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REVIEW

# Glyphosate detection: methods, needs and challenges

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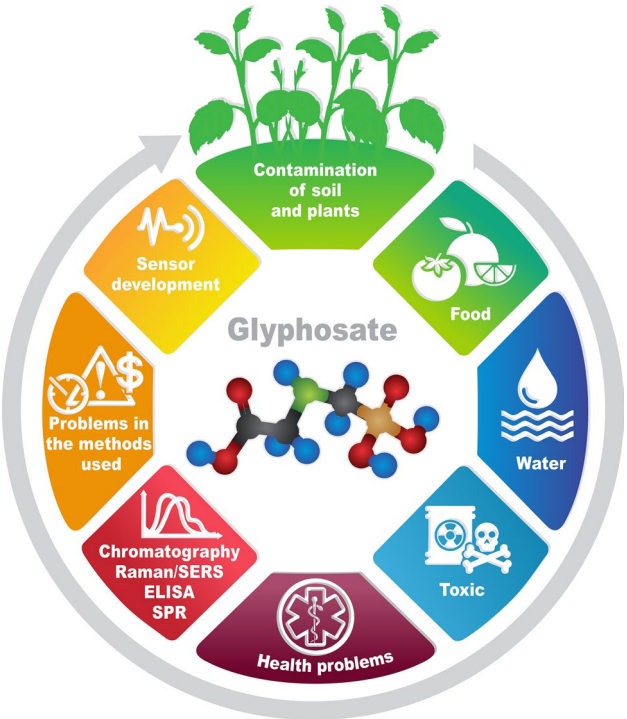
## Abstract

Glyphosate is considered toxicologically harmful and presents potential association with human carcinogenesis and other chronic diseases, including mental and reproductive behaviors. The challenges to analyse and demonstrate its toxicity are likely due to its metal-chelating properties, the interference of organic compounds in the environment, and similarity with its by-products. Whereas there is a link with serious health and environmental problems, there is an absence of public health policies, which is probably due to the difficulties in detecting glyphosate in the environment, further complicated by the undetectable hazard in occupational safety and health. The historical lenient use of glyphosate in transgenic-resistant crops, corroborated by the fact that it is not easily detected, creates the "Glyphosate paradox", by which it is the most widely used herbicide and one of the most hardly determined. In this review, we revisited all available technologies for detection and quantification of glyphosate, including their drawbacks and advantages, and we further discuss the needs and challenges. Briefly, most of the technologies require high-end equipments and resources in low throughput, and none of them are adequate for real-time field tests, which may explain the lack of studies on occupational health associated with the chemical hazard. The real-time detection is an urgent and highly demanded need to improve public policies.

## Graphical Abstract

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## Introduction

### General considerations

Glyphosate [(*N*-phosphonomethyl)glycine] (GLY) is a non-selective and broad-spectrum herbicide and is the most widely used worldwide (Castle et al. 2004; Woodburn 2000). Since the introduction of genetically modified GLY-resistant crops at the end of the twentieth century, its use has increased dramatically (Giesy et al. 2000). The main commercial formulation of GLY is "Roundup", which consists of isopropylamine salt, and the surfactant polyoxyethylene amine is also added according to the manufacturer to increase its efficiency (Tsui and Chu 2003). World Health Organization et al. (1994) had considered GLY as "toxicologically harmless" for humans, other mammals, birds and environment (Tsui and Chu 2003, 2008; Williams et al. 2000) due to its degradability by soil microbes (Zhang et al. 2015a; Napoli et al. 2015) and binding ability to soil colloids (González-Martínez et al. 2005). However, new studies have pointed out GLY as a possibly carcinogenic agent due to its accumulation in the water at the environment. It is believed that this poisonous is probably related to the ability of GLY to form metal complex (Coutinho et al. 2007; Tsui et al. 2005). Actually, the diagnostic strategies and tools have frequently failed to detect GLY and its by-products, and therefore such assumptions need to be confirmed (Simonetti et al. 2015). This review summarizes methods most used during the past 36 years for GLY detection.

