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Spatiotemporal distributions of Cu, Zn, metribuzin, atrazine, and their transformation products in the surface water of a small plain stream in eastern China

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Abstract The intensive use of fertilizers and pesticides in agriculture has led to widespread nonpoint source pollution in surface waterbodies. In this work, the occurrence and distribution of nonpoint source metals (Cu and Zn) and herbicides (metribuzin; atrazine; and its degradates, including desethyl atrazine (DEA), desisoproylatrazine (DIA), and deethyldeisopropylatrazine (DEDIA)) in the surface water of the Baima River, which is located in a region noted for its intense agricultural activities, were investigated during a high water period in August and a low water period in October. The results showed that the heavy metals and herbicides investigated were detected frequently in the surface water of the river during the two periods. The average concentrations of Cu during the high water period and low water period were 9.3 (0–20.7) and 8.7 (0–15.55) μg/L, and the average concentrations of Zn during the two periods were 11.4 (6.65–22.15) and 10.6 (7.55–15.15) μg/L, respectively. The concentrations of atrazine were higher than those of metribuzin, which ranged from 0.07 to 1.12 μg/L during the high water period and 0.01–0.74 μg/L during the low water period. The total concentrations of atrazine and its transformation products in 60.00% of the samples during the high water period exceeded the maximum contaminant level (MCL) of 3 μg/L for the drinking water criteria in the USA, and 33.33% of the samples exceeded the MCL during the low water period. The spatial and temporal distributions of nonpoint source pollutants along the Baima River were influenced by land use and hydrogeomorphic settings. The ecotoxicological risk assessment indicated that atrazine and DIA have moderate risks to aquatic environment in Baima River.

Keywords Baima River watershed · Cu · Zn · Metribuzin · Atrazine · Transformation products

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Introduction

The use of pesticides and fertilizer results in increased crop yields, but their effects are less than desirable because of their contributions to agricultural nonpoint source pollution in rivers and streams (Papadakis et al. 2015; Sun et al. 2013a). Numerous studies have reported substantial residues caused by pesticides in soil, sediments, and surface and ground water throughout the world (Fenelon and Moore 1998; Ryberg and Gilliom 2015; Sun et al. 2013b; Toccalino et al. 2014). Pesticide and nutrient contaminations are some of the main issues in waterbodies in China. In 2014, approximately 1.81 million tons of pesticides and 59.96 million tons of fertilizer were used in China (NBS 2015). The widespread application of pesticides and fertilizers leads to the serious and widespread contamination of soil and adjacent waterbodies, which has been evidenced by a previous study, where herbicides were detected in 97% of the riparian soil samples in the Songhua River Basin, northeastern China (Sun et al. 2013a). Pesticides escape from agricultural fields and enter the surface water via surface runoff, spray drift and drainage. For example, it was found that approximately 98 tons of pesticides (Qi et al. 2014) and 16.4 million tons of nitrogen (Chen et al. 2016a) were flushed into the East Sea through the Yangtze River annually.

In China, herbicides account for 70% of the total use of pesticides. Atrazine is one of the most commonly used herbicides, and its application exceeds 10 thousand tons per year. The vast application of atrazine in agriculture has resulted in extensive environmental contamination. Ecotoxicological data has shown that atrazine is a kind of possible carcinogen and endocrine disrupting chemical, and it is classified as a priority pollutant (Amaral et al. 2014; Jablonowski et al. 2011; Švorc et al. 2013). Moreover, in addition to the parent compound of atrazine, contamination can also happen due to its transformation products, such as deethylatrazine (DEA) and deisopropylatrazine (DIA), which have similar biological activities and exert toxic effects on living organisms (Barchanska et al. 2017). Many studies have documented the contamination of atrazine and its transformation products in surface water, such as in the Guanting Reservoir (Jin and Ke 2002), Liaohe River and Yangtze River (Gfrerer et al. 2002a, b; Yan et al. 2005), Tai Lake (Na et al. 2005), Huaihe River (Zijian et al. 2002), Liaoning province (Gfrerer et al. 2002a, b, Li et al. 2007), Zhejiang province (Chen et al. 2016a, b), and Beijing (Ge et al. 2010), but few studies have investigated small tributary branches in intensive agricultural watersheds in China, where contamination levels are more serious than large trunk rivers because of reduced discharge and deficient dilution capability.

Copper and zinc are the metals with the highest levels in chemical or organic fertilizers (Wang and Li 2014; Yan et al. 2014), which are potentially transported to streams through groundwater discharge (base flow) or overland runoff. The oversaturated input of Cu and Zn makes water unfit for human consumption and causes adverse effects on aquatic organisms. Some studies have shown that the concentrations of Cu and Zn in many aquatic organisms are greater than those of other metals in Taihu Lake, China (Yu et al. 2012). Fu et al. also suggested that Cu and Zn pose the greatest risks to native aquatic species than other priority toxic metals in Taihu Lake (Fu et al. 2016). Current monitoring studies often focus on priority toxic metals, and few studies investigate the occurrence and contamination of Cu and Zn in surface water.

Shandong province is one of the most intensive and productive agricultural regions in eastern China, and pesticides and fertilizer application rank first in the entire country of China. The intensive application of agricultural chemicals has led to the nonpoint source pollution of surface and groundwater throughout this area. In this paper, we selected a typical agricultural watershed in Shandong province as a study area and investigated its nonpoint source pollution. The objectives of the present study were to (i) monitor the concentrations of Cu, Zn, metribuzin, atrazine, and their transformation products in the surface waters of a typical agricultural watershed (i.e., the Baima River watershed); (ii) compare the concentrations of the pollutants found in the present study with those detected in other areas in China; (iii) analyze the impacts of land use, hydrologic properties, and geomorphologic characteristics on the water quality of the watershed; and (iv) assessed ecological risk of heavy metal, herbicides, and their transformation products in the surface waters.

