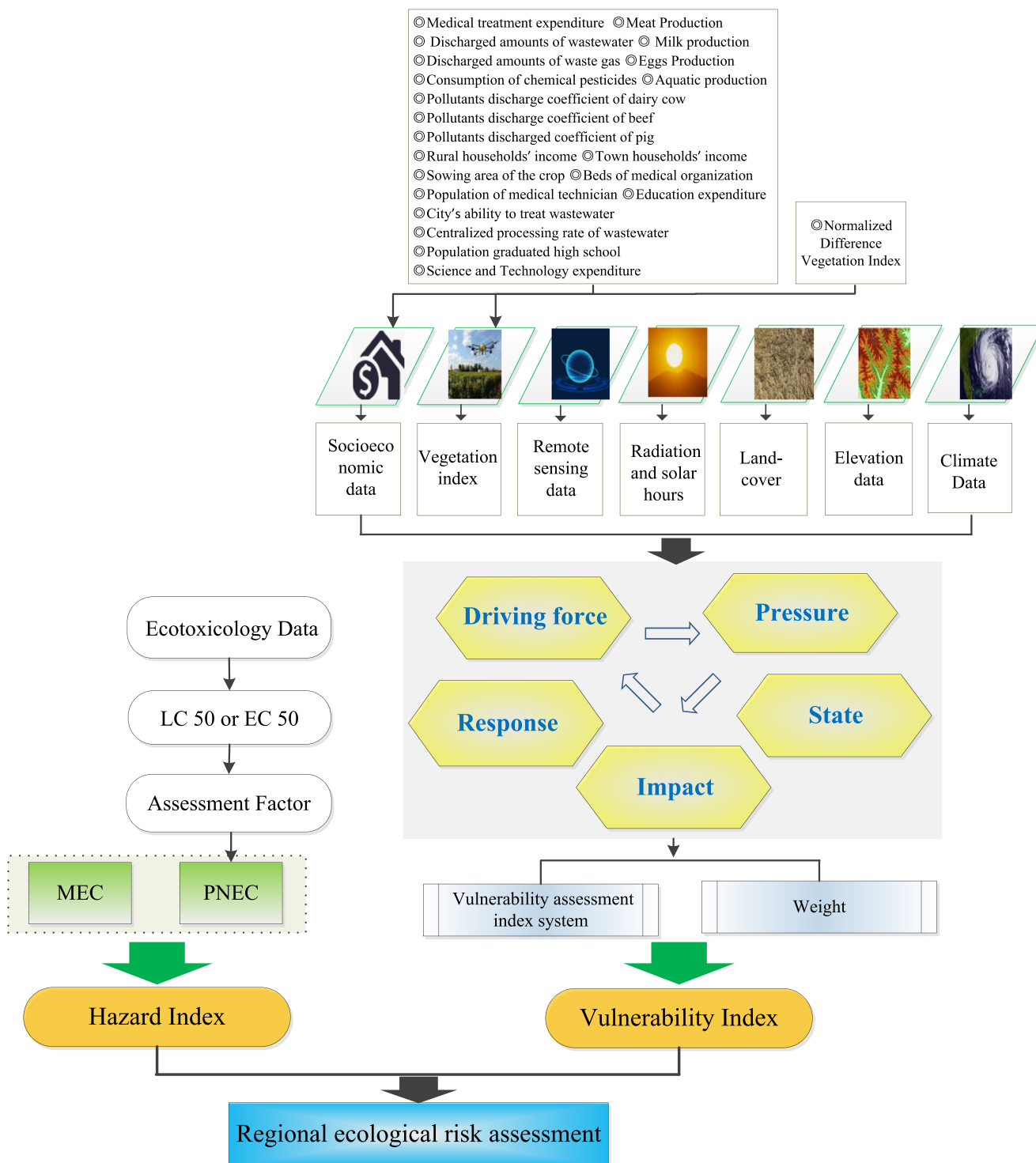


Fig. 2 Antibiotic risk assessment based on a composite function of hazard and vulnerability development framework in the Lake Erlong watershed

(2008), PNEC with different trophic levels can be obtained from available short-term/acute toxicity data (EC50/LC50) with an AF of 1000:

$$PNEC_i = \frac{EC50 (LC50)_i}{1000} \tag{3}$$

where i is the individual antibiotics, and EC50 (LC50) represents acute toxicity. For available long-term/chronic EC10 or NOEC values with AFs of 100, 50, and 10 (Yan et al. 2013; Li et al. 2013),

$$PNEC_i = \frac{chv_i}{AF} \tag{4}$$

where i is the individual antibiotics, and chv is chronic toxicity. In this study, the acute and chronic toxicity data of the selected antibiotics on non-target organisms were collected from other literature (Table S5). Such results give a more realistic picture of the effects on the organisms during their entire life cycle. According to Wang et al. (2017) and Backhaus and Faust (2012), the mixture hazard index ($MHI_{MEC/PNEC}$) of antibiotic mixtures based on the sum of MEC/PNEC values can be calculated by the MHI model, as follows (Eqs. (5) and (6)):

$$MHI_{MEC/PNEC} = \sum_{i=1}^n \frac{MEC_i}{PNEC_i} \quad (5)$$

$$= \frac{\sum_{i=1}^n MEC_i}{\min(EC_{X_{algae}}, EC_{X_{daphnids}}, EC_{X_{fish}})_i \times (1/AF_i)} \quad (6)$$

To further elucidate the hazard levels posed by antibiotics, the different MHI levels were classified into high hazard level ($MHI > 1$), medium hazard level ($0.1 < MHI < 1$) and low hazard level ($0.01 < MHI < 0.1$) (Wang et al. 2017).

