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International Journal of Natural Resources and Environmental Studies
ISSN: 3006-2012 (Print), ISSN: 3006-0834 (Online) | Volume 5, Number 3, Year 2025
DOI: https://doi.org/10.62051/ijnres.v5n3.19
Journal homepage: https://wepub.org/index.php/IJNRES/index

Distribution and Risk Assessment of Triazine Herbicides in the Estuary of the Yangtze River Delta

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ABSTRACT

Triazine herbicides are commonly used and highly effective herbicides. In recent years, many studies have focused on the detection of triazine herbicide residues in the water environment in China and abroad. However, the distribution of triazine herbicides in western Pacific estuaries has not been reported. Therefore, this study utilized high flux solid-phase extraction technology to evaluate the residues of 13 triazine herbicides in the coastal estuaries of the Yangtze River Delta. High-throughput organic analyses combined with high volume solid-phase extraction showed that 11 of the 13 tested triazine herbicides were detected in estuaries along the Yangtze River Delta, namely, atrazine-desethyl, simazine, atrazine, desmetryn, metribuzin, ametryn, prometryn, terbutryn, hexazinone, atratone, and terbuthylazine. The concentration of hexazinone was the highest. To prevent risks to marine aquatic life, policymakers should adopt measures aimed at reducing the entry of triazine herbicides from urban and agricultural sources into the ocean.

KEYWORDS

Triazine Herbicides, Atrazin, Estuarine Transport, The Estuary of the Yangtze River Delta, Ecological Risks

1. INTRODUCTION

Triazine herbicides are traditional selective herbicides developed as early as the 1960s [1] that are characterized by a triazine ring structure, persistence in the environment, high activity, and low volatility [2,3]. These herbicides have the advantages of high herbicidal activity, a wide herbicidal spectrum, and a wide range of application, and they are listed as one of the five most frequently used types of herbicides in the world [4]. Common triazine herbicides include atrazine, prometryne, and simazine. China is the world's second-largest national market for atrazine. Atrazine, which has endocrine-disrupting effects and potential carcinogenicity [5], has been listed as an endocrine disruptor in many countries and regions, including the European Union, the United States, and Japan [6,7,8,9]. However, such herbicides are still widely used in China [10].

Only 10%–30% of triazine herbicides can be absorbed by target plants or soil particles in the process of application, while the remainder will pollute surface water with rainfall, irrigation, or surface runoff and eventually enter the ocean [11]. In addition, a small portion can enter the atmosphere through volatilization and return to the ground through sedimentation, exerting a global impact on the environment [12,13,14]. As a result of their ability to migrate long distances through ocean currents, triazine herbicides have been detected in different environments and organisms in densely populated coastal areas, remote high seas, and polar regions. These effects demonstrate the ecological stress caused by these compounds [15,16,17,18].

At present, most investigations on triazine herbicides have focused on groundwater, surface water, rivers, lakes, and other terrestrial water bodies, while few studies have examined the distribution of herbicides in the western Pacific coastal area. Therefore, studying the spatial distribution characteristics and risk level of triazine herbicides in the estuarine surface water of China is of great significance for marine ecological protection. In this study, high-throughput organic analyses combined with the high-volume solid-phase extraction (Hi-throat/Hi-volume SPE) method were employed to investigate triazine herbicides in the coastal estuary of the Yangtze River Delta in China. The present study aimed to reveal the distribution level and spatial differences in the distribution of triazine herbicides in the main estuaries of eastern China and to provide a scientific basis for strengthening related environmental management measures.

2. MATERIALS AND METHODS

2.1. Sampling

Thirty-one surface water samples were collected using the Hi-throat/Hi-volume SPE method from the coastal areas of Shanghai (SH), Jiangsu (JS), and Zhejiang (ZJ) between July to August 2021. The sampling sites were selected from the seaward runoff areas covering the Yangtze River, Qiantang River, and Oujiang River. Site SH 1 was located at the mouth of the Huangpu River, while sites SH 2–4 points were the farthest from the Huangpu River.

