Glyphosate in Food

Subjects: Public, Environmental & Occupational Health
Contributor: André Pereira

Glyphosate is a systemic, broad-spectrum and post-emergent herbicide. The use of glyphosate has grown in the last decades, and it is currently the most used herbicide worldwide. The rise of glyphosate consumption over the years also brought an increased concern about its possible toxicity and consequences for human health.

: glyphosate   environmental contaminant   food safety

1. Introduction

Glyphosate is an organophosphorus herbicide [1]. The herbicide function of glyphosate was discovered in 1970 by John Franz, a chemist from Monsanto® company (St. Louis, MO, USA), which produced several years later the first glyphosate-based herbicide (GBH), Roundup® [2]. Nowadays, there are hundreds of GBHs commercialized under different brands in more than 100 countries across the world [3]. Currently, glyphosate is the most used herbicide worldwide [4].

The exponential rise in glyphosate use over the years also brought an increased concern about its possible toxicity and the eventual consequences to human health. Therefore, the number of studies about glyphosate effects on the human health increased in recent years [5]. Glyphosate is applied intensively in crop fields, and its residues are frequently detected in the environment, particularly in plants, soil, water, food products and also in human urine [6]. Consequently, concerns increased within the scientific community about the potential impact that this herbicide and its metabolites can have in the environment and humans. Hence, the commercialization of GBHs is highly regulated, and there are maximum residue limits (MRLs) established for glyphosate residues in foods.

2. Physical and Chemical Properties

Glyphosate is a herbicide that belongs to the family of organophosphorus compounds [1]. Currently, glyphosate is widely applied in fields due to its herbicidal properties. However, those properties were not discovered when glyphosate was synthetized for the first time in 1950, being only patented several decades later [7].

Regarding its chemical structure (**Figure 1**), glyphosate is a zwiterrion [8] with phosphonate, carboxylate and amine functions. The zwitterionic structure of glyphosate affords the ability to chelate with trivalent and quadrivalent metals [9][10][11].

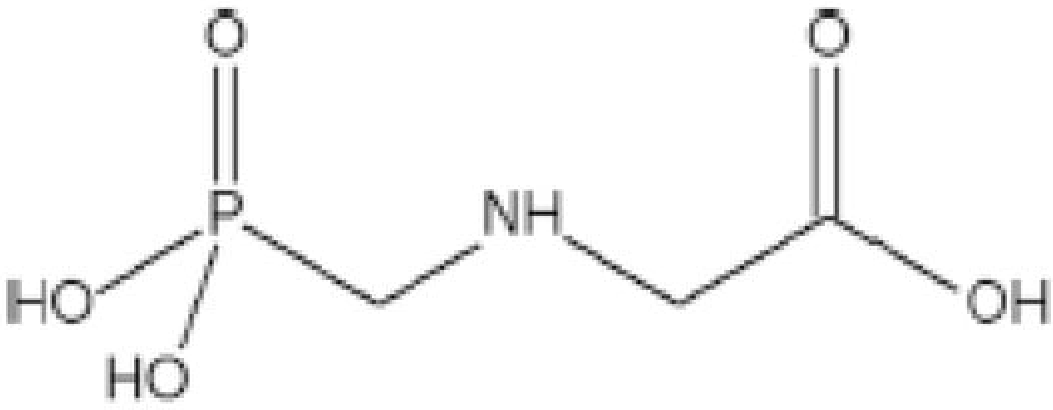

Figure 1. Glyphosate chemical structure.

The covalent bond between the carbon and the phosphorus atoms is characteristic of these organophosphate compounds and provides glyphosate with several chemical and physical specificities, such as high adsorption, high water solubility and compatibility with other chemical substances [9].

Glyphosate is a molecule with high polarity, contributing to its high solubility in water and insolubility in organic solvents [3]. The particular physical and chemical properties of glyphosate, such as the absence of a chromophore or a fluorophore group, the non-existence of absorption in the ultraviolet region, its low ionization, low volatility and high hydrophilicity [12], demand the use of complex analytical methodologies for the detection and quantification of this herbicide in order to achieve the sensitivity and accuracy requested [6][8][13][14].