2.7.2 Vulnerability index

The ecological vulnerability index VI of selected antibiotics in surface waters was calculated in the “driving force”–“pressure”–“state”–“impact”–“response” (DPSIR) model in considering the ecosystem descriptors in the Lake Erlong watershed (Li et al. 2017). The DPSIR model as a comprehensive function of the physiographic factors and socioeconomic factors (Fig. 2) could reflect the exposed characteristic and adaptive capacity of the ecosystem (Zhang et al. 2016). In order to eliminate the influence of the dimension from different environmental descriptors, each descriptor first normalized a relative pressure score value with the ranges between 0 and 1. More detailed descriptions can be found in Li et al. (2017). The normalized vulnerability index (VI) can be calculated from the type of analysis:

$$VI = \sum [D, P, S, I, R (\sum P_{Nij} \times w_{ij}) \cap w_{D,P,S,I,R}] \quad (7)$$

where P_{Nij} is the dimensionless normalized value (between 0 and 1) of the ecosystem descriptors, and w_{ij} is the weight of ecosystem descriptors in the indicator layer. $w_{D,P,S,I,R}$ represents the weight of driving force, pressure, state, impact, and response in the criterion layer. This calculation process was conducted in ArcGIS 10.2 with the raster calculator.

Statistical analysis

Statistical analyses were performed using the SPSS 16.0 software package (Statistical Program for Social Sciences; SPSS Inc., Chicago, IL). Statistical differences between variations were assessed with an independent sample t test. One-way

ANOVA was used to determine the significant difference between different sampling sites and seasonal variations, with the difference regarded as statistically significant when $p < 0.05$. Significance levels are reported as non-significant (NS) ($p > 0.05$), significant (*, $0.05 > p > 0.01$), or highly significant (**, $p < 0.01$ and $p < 0.001$).

Multivariate analyses, e.g., detrended correspondence analysis (DCA) and redundancy analysis (RDA), were used to evaluate the relationship between antibiotic characteristics and environmental parameters. Generally, the RDA should be chosen when the length of the first gradient calculated by DCA is less than 3. Before this process, the variations were first transformed by taking the natural logarithm of a density data (x) to $\ln(1+x)$ to make the residuals more normally distributed. Due to the significant autocorrelation between variations with the inflation factors greater than 20, the extra variations should be removed. Principal component analysis (PCA) was also performed to identify the source of antibiotics in water samples. DCA, RDA, and PCA were processed using Canoco for Windows 4.5.

Results and discussion

Occurrence and concentrations of selected antibiotics

Almost five target antibiotics were detected in the surface water samples from Lake Erlong, and the concentrations are summarized in Table 1. Four antibiotics MET, SMZ, NFX, and CFX were widely detected in this area at a detected frequency of 100%, thereby indicating ubiquitous occurrences in this area. Thus, EFX was only sporadically detected with a frequency of 46%, and this may relate to the usage of EFX in this watershed and the high logKow value by its environmental behavior (Table S1). The concentrations of four frequently detected antibiotics MET, SMZ, NFX, and CFX ranged from 19.36 to 4397.0 ng L⁻¹ at all sampling sites, whereas those of EFX ranged from 0 to 172.4 ng L⁻¹. The mean concentrations decreased in the order of MET (1041.7 ng L⁻¹) > SMZ (771.4 ng L⁻¹) > CFX (646.4 ng L⁻¹) > NFX (179.0 ng L⁻¹) > EFX (15.3 ng L⁻¹). Both the levels of MET, SMZ, and quinolones (NOR, ENR, and CIP) measured in natural surface waters were higher than those in other studies, such as the Huangpu (313.4 ng L⁻¹ for SMZ) (Jiang et al. 2013), Pearl Rivers (9.5 ng L⁻¹ for SMZ, 62.9 ng L⁻¹ for NOR) (Yang et al. 2011), the Po and Arno Rivers in Italy (246 ng L⁻¹ for SMZ, 513 ng L⁻¹ for CIP) (Zuccato et al. 2010), rivers in France (100 ng L⁻¹ for SMZ, 33 ng L⁻¹ for NOR) (Zuccato et al. 2010), 139 streams and Rio Grande in USA (0–300 ng L⁻¹) (Kolpin et al. 2002; Brown et al. 2006), and Lake Baiyangdian in China (0.86–505 ng L⁻¹) (Li et al. 2012).

Among four frequently detected antibiotics, MET and SMZ were present at higher concentrations (Table 1). Sarmah et al.

Table 1 Antibiotic concentrations (ng L⁻¹) in the water samples collected from Lake Erlong

Antibiotics	Abbreviation	Number	Min	Max	Mean	SD
Metronidazole	MET	69	168.5	3593.7	1041.7	589.9
Sulfamethoxazole	SMZ	69	67.85	2231.0	771.4	295.9
Ciprofloxacin	CFX	69	55.8	4397.0	646.4	608.3
Norfloxacin	NFX	69	19.39	390.2	179.0	103.9
Enrofloxacin	EFX	69	0	172.4	15.3	36.6

(2006) reported that SMZ is the frequently used sulfonamide in veterinary medicine. Compared with the highly polluted Yinma River watershed in the northeast part of China (Li et al. 2018a, b, c), the averaged concentration of SMZ in natural surface waters was higher (771.4 ng L⁻¹) with the range from 67.85 to 2231.0 ng L⁻¹. Then, MET exhibited the highest average concentration of 1041.7 ng L⁻¹ (± 589.9 SD), with the range from 168.5 to 3593.7 ng L⁻¹. These findings of antibiotics levels were in agreement with a local study in the Songhua River system, indicating the concentrated economic development and agricultural product processing. For quinolones (NFX, EFX, and CFX) measured in natural surface waters, CFX and NFX showed relatively higher concentrations and frequencies in quinolone antibiotics with the average concentrations of 646.4 ng L⁻¹ (± 608.3 SD) and 179.0 ng L⁻¹ (± 103.9 SD), respectively. This may be due to the fact that ciprofloxacin is the highest prescribed antibiotic in this watershed.