For each sample, 20 L of surface water was filtered through a glass fiber filter (GFF, 0.7 μm, 142 mm) using a custom-made XAD-2/4 resin-filled column (XAD-2: XAD-4=1:1 in mass; particle size, 0.5 mm; Amberlite Company, USA). In brief, each water sample was passed through a Hi-throat/Hi-volume SPE sampler to adsorb the triazine herbicides onto a packed column. The filter and main column were then freeze-dried for 48 h to remove residual moisture, after which they were sealed in custom-made aluminum foil bags and stored at −20°C. All of the samples were pre-treated at the Key Laboratory of Polar Science, State Oceanic Administration, Shanghai, China.

2.2. Analytical methods

The solid-phase extraction (SPE) columns were freeze-dried for 48 h to remove residual water, after which 100 ng of heptachlor-exo-epoxide internal standard was added before extraction. Each column was eluted with dichloromethane (high-performance liquid chromatography (HPLC)-grade, 99.90%) using an in situ internal ultrasound system. The columns were then combined and transferred in triplicate to a 200-mL nitrogen blow-off tube (Biotage, Sweden). Next, n-hexane (HPLC-grade, ≥ 95%, 10 mL) was added to the extraction solution and evaporated to a volume of 0.5 mL under a gentle nitrogen stream. The resulting concentrate was purified through a stainless-steel silica column packed with 7.5 g of dry-weight silica. Following this step, n-hexane (5 mL) was added to the concentrate as a solvent substitute and the final volume was adjusted to 1 mL using n-hexane in a brown chromatography vial. The vials were stored at 4°C before analysis [19,20,21,22].

As a reference, 13 target triazine herbicides were separated in an HP-5 capillary gas chromatography column (30 m × 0.25 μm × 0.25 mm) and analyzed using gas chromatography–tandem mass spectrometry (GC-MS/MS; Agilent 8890-7010B, USA; EI Source, USA). The flow rate of the high-purity helium carrier gas (99.999%) was 1.2 mL $\text{min}{-1}$. A 1.0-μL sample was injected in splitless mode using the ion monitoring mode.

2.3. Quality assurance and quality control

The glass fiber filters, glassware, columns, and custom tools were heated to 450°C for 4 h before use to limit the presence of contaminants. The limits of detection (LODs) for the target triazine herbicides were calculated as the average plus three times the standard deviation of the blank concentration (SD).

For each sample, the concentration of triazine herbicide was corrected based on the LOD and the blank was subtracted. Specifically, the LODs of the 13 triazine herbicides ranged from 0.001–335.068 ng L−1. The external standard recoveries for the detected triazine herbicides were 65%–113%, and the average recovery of the heptachlor-exo-epoxide internal standard in estuarine and riverine waters was 86%, indicating an acceptable instrumental performance.

2.4. Data analysis

Statistical analysis was performed using SPSS ver. 27 and Microsoft Office ver. 2023. Origin ver. 2024 was employed to conduct Spearman correlation analysis. The ArcGIS 10.8 mapping software (ESRI, Redlands, CA, USA) was utilized to map the spatial distribution of triazine herbicides in the coastal estuary of the Yangtze River Delta.

2.5. Ecological risk assessment

The ecological risk of triazine herbicides in the surface water of estuaries in the Yangtze River Delta was evaluated using the risk quotient (RQ) method [23,24]. The formula is as follows:

$$RQ = MEC/PNEC, \tag{1}$$

where MEC is the concentration of triazine herbicides measured in the environment, while PNEC is the predicted no-effect concentration. The PNEC values were calculated as the median lethal concentration (LC50 or EC50) divided by an assessment factor of 1000. Reference LC50 (or EC50) values were obtained from the United States Environmental Protection Agency’s ecotoxicology (US EPA ECOTOX) database. The sum of the individual RQs for all triazine herbicides was considered the total RQ.

The RQs were divided into four potential ecological risk levels: $RQ < 0.01$ (no risk), RQ = 0.01–0.1 (low risk), RQ = 0.1–1.0 (medium risk), and $RQ > 1.0$ (high risk).