### Environmental risks and animal's health

The European Glyphosate Task Force (GTF) published an enormous list of scientific citations about toxicological effects of GLY. Interestingly, GLY has been associated with fungus infestation in wheat plantations (Ho and Cherry 2010), and additionally, it has been related to more than 30 plant diseases (Johal and Huber 2009; Huang et al. 2015). An extensive review has compiled evidences for the widespread contamination of GLY and its derivatives in groundwater, surface waters (creeks, brooks, lakes, rivers and drains), marine sediments, seawater and rain (Watts 2009; Allinson et al. 2016; Bradley et al. 2017; Okada et al. 2018). Furthermore, GLY can also be transported by particles in the air (Humphries et al. 2005) and be deposited in the snow (European Commission 2002). GLY may also affect the marine microbial community (Stachowskihaberkorn et al. 2008). The observed concentration of GLY found in coastal areas may be enough to cause considerable changes in the ecosystem, including the obstruction of biomass trophic transfer to different levels (DeLorenzo et al. 1999).

Chronic exposure of GLY is associated with many human health hazards that include: endocrine function disruption (Gasnier et al. 2009; Chalubinski and Kowalski 2006; Ejaz et al. 2004), attention-deficit/hyperactive disorder (ADHD), colitis, diabetes, heart disease, inflammatory bowel disease, amyotrophic lateral syndrome, multiple sclerosis, obesity, depression, non-Hodgkin lymphoma and Alzheimer's disease (Samsel and Seneff 2013a), anencephaly (Rull 2004), autism (Beecham and Seneff 2015), pineal gland disorders (Seneff et al. 2015), birth defects (Paganelli et al. 2010), brain and breast cancers (Shim et al. 2009; Cattani et al. 2014; Thongprakaisang et al. 2013), celiac disease and gluten intolerance (Samsel and Seneff 2013b), chronic kidney disease (Jayasumana et al. 2014, 2015), Parkinson's disease (Gui et al. 2012), pregnancy problems (Richard et al. 2005; Garry et al. 2002; Benachour and Séralini 2009; Hokanson et al. 2007; Poletta et al. 2009), abnormal cell cycle (Marc et al. 2004), allergies (Slager et al. 2010; Heras-Mendaza et al. 2008; Nielsen et al. 2007) and intestine problems (Shehata et al. 2013).

In fish, GLY has affected the energy metabolism, free radical processes, acetylcholinesterase activity (Glusczak et al. 2006, 2007; do Carmo Langiano and Martinez 2008), modified parameters of the micronucleus test and caused DNA damage as evidenced by the comet assay (Grisolia 2002; Cavalcante et al. 2008; Cavaş and Könen 2007) and caused significant alterations in the immune response (El-Gendy et al. 1998) and in hepatocytes histology (Jiraungkoorskul et al. 2003; Szarek et al. 2000). Besides such effects, preference and avoidance reactions of rainbow trout could also be induced by different GLY concentrations (Tierney et al. 2007). It has been demonstrated that low GLY exposure may induce mild oxidative stress in goldfish tissues by suppressing molecules that modulate reactive oxygen species (ROS), such as superoxide dismutase (SOD), glutathione reductase, glutathione *S*-transferase (GST) and glucose 6-phosphate dehydrogenase (Winfield 1990). Additionally, the increase in alkaline phosphatase activity at the heart and liver of fish with sublethal GLY doses has also affected the oxaloacetic and glutamic-pyruvic transaminases activities, leading to epithelial hyperplasia and subepithelial edema in gills, and morphological changes in the liver (Nešković et al. 1996; Lushchak et al. 2009). In amphibians, it has induced morphological changes on tadpole development, probably breaking their antipredator responses (Relyea 2012). A very broad review on the impact of GLY on native amphibians was published in 2008 (Govindarajulu 2008).

## Reasons to determine precise levels of glyphosate

Detection and quantification of glyphosate (GLY) is expensive and slow; consequently, governmental control measures are ineffective since GLY usually cannot be detected by methods that simultaneously analyze different kinds of chemical and their metabolites in the same assay, in a unique multiresidue method. Therefore, the impact of this knowledge gap on public economy and in the health system is not known. Hence, the concept of the "Glyphosate paradox" is raised, which means that besides GLY being the most widely used agrochemical in the world, it is also the most hardly determined by analytical methods.