Lake Erlong, which is located in the central northeast plain of China, suffers from high-intensity human activities and lack of adequate sewage treatment facilities. Most of domestic sewage and industrial wastewater of Liaoyuan City were exported into this lake. Over 40% of the total area of Lake Erlong is used as aquafarms for high-density culturing of fish, e.g., silver carp. Then, it also undertakes the due obligations to farming irrigation in dry years and drinking water of Siping City. Our investigation showed that the average concentrations of MET and SMZ were several tens of nanograms per liter, with 100% detected frequencies, which are relatively higher than those of quinolones (Table 1). MET and SMZ are widely used in agriculture, aquaculture, and livestock as antibacterial agents and growth promoters due to their low price, high efficiency, and low toxicity despite that MET is banned for use as a veterinary drug (Schmidt and Gierl 2000). For most infection antibiotics, active substances that are not fully metabolized are discharged with liquid manure. Then they could be washed off from the top soil by rain, or directly enter aquatic environments (Li et al. 2018a, b, c). Due to their wide application and high detection frequency and concentration, MET and SMZ could have also been suggested as tracers of antibiotic contaminations in natural waters for their widespread occurrence (Li et al. 2018a, b, c). The relatively lower quinolone concentrations in Lake Erlong areas may be due to their low application in these areas and easy degradability environmental stabilities (Kolpin et al. 2002).

Temporal distributions of selected antibiotics

Seasonal variations of selected antibiotics from natural surface waters in Lake Erlong are presented in Fig. 3. For high levels of MET and SMZ concentrations, the higher averaged concentrations 1186.1 ng L⁻¹ (± 903.2 SD) and 799.6 ng L⁻¹ (± 453.3 SD) were found in May 2018 (normal season), with the ranges of 168.52–3593.7 ng L⁻¹ and 67.9–2231.0 ng L⁻¹, respectively. Likewise, the seasonal MET was in the order of normal season > dry season (1098.7 ng L⁻¹ ± 221.9 SD) > wet season (843.9 ng L⁻¹ ± 265.9 SD). SMZ was in the order of normal season > dry season (755.4 ng L⁻¹ ± 95.9 SD) = wet season (755.4 ng L⁻¹ ± 188.7 SD). There was no significant seasonal variability of MET and SMZ (ANOVA, $p > 0.05$). These results may relate to the increased usage of antibiotics considering the high virus incidence rate during the winter (December to February) and ice-frozen period (November to April). Decreased temperature, increased usage, and limited degradation rate of microbial activity resulted in high levels of suppressed and accumulated antibiotics in winter (Wang et al. 2010). Wang et al. (2017) reported that the high human and livestock infections increased SA usage in this relatively low-temperature season. Moreover, with the increased temperature and thawed ice process during April, rainfall or melted ice flowed across the surface picked-up unmetabolized antibiotics that are carried directly to the soil and washed out into the receiving streams and rivers. Owing to the low adsorption ability of SMZ and MET in the soil or manure (Table S1), these compounds were finally transported into the lake. Similarly, the mean NFX concentrations decreased in the order of normal season (776.1 ng L⁻¹ ± 767.4 SD) > wet season (703.1 ng L⁻¹ ± 589.7 SD) > dry season (416.2 ng L⁻¹ ± 278.4 SD). The higher NFX was also presented in May (normal season) with the ranges of 263.9–1553.2 ng L⁻¹.

Likewise, the antibiotics used in the aquaculture farm in the lake are probably one of the antibiotic pollution sources. The mean CFX concentrations decreased in the order of dry season (316.6 ng L⁻¹ ± 61.5 SD) > normal season (141.8 ng L⁻¹ ± 51.4 SD) > wet season (103.2 ng L⁻¹ ± 46.0 SD). Then, the average higher EFX concentration was found in the dry season, with the ranges of 196.5–390.2 ng L⁻¹. PCA was conducted for the selected five antibiotics to assess their relative distributions at all samplings (Fig. 3f). The first two PCA axes explained 84% of the total variances (PC1 = 73%; PC2 =

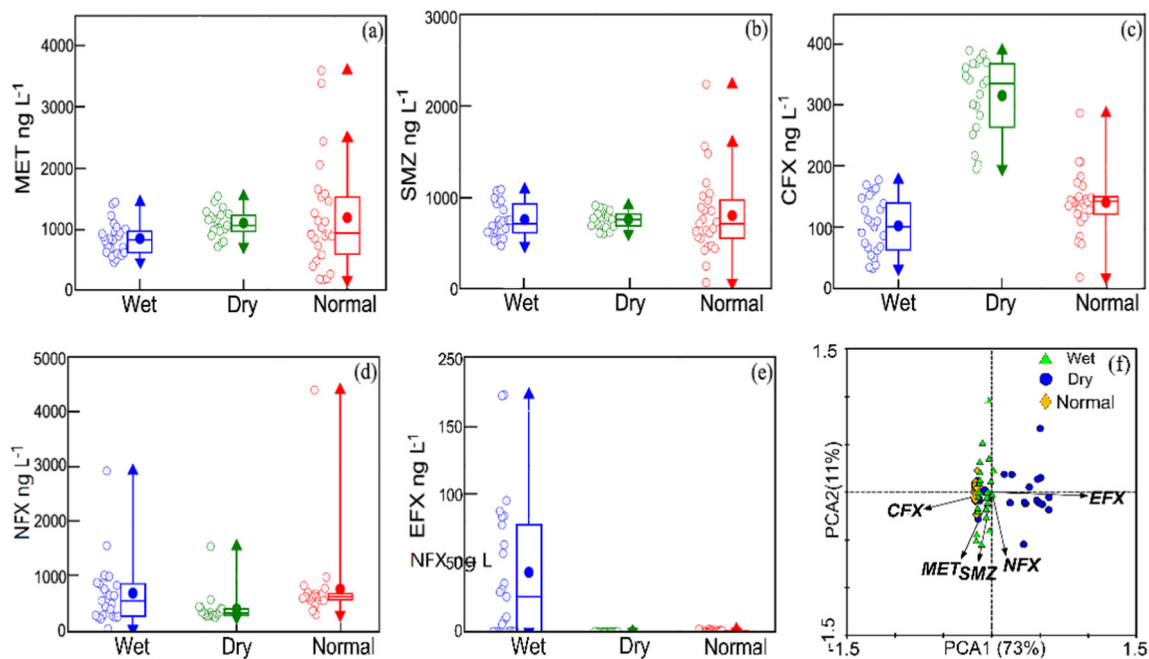


Fig. 3 **a** Box plots of MET in natural surface water ($N=69$) collected in Lake Erlong, **b** SMZ, **c** CFX, **d** NFX, and **e** EFX. In contrast, enrofloxacin was the least frequently detected with a detection frequency of 46%. The black line and the blue circles represent the median and mean values, respectively. **f** The PCA analysis of five

selected antibiotics in all samples. Solid blue circles represent the different samples in October (dry season), green triangles were the samples in June (wet season), and orange rhombus were the samples in April (normal season)