Materials and methods

Study area

The Baima River watershed (936.02 km^2) is a poorly drained agricultural watershed in Shandong province in eastern China. The Baima River, which is 60 km long, is an important river flowing into Nansihu Lake. Nansihu Lake is the largest freshwater lake in this area and is a major water resource for Shandong and Jiangsu provinces. Moreover, the lake is also important to northern China because it serves as a storage reservoir for the eastern region of the Chinese South-to-North Water Transfer Project (SNWTP), which transfers water to cities in northern China, such as Beijing and Tianjin (SNWTPCC 2016). In this case, the protection of the aquatic environments of upstream rivers flowing into Nansihu Lake is very important.

The area of the Baima River watershed is located in the transitionary region between rolling regions in south-central Shandong province and flat areas in southwestern Shandong province (Fig. 1). The values of the average annual runoff at the site of the river inlet into Nansihu Lake have been almost zero in recent years.

Therefore, the downstream areas drain poorly during rainy seasons, which are affected by the high water level of Nansihu Lake. The climate in the watershed is a subhumid continental monsoon climate in the warm temperate zone. The annual rainfall varies between 268.5 and 1225.5 mm, and the multiyear average precipitation is 777.1 mm. Moreover, 76% of the precipitation is concentrated during the period from June to September. Approximately 79% of the entire basin is farmlands, which mainly plant corn. The herbicides applied to farmlands with corn are a mixture of atrazine (22.5%) and nicosulfuron (2.5%). In addition, a small portion of these farmlands is soybeans, and the main herbicide applied there is metribuzin. Zoucheng, the only populous city in the watershed, is situated on the east side of the river. The river receives industrial and domestic wastewater from Zoucheng through the inflow of the anabranch (Fig. 1).

Sampling sites

Fifteen sampling points for surface waters were selected in the trunk stream and main branches of the Baima River during August and October 2015, which represented the high flow period and low flow period, respectively. Monitoring sites were selected and sampled according to protocols established by the Chinese National Standards (CSEPA 2002). During the high flow period, 24 samples were collected from the surface water of the river, but only 15 samples were collected during the low flow period because that part of the tributary dries up. The surface water samples were taken from the middle course of the river from a depth of 30–50 cm. The water temperature (°C), pH, dissolved oxygen (DO) (mg/L), total dissolved solids (TDS) (mg/L), and electrical conductivity (EC) were measured on-site with a portable Hydrolab Surveyer with multiparameter probes (Hach Environmental, Loveland, CO, USA) at a depth of approximately 50 cm to the surface water. All samples were collected in 550-mL plastic bottles, immediately refrigerated by a portable refrigerator and then stored at − 20 °C until they were processed after being carried back to the laboratory. The longitude, latitude, and altitude were determined on-site using a handheld Global Position System (GPS). The distribution of the sampling sites and land use in the Baima River watershed is displayed in Fig. 1.

Chemicals and reagents

All chemical standards, including metribuzin (purity > 99.9%), atrazine (purity > 99.9%), and their metabolites, including DEA (purity > 99.9%), DIA (purity > 99.9%), and deethyldeisopropylatrazine (DEDIA, purity > 99.9%), were purchased from J&K Chemical Technology Co. Ltd. (Beijing, China). N-hexane of chromatographic grade was purchased from Tedia Chemicals (Fairfield, OH, USA). The solid-phase extraction (SPE) pillar of the polymeric cartridges (Oasis®HLB, 6 cm^3, 200 mg) was purchased from the Waters Corporation (Milford, MA, USA). Laboratory glasswares were washed with $K_2Cr_2O_7$–H_2SO_4, rinsed with deionized water, and then dried at 105 °C for 4 h. All reagents were of analytical grade or higher.

Environmental sample extraction and analyses

The samples were extracted and analyzed according to published methods (Xu et al. 2007; Yang et al. 2008). Briefly, every sample was filtered through a glass fiber membrane filter (0.45 μm pore size) to remove insoluble matter. A 50-mL filtered aliquot of each stream sample was used to detect the concentrations of Cu and Zn. Another 500-mL filtered aliquot of each stream sample was passed through the activated SPE cartridge under a vacuum at a flow rate that did not exceed 5 mL/min. After the aliquot passed through the SPE cartridge, the cartridge was rinsed with 10 mL of H_2O and dried under a full vacuum for 30 min. Finally, the pillar was eluted with 5 mL of methanol twice, and then the eluate was evaporated to dryness with nitrogen gas using Organomation Associates (NDK-12W, Gaozhuang Instrument Co., Ltd., Shanghai, China) at 30 °C. The dry residues obtained were redissolved in 1 mL of n-hexane solution. The final extracts were filtered through 0.45 μm Nylon 66 filters (Haide Co. Ltd., Shanghai, China) into gas chromatography (GC) vials and analyzed.

The concentrations of Cu and Zn were determined by an AA-7000 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer. The herbicide concentrations were measured by a 2010 plus Shimadzu (Kyoto, Japan) gas chromatograph, with an a ^{63}Ni electron capture detector (GC-ECD) and a DB-5 (30 m × 0.32 mm × 0.25 mm) chromatography column. The injector and detector were maintained at temperatures of 240 and 300 °C, respectively.