Currently, there is no continuous monitoring of GLY or any systematic information about environmental contaminated areas worldwide. The European Union (EU) authorities conducted 186,852 tests in 2009 on cereal samples for pesticide residues, but such survey was performed in only five countries, reaching only 462 sites, from which 42 tested positive. Since 2010, EU authorities have performed regular monitoring of GLY in cereals, but the challenge still remains in testing GLY residues on imported genetically modified soybeans, in which Brazil is one of the biggest producers in the world with indiscriminate use of GLY. Even in the EU, only a small number of testing laboratories are able to detect this chemical (Poulsen et al. 2009). The consequence of this lack of information means greater difficulties to find out how much GLY people have been daily exposed, and how governments should protect human and environment health from the adverse effects of it.

Our perception is that the Europe Community is more concerned in applying the precautionary principle than many other countries. For example, the Codex Alimentarius Commission and the US Environmental Protection Agency (EPA) established the maximum residue limit (MRL) of 20 mg $kg^{-1}$ for GLY in soybean and, in a most preventive way, the National Health Surveillance Agency (ANVISA) in Brazil set the MRL of 10 mg $kg^{-1}$. For drinking water, the regulatory rules adopted by each country differ significantly. The EU has set a MRL of pesticides independently of the chemical structure or biological activity of the compound in 0.1 ng $mL^{-1}$. The EPA established the MRL in terms of persistence and toxicity of each pesticide individually at 700 ng $mL^{-1}$ (Winfield 1990). The Canadian Drinking Water Guideline recommends a maximum level of 280 ng $mL^{-1}$. In Brazil, the ANVISA and the Ministry of Health has established the MRL in water of max 500 ng $mL^{-1}$. The level of exposure that is deemed safe for humans over a long period of time is called ADI. It has been set at 0.3 mg $kg^{-1}$ of bodyweight per day (bw/d) in EU and Canada and 1.75 mg $kg^{-1}$ bw/d in the USA. The ADI is the highest dose at which no adverse effect is found (the No Observed Adverse Effect Level or NOAEL), which is also lower than the lowest dose that has a toxic effect (the Lowest Observed Adverse Effect Level or LOAEL). However, it is important to emphasize that analyses on the current approvals by the EU and in the USA regarding GLY levels suggest that the established ADIs are questionable (Antoniou et al. 2012), especially because agencies used the information provided by studies performed by the industries, which support regulators to calculate and approve the application of chemical levels without adverse effects. All these facts have raised questions about how safe GLY levels are, which is further complicated by the fact that many approaches present Limits of Detection (LOD) far away from Agency's control interest. GLY has some special characteristics that go far from the fact that it has been broadly used. It is usually applied to soils in the form of aqueous solutions, in high concentrations of around 0.03 mol $L^{-1}$ (Candela et al. 2010; Laitinen et al. 2009; Tuesca and Puricelli 2007).

So, to understand and predict the transport of GLY in soils, one needs to measure it in a wide spectrum of concentrations, focusing on how GLY interacts with the soil complexity under variable conditions. In fact, this challenge is quite difficult, both technically and financially, which is mainly due to the complexity of molecular interactions among GLY, metals, nutrients and organic matter, and also because there is no good technology for real-time and sensitive measurements of GLY. Simple, portable and low-cost methods and instruments are highly desirable, but difficult to attain for all different environmental conditions.

## Glyphosate: metabolites and analogues, formulation toxicity and detection problems

Glyphosate (GLY) is generally formulated by a series of zwitterions with adjuvants or surfactants to improve its activity. It is an aminophosphonic analogue of the natural amino acid glycine, which is protonated and presented in different ionic states depending on pH. The carboxylic and the phosphonic acid can be ionized, and the amine group can be protonated (Winfield 1990; Chenier 2002). The GLY primary natural decomposition pathway occurs through degradation by soil microflora under both aerobic and anaerobic conditions (Franz et al. 1997). The main deactivation path is the hydrolysis to aminoethylphosphonic acid (AMPA). This compound presents a low toxicity weak organic acid with a phosphoric acid group (Winfield 1990; Schuette 1998). AMPA is then broken down further by manganese oxide, which naturally occurs in soil (Barrett and McBride 2005), or to phosphoric acid via bacterial action (Forlani et al. 1999; Pipke and Amrhein 1988), and ultimately to carbon dioxide and inorganic phosphate (Winfield 1990; Tuesca and Puricelli 2007). The second catabolic pathway is sarcosine as intermediate metabolite. In hard water, the decomposition process is slower, and GLY forming salt, mainly by