11%). The PC1 axis presented strong positive loadings on EFX and NFX for most of the samples in the dry season. The PC2 axis exhibited negative loadings on five selected antibiotics. This phenomenon seems incompatible with the seasonal SMZ and MET concentrations in lakes, but possible. On condition of the small amounts of usage CFX and EFX in the local watershed, we can explain this phenomenon as the accumulated CFX and EFX concentrations across the entire spring and summer, and also associated with their environmental stability (Table S1). As the aquaculture farm enclosure was uniformly distributed in the lake, the inputs of antibiotics increased and accumulated (Fig. S3). Also, the action of strong wind and waves of the lake attributed to the resuspension of sediment which bring more antibiotics. In addition, the higher bio- and photodegradation of antibiotics in spring and summer were more positive during the high-temperature season (Karthikeyan and Meyer 2006). It can be seen that the five antibiotic concentrations showed high levels despite of a large-volume lake. This could be due to the heavy use of antibiotics in the local watershed.

Spatial distributions of selected antibiotics

Owing to the sources and environmental stability characteristic, the spatial distributions of antibiotics showed different variations despite of an inter lake. The inverse distance weighted (IDW) interpolation method of ArcGIS 10.2 aimed to map the spatial distributions of five antibiotics in different

seasons, and the nature breaks method was used to classify the gradation standard (Fig. 4). On the whole, the total antibiotic concentrations were relatively higher both in the south and north sections of Lake Erlong, followed by the concentrations in the midsection due to the large depth (Fig. 1), except for some special sites. The south section received most municipal sewage and agricultural effluent by Dongliao River, flowing through Liaoyuan City with approximately 1170,000 population (Fig. S3). Then, the north section of the lake was divided into different private aquaculture ponds by stable floating, and the influent was from discharge channels containing direct aquaculture wastewater and rural sewage near by the lake (Fig. S3).

Generally, MET and SMZ showed a consistent spatial distribution in Fig. 4. In the wet season, the higher MET and SMZ concentrations were exhibited in the south section of the lake, and this could also be found in CFX and EFX. As stated before, this may relate to the more terrestrial contaminants of inflow rivers through the agricultural area and city in the rainy wet season (Fig. S3). Seasonally, all the antibiotics were more evenly distributed in the entire lake in the dry season contrary to other seasons. It is our understanding that this attributed to the dilution effect of a large-volume lake with less precipitation, and also the decreased usage of antibiotics in the harvestable season. It can be seen that the high concentrations of MET and SMZ were located in the north section of the lake in the normal season (Fig. 4). In general, one should keep in mind that the MET and SMZ applications in