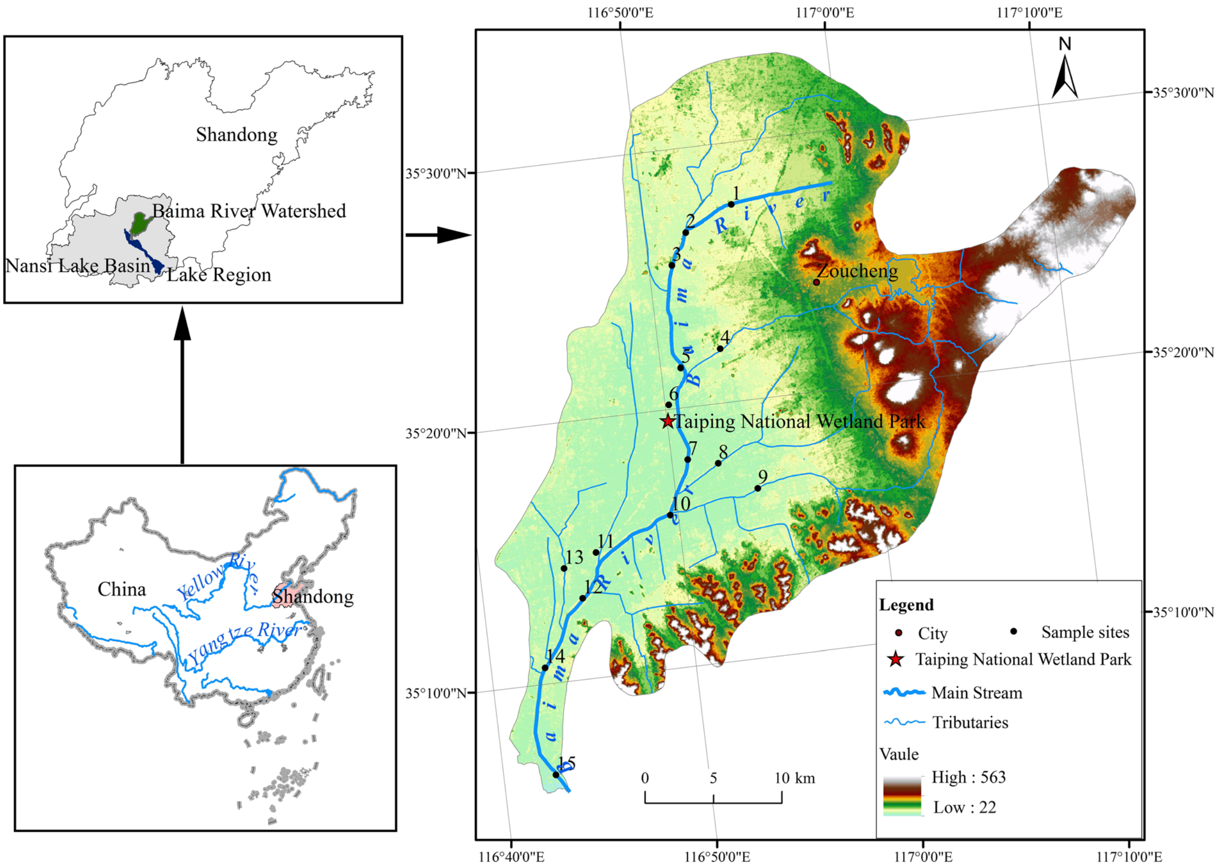


Fig. 1 The distribution of sampling sites in the Baima River watershed

Nitrogen (99.999%) served as the carrier gas, with a constant flow rate of 2.5 mL/min. The oven temperature program was started at 50 °C for 1 min, was increased to 220 °C at 30 °C/min for 2 min, then increased to 240 °C at a rate of 2 °C/min, and was finally increased to 270 °C at a rate of 8 °C/min for 5 min. Sample volumes of 1 mL were injected into the GC-ECD with splitless injection.

All samples were analyzed as a batch experiment, which included one blank sample and one duplicate sample. No heavy metals or herbicides were detected in the blank samples. The method detection limit (MDL) compared to the signal-to-noise ratio (S/N) was 3:1. The recovery was 69.1–98.3%, and the RSD was 7.1–12.3%. The limits of detection for metribuzin, atrazine, DEA, DIA, and DEDIA were 0.005, 0.01, 0.005, 0.005, and 0.01 μg/L, respectively. The recovery was satisfactory for the herbicides and transformation products. Detection limit was 4 μg/L for Zn and 2.5 μg/L for Cu.

Statistical analysis and data processing

All of the data collected from the experiment are performed in Excel 2007 and analyzed by SPSS 21.0. The relationships between the concentrations of herbicides are analyzed using the Pearson correlation. A probability of $p < 0.05$ was considered statistically significant.

Ecological risk assessment

The ecological risk quotient (RQ) is commonly used in risk assessments, which was quantified for each herbicide using the measured environmental concentration (MEC) divided by the predicted no-effect concentration (PNEC). The PNEC of each herbicide was estimated a critical concentration divided by an assessment factor (AF). The critical concentration was the concentration lethal to 50% of test organisms (LC_{50}), 50% effective concentration (EC_{50}), or no-observed-effect concentration (NOEC), which were obtained from the Pesticides Properties Database (PPDB 2018) and previous study

(Ralston-Hooper et al. 2009). An AF of 100 was used when data from one long-term assay were available for fish or zooplankton, and AF of 10 was used when data from three long-term assays were available (ECC 2003). The RQs were classified into three categories, including low risk ($0.01 \leq RQ < 0.1$), medium risk ($0.1 \leq RQ < 1$), or high risk ($RQ \geq 1$).