complexation to $Ca^{2+}$ (Coutinho and Mazo 2005). GLY has more than one thousand analogues (Winfield 1990; Pollegioni et al. 2011), but seems that there are only two, very similar analogues, which are as effective to the same extent as GLY, the *N*-hydroxy-glyphosate and *N*-amino-glyphosate (Winfield 1990; Laitinen et al. 2009; Singh 1998).

Interestingly, the oxidative stress generated by GLY, AMPA and its commercial formulation was examined in a hepatocyte cell line (HepG2) under dilution levels below agricultural applications, but surprisingly, the AMPA exposure produced an increase in glutathione (GSH) levels only, and no effects were observed for GLY. However, the GLY formulation induced a significant increase in reactive oxygen species, nitrotyrosine formation, superoxide dismutase activity and GSH levels, suggesting that adjuvants associated with the active GLY may be causing part of the toxic effects (Chaufan et al. 2014).

The challenge to detect GLY residue using a simple analytical method is due to its ionic character, high polarity and solubility in water, difficult evaporation, poor solubility in common organic solvents, low volatility, low mass and favored complexing behavior (Ibáñez et al. 2006; de Llasera et al. 2005; Koskinen et al. 2016; Skeff et al. 2016). The photometric and fluorometric detection of these substances is not viable due to the absence of chromophore or fluorophore groups in GLY structures. Moreover, similarity with amino acids or other natural plant components can cause interferences. The GLY capacity to adsorb strongly on clay minerals (Hance 1976; Arroyave et al. 2016) and organic (Zheng et al. 2015) or mineral particles in water (Thompson et al. 1989; Rueppel et al. 1977) and its high affinity to metal cations that complex with it, make it hard to detect without a pretreatment method (Glass 1984).

## Measurement methods

### Chromatography techniques

Chromatography can be used to break apart mixtures into their components allowing each part to be analyzed separately. Many approaches to detect glyphosate (GLY) residues use liquid chromatography (LC) or high-performance liquid chromatography (HPLC), gas chromatography (GC) and ion chromatography (IC) (Zelenkova and Vinokurova 2008). Alternatively, the eluates from the chromatographic columns can be fed into mass spectrometer (MS) detectors (LC/MS).

#### Liquid chromatography

Liquid chromatography (LC) is the most suitable method to detect GLY. It needs derivatization procedure, for which several approaches have been used, such as pre-column, e.g., and post-column (Winfield 1990; Patsias et al. 2001; Hogendoorn et al. 1999; Mallat and Barceló 1998). Normally, LC has been used in combination with fluorescence and UV/visible (LC/UV–Vis) detection after derivatization and has also been used with fluorescence detector (LC–FLD) (Khrolenko and Wieczorek 2005; Merás et al. 2005; Nedelkoska and Low 2004; Ridlen et al. 1997). The recommended EPA method for GLY in drinking water uses LC with direct injection of the sample, post-column derivatization and fluorescence detection without pre-concentration (Barcelo 2000). The derivatization reagents for UV detector are *p*-toluenesulfonyl chloride (Si et al. 2009; Kawai et al. 1991), *o*-nitrobenzenesulfonyl chloride (Fang et al. 2011) and 2,5-dimethoxybenzenesulfonyl chloride (Fang et al. 2014). LC methods for GLY often adopt pre-column 9-fluorenylmethyl chloroformate (FMOC-Cl) derivatization and fluorimetric detection. On FLD detections used 9-fluorenylmethyl chloroformate (FMOC) and *o*-phthalaldehyde (OPA) in post-column (Nedelkoska and Low 2004; Zhou et al. 2007; Hidalgo et al. 2004; Sancho et al. 1996; Sun et al. 2017). The pre-column is more precise than post-column derivatization due to the difficulty in controlling reaction in the reflux system of HPLC for post-column. Pre-column derivatization reaches LOD as low as 0.02 ng $mL^{-1}$ in water and 0.02 mg $kg^{-1}$ in soil, while post-column derivatization reaches on aqueous sample 2.0 ng $mL^{-1}$. LC is a fast, sensitive and repeatable method to GLY residue detection, but it needs derivatization processes and requires high-end equipments.