3. RESULTS AND DISCUSSION

3.1. Concentrations of triazine herbicides in estuarine surface water and comparison of concentrations in China and abroads

In this study, 13 kinds of triazine herbicides were examined, among which propazine and dipropetryn were not detected at estuarine sampling points. Table 1 presents the frequency and concentrations of 13 herbicides detected in the coastal surface waters of JS, ZJ, and SH. The detection rate at each site ranged from not detected (nd) to 77.4% for atrazine, and the average concentration ranged from nd to 55.63 ng L−1 for hexazinone. The total concentration of 13 triazine herbicides (∑13) in 31 estuarine surface water samples was nd–569.77 ng L−1 (ZJ-4). Compared with existing studies in China and abroad (Table 2), the concentration of atrazine at the mouth of the Yangtze River Delta was similar to that in other parts of the world, except that atrazine was not detected in the San Francisco Bay in the United States or in Venice in Italy. The average concentration of atrazine in the estuary area of the Yangtze River Delta is lower than that in Liaodong Peninsula, Haizhou Bay, and Jiaozhou Bay, and it is generally at a low level within China [6,25,26]. In addition, the concentration of simazine was lower than that of other estuaries except for that of the Chukchi Sea. The concentration of terbuthylazine was lower than that of Haizhou Bay and the Arad estuary of Portugal [6,18,25,26,27.28]. Therefore, the concentration of triazine herbicides detected in the estuary of the Yangtze River Delta is relatively low in terms of global pesticide concentrations.

At the province and city level, the average contents of 13 triazine herbicides in the waters of JS and ZJ were 22.85 ngL−1 and 155.76 ngL−1, respectively, while only one triazine herbicide was detected at the SH-4 point in the surface water of SH, with a concentration of 0.0229 ng·L−1. The total amount was in the order of ZJ > JS > SH. Previous studies in China have demonstrated that the concentration distribution of triazine herbicides in surface water is basically high in the north and low in the south, which is consistent with the results of the present study [29]. This phenomenon may be related to the scale of agricultural industry in each province. JS mostly consists of plain landforms, and the agricultural planting area is large. There are many mountainous areas in ZJ, and the farmland area is small. In SH, China's economic hub, the area of farmland is the smallest. The scale of local agriculture determines the scale of herbicide application and correspondingly affects the herbicide concentrations in the aquatic environment.

Table 1. Detection rate and concentration of triazine herbicides in surface water of estuaries of the East China Sea [ng/L]

Triazine herbicides	Atrazine-desethyl	Simazine	Atrazine	Propazine	Desmetryn	Metribuzin	Ametryn	Prometryn	Terbutryn	Dipropetryn	Hexazinone	Atratone	Terbuthylazine
DF	0.065	0.097	0.774	nd	0.065	0.032	0.613	0.097	0.097	nd	0.129	0.032	0.419
Min	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Max	9.732	0.451	14.166	nd	0.227	0.262	8.490	0.099	0.759	nd	568.670	3.579	0.521
Mean	0.604	0.033	1.627	nd	0.013	0.008	0.441	0.006	0.030	nd	55.630	0.115	0.036
SD	2.300	0.103	2.651	nd	0.049	0.046	1.499	0.021	0.135	nd	148.678	0.632	0.100
Median	0.000	0.000	0.949	nd	0.000	0.000	0.077	0.000	0.000	nd	0.000	0.000	0.000

DF, detection frequency; Min, minimum; Max, maximum; SD, standard deviation; nd, not detected

Table 2. Concentrations of triazine herbicides in surface water in China and abroad