Results and discussion

Water quality parameters

The aquatic environmental conditions of rivers, such as pH, temperature, electrical conductivity, and other physical parameters of rivers, can influence the levels of pesticides (Ren et al. 2011). The temperature, electrical conductivity (EC), total dissolved solids (TDS), and dissolved oxygen (DO) are presented as median values in Table 1. The pesticide degradation rate depends on the pH, temperature of the water, chemical properties of the pesticide, and the length of time the pesticide was in contact with the water. The half-lives of the herbicides and transformation products are presented in Table 2. The pH of the river water ranged from 7.27 to 9.10 during the high water period and 7.33 to 9.39 during the low water period. The average temperature of the water was 26.12 °C during the high water period and 23.85 °C during the low water period. However, the relationships between the water quality parameters and the levels of pesticides were not significant, which showed that there had other factors probably influenced the variability in the concentrations. In addition, the water quality parameters were not significantly related with the heavy metals (Cu and Zn) either, which also suggested that the concentrations of heavy metals were affected by other factors.

Seasonal variations in the river discharge are influenced by precipitation, surface runoff, interflow and groundwater flow, which subsequently has a strong effect on the concentration of pollutants in rivers. The total dissolved solids (TDS) ranged from 75.5 to 87 mg/L during the rainy season (August) and ranged from 69.3 to 83.3 mg/L during the dry season (October), which showed an increasing trend during the rainy season compared to the dry season and a decreasing trend during the dry season. This was related to rainfall, runoff, and soil erosion during the rainy season in the catchments, and the TDS were the result of the dissolution of soil constituents from these natural processes. Moreover, the concentration of DO in the river water during the high water period was lower (Table 1), which suggested a high load of dissolved oxygen-consumed organic matter or intense bacterial activity. And the DO concentration during low water period exceeded that during high water period, which suggested that the water quality during low water period was superior to high water period. The values of EC and pH in the water were relatively low due to dilution caused by the enormous water load during the rainy season (high water period in August).

In the case of spatial variations in water parameters, the maximum values of EC, TDS, and the minimum values of DO were recorded in the sampling points located in the central part of the basin, which could be related to the presence of higher contamination. Taiping town, which is the most industrial area in Zoucheng, is located in this area, and the urban, industrial, and agricultural pollution sources decreased the water quality in these reaches. The DO concentrations in the middle reaches, which were, on average, 3.92 mg/L during the rainy season and 4.15 mg/L during the dry season, fell short of the class 3 water quality grade to criteria standard (5.00 mg/L) for fisheries water (CSEPB 2002). The pollution level of downstream in the Baima River was classified into second water quality grade in terms of the EC, TDS, and DO levels, and there is a wharf nearby Nansihu Lake, which is an important industrial source of pollution. The aquatic environmental quality in upstream was relatively better than that in the other reaches.

Cu and Zn

The frequencies of Cu detection over the LODs in the high water period and low water period were 93.33% and 86.67%, respectively. However, the detection rates of Zn during the two periods were up to 100%. The temporal and spatial distributions of Cu and Zn are displayed in Fig. 2. The average concentrations of Cu in the high water period and low water period were 9.3 (0–20.7) and 8.7 (0–15.55) μg/L, respectively. The average concentrations of Zn during the two periods were 11.4 (6.65–22.15) and 10.6 (7.55–15.15) μg/L, respectively.

Table 1 Median value and range of the physicochemical parameters of the river water

Parameters	Upstream		Midstream		Downstream	
	Aug.	Oct.	Aug.	Oct.	Aug.	Oct.
Temp. (°C)	26.60 (25.60–27.60)	24.28 (23.80–24.50)	25.22 (21.70–27.40)	22.72 (20.40–25.50)	27.13 (24.20–29.00)	25.03 (24.20–26.30)
EC (μS/cm)	1395.25 (894–1916)	1597.4 (1164–1887)	1882.5 (1321–2880)	2294 (1775–2700)	1753.25 (1573–1905)	1876.75 (1558–2030)
TDS (mg/L)	80.82 (79.20–83.60)	76.54 (74.40–78.40)	81.4 (78.30–84.50)	73.77 (69.30–79.20)	67.12 (24.50–87.10)	77.68 (71.90–83.30)
DO (mg/L)	4.89 (1.37–9.45)	5.2 (1.24–13.79)	5.09 (0.62–7.68)	5.41 (0.55–10.39)	5.55 (0.42–10.35)	6.94 (0.54–11.04)

Temp. temperature, *DO* dissolved oxygen, *TDS* total dissolved solids, *EC* electrical conductivity

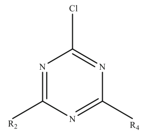
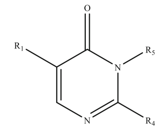
The spatial and temporal distributions of the Cu and Zn concentrations in the water along the Baima River are displayed in Fig. 2. The water samples at sites 14 and 15, which located in downstream, contained higher levels of Cu during the rainy season but decreased to zero during the dry season. This suggested that Cu was carried from the upper reaches via flooding. The Cu concentrations at sites 4 and 11 during the rainy season were higher than those at the other sites because of the nearby city (Taiping town) and industry, respectively. Similarly, the water samples from sites 3, 8, 12, and 14 contained higher Zn during the rainy season than the other samples because of rain, overland runoff, and erosion.

