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Chapter

Glyphosate Residues in Soil and Air: An Integrated Review

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Abstract

Glyphosate [N-(phosphonomethyl) glycine] (GPS) is currently the most commonly applied herbicide worldwide. Given the widespread use of glyphosate, the investigation of the relationship between glyphosate and soil ecosystem is critical and has great significance for its valid application and environmental safety evaluation. However, although the occurrence of glyphosate residues in surface and groundwater is rather well documented, only few information are available for soils and even fewer for air. Due to this, the importance of developing methods that are effective and fast to determine and quantify glyphosate and its major degradation product, aminomethylphosphonic acid (AMPA), is emphasized. Based on its structure, the determination of this pesticide using a simple analytical method remains a challenge, a fact known as the "glyphosate paradox." In this chapter a critical review of the existing literature and data comparison studies regarding the occurrence and the development of analytical methods for the determination of pesticide glyphosate in soil and air is performed.

Keywords: glyphosate, AMPA, soil, air, extraction, analytical methods, quantification

1. Introduction

After World War II, the world was in the need to overcome food scarcity. Therefore, several pest and weed management techniques were adopted by farmers all over the world using various synthetic herbicides. The invention of glyphosate (GLY; N-(phosphonomethyl) glycine) was a big breakthrough in that era. GLY with CAS No. 1071-83-6 is a broad-spectrum, postemergent, nonselective, and synthetic universal herbicide, whose commercial formulations are referred to as glyphosate-based herbicides (GBHs) [1, 2]. Glyphosate was first synthesized in 1950 by Swiss chemist Henry Martin, who worked for the Swiss company Cilag. The work was never published. Its herbicidal activity was not discovered until GBHs were resynthesized and tested in 1970, being used for this purpose since 1974. It was the Monsanto Corporation in 1974 that introduced and made commercially available the herbicidal formulation Roundup containing GLY as active substance. Farmers quickly adopted glyphosate for agricultural weed control, gaining the potential to kill weeds without killing their crops. Indeed, glyphosate proved able to kill weeds without killing their crops, especially annual broadleaf weeds and grasses known to compete with commercial

crops grown around the globe by interfering with the synthesis of the aromatic amino acids phenylalanine, tyrosine, and tryptophan [3].

Since then, its use in agricultural and nonagricultural settings has steadily increased from a total of 0.6 Mg applied in 1974 to a total of 125.5 Mg applied in 2014, and it is currently the most widely used herbicide in the United States and throughout the world [4, 5]. Monsanto's last commercially relevant US patent expired in 2000. Nowadays, GLY formulations that are used as a broad-spectrum systemic herbicide have been widely applied in agronomic crops and orchards. Furthermore, GLY formulations are currently approved by regulatory bodies and marketed worldwide by many agrochemical companies, such as Bayer, Dow AgroSciences, and Monsanto, in different solution strengths and with various adjuvants.

GLY approval is renewed in the European Union (EU) on 16 December 2017, while its approval expires on 15 December 2022. Therefore, GLY can be used as an active substance in plant protection products (PPPs), until 15 December 2022. GLY has been thoroughly assessed, under an intense debate due to a concern about its effects on the environment and human health, by the Member States, the European Chemicals Agency (ECHA), and the European Food Safety Authority (EFSA) in recent years [6, 7]. An important prerequisite for GLY upcoming renewal as an ingredient in PPPs is that GLY should not adversely affect the environment and human and animal health as delineated by European regulation [8].

2. Glyphosate residues in soil

2.1 Environmental fate of glyphosate

2.1.1 Glyphosate in the soil

Given the widespread use of glyphosate, the investigation of the relationship between glyphosate and soil ecosystem is critical and has great significance for its valid application and environmental safety evaluation. Although herbicides containing glyphosate are not intentionally applied directly to the soil, they may contaminate soils in and around the treated areas, via spray drift during their application and after being washed off from leaf surfaces with rainfall.

The fate of glyphosate in soil is complex and attributed to mineralization, degradation, immobilization, and leaching. Several studies trying to identify and understand the mechanisms that control the fate of chemicals as a source of environmental contamination have been published in previous years, especially in soils and water. Some were conducted with the acid form of glyphosate and others with formulated products, since glyphosate is not introduced into the environment as pure active ingredients but as formulated products containing co-formulant chemicals (adjuvants) and other additives. In a recent review, Mesnage et al. presented an overview of the most common surfactants containing co-formulants in glyphosate-based herbicides and explained whether the presence of such surfactant (e.g., Triton CG-110) has the potential to affect adsorption, leaching, and mineralization of glyphosate in the soil [9].

The fate of glyphosate depends on soil composition, its physicochemical properties (texture, organic matter content, pH), its biological properties (microbial community, climatic conditions), the chemical properties of the specific pesticide, as well as the timing between precipitation and pesticide application [10–13]. A recent study by Muskus et al. showed that temperature, pH, and total organic carbon

(TOC) variations influenced the mineralization kinetics of glyphosate as well as the amount of extractable glyphosate and the extent of bio-NER formation over time in a German soil [14].

Glyphosate degrades at a relatively rapid rate in most soils, with a half-life estimated to be between 7 and 60 days. The relatively rapid degradation of glyphosate has the advantage of limiting its role in polluting the environment, especially soil and water resources. However, its degradation could increase the pollution risk by its metabolites: aminomethylphosphonic acid (AMPA) and/or sarcosine. The degradation of the herbicide molecule as described in the literature (**Figure 1**) can follow two paths: the first is based on the breakdown of the carbon-nitrogen bond and leads to the formation of AMPA (main metabolite of glyphosate) via glyphosate oxidoreductase which is further degraded to carbon dioxide, while the second way is based on the splitting of the carbon-phosphorus (C-P) bond that is mediated by C-P lyase enzyme and results in the formation of sarcosine and glycine [15–20]. However, AMPA also exists in the environment as a photodegradation product of aminopolyphosphonates in water [21].

Glyphosate is a small, amphoteric molecule characterized by three polar functional groups. These are the phosphonomethyl, amine, and carboxymethyl groups arranged in a linear manner. As a result of the presence of those groups in its structure, glyphosate is an ionic compound (log KOW = −3.20), highly polar and soluble in water (10.5 g L^{-1} at 20°C). GPS is a polyprotic acid with four pKa values, 0.7, 2.2, 5.9, and 10.6, 8 meaning that the speciation of the molecule is dependent upon the pH value of the solution. Three pKa values, 0.9, 5.6, and 10.2, characterize AMPA. Over the pH values commonly found in soils, mono- and divalent anions are the predominant species present [6, 22].