Location	**Region**	**Name**	**Concentration $[\mathrm{ngL}^{-1}]$**	**Sampling time**	**Sampling point**	**Sampling depth**	**Experimental conditions**	**Data source**
Haeju Bay	China	Atrazine	3.9–61.9 (20.5)	June 2017 (wet season) and November 2017 (dry season)	Nineteen sites were set up along the coast of Haizhou Bay, offshore islands, and in the area of rivers entering the sea, among which sites 7, 8, and 9 were located at the mouths of rivers entering the sea.	0.1–1.0 m	LC-MS/MS	[6]
		Prometryn	<3.0–31.9					
		Desmetryn	<3.0					
		Simazine	<3–3.4 (0.2)					
		Ametryn	<3					
		Terbutryn	<3.0–10.5					
		Hexazinone	<3					
		Dipropetryn	<3.0					
		Propazine	<3.0					
		Terbuthylazine	<3.0–17.6 (0.9)					
Liaodong Peninsula	China	Simazine	1.4–5.3	May 2018	Thirty-two samples were collected in the Bohai Sea and the Yellow Sea near the Liaodong Peninsula	0–0.5 m	SPE	[26]
		Atrazine	8.7–64.8					
Jiaozhou Bay	China	Atrazine	average 35.48	April 2018	Water samples were collected from 34 stations in coastal waters, including seven stations in the estuary area	Water surface layer	SPE, UPLC	[25]
		Atrazine-desethyl	average 5.61					

Arade River estuary	Portugal	Atrazine	2–3	Once a month from August to November 2010	The two sites selected in the Arade River estuary for POCIS deployment were: Site 1 (also referred as the downriver site) located inside the Portimão commercial harbor about 2 km from the river mouth. Site 2 (also referred to as the upriver site) is about 2 km upriver from site 1 and about 4 km from the river mouth	2.5 m, 1.5 m	LC-MS/MS	[27]
		Simazine	1–3					
		Ametryn	0.1					
		Atrazine-desethyl	1–3					
		Prometryn	0–0.2					
		Propazine	nd					
		Terbuthylazine	1–3					
North Pacific	North Pacific	Simazine	nd–0.76	From 12 July to 23 September 2016; from 27 July to 7 October 2017	Ninety water samples were collected from the North Pacific and Chukchi Sea	4 m	SPE, GC-MS	[18]
		Atrazine	nd–6.35					
Chukchi Sea	The Arctic Ocean	Simazine	nd–0.34					
		Atrazine	0.01–0.99					
Baltic Sea	Germany	Atrazine (Max)	1.4	May 2009	A total of 153 samples collected from the shorelines of the Baltic Sea (Germany), Northern Adriatic Sea (Italy), Aegean Sea and Dardanelles (Greece and Turkey), San Francisco Bay (USA), Pacific Ocean (USA), Mediterranean Sea (Israel), and Balearic Sea (Spain)	Water surface layer	HPLC-MS/MS	[28]
Aegean Sea and Dardanelles	Greece & Turkey		33	May 2010 and may 2011				
Northern Adriatic Sea	Italy		1.5	May 2010				
Northern Adriatic Sea	Italy (Venice)		nd	May 2010				
San Francisco Bay	USA		nd	February 2010				
Pacific Ocean	USA		nd	February 2010				
Mediterranean Sea	Israel		25	July 2009 and January 2011				
Balearic Sea	Spain		1.6	October 2010				

LC-MS, Liquid chromatography-tandem mass spectrometry; UPLC, Ultra-performance liquid chromatography; GC-MS, Gas chromatography-mass spectrometry; HPLC-MS, High-performance liquid chromatography-mass spectrometry

3.2. Spatial distribution of triazine herbicides in the estuary of the Yangtze River Delta

Figure 2 and Figure 3 illustrate the specific composition analysis at each sampling point. Atrazine had the highest detection rate in estuarine surface water at 77.4%, and the atrazine concentration ranged from nd to 14.17 ng L−1, with a median of 0.95 ng L−1 and an average of 1.63 ng L−1. Spearman correlation analysis indicated that the correlation coefficient between atrazine and ametryn in estuarine water was large, and in most cases there was a positive correlation (Figure 4). This correlation was more obvious in the JS estuary cross section. There were 16 sites where the concentration of atrazine accounted for the largest proportion of the total concentration of each component. Atrazine-desethyl is a degradation product of atrazine, which can be inferred to be partly derived from atrazine. These results are basically consistent with previous findings indicating that atrazine is a typical agricultural drug in estuarine water bodies in eastern China [29]. Atrazine and ametryn are mainly utilized for weed control in dryland crops such as corn and sugarcane. In 2021, the corn planting area in JS and ZJ reached 7.5 million mu and 419,900 mu, respectively [30,31,32,33]. Atrazine and other pesticides are speculated to be widely used in these areas.

