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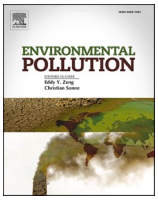

Glyphosate and glufosinate-ammonium in aquaculture ponds and aquatic products: Occurrence and health risk assessment☆

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ABSTRACT

As the two most commonly used organophosphorus herbicides, glyphosate (Gly) and glufosinate-ammonium (Glu) have unique properties for weed control and algae removal in aquaculture. However, the occurrences and health risks of Gly and Glu in aquaculture ponds are rare known. This study aimed to investigate the occurrences of Gly, AMPA (primary metabolity of Gly) and Glu in surface water, sediment and aquatic products from the grass carp (*ctenopharyngodon idella*), crayfish (*procambarus clarkii*) and crab (*eriocheir sinensis*) ponds around Lake Honghu, the largest freshwater lake in Hubei province, China where aquaculture has become the local pillar industry. Three age groups (children, young adults, middle-aged and elderly) exposure to these compounds through edible aquatic products (muscle) consumption were also assessed by target hazard quotient (THQ) method. The results indicated that Gly, AMPA and Glu were widely occurred in surface water, sediment and organisms in the fish, crayfish and crab ponds. AMPA was more likely to accumulate in the intestine of aquatic products than Gly and Glu. According to the total THQ value (1.04 > 1), muscle consumption of grass carp may pose potential risk to children.

1. Introduction

The application of glyphosate-based herbicides (GBHs) worldwide increased 100-fold from the late 1970s to 2016 around the world (Bonny, 2016; Myers et al., 2016). Glyphosate (Gly) is one of the most extensively used organophosphorus compounds in the world with the characteristics of non-selective and post-emergent for agricultural and non-agricultural applications (Agostini et al., 2020). Gly degrades in the environment, primarily by microbial processes, to amino-methylphosphonic acid (AMPA) (Grandcoin et al., 2017). Glufosinate-ammonium (Glu) is another broad-spectrum herbicide listed with the prominent problem of glyphosate-resistant weeds, and its usage is second only to Gly (Takano and Dayan, 2020). Although Gly has unique properties for the control of emergent aquatic weeds in ditches, wetlands, and margins of water bodies, the considerable loss of Gly in use is inevitable (up to 24% of Gly applied to surfaces was runoff) (Imfeld et al., 2013; Solomon and Thompson, 2011). These unused Gly and other compounds continue to accumulate in environmental water and sediment, and even enriched in organisms through the food chain, thus causing a series of health risks (Aparicio et al., 2013; Bonansea et al., 2017; Smedbol et al., 2018).

Honghu lake, a typical shallow lake in the middle reaches of the Yangtze River, is the largest freshwater lake in Hubei province, China and the largest lake type wetland, where is rich in aquatic animal and plant resources (Tadesse et al., 2018). The freshwater area is 810.9 square kilometers, accounting for 32% of the total land area of 2519

Abbreviations: Glyphosate, Gly; Glufosinate-ammonium, Glu; aminomethylphosphonic acid, AMPA; 9-fluorenymethylchloroformate, FMOC-Cl; Ultra-performance liquid chromatography tandem mass spectrometry, UPLC-MS/MS; Predicted no effect concentration, PNEC; Environmental concentration, EC; Risk quotient, RQ; Target hazard quotient, THQ.

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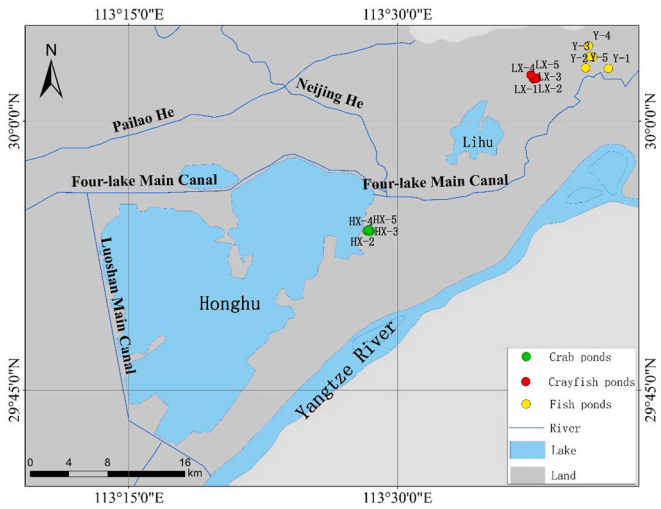

Fig. 1. Map of sampling sites in Honghu aquaculture basins. HX represents crab ponds, LX represents crayfish ponds, and Y represents fish ponds.

square kilometers. In 2016, the Honghu city's aquaculture area was 584.67 square kilometers, aquatic product output was 485,000 tons, and fishery output value was 7.25 billion yuan, accounting for 57 percent of the city's large-scale agricultural output value. Honghu City has been awarded "the first city (county)" of freshwater aquatic products in China, and aquaculture has become the local pillar industry of Honghu (Wang et al., 2017; Zhang et al., 2017). Culture ponds (e.g. fish, crayfish and crab ponds) in this agricultural basins not only made an outstanding contribution to ensuring the safety of aquatic products supply in China, but also had an important impact on the natural water ecosystem. However, the water quality saw to a deterioration tendency in the recent decades, mostly owing to unreasonable human activities such as lake enclosure aquaculture following the rapid social and economic development (Chen et al., 2020). Although lake enclosure aquaculture in this area began in 1980s and the aquaculture area expanded rapidly and reached a peak from 2002 to 2004, there is still a lack of data on the occurrence of organophosphorus herbicides (such as Gly and Glu) in aquaculture ponds (Geng et al., 2020; Zhang et al., 2017). Moreover, the impacts of these compound residues on aquatic organisms (e.g. grass carp, *procambarus clarkii* and *eriocheir sinensis*) and consumers in Honghu aquaculture basin also remain unknown. Therefore, it is of great significance to study the occurrences of Gly, AMPA, and Glu in fish, crayfish and crab ponds in this area.