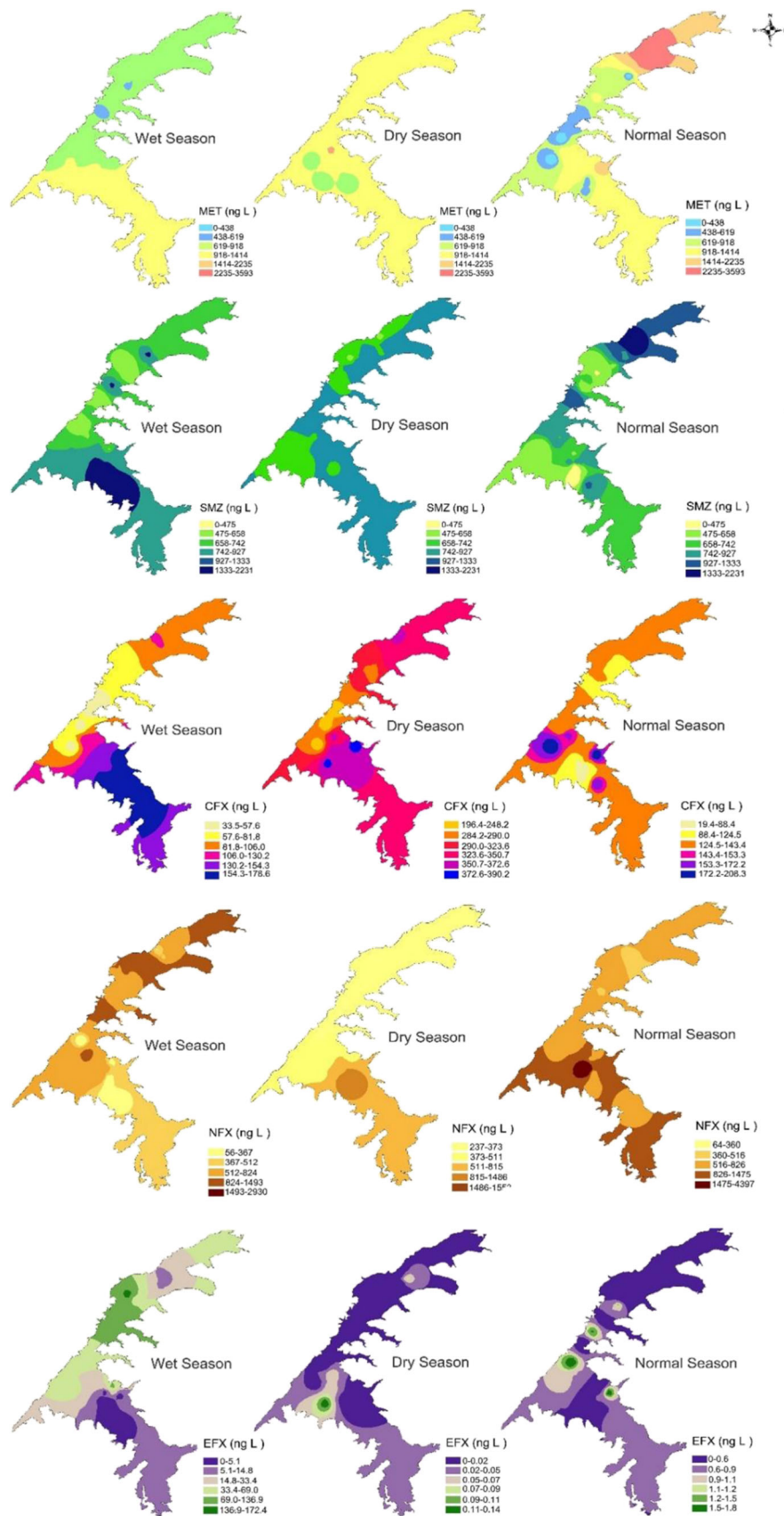


Fig. 4 Selected antibiotic maps of Lake Erlong. The spatial distribution was determined in ArcGIS 10.2

aquaculture farm enclosures in the open water contributed to the high level contamination in Lake Erlong (Fig. S3). Together, for quinolones (CFX, NFX, and EFX), the high concentrations were exhibited in the midsection of the lake with high depth. Recognizing that this may be associated with their environmental stability (Table S1), note also that the antibiotic concentrations from different samples showed sporadic spatial distribution characteristics. Although these aquaculture farm areas were divided in different stable floatings, different managements may exist in areas that belong to different owners.

Correlation between antibiotics and water quality parameters

DCA results indicated that the length of gradient in the first axis was 0.53. Thus, an RDA was used between the distribution of antibiotics and water quality parameters (Table S6) to evaluate the potential relationship. Then all samples ($N = 69$) were analyzed, and separation of samples was clear between sampling times (Fig. 5), indicating the obvious seasonal and

spatial difference in terms of the different environmental parameters. In addition, for all the samples ($N = 69$) and also the samples in the dry season ($N = 20$), TSM, OSM, and ISM were deleted in the RDA model due to the strong autocorrelation with a large inflation factor (> 20). RDA results showed that species–environment correlations in all samples and in the wet season, dry season, and normal season were 0.44, 0.59, 0.70, and 0.65, respectively (Fig. 5). For all samples ($N = 69$), the first two RDA axes accounted for 94.3% of total water biogeochemical variability (axis 1, 84%; axis 2, 10.3%). Coefficients between environmental variables with RDA axes indicated that pH, DOC, and Chl-a correlated with antibiotics, followed by EC and $\text{NH}_3\text{-N}$. RDA indicated that 97.7% of the antibiotic's variations (axis 1, 85.2%; axis 2, 12.5%) for samples in the wet season ($N = 24$) was explained by the environmental parameters we used, including the correlated variations, i.e., EC, COD, pH, and TP. In parallel, for dry season samples ($N = 20$), the first two RDA axes accounted for 87.2% of total water biogeochemical variability (axis 1, 68.8%; axis 2, 19.2%). Then, the correlated environmental variations were EC, pH, DOC, and TP. Moreover, for samples ($N = 25$) from

Fig. 5 Redundancy analysis (RDA) of antibiotic concentrations and environmental parameters. **a** RDA of antibiotic concentrations and environmental parameters for all the samples ($N = 69$), **b** for the samples for the wet season ($N = 24$), **c** for the samples for the dry season ($N = 20$), and **d** for the samples for normal season ($N = 25$). The solid arrows represent the species variables, and hollow arrows represent environmental variables. The units for MET, SMZ, CFX, NFX, and EFX were nanograms per liter; that for Chl-a was micrograms per liter; those for COD, DOC, $\text{NH}_3\text{-N}$, TSM, ISM, OSM, and TP were milligrams per liter; that for EC was microsiemens per centimeter; and that for transparency was centimeters