The Cu concentration exceeded those of the national wetland park in Taiping town (Fig. 1) (we investigated during the high water period in 2014) and the Yihe River (Zhao et al. 2014) in the same region, with a similar geochemical background, whose concentration was too low to be detected. Compared to streams flowing into other lakes or reservoirs in China (Fig. 3), such as Poyang Lake (Cu, 2.79–19.85 μg/L; Zn, 8.67–40.90 μg/L) (Li et al. 2010), Taihu Lake (Zn, 2.0–17.1 μg/L) (Li 2006), and the Dahuofang Reservoir (Cu, 0.79–3.07 μg/L) (Gao et al. 2015), the Baima River contained relatively higher levels of Cu and Zn (Fig. 3). However, the contaminations of Cu and Zn were not serious and did not exceed 1 mg/L, which was the threshold value for grade 2 water quality (CSEPB 2002). The main source of pollution is the erosion of agricultural fertilizer and pesticides from arable soils and the discharge of adjacent industries.

Herbicide and transformation products

During the high water period in August, the frequencies of detection over the LODs for metribuzin, atrazine, and its degradates (DEA and DIA) were 100%, and that of DEDIA was 86.67%. Moreover, the rates of detection over the LODs for herbicides and degradates during this period were higher than those during the low water period in October (Fig. 4). The concentrations of metribuzin in river water during the high water period and low water period were 0.01–0.16 μg/L and 0–0.09 μg/L, respectively. The concentrations of atrazine were relatively higher than those of metribuzin, which ranged from 0.07 to 1.12 μg/L during the high water period and 0.01–0.74 μg/L during the low water period. The application time for metribuzin was similar to that

Table 2 Chemical structures of metribuzin, atrazine and its degradation products

Compound	ATR	DEA	DIA	DEDIA	Metribuzin
Structure					
R1	–	–	–	–	$C(H_3C)_3$
R2	NHCH $(CH_3)_2$	NHCH $(CH_3)_2$	NH_2	NH_2	–
R4	NHC_2H_5	NH_2	NHC_2H_5	NH_2	SCH_3
R5	–	–	–	–	NH2
logPoct	2.7	1.6	1.2	0	–
logKow	2.7	–	–	–	1.7
p*Ka*	1.7	1.3	1.3	1.5	1

of atrazine, but the metribuzin concentrations in river water were substantially lower than those of atrazine. The main reasons were their differences in the amounts of usage, water solubility, half-life, and other properties (Table 1). The usage and persistence of atrazine were higher than those of metribuzin. The average

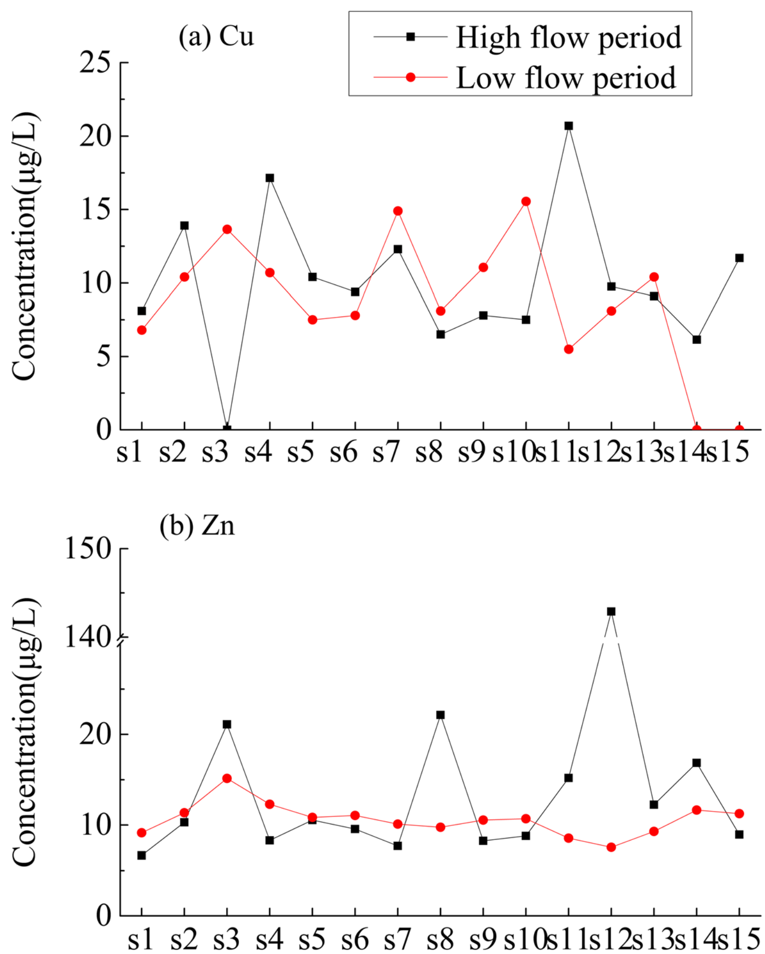


Fig. 2 The distribution of heavy mental concentrations in river water during high water periods and low water periods ((a) Cu concentrations in surface water;(b) Zn concentrations in surface water)