Hexazinone was detected only at the JS-4, ZJ-1, ZJ-2, and ZJ-4 sites, but its concentration was 334.10–568.67 ng L−1, which was much higher than the concentrations of other species in the detected sites. Hexazinone is mainly used for the control and removal of non-farmland weeds, shrubs, and bamboo, as well as for the development and protection of tourist attractions and forest fire prevention roads. In addition, hexazinone can also be used to remove shrubs and weeds near structures such as oil depots, airports, and roads. There are scenic spots near the four hexazinone detection points that go into the sea estuary of the Yangtze River Delta. The JS-4 site is located at the estuary of Bencha Canal, Nantong City, JS Province. There is a scenic spot nearby and a concentrated chemical industrial zone along the coast, including small and medium-sized lubricant production bases, biochemical technology companies, and many chemical enterprises. There are chemical enterprises that produce hexazinone herbicide and hexazinone/dioxalon compound products. This may result in a higher concentration of hexazinone at this site. The ZJ-1, ZJ-2, and ZJ-4 sites in ZJ Province are located at the mouth of the Yongjiang River. Ningbo Botanical Garden and various mountainous scenic spots, tourist resorts, wetland parks, and geoparks are located near the basin. These sites may have a large demand for hexazinone, resulting in a high concentration of hexazinone in the surface waters.

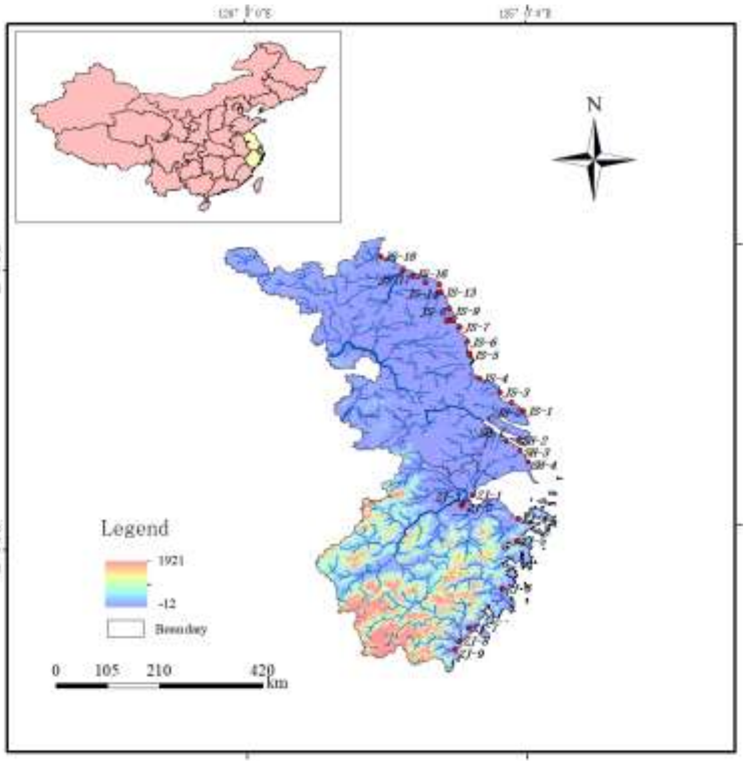

Figure 1. Distribution of sampling points in the estuary of the Yangtze River Delta