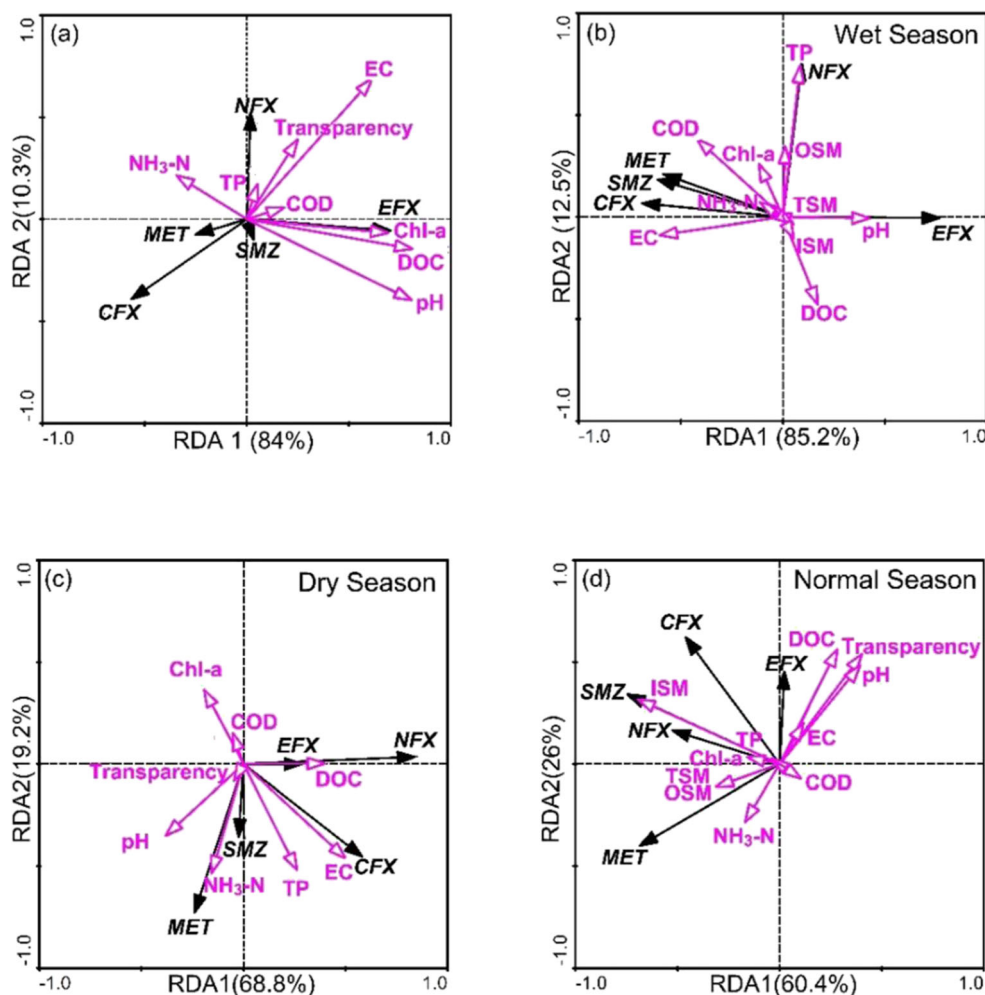


Table 2 Ecological hazard of selected antibiotics in the water samples collected from Lake Erlong

Compounds	Antibiotics	Abb.	Wet season	Dry season	Dry season
			Mean ± SD	Mean ± SD	Mean ± SD
Nitroimidazoles (NI)	Metronidazole	MET	0.026 ± 0.008	0.0342 ± 0.007	0.037 ± 0.028
Sulfonamides (SAs)	Sulfamethoxazole	SMZ	1.759 ± 0.439	1.759 ± 0.223	1.862 ± 1.056
Quinolones (QAs)	Norfloxacin	CFX	6.155 ± 2.741	18.887 ± 3.666	8.455 ± 3.065
	Ciprofloxacin	NFX	0.788 ± 0.661	0.4662 ± 0.312	0.870 ± 0.860
	Enrofloxacin	EFX	0.885 ± 1.064	0.0004 ± 0.0008	0.011 ± 0.013

The MHIs were classified into high hazard level (MHI > 1), medium hazard level (0.1 < MHI < 1), and low hazard level (0.01 < MHI < 0.1)

the normal season, the first two RDA axes accounted for 86.4% of total variability (axis 1, 60.4%; axis 2, 26%) with the correlated environmental variations of ISM, transparency, pH, DOC, etc.

These results showed that antibiotic distributions and concentrations in the surface water samples of Lake Erlong are strongly affected by these environmental variables, e.g., EC, pH, DOC, COD, and nutrient compounds. EC and pH can directly affect the biodegradation and environmental behaviors (photodegradation, adsorption, and hydrolyzation) (Kümmerer 2009b). Then the high DOC concentrations generally could result in strong hydrophobicity, which increases the adsorption of antibiotics under acidic or alkaline conditions (Li et al. 2018a, b, c). Likewise, the antibiotic

concentrations were positively correlative with nutrient compounds, e.g., TP, Chl-a, and NH₃-N, signifying that these nutrients and antibiotics showed similar environmental sources as mainly terrestrial wastewater and aquaculture applications. This result was consistent with the present study of Wang et al. (2017) on the positive correlation between antibiotics and NO₃-N.

Ecological hazard evaluation

Previous studies documented that the use of antibiotics or active metabolites could accelerate the development of antibiotic-resistant bacteria and genes through continual exposure to aquatic organisms, which include algae, daphnids, and

Fig. 6 Ecological hazards of selected antibiotics to algae, daphnids, and fish in different samples by the MHI, shown in Eqs. (5) and (6). Wet, Dry, and Normal represent the samples from June (wet season), October (dry season), and April (normal season), respectively