Glyphosate is soluble in water, but it also binds onto soil particles under certain conditions, particularly in clays. Numerous laboratory studies have shown that the absorption constant of the molecule in the soil varies between 8 and 377 dm^3/kg. This coefficient value indicates a high absorption in the soil. Glyphosate adsorption to soil, and later release from soil, varies depending on the characteristics and

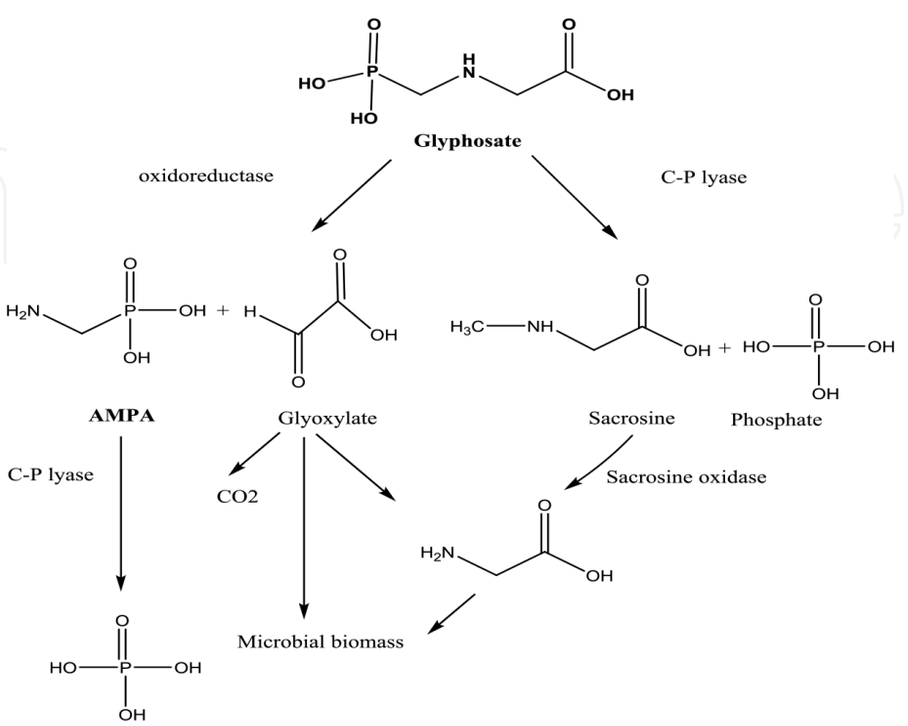


Figure 1.
Main glyphosate biodegradation pathways in the environment [5].

composition of the soil (clay, sand, or gravel), temperature, and soil moisture. So it may quickly wash out of sandy soils or last for more than a year in soils with a high clay content. Even when bound to soil particles, it may dissolve back into soil water later on, for example, in the presence of phosphates. Glyphosate can also form complexes with metal ions, potentially affecting the availability of nutrients in the soil.

The mechanism of glyphosate sorption to soil is similar to that of phosphate fertilizers, the presence of which can reduce glyphosate sorption [23]. Glyphosate compared to most other pesticides strongly absorbs to soil and is not expected to move vertically below the six-inch soil layer, exception made of a colloid-facilitated transport. Its soluble residues are expected to be poorly mobile in the free pore water of soils. The mobility of glyphosate in soil is very low because, as a strong chelating agent through the carboxyl, phosphonate, and amino groups, it creates the complexes that immobilize the mineral micronutrients of the soil (calcium, iron, magnesium, manganese, nickel, zinc, etc.) making them unavailable to plants [11, 24]. Similar to glyphosate, AMPA accumulates in soil and adsorbs in soils with high mineralization rates. Where strong sorption is demonstrated, glyphosate accumulation in soils can be expected. The interaction of pesticide-soil and the diffusion process lead to the formation of non-extractable residues trapped in areas not accessible to water flowing through the soil. The contamination of the environment is therefore considered to be relatively limited.

Nevertheless, this adsorption is not permanent because glyphosate can also be found in lower soil layers. Many studies suggest the possibility of a slow remobilization of these residues, which could explain the low pollution level of groundwater by some pesticides at a long term. Glyphosate does have the potential to contaminate surface waters through erosion, as it adsorbs to soil particles suspended in runoff. Rain events can trigger dissolved glyphosate loss in transport-prone soils [25, 26].

2.2 Glyphosate occurrence in soil

The increase of glyphosate-based herbicides has raised concerns about the occurrence of GLY and AMPA in the environment. Reports of GLY presence in the environment from other parts of the world are numerous. A considerable attention has been given to Argentina [27–30], Canada [31], across the United States [32], Mexico [33], and Portugal [34] as well to Spain [35], New Zealand [36], Austria [37], and French [38].

However, although GLY is the most sold herbicide in Europe, a combined approach on the occurrence and levels of glyphosate residues in European soils and air, in conjunction with analytical methods used for this scope, is still scarce, compared to the magnitude of its use though some research articles and reviews (not only focusing on soil) started to appear (indicatively see [39–41]).

The first large-scale assessment of distribution of GLY and AMPA in soils from agricultural topsoils of the European Union was recently published by Silva, where glyphosate and its metabolite AMPA were tested in 317 EU agricultural topsoils; 21% of the tested EU topsoils contained glyphosate and 42% contained AMPA, while both glyphosate and AMPA displayed a maximum concentration in soil of 2 mg kg^{-1}. Both compounds were present at higher frequencies in northern soils, while eastern and southern regions generally had the most glyphosate- and AMPA-free soils (<0.05 mg kg^{-1}), respectively. In addition, some contaminated soils were observed in areas highly susceptible to water and wind erosion [42]. Therefore, residue threshold values in soils are urgently needed to define potential risks for soil health and off-site effects related to export by wind and water erosion.

2.3 Analytical methods for quantification of GLY and AMPA

In order to detect the presence and quantity of GLY dispersed in the environment, various laboratory analyses are performed on samples taken in situ.

One of the key problems for obtaining reliable results from field samples is the use of the best suitable extraction solution, since sorption and desorption of glyphosate in soils are extremely pH dependent. Some reports showed that humic substances (substances and heterogenic mixtures dispersed and abundant in soils and sediments) adsorb glyphosate strongly due to the hydrogen bonding interactions between the two matrices. Another important aspect is that GLY is a highly polar herbicide, very soluble in water and insoluble in most organic solvents, which does not allow extraction with organic solvents and makes the extraction difficult and the preconcentration step quite lengthy. However, due to the amphoteric character of GLY and AMPA, both anionic and cationic resins have been used for preconcentration and cleanup purposes (commented in the below sections).

2.3.1 Extraction procedure

As already mentioned, GLY has been shown to bind strongly to soils, especially to soils with high amounts of organic matter, iron, and aluminum [43, 44]. There is also evidence that glyphosate binds to clay minerals in a manner similar to inorganic phosphate [44–46]. The strength of the interactions of the phosphonate, carboxyl, and amino groups with iron oxides, silica, alumina, and organic matter depends on factors such as pH, metal cations, phosphate from fertilizers, etc. Therefore, it is hard to detect GLY without a pretreatment method [47].

The choice of the best suitable extraction solution remains a problem that must be addressed accordingly.

Several authors in the past reported different extraction methods of these compounds from soil, mainly using alkaline solutions with different recovery rates [48–51] and most times applicable for one type of soil. In 1980 the FDA's "Pesticide Analytical Manual" (PAM) including a procedure for the analysis of glyphosate residues in soil is published. However low and irreproducible recoveries in soil samples have been reported using this method. Later, Glass in 1983–1984 analyzed soils by alkaline extraction, followed by cleanup using flocculation with $CaCl_2$ and anion exchange [52–54]. Yet, recoveries were still remained poor and ranged from 19 to 55%. Many extractants for soil have been tested in the years that followed with the most commonly used being aqueous bases KOH or NaOH, aqueous NH_4OH or NH_3, or triethylamine. Other extractants include $NaHCO_3$, KH_2PO_4, mixed solutions of KH_2PO_4 and NH_3 or NH_4OH and HPO_4, sodium borate buffers [55–60], or even weak acids such as 10% phosphoric acid buffers [13, 61].