#### Gas chromatography

Gas chromatography (GC) is not commonly used to detect GLY due to the complicated derivatization procedure, but the evaporation properties have been improved through esterification and acylation. Generally, GC is performed after pre-column derivatization of GLY to convert it to volatile and thermally stable derivative (Hu et al. 2008; Kudzin et al. 2002, 2003; Börjesson and Torstensson 2000; Tadeo et al. 2000). The C, P and H in the GLY molecule permit the use of associated techniques as flame photometric detector (GC/FPD) (Tseng et al. 2004; Kataoka et al. 1996), flame ionization detector (GC/FID) (Kudzin et al. 2003), electron capture detector (GC/ECD) and nitrogen phosphorus detector (GC/NPD) (Hu et al. 2008). The most used derivatization reagents are *N*-methyl-*N*-*tert*-butyldimethylsilicontrifluoroacetamide and dimethylformamide (Tsunoda 1993), trifluoroacetic anhydride and 4,4,4-trifluoro-1-butanol (Hu et al. 2007; Lou et al. 2001; Ding et al. 2015), isopropyl chloroformate and diazomethane (Kataoka et al. 1996), trifluoroacetic acid, trifluoroacetic anhydride and trimethyl orthoformate (Kudzin et al. 2002), propionic anhydride and methanol (Ding et al. 2015; Pei and Lai 2004).

Quantification of GLY in soil and water through NPD has reached LOD equivalents of 0.02 mg $kg^{-1}$ (Ding et al. 2015; Pei and Lai 2004) and 0.5 ng $L^{-1}$, respectively (Hu et al. 2007). One point that should be emphasized is the use of less toxic acetone, ethyl acetate and methanol instead of the carcinogenic chloroform, dichloromethane and neurotoxic *n*-hexane as eluent solvents (Tseng et al. 2004). Therefore, GC and LC can determine GLY derivatives in a sensitive and selective way, but the steps to transform GLY in a product that could be read are quite complicated, besides generating unstable products.

#### Ion chromatography

Ion chromatography (IC) is a type of LC in which retention of molecules is based on the attraction between solute ions and charged sites bound to the stationary phase. Once GLY is an ionic compound (p*K*a1 = 2.27, p*K*a2 = 5.58 and p*K*a3 = 10.25), an anion-exchange column can be used followed by elution with an alkaline buffer. IC was used to measure GLY in a simple and sensitive method with emphasis on a simple clean-up procedure based on IC with suppressed conductivity detection (Zhu et al. 1999). The highlight of this study was the very short retention time of common inorganic anions of GLY, such as chloride, phosphate, nitrate and sulfate, without any interference. In a few cases, GLY could be determined directly by IC with UV (Ibáñez et al. 2005) or by suppressing conductivity detection due to its limited sensitivity. Furthermore, an IC method with integrated pulsed amperometric detection (IC/IPAD) could determine GLY with the advantages of not requiring derivatization, pre-concentration and mobile-phase conductivity inhibition (Sato et al. 2001). It is important to consider the complexity of soils, which includes the presence of several competing ions in different concentrations and other environmental variations, such as pH, organic matter and microorganisms that make the extraction methods harder to be attained and leading to unreproducible results.

#### Chromatography–mass spectrometry

Chromatography–mass spectrometry (LC/MS), or alternatively HPLC/MS, is the most common method to detect GLY in environmental samples due to its higher sensitivity (Liao et al. 2018). Low analysis time has been achieved using solid-phase extractions with LC–SPE (Delmonico et al. 2014), but with higher LOD. LC/MS methods are already used with a technique called electrospray ionization (ESI) that works as an ion source (LC/ESI–MS) (Sato et al. 2009). Sensitivity can be significantly improved by LC/MS–MS, which also avoids the derivatization procedure. MS/MS combines two mass analyzers in one instrument, in which the first MS filters the precursor ion followed by its fragmentation with high energy, and the second MS analyzer then filters the produced ions generated by fragmentation. The advantage of the MS/MS is the increased sensitivity due to the noise reduction.