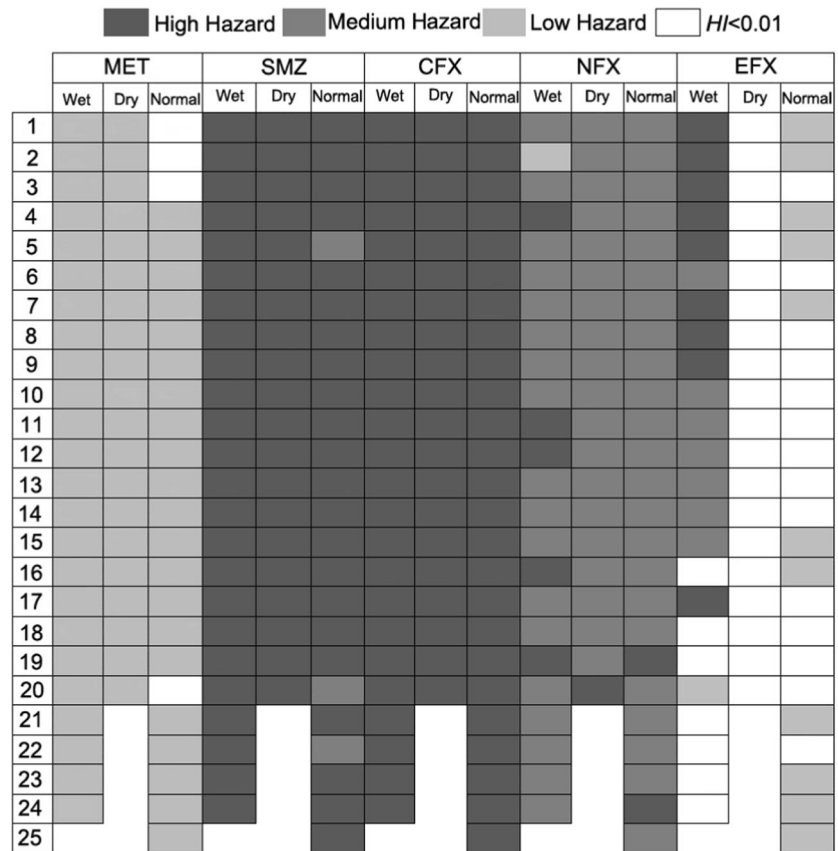


Table 3 Ecosystem vulnerability assessment index system related to antibiotics

Target layer	Criterion layer	Indicator layer	Weight	
Ecological vulnerability	Driving force 0.1446	Population (person) C1	0.4868	
		Average monthly precipitation (in.) C2	0.1040	
		Elevation (m) C3	0.2278	
		Slope (degree) C4	0.0727	
	Pressure 0.3324	Monthly temperature (Fahrenheit) C5	0.1087	
		Meat production (million tons) C6	0.1572	
		Eggs production (million tons) C7	0.0862	
		Milk production (million tons) C8	0.0935	
		Aquatic production (million tons) C9	0.2383	
		Medical treatment expenditure C10	0.4248	
		State 0.1661	Discharged amounts of wastewater (million tons) C11	0.0869
			Discharged amounts of waste gas (million tons) C12	0.0677
	Consumption of chemical pesticides (tons) C13		0.2364	
	Pollutants discharge coefficient of dairy cow C14		0.2030	
	Impact 0.1661	Pollutants discharge coefficient of beef C15	0.2030	
		Pollutants discharge coefficient of pig C16	0.2030	
		Rural households' income (per capita/yuan) C17	0.1121	
		Town household's income (per capita/yuan) C18	0.1216	
		Sowing area of the crop (ha) C19	0.1842	
		Beds of medical organization (number) C20	0.3028	
		Population of medical technician (person) C21	0.2793	
		Response 0.1908	City's ability to treat wastewater (million m ³) C22	0.2570
			Centralized processing rate of wastewater (%) C23	0.2238
			Education expenditure (million yuan) C24	0.1477
	Population of graduated high school (person) C25		0.1477	
	Science and technology expenditure (million yuan) C26		0.2238	

fish, even at small concentrations (Wollenberger et al. 2000; Kümmerer and Henninger 2003; Kümmerer 2009b). The selected antibiotics of water samples may cause adverse ecological and health impacts. In the present study, antibiotics were frequently found in samples collected from Lake Erlong. Hence, the ecological hazards of the five antibiotics were evaluated with calculated individual HI values using Eqs. (2)–(4) in surface water on organisms. Table S5 summarizes the acute median effective concentrations (LC50 or EC50) of the five selected antibiotics to the different aquatic organisms. Then algae and plant are the most sensitive species to antibiotics than daphnids and fish in the aquatic environment. This has been confirmed by previous studies on the sensitivity of the algae to antibiotics (Kümmerer 2009b; Deng et al. 2016). In addition, the co-occurrence of antibiotics shown in Eqs. (5) and (6) was replaced by single antibiotic hazards aiming to assess ecological hazards of antibiotics in the aquatic environment, considering the multicomponent mixtures of antibiotics in the actual conditions. As shown in Table 2 and Fig. 6, the MHI values of SMZ and CFX shown in Eqs. (5) and (6) exhibited high hazard level, indicating that these antibiotics

were harmful to aquatic organisms. Seasonally, there was a significant difference of CFX and EFX (ANOVA, $p < 0.001$) which could relate to their behavior and consumption in the watershed. This was in agreement with earlier studies demonstrating that antibiotics are harmful to algae (Khetan and Collins 2007; Wang et al. 2017; Chen and Guo 2012). NFX showed medium hazard level to algae in most of the surface water samples. Therefore, the current pollution and ecological hazards of antibiotics should be paid attention to, especially SMZ and CFX.

Concerning the signal antibiotic hazard to other aquatic organisms, SMZ and CFX presented MHI values higher than 1 for algae, while the medium hazard level was expected for daphnids in most of the samples (Fig. S4). However, with antibiotics continuously transported into the environment, these organisms are exposed to very high concentrations for a short period of time. This may give somewhat hazard effects on the organisms dwelling in the aquatic environment. Dirany et al. (2012) demonstrated that SMZ contributed more toxic influence than other antibiotics on algae even at a relatively low concentration. The highest hazard level of 22.9 was in the

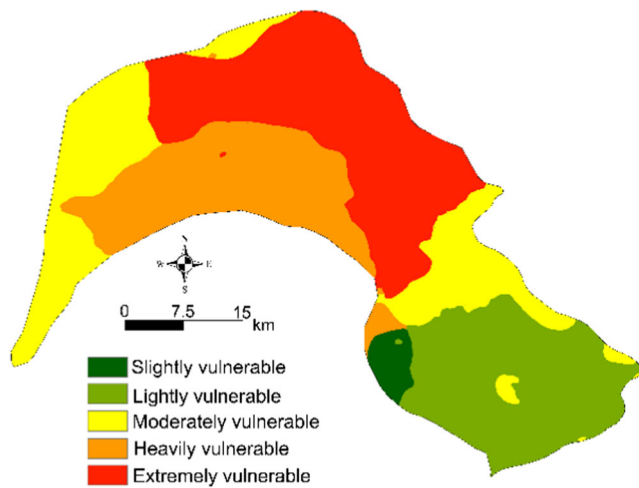


Fig. 7 Ecological vulnerability maps of the Erlong Lake watershed. The ecological vulnerability values were determined in ArcGIS 10.2

dry season, while SMZ obviously is a more important pollution compound for selected antibiotics in Lake Erlong. This result was consistent with the results of Li et al. (2018a, b, c) in Yinma River Watershed about 2 km east of Lake Erlong. Likewise, for other selected antibiotics (MET, EFX, and EFX), there was no fish hazard, and a low hazard level was also found in SMZ and CFX. It revealed that the high consumption of antibiotics does not simultaneously indicate high environmental hazards for the aquatic environment (Wang et al. 2017). Although gaining a full understanding of the dynamics responsible for this hazard to fish is beyond the scope of this manuscript, the bioaccumulation in invertebrate and fish muscles after long-term exposure can be inferred.