The focus of the present study were to (1) investigate the spatial and seasonal distributions of Gly, AMPA and Glu in three typical aquaculture ponds around Honghu lake, China; (2) provide risk assessment of these analytes to the local aquatic environment and evaluate the health risk of human exposure through food consumption.

2. Materials and methods

2.1. Study sites and sample collection

In May, July and October 2020, crab ponds (HX-1, HX-2, HX-3, HX-4, and HX-5), crayfish ponds (LX-1, LX-2, LX-3, LX-4 and LX-5) and fish ponds (Y-1, Y-2, Y-3, Y-4 and Y-5) located in Honghu aquaculture basins were selected for sampling and investigation (Fig. 1). These three months were chosen because May was the first month after the COVID-19 epidemic announced the lifting of the city blockade, July was one of the hottest months of the year, with the growth rate of aquatic products and algae accelerated, and the weather turns cooler in October, the temperature difference between day and night in the south increases, which easily made the water quality worse. Additional detailed information was presented in Table S1.

According to the Technical Specification for Surface water and Sewage Monitoring (HJ T91-2002, China) and the Water quality-Determination of glyphosate-High performance liquid chromatography (HJ 1071-2019, China), surface water were collected by a sampler with 500 mL or 1 L of clean brown glass bottle for a temporary storage and transportation (<24 h). After the sample was collected and filtered through a 0.45 μm membrane, 200 mL was sub-packaged and the pH was adjusted to 9, then sealed and stored in a polyethylene plastic bottle, refrigerated at 4 °C away from light, and the sample detection was completed within 7 days. According to Water Quality Sampling Technical Guidance (HJ 494-2009, China), the wet sediment samples performed 5–20 cm deep were initially collected 200–300 g in polyethylene self-sealed bag and preserved at −20 °C before drying to prevent possible changes. The wet tissue samples were freshly collected 1–5 g by dissecting grass carp caught on the same day, then packed into frozen storage tubes and preserved in liquid nitrogen irrigation.

2.2. UPLC–MS/MS conditions

Analysis of targets was conducted by a Waters Acquity™ UPLC/Xevo TQ MS (Milford, MA, USA), and acquired with MassLynx V4.1 software. Chromatographic separation was carried out at 40 °C using a Waters Acquity C18 column (2.1 mm × 50 mm × 1.7 μm, Milford, MA, USA). The injection volume was 5 μL and the pump flow was set at 0.2 mL/min. Mobile phase A: 10 mM Ammonium solution/0.1% Formic acid water; mobile phase B: 10 mM Ammonium solution/0.1% Formic acid ACN. Dynamic elution with mobile phase A/mobile phase B (v/v): 0 min, 80/20; 3 min, 10/90; 5 min, 10/90; 5 min, 10/90; 5.1 min, 80/20; 7 min, 80/20. The HPLC column was connected to an triple quadrupole mass spectrometer equipped with a turbo ion spray (TIS) source operated in positive electrospray ionization (ESI+) mode and multiple reaction monitoring (MRM) with the following optimized ion transitions: desolvation temp, 350 °C; capillary, 3.00 kV; cone, 25 V; collision gas flow, 0.15 mL/min. The quantitation transition (m/z) and the analytical conditions are listed in Table S2. The positive ion sub-model diagrams of the three target standards are presented in Figure S1. The retention times of FMOC-Gly, FMOC-AMPA and FMOC-Glu are 3.04, 2.89 and 3.18 min, respectively.

2.3. Qualification of Gly, AMPA and Glu

Based on existing methods (Demonte et al., 2018; Han et al., 2016; Geng et al., 2020), we developed an optimized procedure for the determination of Gly, AMPA and Glu in surface water, sediments and biological samples using derivatization with fluorenylmethyl chloroformate (FMOC-Cl), combined with on-line solid phase extraction and ultra-performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS). Details for the pretreatment, analysis and also the quality control were given in the Supporting information (Table S3-5; Figure S2).

2.4. Data analysis

Experimental results were statistically analyzed using GraphPad Prism 8.02 (GraphPad Software Inc., California). The linear correlation was employed to evaluate the association between the concentrations of Gly, Glu and AMPA in surface water and sediments by Cloud_Platform (http://www.ehbio.com/Cloud_Platform/front/#/). The predicted environmental concentrations (PEC) in surface water and sediment were compared under Wilcoxon test by Cloud_Platform for the analytes.

P_{AMPA} (% of AMPA) and Ratio were calculated according to Eqs. (1) and (2):

$$P_{AMPA} = (C_{AMPA} / M_{AMPA}) / (C_{AMPA} / M_{AMPA} + C_{Gly} / M_{Gly}) \quad (1)$$

$$Ratio = C_{AMPA} / C_{Gly} \quad (2)$$

Table 1
Detection rates and concentrations of Gly, AMPA and Glu in surfacewater (n = 15).