3. Occurrence in Food

As already mentioned, the increase in glyphosate consumption in recent decades has raised concerns by the scientific community about the impact it can have on human health. Thus, studies have been conducted in several countries to assess human exposure to glyphosate through the analysis of different food categories.

3.1. Olive Oil

Since Spain is one of the world's largest producers of olives and olive oil, a study was carried out in Almería, southern Spain, to evaluate the glyphosate existing in different types of olive oil and oils, certifying that the levels of glyphosate complied with the MRL of 100 μg/kg defined by the EC [15]. In a total of 25 samples analyzed, no glyphosate residues were detected in any of the samples (the analytical method used had a LOD of 3.3 μg/kg) [16].

3.2. Honey

The application of glyphosate in agricultural fields can lead to the deposition of residues of this herbicide in the environment, particularly in flowers. In addition to bees being pollinators, insects are also honey producers through the collection of nectar from flowers. Thus, several studies were conducted to evaluate glyphosate in honey samples.

Studies in Canada [17] and Switzerland [18] detected the presence of glyphosate in almost all samples, but at values below the MRL of 50 µg/kg [15]. In the Estonian study, although glyphosate was detected in a small number of samples, there were two samples that contained glyphosate levels above the MRL up to 62 µg/kg [19]. In the USA, residues were detected in about 30% of the samples, more than half at levels that were much higher than the MRL, including a sample that was seven times higher than allowed (342 µg/kg) [20]. On the other hand, a multinational study conducted by EFSA revealed that in 186 honey samples, 24 contained glyphosate, 8 of which were higher than legally permitted [21].

3.3. Fruits and Nuts

Several studies have been conducted to evaluate glyphosate in fruit and nut samples.

In France, six samples were analyzed and no glyphosate residues were detected in any of the samples [22]. Another study, conducted in China, detected the presence of glyphosate in a pear sample, but in values below the MRL of 100 µg/kg [15][23]. In a Swiss study, all the fruit juice samples analyzed contained glyphosate up to 3.5 µg/kg, but no sample exceeded the permitted MRL [18].

A multinational study conducted by EFSA, in which a large number of samples of different types of fruit were analyzed, revealed the presence of glyphosate in a small number of samples, with only one pear sample having values higher than legally allowed [21].

In Portugal, DGAV is the authority responsible for controlling pesticide residues in food [24]. The last published report, referring to the year 2017, reveals that in all the products of vegetable origin tested, no glyphosate residues were detected and, consequently, the glyphosate MRL was not exceeded [25].

3.4. Cereals and Cereal Products

The application of glyphosate in agricultural fields where cereals are grown can lead to the accumulation of residues of this herbicide in the soil and cereals. In this way, several studies have determined the levels of glyphosate in several types of cereals as well as in cereal-based foods.

A study conducted in Switzerland detected the presence of glyphosate residues in several samples, with about 90% of wheat samples, 80% of breakfast cereal samples and 70% of bread samples having glyphosate residues. Some samples contained glyphosate values above the MRL, namely one sample of bread with values four times higher than legally allowed and three samples of breakfast cereals with values up to 29 times higher than the MRL of 10 µg/kg defined by the EC [18][15]. Samples of breakfast cereals analyzed in a French study also contained higher levels than legally allowed, up to 34 µg/kg [22].

Another study conducted in Italy has detected levels of glyphosate about 25 times higher than the legally allowed value of 10,000 µg/kg in one wheat seed sample [15][26]. In a multinational study conducted by EFSA in 2017, several samples of the main cereals grown in Europe were analyzed. The results revealed that there were glyphosate residues in a low percentage of samples, with six samples of rye, four of pseudo cereals and one of rice exhibiting levels (243,000 µg/kg) that exceeded the MRL [21].

3.5. Vegetables

In recent years, several countries have conducted studies to evaluate glyphosate levels in vegetables and pulses.

Studies from France [22] and China [23] have not detected the presence of glyphosate in several vegetables. In Ghana, 68 yam samples were analyzed, and 14 presented glyphosate residues, but at levels below the LOQ [13]. In the Swiss study, one third of the analyzed samples contained glyphosate residues, but below the MRLs of 100 µg/kg and 500 µg/kg [15] defined for vegetables and potatoes, respectively, at mean levels of 1.3 µg/kg [18].

