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Glyphosate-Based Herbicides in Aquaculture: An Overview of Aquatic Food Safety Risk Assessment

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Abstract

Aquaculture production has been steadily increasing worldwide due to the growing human population. This growth has resulted in higher consumption of aquatic food products. However, there are concerns about the food safety of aquatic food products due to the increased use of Glyphosate-Based Herbicides (GBHs) in aquaculture applications. This overview examines the complex relationship between aquaculture, GBHs and the associated risks arising from aquaculture. Providing an informative understanding of the research area, an approach to prospective research offers insight into aquatic food safety and risk management strategies. Our goal is to benefit both the aquaculture industry and consumers by emphasizing the importance of ongoing research in ensuring the aquatic food safety and sustainability of aquaculture practices.

Keywords: Glyphosate exposure; Human health; Risk management; Aquatic toxicology

Introduction

Although aquaculture is the fastest-growing food production sector with increasing food demand on a global scale [1-5] aquatic food products have been characterized as a sensitive food due to its suspicions effects on human health [6-9]. Therefore, it is included in the discussion of aquatic food safety planning and its future [10]. Specifically, residues of the common use of harmful substances such as Glyphosate-Based Herbicides (GBHs) in aquaculture, have emerged as a major source of risk to the safety threat of aquatic food products, raising consumer concerns with their worldwide use increasing 100-fold since 1970 [11-15]. Aquaculture holds significant potential due to Turkey convenient geographic position and abundant water resources, making it a key contributor to the production of aquatic food products. Over the years, there has been a steady increase in the quantity of aquatic food derived from aquaculture (Figure 1) [16].

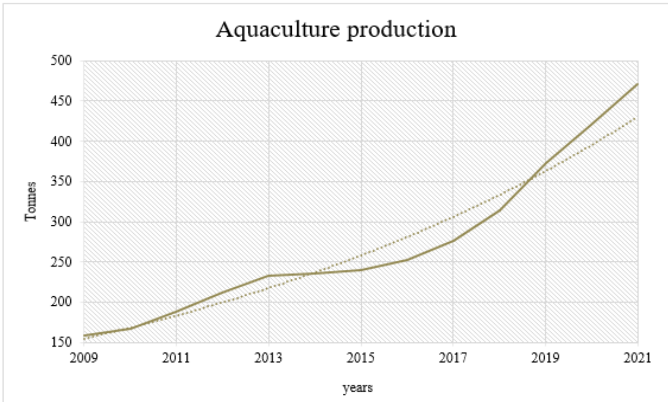

Figure 1: Graph of aquaculture production in Turkey.

The newest data in 2021 show that Turkey produced a remarkable total of 799,851 tons of aquatic food products, with 471,686 tons originating from aquaculture production, while 328,165 tons were obtained through fishing activities. This continuous growth in aquaculture production, showcasing a substantial 60% increase.

It is noteworthy that the per capita consumption of aquatic food products in Turkey ranges between 5.5 and 6.8 kilograms per year. As the aquaculture industry in Turkey continues to experience annual growth, it is expected that the use of glyphosate in aquaculture will also increase with concerning the potential exposure of aquaculture in Turkey to glyphosate. Glyphosate can enter direct application in aquaculture ponds, or contamination of water sources. Once introduced into the water, glyphosate can have harmful effects on both aquatic organisms and ecosystems. Therefore, to ensure the aquatic food safety of Turkey's aquaculture industry, it is important to address the potential risks associated with glyphosate exposure [3].

Therefore, this overview aims to investigate the complex interaction between aquaculture, glyphosate-based herbicides, and the associated risks on aquatic food products in Turkey. Presenting in this overview a suggested study for the future, we expect to capture the substance of the research, generate interest among readers and contribute to future research and valuable information on food safety and risk management strategies in order to benefit both the aquaculture industry and consumers [4-9].

Glyphosate-based herbicides

Glyphosate (Gly) one of the organophosphorus compounds is converted into microbial Aminomethylphosphonic Acid (AMPA) in the environment [17,18]. Glufosinate-ammonium (Glu) is the second most used organophosphorus compounds after Gly (Figure 2). Although these analytes are known to affect human health by being involved in the food chain [19-23], they are still widely used for weed control and algae removal in aquaculture ponds [24].

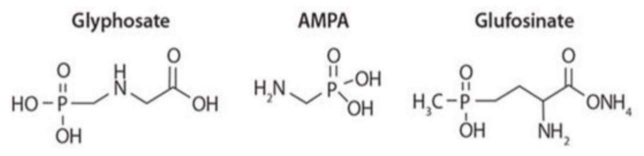

Figure 2: Chemical structures of glyphosate, AMPA and glufosinate.