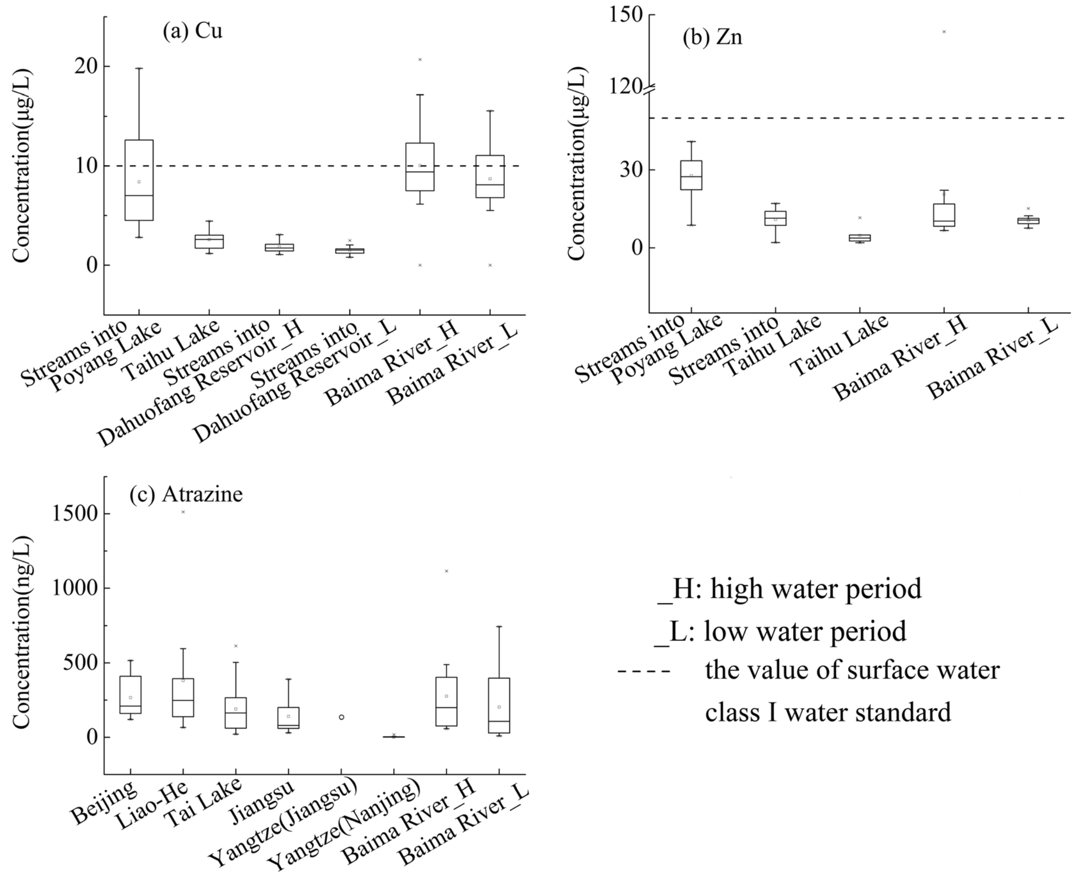


Fig. 3 Box plot for the concentrations of Cu, Zn and atrazine in the surface water in the Baima River watershed and other waterbodies in China. ((**a**) Cu. (**b**) Zn. (**c**) Atrazine)

concentrations of DEDIA, DEA, and DIA in water during the high water period were 0.12, 2.33, and 0.26 μg/L, respectively. However, during the low water period, the average concentration of the atrazine metabolites was mostly lower than that during the high water period, with average concentrations of 0.09, 1.96, and 0.26 μg/L for DEDIA, DEA, and DIA, respectively. The total concentration of the atrazine and transformation products in 60.00% of the river water samples during the high water period exceeded the maximum contaminant level (MCL) of 3 μg/L for drinking water in China, and 33.33% of the water samples exceeded the MCL during the low water period.

Compared with other lakes and rivers (Fig. 3c), such as the Yangtze River (Han et al. 2013; Han et al. 2011), Liaohe River (Gfrerer et al. 2002a, b), Taihu Lake (Na et al. 2005), and surface waterbodies in Beijing (Ge et al. 2010) and Jiangsu province (Han et al. 2013), the atrazine concentrations in the surface water of the Baima River were relatively higher. The main reason was the widespread application of atrazine in croplands and the small amount of discharge from the Baima River, as well as the enormous dilution of the water discharge, which is the reason for the low atrazine level in the Yangtze River.

The spatial and temporal distributions of the herbicide and atrazine metabolite concentrations along the Baima River are shown in Fig. 4. The herbicide concentrations in the river water upstream (from site 1 to site 3) and midstream (from site 4 to site 13) were higher than those in downstream areas which ranged from site 14 to site 15 because of the great water volume in the downstream reaches. The average concentrations of the total herbicides upstream, midstream, and downstream during the high water period were 3.22, 3.99, and 1.31 μg/L, respectively. The spatial distribution of the total herbicide concentrations displayed the same trend during the low water period (Fig. 5).

The concentration correlation coefficients for atrazine, DEA, and DIA between the high water period and low water period were 0.78 ($p < 0.01$), 0.66 ($p < 0.05$), and