Targets	Sampling position	May		July		October	
		Detection rate (%)	Concentration range (μg/L)	Detection rate (%)	Concentration range (μg/L)	Detection rate (%)	Concentration range (μg/L)
Gly	Crab ponds	40.0	< LOD - 1.49	100	<LOQ - 1.27	100	21.7–89.0
	Crayfish ponds	60.0	< LOD - 0.940	100	<LOQ - 0.570	100	10.6–61.4
	Fish ponds	20.0	< LOD - 0.830	100	0.750–2.44	100	8.89–100
AMPA	Crab ponds	100	<LOQ - 2.59	100	1.97–8.16	100	<LOQ -1.93
	Crayfish ponds	100	<LOQ - 1.90	100	1.75–40.3	100	1.72–28.3
	Fish ponds	80.0	< LOD - 3.99	100	7.95–15.8	100	6.12–21.2
Glu	Crab ponds	20.0	< LOD - 6.13	20.0	<LOQ	100	<LOQ - 2.94
	Crayfish ponds	40.0	< LOD - 0.610	60.0	< LOD - 0.990	100	<LOQ - 2.58
	Fish ponds	0.00	< LOD	100	<LOQ	80.0	<LOQ

Note: The LOD and LOQ obtained in surfacewater with the present technique is 0.1 and 0.4 μg/L, respectively.

where C_{AMPA} and C_{Gly} are their concentrations in the positive water samples (μg/L), C_{AMPA} or C_{Gly} is set to 0 μg/L when below the LOD, C_{AMPA} or C_{Gly} is set to 0.05 μg/L when between the LOD and the LOQ. M_{AMPA} and M_{Gly}, their molar mass (g/mol), is 94.97 and 169.07, respectively. $P_{AMPA} \geq 0.5$ represents the molar concentration $C_{AMPA} \geq C_{Gly}$ under aged Gly treatment; $P_{AMPA} < 0.5$ represents the molar concentration $C_{AMPA} < C_{Gly}$ under freshly Gly treatment (Geng et al., 2020).

2.5. Ecological risk assessment of water consumption for aquatic organisms

The evaluation model of this part refers to Geng et al. (2020). PNEC (predicted no effect concentration for water, μg/L) was calculated by Eq. (3):

$$PNEC_{water} = (ADI * bw * P * 1000) / C \quad (3)$$

where ADI (acceptable daily intake, mg kg/bw/day), P and C of the targets have been listed in Table S6.

The risk to drinking water and aquatic ecological safety was assessed by risk quotient (RQ) method according to Eq. (4).

$$RQ = EC / PNEC \quad (4)$$

EC means the monitoring environmental concentration. RQ > 1, the risk of the target for groundwater/surface water safety is unacceptable. RQ ≤ 1, the risk is acceptable.

2.6. Dietary expose risk assessment of muscle consumption for consumers

The target hazard quotient (THQ) method was used to evaluate dietary expose risk form aquatic products (fish, crayfish and crab) containing Gly, AMPA and Glu in three age groups (children, young adults, middle-aged and elderly) of human consumers (Zhu et al., 2020).

$$THQ_i = (EF_i * ED_i * F_{IR} * C_i / RfDi * W_{i\ AB} * AT_n) * 10^{-3} \quad (5)$$

$$TTHQ = \sum_i THQi \quad (6)$$

THQ_i is the hazard quotient of target i, TTHQ is the total target risk coefficient of Gly, AMPA and Glu in meat products. EF_i, 365 d/year, is the exposure frequency of chemical i. ED_i is the exposure persistence of chemical i, average exposure period is 30 years. F_{IR} is the average daily dietary intake of meat. Residents are divided into three groups: children (3 ~ < 12 years old), young adults (12–45 years old) and middle-aged and elderly (>45 years old), and their F_{IR} values are 22.34 g/d, 35.50 g/d and 36.64 g/d, respectively. C_i is the concentration of Gly, AMPA, and Glu in the edible muscle. RfD_i is the reference dose of chemical i in aquatic products, and the RfD of Gly is 0.100 mg/(kg·d). W_{AB} is per body weight, and W_{AB} values of the above-mentioned groups are 24.5 kg, 60.3 kg and 59.4 kg respectively. AT_n is the average exposure time (d).

3. Results and discussion

3.1. Occurrence of Gly, AMPA and Glu in surface water and sediment

The detection rates and concentrations of Gly, AMPA and Glu from three typical aquaculture ponds in surface water and sediment are shown in Tables 1 and 2. According to the Surface Water Environmental quality Standard (GB 3838-2002, China), the water quality of aquaculture ponds belongs to Class III, none of the sample sites exceeded 0.7 μg/L (GB/T 14848-2017, China; suitable for aquaculture) (Table S7). In the present study, we observed that, the contents of three analytes in culture ponds fluctuated significantly in surface water, while the corresponding analytes in sediments did not fluctuate significantly. Higher concentrations in surface water were observed in October for Gly and AMPA, while the trends of Gly and AMPA in sediment are the same. Particularly, the maximum in October was observed for AMPA in sediment. The detection rate of AMPA from crab ponds and crayfish ponds was 100%, and that in fish ponds was more than 80%. It can be

Table 2
Detection rates and concentrations of Gly, AMPA and Glu in sediment (n = 15).

Targets	Sampling position	May		July		October	
		Detection rate (%)	Concentration range (ng/g dw)	Detection rate (%)	Concentration range (ng/g dw)	Detection rate (%)	Concentration range (ng/g dw)
Gly	Crab ponds	80.0	< LOD - 14.0	100	< LOQ - 10.8	80.0	< LOD - 15.7
	Crayfish ponds	100	< LOQ - 10.6	100	< LOQ - 10.5	20.0	< LOD - 46.5
	Fish ponds	100	< LOQ - 14.3	80.0	< LOQ - 14.3	100	< LOQ - 16.6
AMPA	Crab ponds	100	39.3–89.0	80.0	30.9–121	100	35.3–120
	Crayfish ponds	100	17.9–66.5	100	40.3–78.3	100	23.8–125
	Fish ponds	100	89.5–185	100	77.2–223	100	138–398
Glu	Crab ponds	100	< LOQ	100	< LOQ - 14.1	100	< LOQ - 10.8
	Crayfish ponds	100	< LOQ - 14.9	100	< LOQ - 13.1	100	< LOQ - 14.5
	Fish ponds	100	< LOQ - 12.9	100	< LOQ - 11.6	60.0	< LOD - 10.6

Note: The LOD and LOQ obtained in sediment with the present technique were 5 and 10 ng/g dry weight, respectively.