Moreover, it is vital to adjust the concentration of the extraction media in such a way that high recovery rates can be obtained while avoiding matrix problems provoked by excessively aggressive alkaline media, which may enrich the dissolved humic substances in the extraction solution [49]. Humic acids interfere, for example, with the derivatization and suppress the ionization in ESI-MS/MS detectors.

2.3.2 Analytical methods

Although GLY is the most widely used agrochemical in the world, it is also the most cumbersome in its determination in analytical methods, a fact known as the "glyphosate paradox." The challenge to detect GLY using a simple analytical method is an outcome of its ionic character, low volatility and low mass, high polarity and solubility in water, poor solubility in common organic solvents, high boiling points,

difficult evaporation, and poor retention on traditional analysis columns. The quantitative and qualitative analyses of GLY (and AMPA) are extremely difficult due to the absence of fluorophores or chromophores in their structure. Furthermore, its determination at the low concentration levels required for residue analysis in different matrices is very difficult. In soil its determination is even more difficult due to the complexity of this matrix and subsequent matrix effects. The derivatization process using different derivatization reagents has been extensively used to overcome some of the above problems [62].

Prior to any attempt, it is important that all analysts to work with a glass that is not silanized to avoid the typical pitfall of GLY analysis. GLY has a profound affinity to glass, and any analytical solution prepared by this way will deviate substantially from its nominal concentration.

Chromatography is the most used and powerful method for the determination of GLY and its main metabolite AMPA, utilizing gas chromatography (GC) and liquid chromatography (LC) after derivatization or directly and capillary electrophoresis (CE). Conventional detectors are difficult to be used (especially for a straightforward analysis) due to the lack of chromophore and fluorophore groups in GLY. Usually, the limits of detection for GLY in soil vary between 0.01 and 0.3 mg/kg.

In all cases, the analytical methodology is practically exclusive for this analyte, since the working conditions cannot be applied to the determination of pesticides different from glyphosate, except for some organophosphorus, such as glufosinate and other polar compounds, and this chemical is difficult to incorporate in the vast majority of multiresidue methods. However, many of the methods published for the determination of GLY are also suitable and report results for the determination of AMPA. The majority of developed analytical methods concerned a single matrix (most often water) and may not be suitable for other matrices. Therefore, the last decade, numerous revised methods have been published on the analysis of glyphosate and AMPA in different matrices such as water, plants, or soils. Many of them just modify several parameters of previously published methods, as the pH of the water in the extraction, cleanup procedure, and derivatization step (volume and/or concentration of the samples or reagents). Other modifications include the use of different separation techniques or detection systems or even new matrices. Fewer new methods have been reported in the past 5 years for more complex matrices such as soil. Very few articles have been published on multimatrix methods.

In **Table 1** numerous analytical methods that have been used for the determination of GLY and AMPA in soil matrices are summarized. Based on the given information, at present LC is the most used method since it is considered the most suitable technique for the detection of phosphonic and amino acid-type herbicides at low concentrations. Hence, the lack of chromophore or fluorophore groups makes it difficult to use conventional detection methods such as ultraviolet (UV) absorption or fluorimetry. LC–MS/MS is currently the method of choice for polar analytes due to its high selectivity and sensitivity.

2.3.3 Gas chromatography - Derivatization

Gas chromatography methods are used after derivatization by simultaneous acylation, esterification, or trialkylsilylation reactions to convert the analytes into volatile compounds [69, 91, 92]. Typically used derivatization reagents are the mixture of trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) or N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) containing 1% tertbutyldimethylchlorosilane (TBDMCS) in excess producing sufficiently

Year	Sample preparation (extraction/ cleanup)	Derivatization (pre- or post-column)	Analytical method	LOD/LOQ μg/g	Other information	Reference
1986	0.1 M $(C_2H_5)_3$ N/ SAX cleanup	FDNB	HPLC-UV (405 nm)	0.05 GLY 0.1 AMPA		[63]
1988	0.1 M KH_2PO_4 or 0.2 M KOH	FMOC-CI	HPLC-FLD (λex = 270 nm, λem = 315 nm)	0.5–1.0 GLY	Minutes till some days of analysis time 0.1 M KH_2PO_4 (sandy soils)/0.2 M KOH (high clay soils)	[50]
1989	0.1 M KH_2PO_4	TFAA-TFE	GC-NPD	0.01/0.05	Recoveries 66–75%	[64]
1991, 1999		TsCl	HPLC-UV (240 nm or 280 nm)	8 mg/L GLY 10 mg/L AMPA		[64–66]
1994	0.25 M NH_4OH and 0.1 M KH_2PO_4	HFB/TFAA (1:2)	GC–MS (EI-SIM)	0.01/0.05 GLU, 0.01/0.05 AMPA	Recoveries 84–97%	[67]
1996	0.6 M KOH	FMOC-CI	LC–LC/FLD (263 nm λex = excitation, λem = 317 nm)	0.01/0.05 GLY 0.01/0.05 AMPA	Concerning soil organic matter and clay contents, the LOQ can reach 0.01 μg/g for both analytes for sandy samples, and for soil samples with a high organic matter and clay contents, LOQ is of 0.04 μg/g for glyphosate and 0.1 μg/g for AMPA	[68]
1996	NaOH 0.2 M	iso-PCF	GC-FPD	0.8/8.0 GLY 1.2/12 AMPA	Recoveries 91–106%	[69]
2000	1 M NaOH	TFAA/TFE (2:1)	GC–MS (EI)	0.003/0.006 GLY 0.003/0.006 AMPA	Recoveries 75–78%	[48]
2002			Cyan sensor	0.45 GLY	Phosphonomethyl glycine Inhibits amino acid biosynthesis	[70]
2005	0.6 M KOH	FMOC-CI	LC-ESI-MS/MS	0.005/0.05 GLY 0.005/0.05 AMPA	Recoveries 88–92%	[49]
2007	0.1 N NaOH/ SAX-SPE	FMOC-CI	HPLC-ESI-MS/MS	0.02/0.035 GLY 0.03/0.05 AMPA	Mean recovery values were 70% (7%) for GLU and 63% (3%) for AMPA	[71]

Year	Sample preparation (extraction/ cleanup)	Derivatization (pre- or post-column)	Analytical method	LOD/LOQ μg/g	Other information	Reference
2008	2 M NH_4OH	TFAA/TFE	GC-NPD	0.01 GLY	Recoveries 88–94%	[72]
2009	0.1 M KOH/CAX cleaned up	FMOC-CI	HPLC-FLD	0.025		[55]
2009	2 M NH_4OH	1. CS2 2. Ammonical solution of Cu(II)	UV 435 nm	1.1./3.7 μg/mL GLY	80–87%	[73]
2010	Water		CE/MS (negative with amino capillary)	20 GLY 40 AMPA	Recoveries 76–121% (20/200/2000) for GLY and 83–89% (40/400/4000) for AMPA	[74]
2011	Water	1. $Ca(ClO)_2$ 2.OPA/ME	SIA-FLD (λex =270 nm, λem =315 nm)	0.08/0.25 mmol/L GLY	Pre-column conversion: 1. of glyphosate to glycine by $Ca(ClO)_2$; 2. followed by reaction with OPA/ME in borate buffer (pH 9.5) to produce the fluorescent 1-(2′-hydroxyethylthio)-2-N-alkylisoindole	[75]
2012	0.2 M KOH		SWV using CFME	25/83 μg/L GLY	Recoveries 89–102%	[76]
2013	0.1 M KOH/SPE	FMOC-CI	HPLC-ESI-MS/MS using reversed-phase C18	0.02/0.05 GLY 0.01/0.03 AMPA	Recoveries 79–117%	[77]
2014	0.6 M KOH	FMOC-CI	HPLC-FLD (λex = 267, λem =317 nm) using reversed-phase C18	0.5 GLY 0.5 AMPA		[57]
2014	10% H_3PO_4		SPE-HPLC-ESI-MS/MS (using HILIC)	0.37 GLY 0.61 AMPA	Recoveries 85–126%	[61]
2014	0.01 M	FMOC-CI	SPE-HPLC-FLD (λex =263 nm and λem =317 nm)	0.6/2.0 ng/mL GLY 0.4/1.3 ng/mL AMPA		[78]