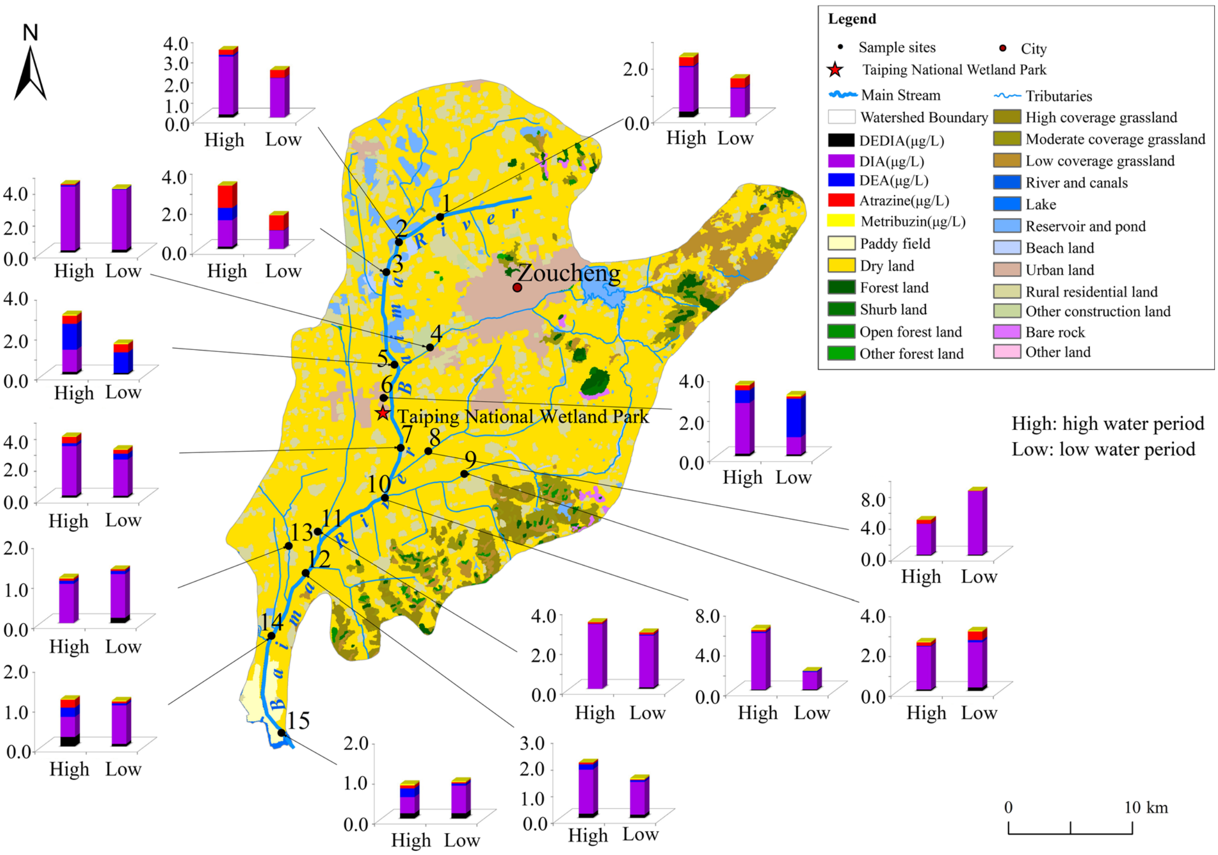
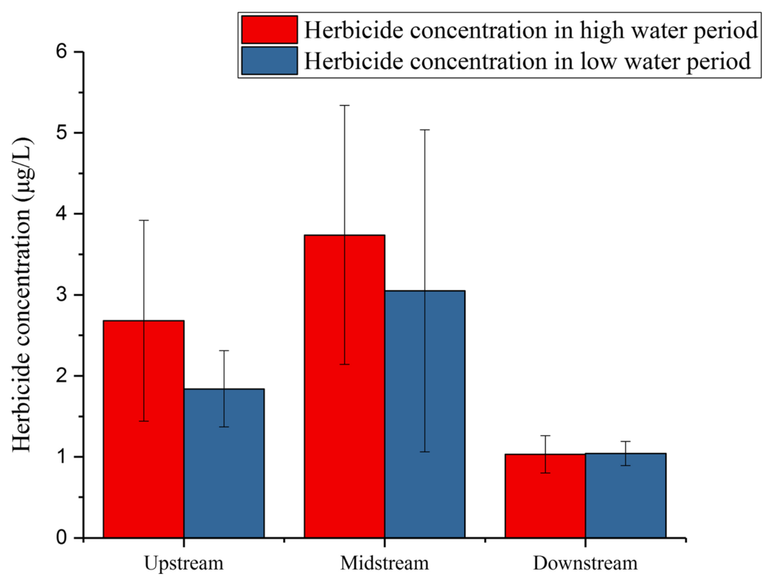


Fig. 4 The distribution of total herbicide concentrations in river water during the high water period and low water period

0.56 ($p < 0.05$), respectively. However, the concentration correlations for metribuzin and DEDIA between the two periods were not significant. The atrazine concentration in river water during the high water period in August was not significantly related to its transformation products during the low water period in October. The sources of

Fig. 5 The average concentrations of total herbicides upstream, midstream, and downstream during two periods



the atrazine transformation products might come from the degradation of the parent compound, the transportation of underground water, and surface runoff.

Factors affecting the spatial distribution of nonpoint source pollution

Many studies have shown that the land use, hydrological properties, and geomorphological characteristics of watersheds have strong impacts on water quality (Sun et al. 2013b; Tu 2009; Tu and Xia 2009). The results of this study suggest that the hydrological and geomorphological characteristics influence water chemistry. The downstream region of the Baima River is located on lowland plain areas, which has poor water discharge conditions, and the water of Nansihu Lake flowed backward into the adjacent downstream reach through underground water during the high water level period. Therefore, the concentrations of heavy metals and herbicides were low in downstream areas because of the hydrogeomorphic setting and the substantial volume of dilution. As displayed in Fig. 5, the average concentrations of the total herbicides in the downstream water were 1.31 μg/L during the high water period and 1.23 μg/L during the low water period, which were below those of the other reaches. The heavy metals also displayed the same trend (Fig. 3).