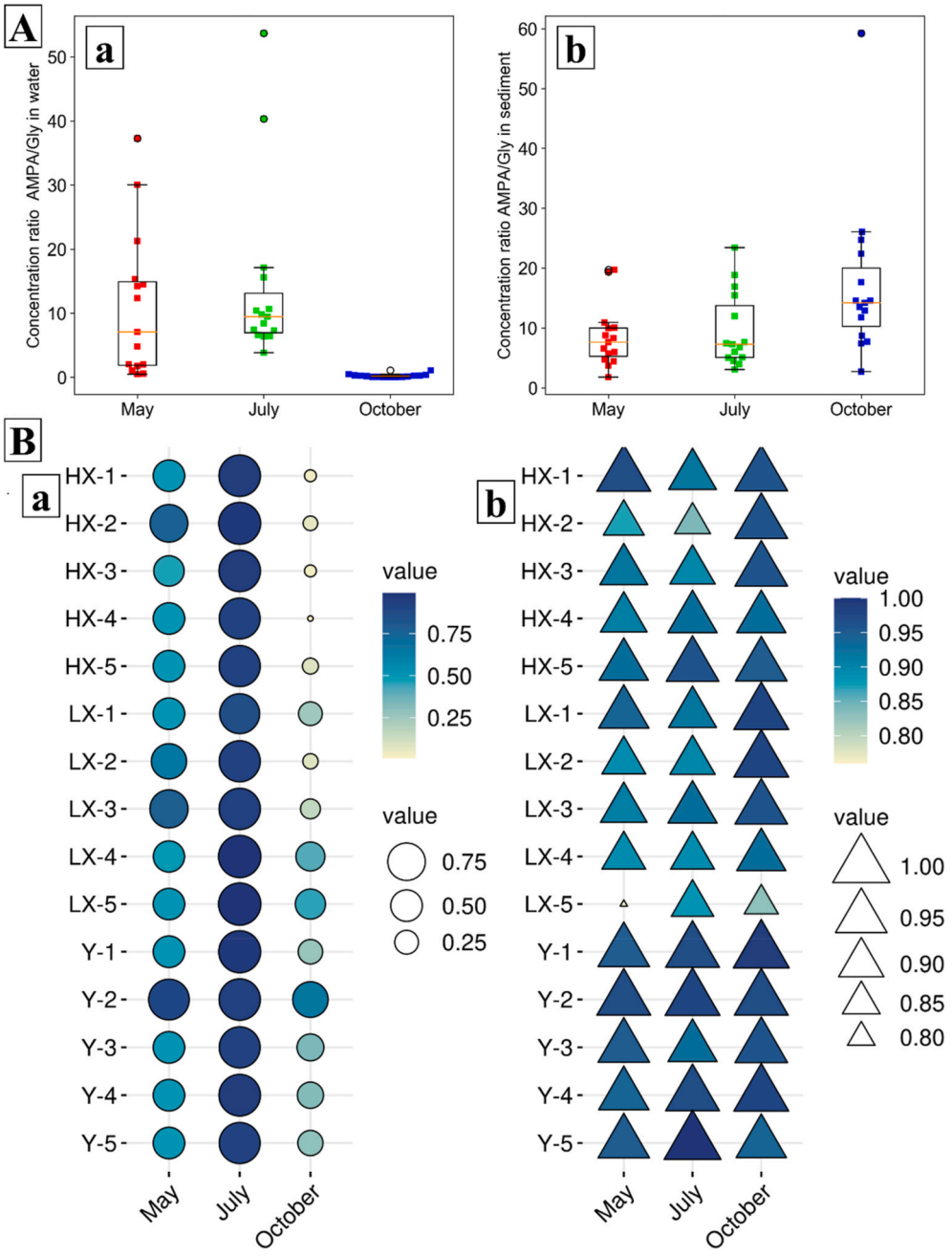

Fig. 2. The seasonal variation of AMPA/Gly concentration ratios in surfacewater and sediment. A represents AMPA/Gly concentration ratios in different sampling time and B represents AMPA/Gly concentration ratios in different sampling sites. a, surfacewater; b, sediment (HX: crab ponds, LX: crayfish ponds and Y: fish ponds). Values outside this range are plotted individually.

concluded that the main reason for the high total residues in fish ponds is that the content of AMPA is relatively high.

Gly and AMPA have been detected in multiple surface water samples from Europe, North America and South America, ranged from 1.8 to 427 μg/L for Gly and 1.4–397 μg/L for AMPA (Geng et al., 2020). The main source of Gly and other compounds in the culture area is attributed to the herbicidal application of Gly formulations or other Gly-based herbicides (Tzanetou and Karasali, 2020). Soil is an important destination of Gly herbicides, but affected by run off or wind, it may also be accepted by the surrounding lakes (Lupi et al., 2019; Silva et al., 2018). In the runoff test, 88.1% Gly was retained in the surface soil layer (0–9 cm) and 3.9% in the runoff, and Gly was detected in rain water's samples (Richards et al., 2018). Generally, the persistence of Gly in water was lower than that in soil, and the persistence observed in Canadian ponds ranged from 12 to 60 days, although the persistence was recorded in the sediments of American ponds for more than one year (Islas et al., 2014). And sediment could also be contaminated where its degradation is even slower than in dissolved water (EFSA, 2015; Van Bruggen et al., 2018). In this study, compared with the water body, the detection rates of the three substances in the sediment is higher, this mainly depends on which substances may have adsorption properties in the sediment. Compared with Gly, the content of Glu in water samples and sediments was lower. A survey from 10 provinces in China also showed that the detection rate of Glu in 196 surface water samples was 2.6% (Geng et al., 2020). In addition, AMPA (lasts for more than a year in soil) was detected in all the month surveyed, which may be due to its longer half-life than Gly (its half-life in water is between 12 days and 10 weeks, a typical field half-life of 47 days has been suggested in soil) and Glu (its half-life which