Year	Sample preparation (extraction/ cleanup)	Derivatization (pre- or post-column)	Analytical method	LOD/LOQ µg/g	Other information	Reference
2014	Water	$HCl/NaNO_2$	DIPN-GNPs-PGE	0.35 ng/mL GLY	1.0 g soil was suspended in a 30 mL water Recoveries 98.6–102.8%	[79]
2016	Water		IS-FLD using lgG-CDs	0.35 ng/mL GLY	Recoveries 87.4–105.5%	[80]
2015	1 M $Na_2B_4O_7$	FMOC-Cl	HPLC-PDA (206 nm)	0.01/0.1 GLY 0.01/0.1 AMPA	Recoveries 70–76% Confirmation with QTOF MS	[16]
2015	NaOH	FMOC-Cl	HPLC-UV (254 nm)	—		[3]
2015, 2016, 2018	0.6 M KOH	FMOC-CI	HPLCMS/MS/using reversed-phase C18	0.02/0.05 GLY 0.03/0.05 AMPA	Recoveries 77–87%	[81–83]
2016	NaOH	FMOC-CI	SPE-HPLC–MS	0.02 mg/L GLY 0.05 mg/L AMPA		[84]
2018	NH_4Cl	FMOC-CI	UV–Vis (264 nm)	20 GLY		[85]
2018	KOH	FMOC-CI	SPE-HPLC–MS		0.001 GLY 0.001 AMPA	[86]
2018	0.1 M K_2PO_4	FMOC-CI	HPLC-MS (negative ionization)	0.002 GLY 0.005 AMPA	Recovery 80%	[27]
2018	40 mM $Na_2B_4O_7$ or $NaHCO_3$ 0.5 M	2% succinic anhydride IN DMSO	L'ELISA (via microtiter plate reader at 450 nm)	0.8 10–3/0.1 GLY	Recoveries 87.4–97.2% (0.1–10 µg/g) confirmed with HPLC-FLD (by Ibanez)	[87]
2019	0.6 M KOH	FMOC-CI	LC-ESI-MS/MS using reversed-phase C18	GLY 0.01 AMPA	Recoveries from 89.6 to 118.8% for GLY and from 68 to 94.6% for AMPA	[88]
2019	Water	HFBA/FBA	SPE-GC-FPD	0.10/0.37 ng/mL GLY 0.22/0.81 ng/mL AMPA	Recoveries 94–110%	[89]

Year	Sample preparation (extraction/ cleanup)	Derivatization (pre- or post-column)	Analytical method	LOD/LOQ μg/g	Other information	Reference
2019		1. $Ca(ClO)_2$ 2.OPA/ME	SIC-FLD	0.03/0.10 GLY	Pre-column conversion: 1. of glyphosate to glycine by $Ca(ClO)_2$; 2. followed by reaction with OPA/ME in borate buffer (pH 9.5) to produce the fluorescent 1-(2′-hydroxyethylthio)-2-N-alkylisoindole	[90]

Solid-phase extraction = SPE; anion exchange = SAX; cation exchange = CAX; Flame photometric detector = FPD; nitrogen-phosphorus detector = NPD; fluorescence detector = FLD (λex = excitation; λem = emission); capillary electrophoresis = CE; immunosensor = IS; square wave voltammetry = SWV; carbon-fiber microelectrode = CFME; double template imprinted polymer film-gold nanoparticle-modified pencil graphite electrode = DIPN-GNPs-PGE; carbon dot-labeled antibodies = lgG-CDs; sequential injection chromatography = SIC; sequential injection analysis = SIA; linker-assisted enzyme-linked immunosorbent assay = L'ELISA; laser-induced fluorescence detection = LIF; Fluorenylmethylchloroformate = FMOC-Cl; 1-fluoro-2,4-dinitrobenzene = FDNB; trifluoroethanol = TFE; N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide = MTBSTFA; 2,2,3,3,4,4,4-heptafluoro-1-butanol = HFB; trifluoroacetic anhydride = TFAA; heptafluorobutyric anhydride = HFBA; isopropyl chloroformate = iso-PCF; o-phthalaldehyde/2-mercaptoethanol = OPA/ME; 4-toluenesulfonyl chloride = TsCl.

Table 1.
Main characteristics on the methods used for the determination of GLY and its main metabolite in soil matrices.

volatile derivatives for GC analysis. These derivatization approaches can be applied not only to soil (or sediment) but to other commodities as well [91].

GLY as a compound permits its detection (in conjunction with GC) by several detectors such as the flame photometric detector (FPD), flame ionization detector (FID), electron capture detector (ECD), nitrogen-phosphorus detector (NPD),and also the more sensitive and selective mass spectrometer detector (MSD). The quantification of GLY in the soil through NPD has reached an limit of quantification (LOQ) equivalent of 0.02 mg/kg [93, 94]. GC analytical methods are reliable, sensitive, and selective, but the sample preparation is very time-consuming, complicated, and tedious as all ionic groups must be derivatized. In addition, they involve anhydrous conditions, extensive cleanup using solvent partitioning steps, charcoal elimination of pigments, and a large-volume anion of cation exchange.

2.3.3.1 GC-MS

Borjesson and Torstensson using GC-MS managed to sensitively detect GLY and AMPA in soil [48]. One point that should have been addressed was the content of humic acids a problem mentioned above as well. Extraction was tedious, involving extraction under basic conditions, adjustment of the pH to acidic, and then subjected to column purifications to achieve ligand-anion exchanges. To derivatize GLY and AMPA TFE and TFAA were used. By this way the respective ester and acetyl derivative are formed suitable for GC analysis.

Utilizing the S/N approach, they presented one of the lower LOQs of the bibliography for GLY, established at 0.006 mg/kg. The application of the method in soils collected from Swedish embankments after being treated with GLY revealed the gradual degradation of GLY along with the presence of AMPA.

Bergstrom et al. investigated at laboratory level GLY and AMPA in sand and clay soils [13]. More specifically, its degradation was monitored using a GC-MS method, after derivatization with TFE and TFAA. The extraction of the soil was accomplished using an alkaline solution. Selected ion monitoring was utilized to enhance selectivity and optimize sensitivity of the method. The LOQ of the method was established at 0.01 mg/kg. The studied kinetics demonstrated that GLY had a very slow degradation rate in the clay soil. Concerning AMPA, though it is more tenacious than GLY (when derived from GLY), it degrades faster than GLY.