On the other hand, another study carried out in Italy [27], as well as a multinational study carried out by EFSA [21], detected glyphosate residues above the legally permitted value in two canned vegetable samples and one asparagus sample, respectively.

A study in Switzerland [18] detected the presence of glyphosate residues in about half of the analyzed legume samples, but none of the samples exceeded the MRL of 10,000 µg/kg set by the EC [15]. A multinational study conducted by EFSA in 2017 [21] in samples of dried lentils, beans and soybeans also detected the presence of glyphosate in several samples, but with values below the legal limit.

3.6. Animal-Derived Products

Due to the exponential increase in the use of glyphosate in agriculture in recent decades, a study carried out in Switzerland [18] aimed to detect and quantify existing glyphosate residues in different samples of animal products.

The results, ranging between <1 and 4.9 µg/kg, showed the presence of glyphosate residues in 23.1% of the meat and fish samples, but none showed values above the MRL of 50 µg/kg established [15].

3.7. Baby Food

Baby food has also been analyzed in several studies. Studies in France [22] and Switzerland [18] did not detect the presence of glyphosate, while an Italian study detected the presence of glyphosate in 2 samples, but none had levels above the MRL of 10 µg/kg defined [21].

3.8. Water

In recent years, studies have been conducted to assess the presence of glyphosate in water.

A study in Switzerland did not detect the presence of glyphosate in the surface water samples analyzed [28]. Another study, conducted in Mexico, detected the presence of glyphosate in practically all of the water samples analyzed, all of which had values (up to 0.78 μg/L) much higher than those legally allowed [29]. A German study also revealed the presence of glyphosate in 23 of the 39 samples analyzed. Of these, 10 contained glyphosate residues, in mean levels of 0.12 μg/L, above the MRL (0.1 μg/L) [30][31].

Another study conducted in the United States, involving several types of water samples, detected the presence of glyphosate in 1470 of the 3732 samples analyzed. One sample had values about 5000 times higher than the legally allowed value [32]. In a European study, thousands of surface water and groundwater samples from several countries were analyzed. Glyphosate residues were detected in about 30% of surface water samples. In 80% of these samples, the values were much higher than the MRL, including a sample that was 500 times higher than allowed. Only 1% of the groundwater samples contained glyphosate, of which more than half had values that exceeded the MRL, including a sample with 24 μg/L, a value 240 times above the limit [33].

3.9. Alcoholic Beverages

Although the EC does not define MRLs in wine and beer [15], studies have been conducted to evaluate glyphosate in these alcoholic beverages.

A study conducted in Switzerland revealed the presence of glyphosate residues in all the wine samples analyzed, up to a maximum of 18.9 μg/L, and the presence of glyphosate in 2 of the 15 beer samples [18]. Although there is no MRL in wine, for data analysis purposes, researchers take as reference the MRL for water, which is 0.1 μg/L, and verify that all samples detected exceeded this value [31].

Another study conducted in Latvia analyzed the levels of glyphosate in 100 beer samples. The results revealed the presence of residues of this herbicide in 92 samples, with one sample showing glyphosate levels of 150 μg/L. Taking into account the MRL of the water, we found that all positive samples significantly exceeded this value [34].

Given the results of the studies, it is concluded that it is urgent to establish an MRL for alcoholic beverages.

In general, glyphosate residues are often detected in various food groups. Although, in the vast majority of cases, the values detected are within the legally allowed values, there are food groups where the MRLs were exceeded. In descending order of frequency of detection, these are water, honey, cereals and cereal products and vegetables. Regarding the values detected, the food group that generates the greatest concern is water, since it is the one with higher values in comparison to the MRL, and several samples are up to 5000 times higher than allowed.