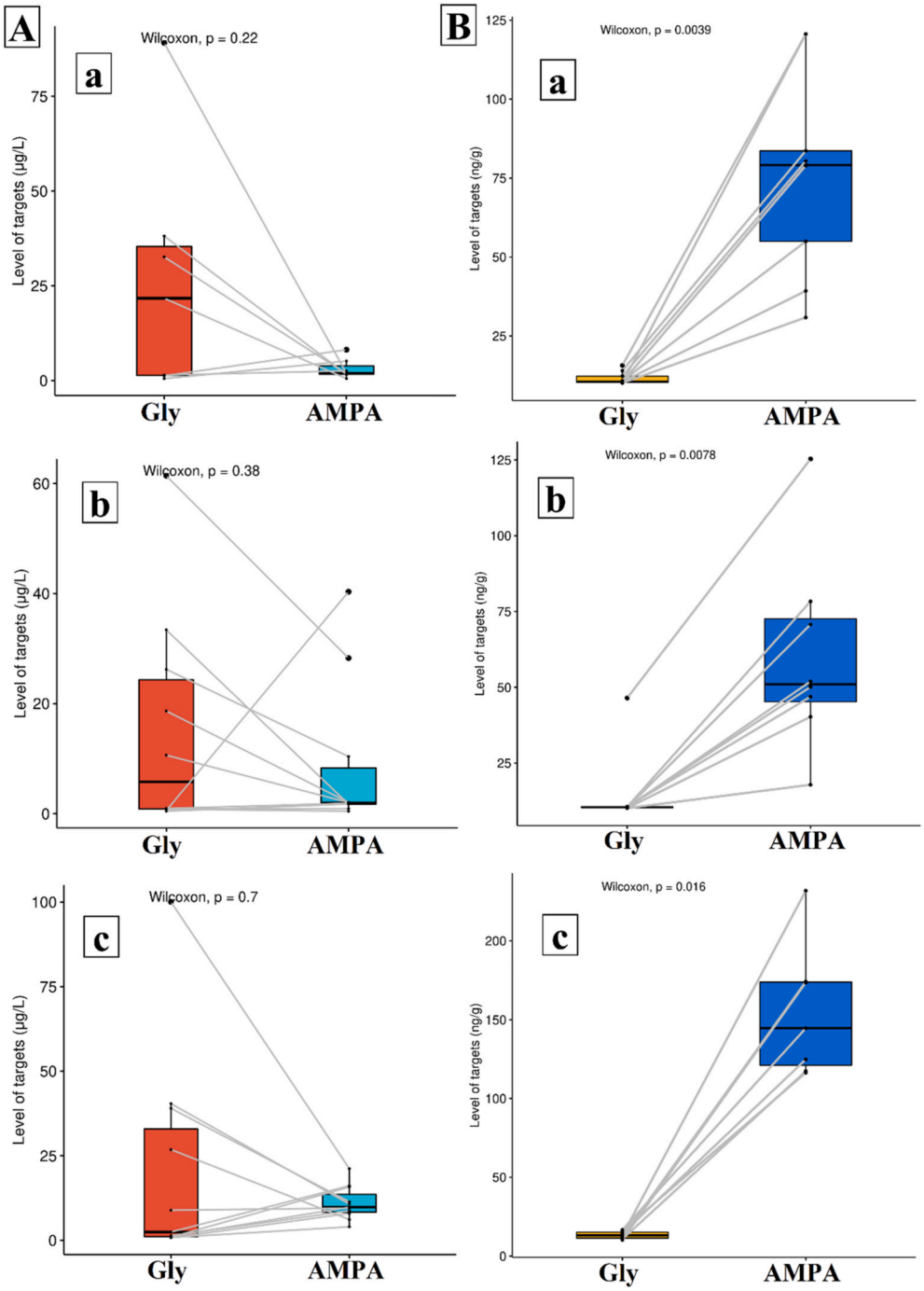

Fig. 3. Levels of Gly and AMPA in surfacewater and sediment. Paired Wilcoxon test, boxplots were performed for the levels of Gly and AMPA in samples grouped by surfacewater and sediment, only samples with either Gly or AMPA detected were plotted. A represents surfacewater and B represents sediment; a, May; b, July; c, October.

varies from 3 to 70 days in soil) (Bento et al., 2019).

3.2. Spatial and seasonal variation of Gly, AMPA and Glu in surface water and sediment

The seasonal variation of Gly and AMPA concentrations was calculated in three different ponds. AMPA is the metabolite of Gly but their contaminated levels were not always consistent. The ratio of AMPA to Gly was calculated for a better understand on the dynamic changes of the both pollutants across different seasons and environmental medium. In addition, the ratio of AMPA to Gly shows more sensitivity than the ratio of AMPA to the sum of AMPA and Gly. Fig. 2A showed that there is a trend toward lower ratio in October for surface water, when AMPA levels are at their minimum. Instead, AMPA/Gly in sediment in October has a higher ratio than other months. Fig. 2B showed that the AMPA/Gly ratio of 15 monitored ponds for surface water was higher in July. Except for LX-5, the AMPA/Gly ratio of 15 monitored ponds for sediment was higher in October.

Concentrations of AMPA in the same samples in surface water varied much less. On a sample-by-sample basis, in only 26.7% of surface water samples, concentrations of AMPA were lower than those of Gly. Similarly, concentrations of Gly in the same samples in sediment varied

Table 3
Detection rates and concentrations of Gly, AMPA and Glu in organisms from fish ponds (n = 15).