2.3.3.2 GC-FPD

A 2019 study on GLY and AMPA analysis in soil showed that still GC-FPD can function as an adequate tool for such demanding analyses [89]. This research was intrigued by the obstacles observed in derivatization in connection with the by-product interferences in high-performance liquid chromatography (HPLC) analysis (when MS/MS mode is not utilized), which lead to inferior selectivity. Consequently, the soil samples were mixed, turned to powder, and then ultrasonic extracted using water assisted by a solid-phase extraction (SPE). After derivatization, the samples were subjected to chemical analysis. A breakthrough of this process was the three-cross derivatization, and the elaborate investigation of its optimization, aided by the orthogonal experimental design. Such design is fundamental in the selection of the optimum conditions, in this case, reaction temperature, time, and ratio of the derivatizing-coupling reagents.

2.3.3.3 GC-NPD

GC-NPD was utilized by Hu and coworkers to analyze GLY in soil, using GC-MS for verification [72]. Extraction was performed in alkaline environment, followed

by acidification in the dry extract. The authors stated that NH_4OH was the most adequate extractant due to lesser extracted interferences than other alkaline agents, though in other works other agents are selected [48]. Derivatization was accomplished by the use of TFE and TFAA, followed by a liquid extraction using methylene chloride. The method verified the degradation of GLY in soil in apple orchards.

2.3.4 Liquid chromatography and derivatization

2.3.4.1 Fundamentals

The availability of derivatization techniques compatible with an aqueous extract or sample and the chromatographic separation makes LC a more attractive pre-column derivatization [91]. Derivatization approach is used to produce fluorescent derivatives and to enhance their retention in hydrophobic stationary phases prior to detection by fluorescence detection (FLD), UV detection, electrochemical detection (ECD), or tandem mass spectrometry (MS/MS). In post-column procedures, the most known reactions are ninhydrin derivatization accompanied by UV detection and fluorogenic labeling with o-phthalaldehyde (OPA) in mercaptoethanol or N,N-dimethyl-2-mercaptoethylamine after oxidation of glyphosate to glycine.

Although GLY and its derivatives show high sensitivity in LC determination, a laborious cleanup procedure such as ion-exchange column chromatography is required which may result in some sample loss and lower reproducibility, or many laboratories do not have the facilities required for this type of pre- or post-column fluorogenic labeling. The use of either hydrophilic/weak exchange or reversed-phase/weak exchange mixed-mode chromatography without any derivatization, followed by diverse detection techniques including tandem mass spectrometry detection, is gaining interest [77, 95]. HPLC methods are highly sensitive with fluorogenic labeling, but they lack specificity and usually require a laborious cleanup procedure such as ion-exchange column chromatography, which may result in some sample loss and lower reproducibility.

2.3.4.2 Pre-column procedures

2.3.4.2.1 FMOC derivatization

Pre-column procedures are a good alternative to post-column ones, and this has gradually come to play an important role in the analysis of glyphosate. The easier, less demanding and more current popular method to analyze these compounds is derivatization with 9-fluorenylmethylchloroformate (FMOC-Cl) followed by HPLC with FLD or MS/MS. A factorial experimental design was applied by a Chilean group in a critical analysis of this derivatization reaction [78]. The design was studied in aqueous soil extracts, unveiling the proper equilibrium between agents for the successful completion of the reaction. For example, excess of FMOC-Cl is required since there are also other active centers (amine-hydroxy groups) with which FMOC-Cl can react. Isotherm data verified the broad applicability of this method.

Back in the 1990s, Sancho et al. established a method for the analysis of GLY in soil samples that involved a pre-column derivatization step with FMOC-Cl and subsequent estimation by coupled-column liquid chromatography with fluorescence detection (LC–LC/FLD) [68]. However, for the determination of glyphosate in soils based on FMOC derivatization analytics, an extraction procedure including an SPE cleanup step has been used in many studies and considered more efficient [37]. In particular, Todorovic et al. extracted soils using sodium tetraborate. Once

again, a group devoted substantial time in the extraction of GLY and AMPA from soil due to the complex sorption and desorption in soil which is also pH dependent. The sodium tetraborate performed better in terms of chromatographic efficiency than KOH extraction (more matrix interferences, more humic substances, etc.). The authors after derivatizing GLY and AMPA with FMOC-Cl cleaned up-enriched the extract with a polymeric SPE cartridge. Overall, the method was fit for purpose based on the analytical results on three different types of soils.

Botero-Coy et al. have established a method based on LC–MS/MS, which was successfully applied to soil samples from Colombia and Argentina [77]. This work was an improvement of the previous work in the same domain [49]. In that work, the soil samples were extracted with potassium hydroxide solution and purified with SPE Oasis HLB cartridges. A pre-column derivatization step was also required in this method for which 9-fluorenylmethylchloroformate (FMOC-Cl) was used and the purification method using SPE cartridges was troublesome and expensive. Despite these difficulties, the analysis was conducted in Spanish soils with success. But, when soil samples from the mentioned countries were analyzed by the specific protocol, their high organic content proved an obstacle in the analysis. For this reason the authors introduced a dilution step of the extract assisted by pH adjustment to 9, before the SPE step. For SPE the polymeric reversed-phase Oasis HLB cartridges proved better in retaining-releasing the FMOC derivative than Oasis MAX used with good results.

Internal standard's use compensated possible downsides during sample preparation and corrected matrix effects. An additional tool in this work was the use of high-resolution mass spectrometry exploiting the time-of-flight technology. By this way additional interferences that would affect the analysis were further elucidated using the accurate mass full-acquisition data. It is noteworthy that the authors investigated MS ions used in the MS/MS mode. Interestingly, MRM transition containing the m/z 179 was problematic since it is related to FMOC and lacks specificity. In our work (see below), the specific ion was monitored only in AMPA transition, solving this issue [88]. Overall, the analysis verified the presence of GLY and AMPA in the majority of samples.

Another work in the field of GLY analysis in soil/sludge using FMOC-Cl as a derivatizing agent was presented by Sun and coworkers [96]. In this context, an optimized sample preparation protocol was developed, applying extraction with sodium phosphate and trisodium citrate solutions (aqueous) and a purification step using hexane in acidified soil. The rationale behind the use of trisodium citrate was to counteract the effect of other metal ion complexing agents (such as Mg^{2+}, Ca^{2+}, etc.), in which GLY binds. The method was validated in three types of soils (and sludge samples) verifying that it was fit for purpose. The demonstrated LOQ was determined at 0.04 mg/kg.

A pre-column derivatization was applied by Druart and coworkers, embracing glufosinate also in their portfolio [60]. A detailed study was conducted on the parameters governing the extraction of the analytes from the matrix. Accelerated solvent extraction, ultrasonic extraction, and magnetic stirring agitation were tested to achieve optimum conditions. In the end agitation was selected. The group also optimized derivatization by selecting water as the solvent of the reaction, though the previous study showed that an equivalent mixture of H_2O:ACN would compromise the solubility of both GLY and FMOC-Cl reagents [97]. In the same study, it was demonstrated that a C18 column of 30 cm superseded other columns tested, even a respective NH_2 column broadly used for such separations.

In addition our group has developed a methodology for GLY and AMPA detection in topsoils originating from Greece [88]. The sample preparation was envisaged by previous works (one of our group) [49, 98]. The LC–MS/MS method developed

was adequate for the analysis of both active substances, showing that GLY and AMPA were detected in 37 and 45%, respectively, of the samples investigated. A breakthrough of this work was the association of the results with the land use utilizing geographical information system (GIS) databases.