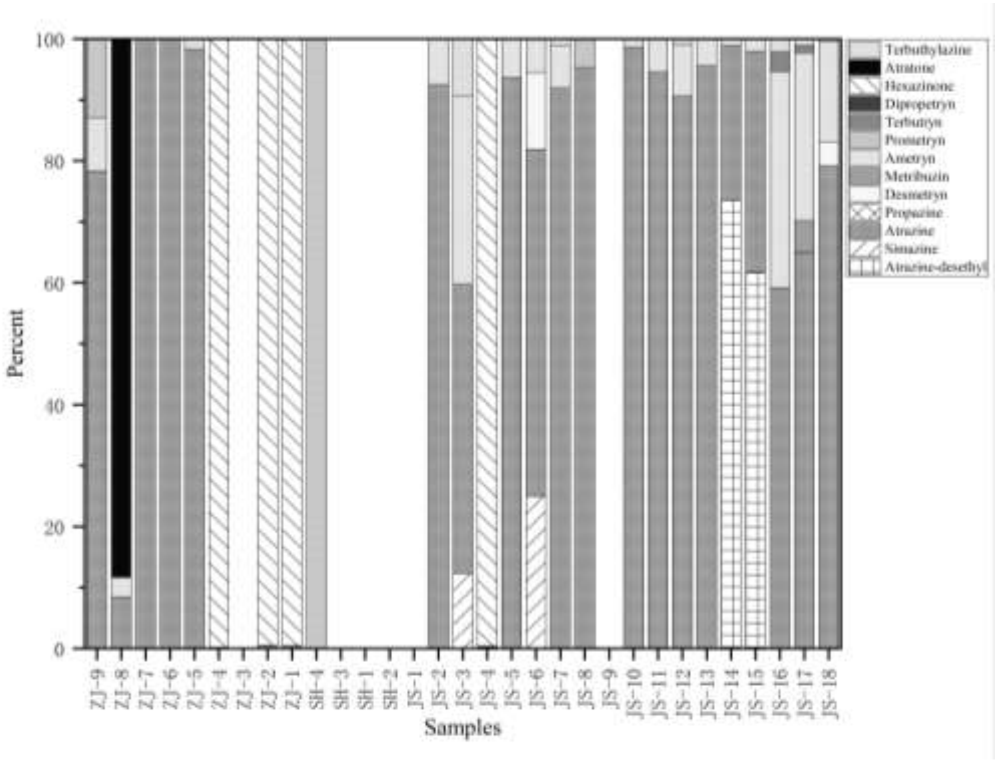

Figure 2. Cumulative column chart of the percentage concentrations of 13 triazine herbicides at each point in the Yangtze River Delta estuary