Targets	Tissues	May		July		October	
		Detection rate (%)	Concentration range (ng/g dw)	Detection rate (%)	Concentration range (ng/g dw)	Detection rate (%)	Concentration range (ng/g dw)
Gly	Brain	60.0	< LOD - 1.11	50.0	< LOD	60.0	< LOQ
	Liver	33.0	2.61–6.55	50.0	< LOD	57.0	< LOQ
	Muscle	33.0	< LOD	100	< LOQ	80.0	< LOQ
	Intestine	93.0	< LOQ	50.0	< LOQ	73.0	< LOQ
AMPA	Brain	40.0	< LOQ	25.0	< LOQ	40.0	< LOQ
	Liver	93.0	2.53–16.6	50.0	2.17–5.97	80.0	1.08–3.66
	Muscle	47.0	< LOD	75.0	2.25–6.86	57.0	< LOD - 14.6
	Intestine	100	12.0–250	100	30.7–202	73.0	15.0–267
Glu	Brain	50.0	< LOQ	0.00	< LOD	40.0	< LOD
	Liver	7.00	< LOD	0.00	< LOD	71.0	< LOD - 0.980
	Muscle	7.00	< LOD	25.0	< LOQ	80.0	< LOD
	Intestine	33.0	0.650–3.81	25.0	< LOQ	47.0	0.582–3.00

Note: The LOD and LOQ for the selected matrices ranged from 0.3 to 3.3 ng/g and from 1 to 10 ng/g, respectively.

much less. On average, concentrations of AMPA in sediment were higher than those of Gly. The positive detected concentration of AMPA was significantly higher than its parent (Gly) under paired Wilcoxon test in sediment (Fig. 3B, $P < 0.02$) but not in surfacewater, the significant difference was $P = 0.0039$ in May, $P = 0.0078$ in July and $P = 0.016$ in October.

Through the analysis of AMPA/Gly concentration ratios, we speculate that the accumulation or high level of AMPA in sediment is not affected by the season. By Paired Wilcoxon test comparison, we also confirmed that there was a high residue of AMPA in the environment. Other studies have also reported that AMPA is still highly detected in different regions (Bento et al., 2019; Grandcoin et al., 2017; Silva et al., 2018). In Europe, AMPA was the predominant form, being present in 42% of the soils while Gly was present in 21% (Silva et al., 2018). Grandcoin et al. (2017) pointed out that sediments tend to accumulate AMPA. Bento et al. (2019) also concluded that AMPA persists and may accumulate in soil.

3.3. Occurrence of Gly, AMPA and Glu in aquatic products

The brain, liver, muscle and intestine of grass carp from fish ponds were used for analysis in Table 3. Specifically, Table 3 showed that Gly, AMPA, and Glu can be detected in the intestine of grass carp, with the detection rates were 50–93.3%, 73.7–100%, 25–44.0%, and the concentration ranges were < LOQ, 12.0–267 ng/g, 0.582–3.81 ng/g, respectively. Obviously, the concentration of AMPA in the intestine was higher than that in other biological tissues. Similarly, the detection concentrations and rates of AMPA in intestines of crab and crayfish were higher than those in liver and muscle (Table S8-9). The study found that the detection rates of the three analytes in the intestine were higher than those in the brain, muscle and liver, consistent with the fact that mammals do not absorb Gly and it is rapidly excreted (Solomon and Thompson, 2011; Van Eenennaam and Young, 2017). Although the levels of Gly in cattle, pigs and poultry are negligible, the study found that AMPA level was much higher than Gly, and the available data do not provide evidence that aquatic products containing AMPA do not pose a potential risk.

In general, the bioaccumulation of these chemicals is a result of the joint actions of multiple factors including the physicochemical properties of the chemicals involved, physiological deposition of organisms and the surrounding environmental conditions (Fantón et al., 2021). Pesticides have a high potential to accumulate in aquatic organisms if log Kow is greater than 3 and a soil half-life greater than 30 day (Fantón et al., 2021). Gly (log Kow = - 3.2, half-life: 15 days) is neither persistent nor lipophilic (IUPAC, 2020). The estimated AMPA log Kow (- 1.63) shows that this compound is considered to have a low bioaccumulation potential (IUPAC, 2020). However, AMPA is very persistent (half-life: 121 days). Thus, AMPA is easier to be bioaccumulated than the Gly. In addition, the tissues with a lower metabolic rate, such as muscle, have a lower bioaccumulation potential (Fantón et al., 2021). So, the organs with intense metabolic activities, like the intestine and liver, accumulated higher levels of these herbicides than the brain and muscle. This is consistent with our present results. Bioaccumulation also occurs through the dietary uptake. Gly is highly soluble in water phase and insoluble in most organics. It might not be easily absorbed by the gastrointestinal tract of animals and might quickly excreted by the intestines without metabolism, which leading to less accumulation in other organs. In our present work, the higher levels of these substances in the intestines may largely due to the enrichment along the food chain. Because, the Food and Agriculture Organization (FAO) reported that Gly and its major metabolite (AMPA), mainly as a result of accumulation of residues in the food chain (Bai et al., 2016).

Table 4
THQ and TTHQ values in muscle of grass carp, crayfish and crab of three typical aquaculture ponds from Honghu.

Groups	Muscle	THQ			TTHQ
		Gly	AMPA	Glu	
Children (3 ~ < 12 years old)	grass carp	0.0470	0.796	0.193	1.04 [a]
	crayfish	0.0350	0.110	0.123	0.268
	crab	0.0670	0.241	0.174	0.482
Young adults (12–45 years old)	grass carp	0.306	0.514	0.125	0.944
	crayfish	0.0230	0.071	0.795	0.889
	crab	0.0430	0.156	0.112	0.311
Middle-aged and elderly (>45 years old)	grass carp	0.320	0.538	0.131	0.989
	crayfish	0.0240	0.074	0.833	0.931
	crab	0.0450	0.163	0.117	0.326
	Mean value	0.101	0.296	0.289	0.687

[a] : TTHQ >1. TTHQ ≤1 indicates that the risk of chemicals entering the human body through edible meat is low, and the effect on the human is not obvious; TTHQ >1 indicates that the risk of chemicals entering the human body through edible meat is higher, which may affect human health, and the higher the value, the higher the risk.