Moreover, these analytes also contaminate freshwater aquatic food products since they can reach freshwater sources through rain, underwater sources, and agricultural activities near freshwater sources [25-30].

Applications of glyphosate in aquaculture

An aquatic formulation (Rodeo®) of glyphosate is used to treat aquatic weeds in waterbodies and drainage canals. Because of its extended use, glyphosate can run off or be sprayed directly into waterbodies, and chronically expose aquatic wildlife, including weed control, algae management, pond preparation, disease prevention, waterbody management, and habitat restoration [31]. It is employed to manage and eliminate aquatic weeds, ensuring optimal growing conditions for aquatic organisms. Glyphosate effectively controls algae blooms, maintains a balanced environment, and improves water quality [32].

It aids in clearing vegetation and creating a favourable environment for aquatic species prior to stocking fish. It also facilitates waterbody management and promotes habitat restoration by removing invasive plant species [33-35]. However, contamination of water resources with glyphosate residues can have significant consequences. The presence of glyphosate residues in water can disrupt the balance of aquatic ecosystems, affecting the well-being of various organisms and ultimately impacting the availability of aquatic food sources [36]. This includes careful application techniques, adherence to residue limits, monitoring of water quality parameters, and considering alternative methods for weed control. Regular assessment of the environmental impacts of glyphosate in aquaculture is essential to ensure long-term sustainability.

Ensuring aquatic food safety

Glyphosate has a significant increase in global usage, with estimates suggesting that it will reach 1 million tons in the coming years [37]. Glyphosate residue levels, measured as Maximum Residue Limits (MRLs) in food, vary among different standards, including those set by FAO/WHO, the European Commission, and the US EPA. Notably, the impact of glyphosate on rice appears to be minimal compared to other crops due to the high-water levels in rice fields during the reproductive stage, which suppress weed growth. However, glyphosate usage can still decrease crop yields and lead to contamination during harvesting and processing.

As a result, residues of glyphosate can be found in grains and legumes after processing, entering the food chain [38]. Additionally, trace amounts of glyphosate and its residues have been detected in various food products such as fruits, honey, vegetables, cereals, legumes, and manufactured goods [39]. Given the potential risks to public health, Maximum Residue Limits (MRLs) for glyphosate residues in food products have been established in the food codex [39,40]. However, limited data is available regarding glyphosate residue limits in aquaculture worldwide [41-44].

Additionally, it is important to consider the maximum residue limits of glyphosate in foods according to the European Food Safety Authority (EFSA) and Turkish food codex maximum residue limits of herbicides regulation. Despite its extensive use, regulatory agencies such as the US EPA and the European Food Safety Authority (EFSA) consider glyphosate as unlikely to be carcinogenic to humans. The EFSA has set the Acceptable Daily Intake (ADI) of glyphosate at 0.5 mg/kg/d. However, the specific maximum residue limit for glyphosate in aquatic foods is not provided in the regulations of both the European Food Safety Authority (EFSA) and the Turkish Food Codex.

Literature Review

An approach to prospective research

Investigating the spatial and seasonal distributions of Gly, AMPA and Glu in fish farms will provide an opportunity to assess the potential risk to human health through food consumption by contributing to the missing data in the literature on the glyphosate limit in aquaculture food safety, as well as identifying the source affecting food safety. Moreover, the results of the project are likely to allow for larger long-term projects at the international level.

Research question 1: Is there Gly, AMPA and Glu formation in Fish farms?/What is its seasonal and spatial distribution?

Research question 2: I s there a potential non-carcinogenic risk to human health?/(THQ>1)

The first research question is to understand the source of the main problem in which space (cage/pond) and seasonal distribution (in which seasons and months) in aquaculture farms. For example: Is the majority of Gly, AMPA and Glu formation from groundwater or from herbicide applications in ponds? The second research question is more focused on determining its impact on food safety.

Based on the findings from the first research question, the next step will be to determine the probability of causing any adverse health effects by calculating the Target Hazard Coefficient (THQ>1) with the data of Gly, AMPA and Glu concentrations. Therefore, this research question, based on the information gained in the research, contributes to the missing information in the literature and the regulation, in which limits (mg/kg) and in which age group (3<12/12-45/>45) the spatial and temporal food safety of fish is determined may pose a risk to human health.

Experimental section

In general, the practical work can be divided into six Work Packages (WP) and workflow chart show in Figure 3.

WP 1: Sampling of water and fish will be collected according to the method described by Yan et al.

WP 2: Adaptation of the extraction process, according to the method described by Chiesa et al. For water samples will be carried out according to the method described by Lin et al. The resulting extracts will be analysed by LC-MS/MS applying the compound-specific mass transitions as published by [45].