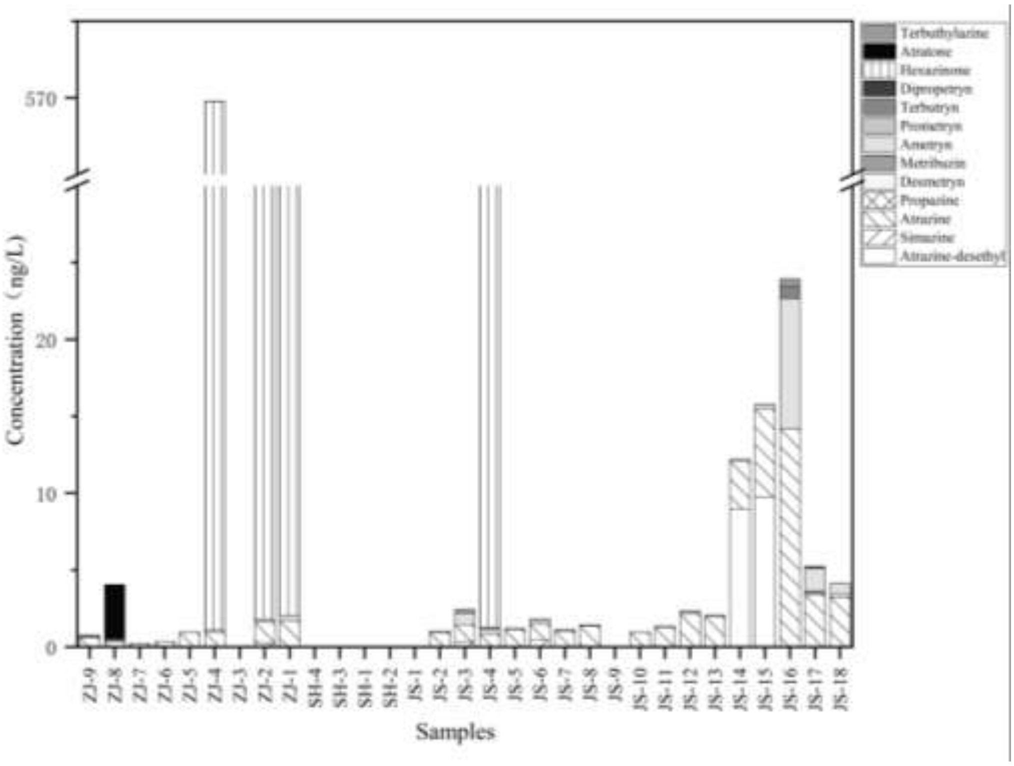

Figure 3. Column diagram of the concentration accumulation of 13 triazine herbicides at each point in the Yangtze River Delta estuary

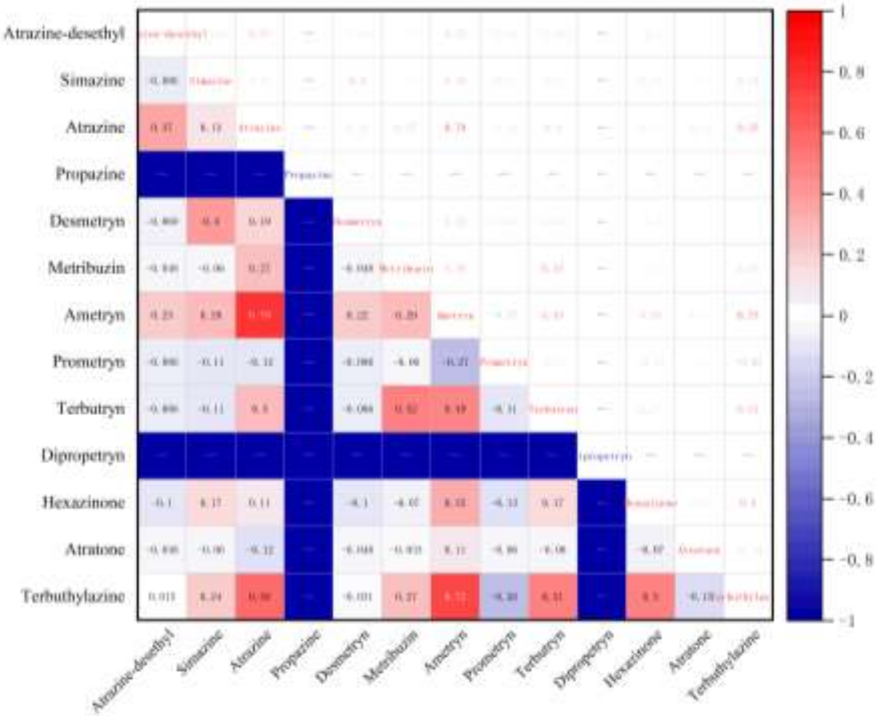

Figure 4. Spearman correlation analysis of 13 triazine herbicides in the Yangtze River Delta estuary. Positive values indicate a positive correlation, negative values indicate a negative correlation, and a value of 0 indicates no correlation

3.3. Ecological risk assessment

Estuaries are important import channels through which marine pollutants enter the sea, where these pollutants pose serious threats to the early life stages of aquatic organisms and sensitive species. The ecological risk assessment data for 10 herbicides in the estuary of Yangtze River Delta are presented in the table below.