Ecological vulnerability evaluation

Evaluation of ecological vulnerability of a valued ecological server lake or reservoir for a local region to one or more antibiotic-related hazards could serve as a planning tool in environmental decision-making and ecosystem management. This process could identify the highly vulnerable communities and allocate adaptation resources (Shen et al. 2016). As was shown in the DPSIR model, 26 descriptors were selected for the five-criterion layer with their weights (Table 3). The widely used analytic hierarchy

process (AHP) method linked with multiple assessments of five experts was conducted to determine the importance of the descriptors (Li et al. 2017; Sener and Davraz 2013). Then AHP results need to undergo a consistency test, while the coefficient of consistence values should be less than 0.1.

The ecological vulnerability result linked with antibiotics in Lake Erlong is shown in Fig. 7; the extremely and heavily vulnerable levels were concentrated in the central and northwest regions of the watershed, i.e., Changling county and Lishu county. They were in the center of the Corn Belt of Northeast China, especially Lishu county which produced 2,099,025 t corn grain and is representative of the high corn production zone (Li and Sun 2016). Then the slightly and lightly vulnerable levels were located in the Southeast region with more forest cover (Fig. 1). These results were consistent with Li et al. (2017) and Zhang et al. (2016) that elevation and forest coverage limited the agricultural land and decreased human disturbances.

Ecological risk assessment

In this present study, antibiotics were frequently detected in surface waters in Lake Erlong (Table 2). Thus, it is necessary to evaluate the ecological risk of these antibiotics both considering the effects of hazard ($MHI_{MEC/PENC}$) and vulnerability (VI) linked with environmental factors within a group, rather than those of the individual substances in a certain environment. As shown in Fig. 8, according to the natural breaks method, ecological risk was divided into 5 levels, with $0 < risk \leq 2.4$ as slight risk, $2.4 < risk \leq 3.2$ as light risk, $3.2 < risk \leq 3.6$ as moderate risk, $3.6 < risk \leq 4.3$ as heavy risk, and $4.6 < risk \leq 5.5$ as extreme risk, respectively. The distributions of extreme risk and heavy risk were located in Changling county and Lishu county in the dry season, respectively, as well as in the wet season or normal season. Among them, for signal antibiotics, these counties also presented high ecological risks, while risk values were calculated for HI and vulnerability VI (Fig. S5). These results showed consistent tendency with ecological vulnerability (Fig. 7), indicating the influence of different geographical extents and varied concentrations of antibiotic residues in the natural environment. Hence, with the highest risk values of greatest public concern, these counties indicated a sector with top priority for environmental

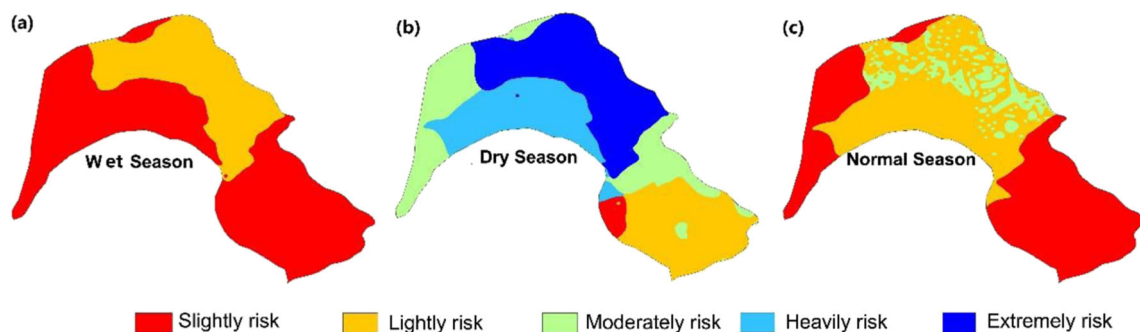


Fig. 8 Ecological risk maps of the Lake Erlong watershed in the a wet season, b dry season, and c normal season

preservation and pollution prevention. Note that the high-risk values should exist in the natural environment due to the environmental behavior of antibiotics, e.g., sediment and particulates (Table S1). In a regional practice, our investigation revealed excessive or illegal antibiotic usage despite the implementation of regulatory policies in aquaculture and livestock (Fig. S3). More antibiotic data on environmental levels and various exposure routes under different geographical backgrounds could be helpful in assessing the actual ecological risk. It clearly demonstrated the need for ranking the spatial characteristic of antibiotic contamination in different periodical samplings, and the prioritization of the sectors seeking urgent attention.

Conclusion

Overall, in this study, we investigated the occurrence and distribution of five common antibiotics and ecological risk assessment in the surface of Lake Erlong in different seasons. The results allowed for a comprehensive regional analysis of the highly variant spatial and temporal distributions of antibiotics. Antibiotic concentrations were mainly affected by the complicated processes of discharge, aquaculture usage, and industrial/domestic wastewater and also their environment fate. Considering the anthropogenic factors and social-cultural and economic developments, 26 descriptors related to the regional antibiotics were selected to evaluate the ecological vulnerability. It was apparent that high ecological vulnerability can be accurately estimated in the center and northwest with more agricultural land. Most importantly, ecological risk assessment results ranked the distributions of extreme risk and heavy risk mainly located in Changling county and Lishu county.

The results of antibiotic ecological risk assessment can support decision-makers to find out the relevant regional high-risk areas and take specific measures to preserve the human health and environment. Further studies should be focused on better understanding the migration mechanism of selected antibiotics in this aquatic environment. The interdisciplinary approach for ecological risk of pollutants and multivariate analyses linked with multisource dataset is a potential tool to environmental monitoring and evaluation, especially in limited and remote regions.

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