Riparian land use was another important factor affecting the aquatic environmental quality. There are two land use types in the riparian zones of the Baima River watershed: drylands and rural settlements. The results indicated that the total herbicide concentrations in the river water adjacent to the drylands were higher than those in the adjacent rural settlements (Fig. 6a). However, the concentrations of Cu and Zn in the river water were not significantly different between the two types of riparian lands (Fig. 6b); the main reason might be that rural domestic wastewater also contains Cu and Zn.

Ecological risk assessment

Since the contaminations of Cu and Zn were not serious and did not exceed the threshold value for the criteria of grade 2 water quality (CSEPB 2002) which was suitable to drank water source and habitat for scarce aquatic organisms, we assessed the ecological risk of metribuzin, atrazine, and their transformation products, DEA and DIA. Due to the lack of toxicity data (e.g., LC_{50} or EC_{50}), ecological risk of DEDIA was not evaluated.

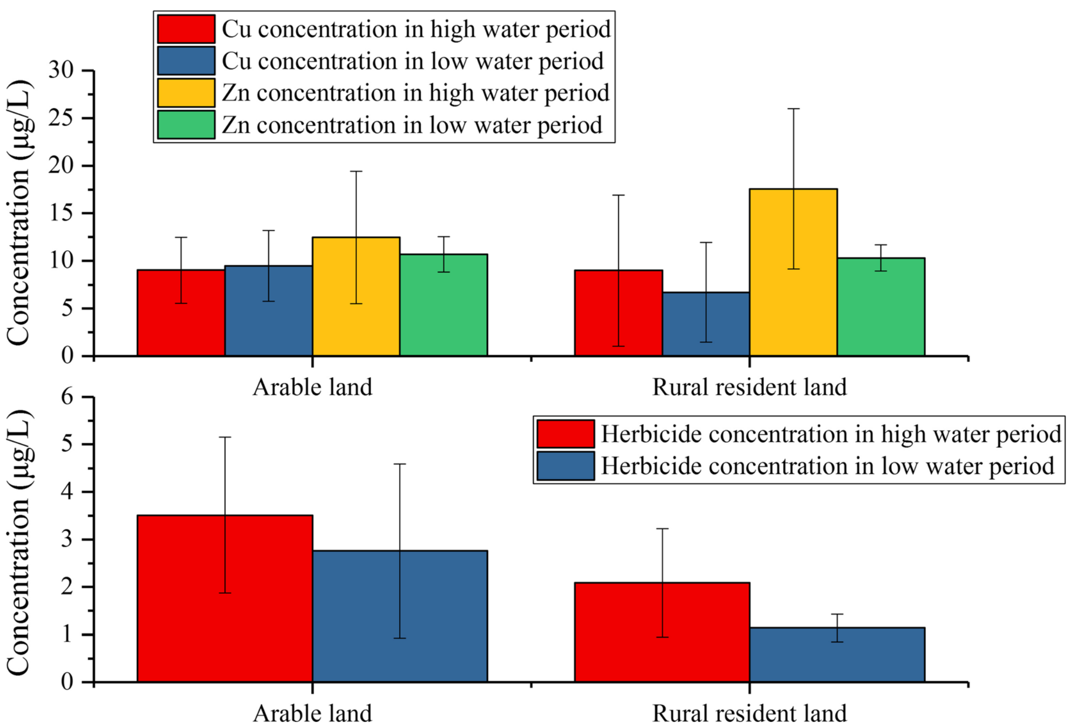


Fig. 6 The average concentrations of heavy metals and the herbicides in river waters adjacent to different land use types

Table 3 Ecotoxicity endpoints for fish, aquatic invertebrates, and algae and related PNEC values (μg/L) for the herbicides

	Fish	Aquatic invertebrate	Algae	Critical concentration	Assessment factor	PNEC (μg/L)
Atrazine	2000	250	100	NOEC:100	10	10
Deethylatrazine		5100	2000	LC50:2000	100	20
Deisopropylatrazine	–	7200	3000	LC50:3000	100	30
Metribuzin	5600	320	19	NOEC:19	10	1.9

The data of ecological toxicity are listed in Table 3. The RQ values of metribuzin, atrazine, DEA, and DIA were 0.001–0.074, 0.001–0.112, 0.001–0.065, and 0.023–0.206, respectively. Atrazine and DIA pose medium risks ($0.1 < RQ < 1$) than metribuzin and DEA ($RQ < 0.1$). Atrazine of one sample in upstream during high water period poses medium risk (RQ 0.112), and other samples pose low risk. However, to the ecological risk of DIA, 8 samples during high water period and 2 samples during low water period pose medium risk. Furthermore, the RQ displayed significant differences in geographical location. In general, the RQs of DIA in midstream were more than other reaches and the contamination of herbicides was more serious in midstream of Baima River.

Conclusions

The Baima River is located in a typical small agricultural watershed, where corn is the main plant, and atrazine is the main kind of herbicide applied to croplands. In this study, we found that nonpoint source metals (Cu and Zn) and herbicides, including metribuzin, atrazine, and its degradates, were detected widely in the surface waters of the Baima River. As expected, atrazine and its degradates were not only the most frequently detected herbicides but also those detected at the highest concentrations. The sum of atrazine and its degraded concentrations in most of the river water samples exceeded the maximum contaminant level (MCL) of 3 μg/L for drinking water criteria in the USA, which was higher compared to those from other surface waters in China because of the small water volume and deficient dilution capability. Our study suggested serious nonpoint pollution in small agricultural watersheds in China. The spatial and temporal distributions of aquatic nonpoint source pollutants alongside the Baima River were influenced by land use and hydrogeomorphic settings. The concentrations of nonpoint source pollutants were lower in downstream areas compared to those in other reaches because of water logging and the substantial volume of dilution.

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