WP 3: Estimation of the recovery rate will be calculated based on existing methods [46-48], and will optimize the procedure for the determination of Gly, AMPA and Glu in water 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 (LC-MS/MS). For quantification, a matrix-matched calibration will be utilised. A Glyphosate free matrix extract is produced and increasing amounts of Glyphosate are added to the extract prior to analysis. Recovery rates will be derived for the spiked samples with recovery rates of 70% to 110% being considered acceptable.

WP 4: Evaluation of the detection limit and working range, In WP1 the most suitable sample clean-up strategy will be identified, and state-of-the-art LC-MS/MS instrumentation will be available for analysis. Consequently, a highly sensitive overall analytical methodology can be expected. To verify the performance of the method, the Limit Of Detection (LOD) and linear detection range will be elucidated to further characterise the method's performance. Determination of LOD will be conducted using ten replicate blank samples spiked at a low level according to Wenzl et al. The standard deviation of the spiked samples will be compared to the standard deviation of unspiked blanks. As soon as the signal for a sample is significantly different from blank, the LOD is reached. Additionally, the dynamic range of the method will be elucidated in order to test the reliability of the method for a wide range of potentially highly contaminated samples.

WP 5: Screening of a collected water and fish samples, after adaptation and characterisation of the analytical method, it will be applied for the analysis of samples for four seasons in fishpond and cage farms located in Turkey. samples will be obtained from determined 10 stations.

WP 6: Health risk assessment of fish consumption for consumers, the Target Hazard Quotient (THQ) method will be used to evaluate dietary exposure risk from fish Gly, AMPA and Glu in three age groups of human consumers. It is divided into three groups according to Zhu et al., and Yan et al. children (3～< 12 years old), young adults (12 years-45 years old) and middle-aged and elderly (>45 years old)."Edible Daily Intake (EDI), Target Hazard Coefficient (THQ), and "Hazard Index (HI)" will be calculated to assess the health risks of Gly, AMPA and Glu in fish in adult humans. The EDI value (EDI=mg/kg bodyweight/day) of Edible Daily Intake (EDI) glyphosate for children, young adults and middle-aged and elderly is calculated according to the following formula [49]:

$$EDI = C \times D\ food\ intake / BW \qquad (1)$$

The EDI values will be calculated in this study were compared with the oral reference dose (RfDo) values recommended by the USEPA. The Target Hazard Coefficient (THQ) is an estimate of the level of risk (non-carcinogenic) based on pollutant exposure. The method used to determine the THQ of each heavy metal was calculated with the following formula [50]:

$$THQ = (EF \times ED \times FIR \times C / RfDo \times BW \times AT) \times 10^{-3} \qquad (2)$$

Where,

EF: Frequency of exposure (365 days/year),

ED: Exposure time (average life expectancy: 30 years),

FIR: Food intake rate (20 g/day),

C: Average concentration of Gly, AMPA, and Glu in fish muscle tissue (mg/kg),

RfDo: Oral reference dose (mg/kg/day), 0.100 mg/(kg d),

AT: Average duration of exposure for non-carcinogenic (365 days/year × number of years of exposure 30),

D food intake: Daily average fish consumption (g/person/day) (16.71 gr/person/day in Turkey) (TURKSTAT, 2019),

BW: Average body weight.

If THQ values exceed 1, there may be potential for adverse non-carcinogenic health effects to occur. If the values are less than 1, non-carcinogenic health effects are not expected [51,52].

Hazard Index (HI) HI is the sum of THQ for all observed glyphosate (hazardous if HI>1) [53].