It was reported that the LC/MS–MS method sufficiently detects GLY, but this method requires longer equilibration time, suffers from poor robustness and still has adverse impacts on column lifetime (Liao et al. 2018). Kaczyński and Łozowicka compared LC/MS–MS and LC/FLD to detect traces of GLY in rapeseeds. Good results have been achieved with LC/MS–MS, but some factors may have affected the method's performance such as metal ions, sample preservation and storage time (Kaczyński and Łozowicka 2015). However, while LC/FLD requires less expensive equipment, the LC/MS–MS presents simpler sample preparation, easier procedure, faster and more sensitive (Hao et al. 2011). Routine analysis can be performed without laborious instrumental changes using this technique. The results suggest that LC/MS–MS may also be used to analyze residues of these compounds in oil plants, where GLY is widely used. Flow injection associated with tandem mass spectrometry (MS/MS) was researched for the rapid detection of polar pesticides, such as GLY (Mol and van Dam 2014).

Searching for an analysis without derivatization procedures has led to the development of an alternative methodology to determine GLY and AMPA residues using a fast-chromatographic analysis with sensitive detection, with calibration curves prepared in the matrix after a simple sample extraction and liquid–liquid partition followed by protein precipitation step with organic solvent to minimize the complexity of the sample (Martins-Júnior et al. 2009, 2011). These authors investigated the potential of reversed-phase LC–ESI/MS/MS for the quantification of these residues in soybean-spiked samples, suggesting that this method could be expanded to corn and cotton crops. LC–ESI–MS/MS does not need derivatization procedure, but the instrumentation demands are substantial (Byer et al. 2008). A fully automated SPE–LC–ESI–MS/MS was developed and validated to analyze potable water, surface water and wastewater with good LOD, but with derivatizations (Vreeken et al. 1998). Similarly, a selective and sensitive online SPE–LC–ESI–MS/MS approach reached incredible LOD for GLY and AMPA in soil and water samples, reaching as low as 50 ng $g^{-1}$ and 0.0005 ng $mL^{-1}$, respectively (Ibáñez et al. 2005, 2006; Hanke et al. 2008). It is also interesting to highlight that using labeled GLY as internal standard, even applying powerful approaches as SPE–LC–ESI–MS/MS detection, its application to real-world samples failed. Most reported methods for GLY analysis did not perform acidification of sample before derivatization, and some data reported on GLY concentrations in water might be questionable due to the presence of some organic compounds and metal ions that were neglected, which act as chelating

agents that form complexes with GLY, becoming unavailable for the derivatization step. The nature of the formed complex was not elucidated yet, and more studies are necessary to establish whether acidification of samples is a general approach that should be applied to all water samples (Ibáñez et al. 2006).

GC/MS is another method that requires derivatization to confer volatility to GLY (de Llasera et al. 2005; Kudzin et al. 2003). Three technologies based on GC/MS have been used to detect GLY: GC–CI (chemical ionization)–MS, GC–FID (flame ionization detector)–MS and GC–EI (electron impact)–MS. Generally, the methods are time-consuming, tedious and require a substantial amount of sample manipulation. Although these methods present high sensitivity and capability of detecting very low GLY concentrations, they are laborious and require the use of high-end specialized equipments. Tsunoda developed a sensitive GC/ion-trap-MS (GC/IT-MS) method to determine simultaneously GLY, glufosinate (GLU) and bialaphos (BIA), their major metabolites, besides other nineteen amino acids (Tsunoda 1993). Royer et al. (2000) used this method to determine GLY and AMPA in water with different hardnesses. Börjesson and Torstensson (2000) reached LOD as low as 0.1 ng $mL^{-1}$ in groundwater and 6 ng $g^{-1}$ for both compounds in soil. The preferred detection system according to many scientists is MS (Kudzin et al. 2002; Börjesson and Torstensson 2000; Royer et al. 2000; Alferness and Iwata 1994).