References

1. Comission Regulation (EU) 2017/269 of 16 February 2017; Official Journal of the European Union: Brussels, Belgium, 2017; L. 40/4.
2. Davoren, M.J.; Schiestl, R.H. Glyphosate-based herbicides and cancer risk: A post-IARC decision review of potential mechanisms, policy and avenues of research. Carcinogenesis 2018, 39, 1207–1215.
3. Williams, G.M.; Kroes, R.; Munro, I.C. Safety Evaluation and Risk Assessment of the Herbicide Roundup and Its Active Ingredient, Glyphosate, for Humans. Regul. Toxicol. Pharmacol. 2000, 31, 117–165.
4. Benbrook, C.M. Trends in glyphosate herbicide use in the United States and globally. Environ. Sci. Eur. 2016, 28, 1–15.
5. Tarazona, J.V.; Court-Marques, D.; Tiramani, M.; Reich, H.; Pfeil, R.; Istace, F.; Crivellente, F. Glyphosate toxicity and carcinogenicity: A review of the scientific basis of the European Union assessment and its differences with IARC. Arch. Toxicol. 2017, 91, 2723–2743.
6. Chiesa, L.M.; Nobile, M.; Panseri, S.; Arioli, F. Detection of glyphosate and its metabolites in food of animal origin based on ion-chromatography-high resolution mass spectrometry (IC-HRMS). Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 2019, 36, 592–600.
7. Bai, S.H.; Ogbourne, S.M. Glyphosate: Environmental contamination, toxicity and potential risks to human health via food contamination. Environ. Sci. Pollut. Res. 2016, 23, 18988–19001.
8. Compound Summary-Glyphosate. Available online: https://pubchem.ncbi.nlm.nih.gov/compound/Glyphosate (accessed on 29 October 2021).
9. Villarreal-Chiu, J.F.; Acosta-Cortés, A.G.; Kumar, S.; Kaushik, G.; Singh, R. Green Technologies and Environmental Sustainability; Singh, R., Kumar, S., Eds.; Springer International Publishing: Cham, Switzerland, 2017; ISBN 978-3-319-50653-1.
10. Oliveira, P.C.; Maximiano, E.M.; Oliveira, P.A.; Camargo, J.S.; Fiorucci, A.R.; Arruda, G.J. Direct electrochemical detection of glyphosate at carbon paste electrode and its determination in samples of milk, orange juice, and agricultural formulation. J. Environ. Sci. Health Part B Pestic. Food Contam. Agric. Wastes 2018, 53, 817–823.
11. Zhan, H.; Feng, Y.; Fan, X.; Chen, S. Recent advances in glyphosate biodegradation. Appl. Microbiol. Biotechnol. 2018, 102, 5033–5043.
12. Simonetti, E.; Cartaud, G.; Quinn, R.M.; Marotti, I.; Dinelli, G. An interlaboratory comparative study on the quantitative determination of glyphosate at low levels in wheat flour. J. AOAC Int. 2015, 98, 1760–1768.
13. Wumbei, A.; Goeteyn, L.; Lopez, E.; Houbraken, M.; Spanoghe, P. Glyphosate in yam from Ghana. Food Addit. Contam. Part B Surveill. 2019, 12, 231–235.