Table 3. Ecological risk assessment of 10 herbicides in the estuary of the Yangtze River Delta [34]

Name	Property	Value	Mean RQ value	Potential ecological risk level
Atrazine	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	>4.5	0.357	medium risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	1.0	1.608	high risk
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.059	27.258	high risk
Prometryn	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	5.5	0.001	no risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	1.4	0.004	no risk
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.002	3.091	high risk
Hexazinone	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	>320	0.174	low risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	-	-	-
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.0145	3836.528	high risk
Simazine	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	90	0.000363	no risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	-	-	-
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.04	0.81576	medium risk
desmetryn	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	2.2	0.00572	no risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	-	-	-
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.025	0.503	medium risk
Metribuzin	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	74.6	0.000113	no risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	-	-	-
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.0266	0.318	medium risk
Ametryn	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	5	0.0882	low risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	1.7	0.259	medium risk
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.0036	122.478	high risk
Terbutryn	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	>1.1	0.0272	low risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	-	-	-
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.0024	12.454	high risk
Atratone	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	-	-	-
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	-	-	-
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.0799	1.445	high risk
Terbuthylazine	Temperate freshwater fish-acute 96-hour LC$_{50}$ [mg L^{-1}]	2.2	0.0164	low risk
	Aquatic crustaceans-acute 96-hour LC$_{50}$[mg L^{-1}]	0.167	0.217	medium risk
	Algae-acute 72-hour EC$_{50}$, growth [mg L^{-1}]	0.012	3.016	high risk

As can be seen from Table 3, the ecological risk of various triazine herbicides to algae is generally higher than that of temperate freshwater fish and aquatic crustaceans of the same species. Algae was found to be the most sensitive group of organisms, but the lack of toxicity data for algae may have led to the overestimation of risk, necessitating further study. Hexazinone was the triazine herbicide with the highest concentration detected in the Yangtze River estuary, but its ecological risk level to temperate freshwater fish was low. The results showed that the risk level of each pollutant was not directly related to its concentration. As shown in Figures 5–6, the ecological risk to temperate freshwater fish and aquatic crustaceans at the JS-16 point was much higher than that at other sampling points. The JS-16 site is located at the mouth of the Guanhe River, which is close to many farmlands nearby receives the flow of several rivers. It is recommended that herbicides should be applied rationally to reduce their associated ecological risks. The results indicated that the ecological risk of atrazine to temperate freshwater fish was generally higher than that of other triazine herbicides at the same site. China's surface water environmental quality standard stipulates that the standard limit of atrazine in surface water is 3 μg/L, while the standard limits for other triazine herbicides are not specified. Atrazine is considered a priority substance in the European Water Framework Directive, with an annual mean value of 0.6 μg L−1 as defined by the European Commission in the Environmental Quality Standard [35]. The concentration of atrazine in the Yangtze River Delta estuary did not exceed the above two standards. As shown in Figure 7, atrazine at the ZJ-3 site displayed the highest risk entropy for algae. This site is located in the Caoejiang River, near many farmlands and printing and dyeing enterprises. Printing and dyeing wastewater contains many organic pollutants, which may have synergistic toxic effects on algae. Studies have shown that marine microalgae are significantly affected by mixtures of atrazine and other herbicides, and the criteria defined do not reflect the synergies of the mixtures and are insufficient to protect marine microalgae [36].

In the ecological risk assessment of estuarine triazine herbicides in China and abroad, the ecological risk degree of atrazine and prometryn in the relevant waters off Haizhou Bay is low [6]. In Europe, atrazine contributes the most to ecological risks based on acute toxicity in the Ebro, Luros, and Rhone rivers [37]. The risk of atrazine in Liaodong Peninsula and Camps Bay in Cape Town, South Africa is low for fish and high for algae [26,38], which is consistent with the results of the present study. It can be seen that the ecological risk of atrazine in estuarine water bodies is generally high, which necessitates further attention and improved monitoring, management, and remediation efforts.

4. CONCLUSION

This study determined the distribution of 13 triazine herbicides in estuaries along the Yangtze River Delta for the first time and conducted preliminary analyses. The results showed that the overall concentration of triazine herbicides in the estuaries of the Yangtze River Delta was JS > ZJ > SH. Atrazine and hexazinone were the main components. The ecological risk of atrazine in estuarine water bodies should receive greater attention, and measures should be taken to reduce atrazine pollution.

CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

ACKNOWLEDGEMENTS

We thank LetPub (www.letpub.com.cn) for its linguistic assistance during the preparation of this manuscript.

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