Another approach based on by ion-pairing reversed-phase liquid (RP-LC) coupled to inductively coupled plasma mass spectrometry with octapole (ICP/MS) did not require derivation and obtained lower sensitivity with LOD at 25–32 ng $mL^{-1}$ (Sadi et al. 2004). Guo and colleagues also built an IC/ICP–MS method in order to determine the GLY in water. The method was sensitive, simple, did not require sample pre-concentration or mobile-phase conductivity suppression and did not suffer anions' interference (nitrate, nitrite, sulfate, chloride, etc.) and metallic ions from the matrix (Guo et al. 2005). Later in 2007, they developed an IC/ICP–MS method to determine simultaneously four water-soluble organophosphorus herbicides. The detection was fast, simple, selective and free from tedious sample preparation or chemical derivatization and was applicable to highly polluted water samples. However, environmental water applicability depends on further research using instrumental upgrading or applying a pre-concentration step to improve its sensitivity (Guo et al. 2007). Yoshioka and colleagues also avoided derivatization and ion-pair reagents and aimed the study to the emergency medicine, where time is the utmost aim, especially in poisonings cases. In this situation, a rapid method for detecting multiple herbicides would allow rapid treatment. Besides GLY, this method could also detect GLU, BIA, AMPA and 3-methylphosphinicopropionic acid (3-MPPA) in human serum. These amphoteric and polar phosphorus herbicides contain amino acids. Their detection without derivatization or ion-pair reagents, and under the use of conventional columns, such as reversed-phase (RP) or ion-exchange column may lead to poor peak shapes and insufficient peak separation in LC chromatograms (Yoshioka et al. 2011). In order to solve this problem, hydrophilic interaction chromatography (HILIC) columns were used (Coutinho et al. 2007; Li et al. 2009; Vass et al. 2016). Once hydrophilic and polar compounds cannot be retained by conventional RP chromatography, the HILIC column is suitable. The greatest advantage of IC testing is the simple treatment for samples. However, it is only applied in water and soil analysis.

## Spectroscopic methods

Spectroscopy analysis studies the interaction between matter and electromagnetic radiation as a function of its wavelength or frequency. The data are represented by a plot of the response of interest as a function of the wavelength, wavenumber or frequency.

### Methods of absorption and emission

Although accurate and sensitive, the technologies related to atomic absorption spectrometry, electrothermal atomization atomic absorption spectrometry, flame atomic absorption spectrometry, fluorimetry and fading spectrophotometry, suffer from the requirement of well-established laboratory settings, high complexity and long testing times. However, a simple and cost-effective fluorimetric sensor (FS) has been developed, which is based on the detection of oligonucleotides by fluorescence. It is based on fluorescence magnetic nanoparticles (FMPs) coupled to specific DNA probe (FS-FPMs/DNA). The principle of detection was based on a competitive inhibition of conjugated GLY-double target/probe-FMP (Lee et al. 2013). GLY could be easily quantified using confocal laser scanning microscopy and low-cost UV photometric analysis. Unfortunately, this study did not explore the possible cross-reactions with GLY analogues and possible environmental interferents. This study further improves the previous report by the same authors, who developed a competitive inhibition assay by free GLY using GLY-dsDNA-gold conjugate nanoparticles, which was used to quantify fluorescence intensity through an immunoassay (FS-AU/DNA) (Lee et al. 2010).

Another immunosensor (IS) was developed using carbon dot-labeled antibodies (lgG-CDs) that were able to specifically recognize GLY (Wang et al. 2016a). The fluorescent properties of this IS allowed the visualization of the GLY distribution into plant tissues. The excess of IgG-CDs is removed from the system using magnetic nanoparticles

$Fe_3O_4$ allowing a linear relationship between the fluorescence intensity of IgG-CDs and the logarithmic concentration of GLY.

Silva and colleagues employed diffuse reflectance spectroscopy (DRS) using a spot test on a filter paper (da Silva et al. 2011; Metzger 1997). Although the technique is simple, precise, inexpensive, environmentally friendly, requires minimal amounts of samples and reagents and is applicable to environmental, drinking water and commercial formulations, it presents very low sensitivity and may not be applicable to soil samples.