3.4. Health risk assessment results through consumption

Gly was positively detected in 45 surface water samples with ECs ranging from 0.1 (LOD) to 100.09 μg/L, and posed low risks with RQs<0.04 (Figure S3), suggesting that the risk of the analytes for surface water safety is acceptable. Besides the same as parent, AMPA was detected at 0.1 (LOD) - 40.3 μg/L in 45 surface water samples with RQs<0.2 (Figure S3), implying acceptable risks to aquatic organisms. Also Glu was detected at 0.1 (LOD) - 6.13 μg/L in 45 surface water samples with the RQs were all below 0.05, indicating low risks to aquatic species (Figure S3). In general, Gly, AMPA and Glu in the three types of

ponds were acceptable and relatively low-risk, yet a few crab ponds (i.e. HX-5) still had a tendency to deteriorate. While several studies had shown that Gly-herbicides was not targeted for aquatic organisms, the risk of various Gly formulations to aquatic systems was still not negligible (EFSA, 2009; Solomon and Thompson, 2011; EFSA, 2015).

Aquatic products such as domestic fish, crayfish and crabs are important sources of animal protein nutrients in the human diet, yet the consumption of different people eating meat (especially muscle) containing Gly and its related substances is unknown. Table 4 showed that the TTHQ values from high to low were AMPA, Glu and Gly, and the TTHQ values from high to low in different aquatic products were fish, crayfish and crab. The TTHQ value in grass carp muscle consumed by children is more than 1 (which is largely related to the detected concentration of AMPA), that is, the risk of analytes entering into the human body through food consumption is higher, which may have a certain impact on children health. This may be related to the increasing production and use of herbicides in China and the continuous expansion of the planting area of genetically modified crops in the south (Benbrook, 2016; De Castilhos et al., 2020).

4. Conclusion

This study is, to our knowledge, the first dealing with the occurrence of Gly, AMPA and Glu in fish, crayfish and crab ponds around Honghu lake, and draw the following conclusions that (1) none of the water samples at each site exceeded 0.7 μg/L of Gly (the Chinese class III groundwater standard, GB/T 14848-2017), indicating that these ponds have not been seriously polluted; (2) the concentration of AMPA in sediment was much higher than that in surface water (Wilcoxon test, $P < 0.02$); (3) AMPA was more likely to accumulate in the intestine than Gly and Glu; (4) despite the THQ results show that the risk exposed to these contaminants is low, some residues are still detected in biological samples, especially the detection rates of Gly, AMPA and Glu in the intestines of grass carp were all more than 25%, suggesting that these substances may be enriched in the intestines and need to be further studied.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.118742.

References

Agostini, L.P., Dettogni, R.S., Dos Reis, R.S., Stur, E., Dos Santos, E.V.W., Ventorim, D.P., Garcia, F.M., Cardoso, R.C., Graceli, J.B., Louro, I.D., 2020. Effects of glyphosate exposure on human health: insights from epidemiological and in vitro studies. Sci. Total Environ. 705, 135808.

Aparicio, V.C., De Gerónimo, E., Marino, D., Primost, J., Carriquiriborde, P., Costa, J.L., 2013. Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins. Chemosphere 93 (9), 1866–1873.

Bai, S.H., Ogbourne, S.M., 2016. Glyphosate: environmental contamination, toxicity and potential risks to human health via food contamination. Environ. Sci. Pollut. Res. Int. 23 (19), 18988–19001.

Benbrook, C.M., 2016. Trends in glyphosate herbicide use in the United States and globally. Environ. Sci. Eur. 28 (1), 3.

Bento, C.P.M., van der Hoeven, S., Yang, X., Riksen, M.M.J.P.M., Mol, H.G.J., Ritsema, C. J., Geissen, V., 2019. Dynamics of glyphosate and AMPA in the soil surface layer of glyphosate-resistant crop cultivations in the loess Pampas of Argentina. Environ. Pollut. 244, 323–331.

Bonansea, R.I., Filippi, I., Wunderlin, D.A., Marino, D.J.G., Amé, M.V., 2017. The fate of Glyphosate and AMPA in a freshwater endorheic basin: an ecotoxicological risk assessment. Toxics 6 (1), 3–15.

Bonny, S., 2016. Genetically modified herbicide-tolerant crops, weeds, and herbicides: overview and impact. Environ. Manag. 57 (1), 31–48.

Chen, L., Tian, Z., Zou, K., 2020. Water quality evaluation based on the water quality index method in Honghu Lake: one of the largest shallow lakes in the Yangtze River Economic Zone. Water Sci. Technol. Water Supply 20 (6), 2145–2155.

De Castilhos, G.N., Zuanazzi, N.R., Fabrin, T.M.C., Oliveira, E.C., 2020. Glyphosate and its toxicology: a scientometric review. Sci. Total Environ. 733, 139359.

Demonte, L.D., Michlig, N., Gaggiotti, M., Adam, C.G., Beldoménico, H.R., Repetti, M.R., 2018. Determination of glyphosate, AMPA and glufosinate in dairy farm water from Argentina using a simplified UHPLC-MS/MS method. Sci. Total Environ. 645, 34–43.

EFSA, 2009. Conclusion regarding the peer review of the pesticide risk assessment of the active substance glufosinate. EFSA J. 3, 27r.

EFSA, 2015. Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate. EFSA J. 13.

Fantón, N., Cazenave, J., Michlig, M.P., Repetti, M.R., Rossi, A., 2021. Biomarkers of exposure and effect in the armoured catfish *Hoplosternum littorale* during a rice production cycle. Environ. Pollut. 287, 117356.

GB3838-2002, 2002. Environmental Quality Standards for Surface Water. China State Environmental Protection Administration, Beijing.