GLY in soil is studied for registering not only its residual prevalence (including AMPA's) but also its degradation dynamics. With this in view, Zhang et al. investigated its dynamics using an HPLC-FD method, utilizing FMOC derivatization [3]. Results of this study showed that the degradation is dependent on the physicochemical parameters of the soil, exemplified by the pH. The behavior of GLY and AMPA was investigated in compost-amended soils by Erban and colleagues [86]. Soil depth was disclosed as a key factor on the concentrations detected. GLY and AMPA though showed a different behavior when moisture and saturated hydraulic conductivity are considered. More specifically, GLY was affected principally by moisture, whereas AMPA was impacted by this conductivity.

2.3.4.2.2 Other fluorophores

Oliveira-Pereira and colleagues, in the context of adsorption studies, determined GLY and AMPA using a low-cost reversed-phase sequential injection chromatography method [90]. More specifically, GLY was converted (pre-column) to glycine (using hypochlorite). Then, by reaction with o-phthaldialdehyde, the respective fluorescent indole was formed. Expectedly, this reaction reduces the polarity of the indole derivative making it adequate for analysis under reversed-phase conditions (e.g., C18).

2.3.5 Direct analysis: a recent cornerstone

Direct analysis of GLY and AMPA, avoiding the derivatization step, is still a challenge for the analysts. In this context, Marek and Koskinen developed a method for the straightforward analysis of GLY and AMPA in soil using for separation a Bio-Rad cation H exchange column coupled to LC–MS/MS [61]. The sample preparation involved mixing of soil with phosphoric acid solutions and sequential extractions advancing from a specific SPE technology. The combined extracts were purified using IC-Chelate cartridges known for their ability to exchange transition metals and divalent cations. A portion of the end extract was reacidified and passed through an IC-RP SPE cartridge to eliminate hydrophobic interferences prior to analysis. This work managed to provide very high recoveries for both substances regardless of the type of soil, which is a clear advantage.

2.3.6 Hydrophilic interaction liquid chromatography (HILIC) and normal phase, a new frontier for GLY and AMPA in soil analysis

Due to the chemical nature of GLY, its analysis can be pursued under normal phase conditions, utilizing the same framework, the golden standard—HILIC. The latter is used in the efficient separation of a plethora of polar compounds, including pesticides. Despite its application for the separation of challenging polar pesticides, including GLY, in a variety of commodities [99], seldom are the reports for GLY analysis in soil. Marek reported a poor chromatographic performance when HILIC conditions (only one HILIC column was used; data were not shown) were used in the determination of GLY in soil and other matrices [61]. Hence, efforts need to be made in this direction, considering the inherent advantages of analyses of polar compounds under these conditions.

2.3.7 Other methods

Capillary electrophoresis methods have been reported in recent years using detection systems such as contactless conductivity, electrochemiluminescence [100], and laser-induced fluorescence [101, 102], as reviewed by Gauglitz et al. [103]. Ion chromatography [104], electrochemical method, surface resonance-enhanced spectrometry, enzyme-linked immunosorbent assay also called ELISA methods [87], spectrophotometry [73, 85], and fluorescent spectrometry [50, 55, 57, 75, 78, 80, 90, 96] were also reported to detect GLY in current literatures. However, the selectivity of ion chromatography was limited. Unlike other pesticides, the application of immunoanalytical techniques for glyphosate determination has been troublesome, although they have made some improvements.

Indicatively, El-Gendy and coworkers studied GLY in Egyptian soil samples using an optimized and sensitive linker-assisted enzyme-linked immunosorbent assay (L'ELISA) [87]. To derivatize GLY succinic anhydride was used. The method was well correlated with an HPLC-FD method that used sodium tetraborate for the extraction.

The advances in cutting-edge technologies can further hyphen such methods with modern mass spectrometers to provide solutions that currently are disregarded or seem problematic.

3. Glyphosate residues in the atmosphere

3.1 General aspects

The environmental pollution instigated by the use of plant protection products, commonly referred to as pesticides, is one of the most serious problems that facing the world due to their potential toxicity, high persistence, and slow degradation. Pesticide fate in the environment is characterized by a number of complex processes occurring in different environmental compartments, such as air, soils, and plants [105]. A wide variety of pesticides has been detected in different environmental media, including water bodies, soil, and the atmosphere. The extended use of pesticides containing persistent active ingredients can lead to raised concentrations due to the accumulation in the environment and long-term exposure to nontarget organisms.

Since the last decades, there has been an increasing global concern over the human health impacts attributed to the environmental pollution and specifically to air pollution. During applications, a noteworthy segment of applied pesticides ranged from 15 to 40% is dispersed in the atmosphere and can travel with long-range atmospheric transport [106]. Thus, the atmosphere has been considered as an important spread vector at local, regional, and global scales. It has been reported in the international literature that air pesticide contamination was observed both in urban and rural areas with concentration levels ranging from some picograms to several nanograms per cubic meter [107]. However, the contamination of air by pesticides is an aspect of atmospheric pollution that remains less documented than that of other environments.

Worry over the transport of pesticides in air started in the 1960s with the detection of persistent and volatile substances such as DDT, dieldrin, and aldrin far from their application sites. The first legislation to consider air as an exposure route was in the United States in 1971. Since then the issue of pesticides in air has been subject to sporadic regulatory concern, especially in Europe [108].

Milestone legislation in Europe concerning pesticides in the atmosphere occurred in 1996 with the Stockholm convention on persistent organic pollutants (POPs). This regulation covers all chemicals, including pesticides, and lays down principles to identify substances for which aerial transport may be noteworthy [108].

Long-range transport in air and water can result in the exposure of remote and particularly vulnerable ecosystems such as the Arctic [109, 110].

Pesticides enter into the atmosphere, and their residues can move away from the application sites resulting in accidental exposure for humans, animals, and plants, close or distant the treated sites. It is well recognized that the exposure and effect assessment of pesticides should not be constrained to the target area, and its close zone because this does not adequately cover possible hazards associated with their use.

The most common routes of pesticide entry into the atmosphere could be the drift during their application, volatilization from the soil, surface water or crop foliage, as well as wind erosion of deposited residues [111–113]. Once they enter in the atmosphere, pesticides are distributed between the gaseous and particulate phases depending on parameters such as:

- Octanol-air partition coefficient
- Vapor pressure
- Henry's law constant
- Water solubility
- Total suspended particulate matter
- Weather conditions [114]

In the atmosphere, pesticides are distributed between particle and vapor phases based on their vapor pressure, the ambient temperature, and the concentration of suspended particulate matter. Taking into account the low volatility of the majority of the most commonly used pesticides; it could be considered that they are often absorbed on the surface of atmospheric particles. In that way they may incur transformation processes resulting in the formation of secondary metabolites which could be even more hazardous than the parent released compounds [106]. Pesticides released into the atmosphere can settle to the ground, be broken down by sunlight and water, or dissipate into the surrounding air.

3.1.1 Transfer processes of pesticides in the air

During and after the application of a pesticide, a considerable portion of the amount applied may enter into the atmosphere through many different routes (the most important will be briefly discussed) and consequently may be transported over shorter and longer distance.

Through spray application of pesticides, a fraction of the spray would exist as pesticides in the gas phase and as small droplets or particles. The latter do not reach their target due to their extremely small size and cannot be captured by drift collectors. This fraction that exists in the gas phase and as aerosol should be taken into account along with drift.