$$HI = \sum_{i=1}^{n} THQ$$

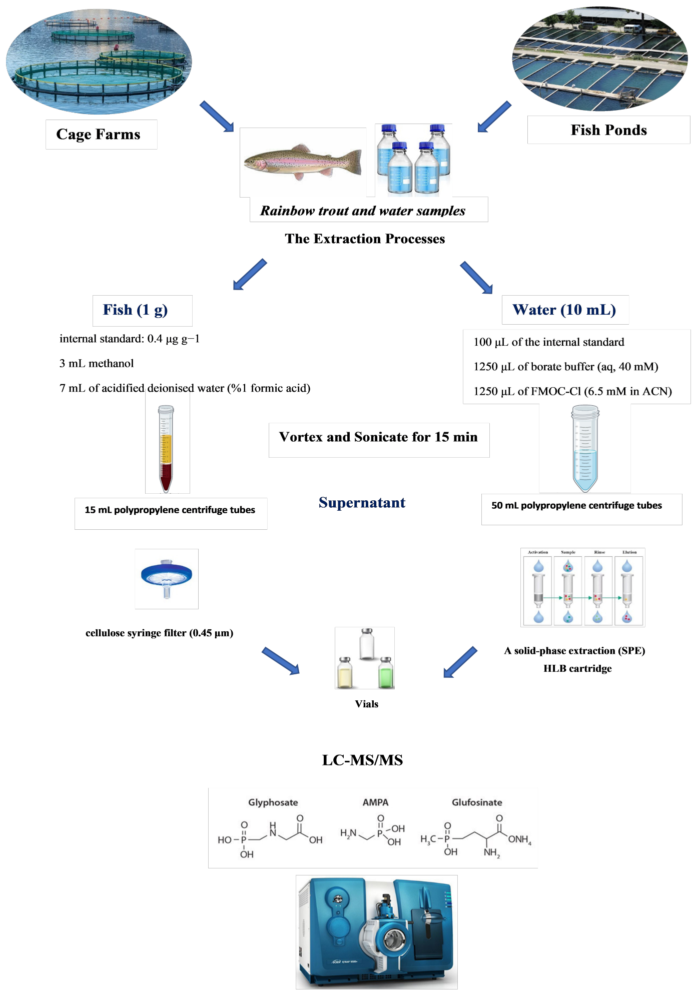

Figure 3: Workflow chart.

Discussion

Aquatic food safety is a crucial aspect of human health, and several recent studies show the potential risks associated with herbicide contamination in aquatic environments and its impact on human health.

Investigated the presence of glyphosate and glufosinate-ammonium in aquaculture ponds and assessed the associated health risks [21]. Their findings revealed the occurrence of these herbicides in the samples collected, indicating the potential for herbicide contamination in aquaculture systems. The study emphasized the need for effective monitoring and management strategies to ensure the safety of aquatic products and protect human health. The health risk assessment conducted by the researchers indicated that the estimated daily intake of glyphosate and glufosinate-ammonium through the consumption of aquatic products was generally within acceptable limits for most individuals.

Another study by Thanomsit et al. examined the fate of glyphosate in aquatic environments, as well as its adverse effects and toxicity on aquatic organisms [54]. The research provided valuable insights into glyphosate's behavior, including its persistence, degradation, and potential impacts on aquatic ecosystems. Understanding these factors is crucial for assessing the risks associated with glyphosate exposure and implementing appropriate mitigation measures to safeguard aquatic food safety and human health.

Lares et al. conducted a synthetic review focusing on the effects of glyphosate on aquatic organism, an important group of aquatic organisms [55]. The study synthesized existing research and highlighted the potential impacts of glyphosate exposure on cladocera populations and their ecological roles in aquatic ecosystems. The findings underscored the importance of considering the effects of glyphosate on non-target organisms and the potential consequences for overall aquatic ecosystem health.

In addition to herbicides' effects on aquatic organisms, the study by Biandolino et al. investigated the potential influence of glyphosate and temperature on the nutritional lipid quality of the mussel species *Mytilus galloprovincialis* [56]. By examining the interplay between glyphosate exposure, temperature variations, and lipid quality, the researchers provided valuable insights into the potential implications for human consumption of aquatic food products. Understanding the influence of environmental factors on the nutritional composition of aquatic organisms is essential for assessing their overall quality and potential impacts on human health [57].

Collectively, these studies underscore the importance of monitoring herbicide residues in aquaculture systems, evaluating their potential health risks, and considering the effects of herbicides on aquatic organisms and the nutritional quality of aquatic food products. Such insights contribute to the development of appropriate regulations, mitigation strategies, and monitoring programs to ensure the safety and quality of aquatic food products for human consumption and protect human health. Further research in this area is crucial for continually improving our understanding of the complex interactions between herbicides, aquatic ecosystems, and human health.

Conclusion

This overview examines the complex relationship between glyphosate-based herbicides and the risks associated with aquaculture in Turkey. This overview highlighted the ongoing research in this field and emphasizes the continuous efforts required to assess and manage the potential risks associated with glyphosate in aquaculture.

We reviewed the potential risks of glyphosate in aquaculture, underlining the importance of understanding its implications for both the industry and consumers. Our emphasis on food safety measures and risk management strategies aims to contribute to effective measures that protect the aquaculture sector and the consumer of aquatic food products in Turkey. The existing lack of clarity surrounding glyphosate limits in aquatic foods presents challenges in terms of food safety and public health. This knowledge gap highlights the necessity for further research and data collection to ascertain the extent of glyphosate contamination in aquatic food products and its potential consequences for human health.

Finally, we expect that this overview will act as a catalyst to encourage collaboration among researchers and facilitate discussions. Efforts should be made for the safety and sustainability of aquaculture practices in Turkey, while ensuring the quality and integrity of aquaculture for human health.

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.

Data Availability Statement

No data were used to support this review.

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