14. EFSA. Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate. EFSA J. 2016, 13.
15. European Comission EU. Pesticides Database-Pesticides Residues and Maximum Residue Levels. Available online: https://eurlex.europa.eu/legal.content/EN/ALL/?uri=CELEZ%3A32013R0293 (accessed on 25 August 2021).
16. Chiarello, M.; Jiménez-Medina, M.L.; Marín Saéz, J.; Moura, S.; Garrido Frenich, A.; Romero-González, R. Fast analysis of glufosinate, glyphosate and its main metabolite, aminomethylphosphonic acid, in edible oils, by liquid chromatographycoupled with electrospray tandem mass spectrometry. Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 2019, 36, 1376–1384.
17. Thompson, T.S.; van den Heever, J.P.; Limanowka, R.E. Determination of glyphosate, AMPA, and glufosinate in honey by online solid-phase extraction-liquid chromatography-tandem mass spectrometry. Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 2019, 36, 434–446.
18. Zoller, O.; Rhyn, P.; Rupp, H.; Zarn, J.A.; Geiser, C. Glyphosate residues in Swiss market foods: Monitoring and risk evaluation. Food Addit. Contam. Part B Surveill. 2018, 11, 83–91.
19. Karise, R.; Raimets, R.; Bartkevics, V.; Pugajeva, I.; Pihlik, P.; Keres, I.; Williams, I.H.; Viinalass, H.; Mänd, M. Are pesticide residues in honey related to oilseed rape treatments? Chemosphere 2017, 188, 389–396.
20. Berg, C.J.; Peter King, H.; Delenstarr, G.; Kumar, R.; Rubio, F.; Glaze, T. Glyphosate residue concentrations in honey attributed through geospatial analysis to proximity of large-scale agriculture and transfer off-site by bees. PLoS ONE 2018, 13, e0198876.
21. EFSA. The 2017 European Union report on pesticide residues in food. EFSA J. 2019, 17, e05743.
22. Liao, Y.; Berthion, J.M.; Colet, I.; Merlo, M.; Nougadère, A.; Hu, R. Validation and application of analytical method for glyphosate and glufosinate in foods by liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 2018, 1549, 31–38.
23. Chen, M.-X.; Cao, Z.-Y.; Jiang, Y.; Zhu, Z.-W. Direct determination of glyphosate and its major metabolite, aminomethylphosphonic acid, in fruits and vegetables by mixed-mode hydrophilic interaction/weak anion-exchange liquid chromatography coupled with electrospray tandem mass spectrometry. J. Chromatogr. A 2013, 1272, 90–99.
24. Autoridade de Segurança Alimentar. e Económica Sabe o que é o Glifosato. Available online: https://asae.gov.pt/ficheiros-externos-2016/sabe-o-que-e-o-glifosato-maio-aspx. (accessed on 30 July 2021).
25. Direção Geral de Alimentação e Veterinára. Controlo Nacional de Resíduos de Pesticidas em Produtos de Origem Vegetal no ano de 2017. Available online: https://www.dgav.pt/wp-

content/uploads/2021/03/Controlo-residuos-2017.pdf (accessed on 24 June 2021).

26. Gotti, R.; Fiori, J.; Bosi, S.; Dinelli, G. Field-amplified sample injection and sweeping micellar electrokinetic chromatography in analysis of glyphosate and aminomethylphosphonic acid in wheat. J. Chromatogr. A 2019, 1601, 357–364.
27. Savini, S.; Bandini, M.; Sannino, A. An Improved, Rapid, and Sensitive Ultra-High-Performance Liquid Chromatography-High-Resolution Orbitrap Mass Spectrometry Analysis for the Determination of Highly Polar Pesticides and Contaminants in Processed Fruits and Vegetables. J. Agric. Food Chem. 2019, 67, 2716–2722.
28. Gauch, R.; Leuenberger, U.; Müller, U. Bestimmung des Herbicids Glyphosat und dessen Hauptmetabolit Aminomethylphosphonsäure (AMPA) in Trinkwasser mit Hilfe der HPLC. Z. Lebensm. Unters. Forsch. 1989, 188, 36–38.
29. Rendón-Von Osten, J.; Dzul-Caamal, R. Glyphosate residues in groundwater, drinking water and urine of subsistence farmers from intensive agriculture localities: A survey in Hopelchén, Campeche, Mexico. Int. J. Environ. Res. Public Health 2017, 14, 595.
30. Skark, C.; Zullei-Seibert, N.; Schöttler, U.; Schlett, C. The occurrence of glyphosate in surface water. Int. J. Environ. Anal. Chem. 1998, 70, 93–104.
31. The Council of the European Union. Council Directive 98/83/EC of November 1998 on the Quality of Water Intended for Human Consumption. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31998L0083&from=EN (accessed on 6 August 2021).
32. Battaglin, W.A.; Meyer, M.T.; Kuivila, K.M.; Dietze, J.E. Glyphosate and its degradation product AMPA occur frequently and widely in U.S. soils, surface water, groundwater, and precipitation. J. Am. Water Resour. Assoc. 2014, 50, 275–290.
33. Horth, H.; Blackmore, K. Survey of Glyphosate and AMPA in Groundwaters and Surface Waters in Europe. Available online: http://www.egeis.org/cd-info/WRC-report-UC8073-02-December-2009-Glyphosate-monitoring-in-water.pdf (accessed on 7 August 2021).
34. Jansons, M.; Pugajeva, I.; Bartkevičs, V. Occurrence of glyphosate in beer from the Latvian market. Food Addit. Contam. Part A Chem. Anal. Control Expo. Risk Assess. 2018, 35, 1767–1775.