Volatilization is defined as the transfer of pesticide residues into the gas phase after application. Volatilization from treated areas is a constant process and could be

the main dissipative route for numerous pesticides [115]. Its extent is governed by the physical and chemical properties of the pesticide such as vapor pressure and Henry's law constant; the application parameters such as the droplet size and the water volume; and finally the climatic conditions during and after application [108, 116]. Volatilization may be swayed by relative humidity, the atmospheric pressure, and the wind velocity [117]. The compound's volatility with medium vapor pressure values is significantly influenced by environmental and application factors, whereas substances with high vapor pressure values present high volatilization which does not depend on other factors. It is broadly established in the literature that vapor pressure can be used to categorize pesticides with a very high or with no volatilization potential. Vapor pressure also rules the partitioning of a semi-volatile constituent between the gas and the airborne particle phases. According to Bidleman substances with a vapor pressure value higher than 10^{-2} Pa are mainly expected in the vapor phase, while those with vapor pressure value lower 10^{-5} Pa solely exist in the particle-adsorbed phase [118]. Pesticides with vapor pressure between 10^{-2} and 10^{-5} Pa values partition between these phases.

A significant amount of pesticides entering into the atmosphere for several days or weeks after pesticide application comprises volatilization from the soil and plant surfaces as well as wind erosion of soil particles containing sorbed pesticides [119, 120]. Many parameters such as the physicochemical properties of the pesticide (vapor pressure, solubility, adsorption coefficient, molecular mass, and chemical nature), the soil properties (water content, soil density, soil organic matter content, clay content/texture, soil pH), the weather conditions (air temperature, solar radiation, rain, air humidity, and wind), and the agricultural practices used (application date and rate and formulation type) may influence the volatilization process [111].

Volatilization from plants is considered up to three times higher than soil volatilization under similar meteorological conditions. The vapor pressure and Henry's law constant are the physicochemical characteristics of the compound that seem to be related with the degree of volatilization. Additionally, application methods and weather conditions may also play an important role in the volatilization process from plants [121].

The Focus Air group has deemed that vapor pressure is the most significant factor affecting volatilization and deemed that active ingredients applied to soil with vapor pressure values higher than 10^{-4} Pa and active ingredients applied to plants with vapor pressure values higher than 10^{-5} Pa have a high possibility to enter in the air and for that reason require a risk assessment evaluation before authorization [108].

Pesticides existing in the aerial phase could be carried by wind and deposited accidentally in untreated areas by dry (gas and particle) and wet (rain and snow) deposition [122].

The atmosphere could be efficiently cleaned of suspended particulate matter to which pesticides might be sorbed by rainfall, and thus gas-phase pesticides can partition directly into a falling raindrop [122].

High pesticide concentrations in the air could be considered seasonal and often associated with local use and thus occur during the spraying months [123]. The physical and chemical properties of each pesticide also play a significant role in determining if a pesticide converts airborne, whether it then exists primarily in the gaseous or particle phase, and how efficiently rainfall removes it from the atmosphere. The period of time that a pesticide is applied, its amount, and the cultivated area play also significant roles in whether a pesticide exists in the atmosphere and at which concentration [113].

3.1.2 Glyphosate occurrence in the air

Glyphosate (N-[phosphonomethyl] glycine), a broad-spectrum, nonselective, and post emergence herbicide, is the most widely used pesticide worldwide.

Although numerous laboratory and field studies have been carried out for the determination of glyphosate and AMPA in the aquatic environment, there are limited studies in field soils. Furthermore, atmospheric concentrations of glyphosate and AMPA are shabbily documented as very few studies have monitored them in the atmosphere [124].

The first report about the atmospheric concentrations of glyphosate and AMPA had been published in 1991 in order to present the results of a study that had been conducted in 1988 in northeastern Finland for measuring the workers' exposure to glyphosate when they used sprayers connected to brush saws. In that study glyphosate was determined from the breathing zone and from urine samples. Based on the results of this study and at the end of the spraying week, two air samples were found to have measurable levels of glyphosate at concentrations 2.8 and 15.7 μg m^{-3}. AMPA had not been detected in any of the air samples [125].

In 2002, Humphries et al. examined the atmospheric samples at three different sites in east-central Alberta. For the purposes of the study, air samples were collected before the application of glyphosate and after its application and for 24 h time period at regular intervals. Glyphosate was not detected in any of the collected air samples at levels above the method LOQ; however, it was detected in few particulate samples [126]. The nonexistence of glyphosate in the polyurethane foam indicates that glyphosate is not released as the vapor forms into the atmosphere but rather is carried by a particulate matter.

In 2004, glyphosate was examined in 59 atmospheric samples in Hauts-de-France Region in France, with a detection occurrence of 14% and a maximum concentration of 0.19 ng m^{-3} [124, 127].

Chang et al. reported that both glyphosate and AMPA had been detected in the ambient air of Iowa, Indiana, and Mississippi during two growing seasons of the years 2007 and 2008. Atmospheric concentrations of glyphosate reached 9.1 and 5.4 ngm^{-3} in Mississippi and Iowa agricultural areas, respectively; however atmospheric concentrations of AMPA touched 0.49 and 0.97 ngm^{-3} in Mississippi and Iowa, correspondingly. It had been concluded that the existence of glyphosate in air is due to spray drift or wind erosion as it is not a volatile compound whereas AMPA presence is due to wind erosion as it is a glyphosate degradation product and it is formed in soil [128]. The authors provided also measurements in rainwater and estimated that 97% of glyphosate existing in the atmosphere could be removed by weekly rainfall greater than 30 mm [129].

Morshed et al. determined the atmospheric concentrations of glyphosate in treated fields in Malaysia during spray applications by a mist blower [129]. The maximum concentration of 42.96 μgm^{-3} was measured for glyphosate, and additionally a first modeling attempt for the estimation of glyphosate emission to the atmosphere at regional level was done; however, there were no measurements to confirm the model output.

In 2014, and specifically from July to November, Sousa et al. performed a study in northeastern Brazil, in the municipality of Limoeiro do Norte-Ceará, in urban and rural areas, for the determination of the atmospheric concentrations of glyphosate. Glyphosate detected at concentrations ranged between 0.313 and 2.939 μg m^3 in all collected atmospheric samples [130].

During the years 2015–2016, glyphosate and AMPA were searched in 142 air samples during a 2-year field campaign in France. Samples were taken from both non-agricultural and agricultural areas, while atmospheric concentrations of glyphosate

were detected at an overall frequency of 7%. AMPA was not detected in any sample. The maximum concentration of 1.04 ng m^{-3} was measured for glyphosate in the rural site of Cavaillon. As regards the temporal distribution of glyphosate, it had been pointed out that there was no reproducible detection pattern from 2015 to 2016 [125].

3.1.3 Monitoring studies for pesticides in the air

Generally, a few number of monitoring studies have been conducted for the determination of pesticide residues in atmospheric samples. These studies could not provide consistent results due to the variability in experimental conditions, the lack of consistency in sampling methodologies, the variation in collection time and duration, the analytes selected, the analytical methods used [131], as well as the method detection limits. Most of the studies have been performed at the national level, they are short-term as they lasted from 1 to 2 years, and for that reason, the overall conclusion on the long-term trends and the atmospheric movements of pesticides could not been reached [108].

3.2 Determination of glyphosate

3.2.1 Sampling and extraction procedures

Pesticides existing in the atmosphere are usually at very low concentrations, and thus appropriate sampling and techniques are necessary. The most common sampling techniques used for pesticides in the ambient air could be separated into two categories: the active and the passive or diffuse samplers [132].

3.2.1.1 Active sampling

Active samplers allow the pesticides existing in gaseous and particulate phases to be trapped by pumping air through a filter followed by a solid adsorbent. Thus, pesticides standing in the gas phase are stacked by the solid adsorbent, whereas pesticides in the particulate phase are maintained in the filter.