GB/T 14848-2017, 2017. Standard for groundwater quality. In: General Administration of Quality Supervision Inspection and Quarantine of the People's Republic of China (Beijing).

Geng, Y., Jiang, L., Zhang, D., Liu, B., Zhang, J., Cheng, H., Wang, L., Peng, Y., Wang, Y., Zhao, Y., Xu, Y., Liu, X., 2020. Glyphosate, aminomethylphosphonic acid, and glufosinate ammonium in agricultural groundwater and surface water in China from 2017 to 2018: occurrence, main drivers, and environmental risk assessment. Sci. Total Environ. 769, 144396.

Grandcoin, A., Piel, S., Baurès, E., 2017. AminoMethylPhosphonic acid (AMPA) in natural waters: its sources, behavior and environmental fate. Water Res. 117, 187–197.

Han, Y., Song, L., Zhao, P., Li, Y., Zou, N., Qin, Y., Li, X., Pan, C., 2016. Residue determination of glufosinate in plant origin foods using modified Quick Polar Pesticides (QuPPe) method and liquid chromatography coupled with tandem mass spectrometry. Food Chem. 197 (Pt A), 730–736.

HJ 1071-2019, 2019. Water quality-Determination of glyphosate-High performance liquid chromatography. In: Ministry of Ecology and Environment of the People's Republic of China (Beijing, China).

HJ T91-2002, 2003. Technical Specification for Surface Water and Sewage Monitoring. China Environmental Monitoring General Station, Beijing, China.

HJ 494-2009, 2009. Water quality-Guidance on sampling techniques. In: Ministry of Ecology and Environment of the People's Republic of China (Beijing, China).

Imfeld, G., Lefrancq, M., Maillard, E., Payraudeau, S., 2013. Transport and attenuation of dissolved glyphosate and AMPA in a stormwater wetland. Chemosphere 90 (4), 1333–1339.

Islas, G., Rodriguez, J.A., Mendoza-Huizar, L.H., Pérez-Moreno, F., Carrillo, E.G., 2014. Determination of glyphosate and aminomethylphosphonic acid in soils by HPLC with pre-column derivatization using 1,2-naphthoquinone-4-sulfonate. J. Liq. Chromatogr. Relat. Technol. 37 (9), 1298–1309.

IUPAC, 2020. Pesticide Properties Database. Agric. Environ. Res. Unit (AERU), Univ. Hertfordsh.

Lupi, L., Bedmar, F., Puricelli, M., Marino, D., Aparicio, V.C., Wunderlin, Daniel, Miglioranza, K.S.B., 2019. Glyphosate runoff and its occurrence in rainwater and subsurface soil in the nearby area of agricultural fields in Argentina. Chemosphere 225, 906–914.

Myers, J.P., Antoniou, M.N., Blumberg, B., et al., 2016. Concerns over use of glyphosate-based herbicides and risks associated with exposures: a consensus statement. Environ. Health 15 (1), 1–13.

Richards, B.K., Pacenka, S., Meyer, M.T., et al., 2018. Antecedent and post-application rain events trigger Glyphosate transport from runoff-prone soils. Environ. Sci. Technol. Lett. 5 (5), 249–254.
Silva, V., Montanarella, L., Jones, A., Fernández-Ugalde, O., Mol, H.G.J., Ritsema, C.J., Geissen, V., 2018. Distribution of glyphosate and aminomethylphosphonic acid (AMPA) in agricultural topsoils of the European Union. Sci. Total Environ. 621, 1352–1359.
Smedbol, E., Gomes, M.P., Paquet, S., Labrecque, M., Lepage, L., Lucotte, M., Juneau, P., 2018. Effects of low concentrations of glyphosate-based herbicide factor 540® on an agricultural stream freshwater phytoplankton community. Chemosphere 192, 133–141.
Solomon, K.R., Thompson, D.G., 2011. Ecological risk assessment for aquatic organisms from over-water uses of glyphosate. J. Toxicol. Environ. Health B. 6 (3), 289–294.
Tadesse, A.W., Gereslassie, T., Xu, Q., Tang, X., Wang, J., 2018. Concentrations, distribution, sources and ecological risk assessment of trace elements in soils from Wuhan, Central China. Int. J. Environ. Res. Publ. Health 15 (12), 2873.
Takano, H.K., Dayan, F.E., 2020. Glufosinate-ammonium: a review of the current state of knowledge. Pest Manag. Sci. 76 (12), 3911–3925.
Tzanetou, E., Karasali, H., 2020. Glyphosate Residues in Soil and Air: an Integrated Review.
Van Bruggen, A.H.C., He, M.M., Shin, K., Mai, V., Jeong, K.C., Finckh, M.R., Morris Jr., J., 2018. Environmental and health effects of the herbicide glyphosate. Sci. Total Environ. 616, 255–268.
Van Eenennaam, A.L., Young, A.E., 2017. Detection of dietary DNA, protein, and glyphosate in meat, milk, and eggs. J. Anim. Sci. 95 (7), 3247–3269.
Wang, Z., Du, Y., Yang, C., Liu, X., Zhang, J., Li, E., Zhang, Q., Wang, X., 2017. Occurrence and ecological hazard assessment of selected antibiotics in the surface waters in and around Lake Honghu, China. Sci. Total Environ. 609, 1423–1432.
Zhang, T., Ban, X., Wang, X., Cai, X., Li, E., Wang, Z., Yang, C., Zhang, Q., Lu, X., 2017. Analysis of nutrient transport and ecological response in Honghu Lake, China by using a mathematical model. Sci. Total Environ. 575, 418–428.
Zhu, G., Noman, M.A., Narale, D.D., Feng, W., Pujari, L., Sun, J., 2020. Evaluation of ecosystem health and potential human health hazards in the Hangzhou Bay and Qiantang Estuary region through multiple assessment approaches. Environ. Pollut. 264, 114791.