Pesticides present in the atmosphere could be sampled through low-volume or high-volume samplers. As pesticide residues in the atmosphere are at very low concentrations, high-volume samplers are usually used [121].

For sampling of semi-volatile pesticides, the use of diffusion denuder systems, which consist of a series of coaxial glass tubes coated with an appropriate adsorbent through which the air flows, is proposed [121].

3.2.1.2 Passive sampling

Passive air samplers are devices that collect pesticides from the air without the use of pump, and they are comprised of an accumulating intermediate which has a high retention capacity for the target analytes. Passive samplers are able to gather only the free gaseous phase pesticides, while the length of sampling range from few weeks to several months, considerably larger than the usual time required using the active ones [121].

In 1991, Jauhiainen et al. collected air samples for the determination of glyphosate from the breathing zone through a portable pump onto an absorption liquid [125]. The air samples collected were first evaporated to dryness and then dissolved with trifluoroethanol and trifluoroacetic anhydrite.

Chang et al. used high-volume active samplers for collecting air samples for the determination of glyphosate. The glass fiber filters used were baked at 550°C,

cooled to the room temperature, and enfolded in aluminum foil before sampling [128, 130]. The glass fiber filters after sampling were slowly grounded in a polypropylene tube and then extracted with hydrochloric acid (pH 2) and further with a potassium hydroxide solution (pH 11). Cellulose nitrate filters were used under vacuum for filtration [128].

Ravier et al. used also high-volume samplers, and the particulate samples were collected on quartz microfiber filters. The filters after sampling were protected from the light and stored at −20°C [124]. Field air blank samples were also collected for the determination of the background contamination through handling and storage. The extraction of all the samples was performed in polytetrafluoroethylene or polypropylene vessels in order to avoid loss of the studied compounds via wall adsorption. According to Ravier et al., filters were extracted with ultrahigh quality water with the addition of appropriate quantities of Borax (0.05 M) and EDTA solutions. Polyethersulfone membranes were used for sample filtration. FMOC-Cl was used as a derivatization agent.

Morshed et al. performed a study for the determination of glyphosate in the atmosphere by using both active and passive sampling methods. For the purposes of the study, three different air samplers were used. Cellulose filter patches and polyurethane foam were used for passive samplers. Active samplers were also used for sampling and were connected to polyurethane foam plug for the determination of glyphosate existing in the vapor phase and a quartz fiber filter for the particulate phase of airborne glyphosate [129]. Sample extraction for both active and passive extraction methods was performed with borate buffer. FMOC-Cl was used as a derivatizing agent.

High-volume air samplers were used to collect suspended, airborne particulates and trap airborne glyphosate vapors in a study conducted in Alberta's area. A volatile glyphosate was collected on a polyurethane foam plug and particulate glyphosate on a filter paper [126, 133].

Sousa et al. used a glass sample holder in which a polyurethane foam (adsorbent medium) was placed. The particulate material was collected from the glass fiber filters. Glyphosate was determined in the atmosphere after extraction from polyurethane foams with a solution comprising of monobasic potassium phosphate and methanol in ultrapure water while the pH of the solution was maintained at 2 using concentrated phosphoric acid. The samples were concentrated in a C18 solid-phase extraction cartridge.

3.2.2 Analytical method

The chromatographic analysis of glyphosate and AMPA is considered tough in trace analysis. Due to their low molecular weight, low volatility, thermal lability, and excellent water solubility, their extraction and determination are complex.

The main analytical techniques used for the analysis of glyphosate in atmospheric samples are liquid chromatography equipped with diode array or fluorescence detectors and liquid chromatography interfaced with a quadrupole-time-of-flight mass spectrometer or mass spectrometry. However, gas chromatographic technique with ECD has also been used.

In 1991 Jauhiainen et al. reported that a gas chromatographic system equipped with ECD and fused silica has been used for glyphosate determination in air samples. Additionally a triple-quadrupole mass spectrometer equipped with fused silica was used for identification purposes.

In 2011 a liquid chromatographic method for the determination of glyphosate in air samples was reported [129]. The analytical standards (stock and working) were prepared in a 0.025 M sodium borate buffer (pH 9) solution. Prior to HPLC

chromatographic analysis, working standards were pre-column derivatized with a derivatizing agent (0.002 M FMOC-Cl). The liquid chromatographic system consisted of a florescence detector and a Hypersil NH2 chromatographic column, while the mobile phase comprised of 50% phosphate buffer (0.05 M potassium phosphate monobasic KH2PO4 adjusted to pH 6.0 with 7 N KOH). The glyphosate retention time was 5.6 min and the total run time was 10 min. The LOD of the method was 0.015 μg ml^{-1}, while the LOQ was 0.05 μg ml^{-1} and determined through the linear calibration curve.

Chang et al. reported another method for the determination of glyphosate and AMPA by using a liquid chromatography tandem mass spectrometer. Both glyphosate and AMPA were derivatized with 9-fluorenylmethylchloroformate before analysis. A gradient elution system comprised of 95% of 5 mM ammonium acetate in HPLC-MS-grade water to 100% HPLC-grade acetonitrile was used. The molecular ion and the fragment ion for glyphosate were 390 and 168. In the case of AMPA the molecular ion and the fragment ions were 332, 110, and 136 [128].

Zhang et al. performed the analyses for the determination of glyphosate in the air samples of workplaces by ion chromatography using a conductivity detector. The limit of detection was found to be 0.003 mg/m^3. The recovery ranged between 94.8 and 97.4% [134].

According to Maria Gizeuda de F. Sousa et al., glyphosate was determined by liquid chromatography equipped with a diode array detector and a C-18 chromatographic column at 195 nm. The mobile phase consisted of 0.006 mM KH2PO4, and the flow rate set at 1.0 mL/min. Under these conditions glyphosate is eluted at 2.97 min, whereas the total analysis time was 7 min. The analytical method LOD was 0.09 μg mL^{-1}, whereas the LOQ was 0.27 μg mL^{-1} [130].

For the determination of glyphosate and its major metabolite AMPA, Ravier et al. used an ultra-performance liquid chromatographic (UPLC) system interfaced with a quadrupole-time-of-flight mass spectrometer and equipped with an electrospray ion source and a C18 UPLC column. The elution system consisted of water with 5 mM ammonium formate and acetonitrile. The analyses are performed in the negative ionization mode. Both the LOD and the LOQ were determined by the calibration curve and were 0.05 and 0.14 ngm^{-3}, respectively, for glyphosate and 0.30 and 0.90 ngm^{-3}, respectively, for AMPA [124].

4. Conclusions

HPLC methods are highly sensitive especially with fluorogenic labeling, but they lack specificity and usually require a laborious cleanup procedure such as ion-exchange column chromatography, which may result in some sample loss and lower reproducibility. At present LC-MS in tandem mode (MS/MS) is considered the most suitable technique for the detection of phosphoric and amino acid-type herbicides at low concentrations. Derivatization is the most common way to analyze GLY and AMPA using LC-ESI-MS/MS systems, a procedure that is described in soil matrix as well.

The maximum concentrations of glyphosate in atmospheric samples correspond to the time of its application. Due to the limited number of monitoring studies for monitoring pesticides and specifically glyphosate in the air, a reliable conclusion about its fate could not be reached.

Conflict of interest

The authors declare no conflict of interest.

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