Most of the spectrophotometric methods require colored reagents and chromophore groups. To surpass this difficulty, a simple and rapid method was developed by transforming the amino group of GLY into a dithiocarbamate derivative. A copper (I) perchlorate reaction formed a yellowish green-colored complex with maximum absorbance at 392 nm (Sharma et al. 2012). The color intensity and stability were obtained at 60 s, and remained for at least 90 min, which was an advantage over the commonly used spectrophotometric methods. In some cases, it is useful to apply a low-cost, simple and fast method, despite its lower sensitivity, when compared with chromatographic methods or CE. For example, some researchers have used UV–Vis spectroscopy for GLY quantification in laboratory experiments to evaluate the adsorption capacity in soil sample under different pH values by performing adsorption isotherms under well-controlled conditions and was able to quantify GLY in the range from 0.084 to 21.8 mg $L^{-1}$ (Waiman et al. 2012). However, a derivatization step was performed, in which the GLY amine group was modified by FMOC-Cl in acetonitrile at pH 9.0. Besides, a non-characterized soil sample was incubated overnight in buffer solution and adjusted to different pH values, and therefore, the potential use for field conditions with different soils is yet to be demonstrated, since differences in the concentration of organic compounds and metal ions were not referred to, or considered (Waiman et al. 2012). Another method has also been proposed, which uses carbon disulfide to convert the GLY amine group into dithiocarbamic acid. Dithiocarbamate by-product is then used as a copper-chelating group that results in a yellowish-colored complex used for measurements (Jan et al. 2009).

Another colorimetric sensor for GLY detection has specifically been made by aggregating 2-mercapto-5-nitrobenzimidazole-capped silver nanoparticles (MNBZ-Ag NPs) and $Mg^{2+}$ ions. This structure suffers a reduction in the distance of its interparticle complex formation between MNBZ-Ag NPs–$Mg^{2+}$ ion and GLY, which promotes a color switch from yellow to orange-red (Rawat et al. 2016). The colorimetric property was based on the inhibition of peroxidase-like activity of $Cu^{2+}$ through the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB). The color solution changed according to the concentration of GLY when complexed with $Cu^{2+}$ (Chang et al. 2016a). The indirect colorimetric determination method of GLY was developed after its oxidation with hydrogen peroxide to orthophosphate, reaching levels between 1000 and 20,000 ng $mL^{-1}$ (Glass 1981). Although the complex is pH dependent and needs a preconcentration step before measurement, it can detect GLY in different samples.

Recently, the dithiocarbamic acid was used as an optical color changer of the polyvinyl alcohol (cd-PVA; copper-doped polyvinyl alcohol) nanofiber from blue to yellow (De Almeida et al. 2015). Although advantageous, requiring small sample volume, with a fast response time (~ 1–3 s), good color spot stability (4 h) and low cross-reactivity with GLY derivatives and structural analogues, AMPA and glycine, respectively, the sensor was not very sensitive and could not keep stability for longer periods (> 20 days). Another drawback was the system susceptibility to compounds and ions commonly found in environmental waters at a lower concentration (60,000 ng $mL^{-1}$), which could require pre-treatment, besides being strongly dependent on pH 11–12.

An additional colorimetric sensor strip was capable to detect not only GLY, but also three other organophosphorus compounds: dimethoate, dichlorvos and chlorpyrifos (Liu et al. 2015). It presents some advantages, such as easy readout, fast analysis, easy operation, low cost, simple transportation and storage. However, although its detection limit has met the maximum residue limits reported in the EU pesticides database, naked eyes cannot distinguish very large ranges, so specific photonic equipments are required for measurements. Briefly, stabilized gold nanoparticles (NPs) with cysteamine (CS-AuNPs) without aggregation present a red color, and when GLY aggregates to these NPs, the color switches to blue or purple color (Zheng et al. 2013).

Another optical sensor was designed using hollow-core metal-cladded waveguide (HCMW) with double-metal surface. The insertion of chromogenic GLY in the hollow core promoted the orientation for the wave propagation exciting highly sensitive ultra-high-order modes, through small incident angle coupling (Dai et al. 2014). Detection of GLY concentrations as low as 0.23 ng $mL^{-1}$ was unambiguously identified within several minutes. Several interesting advantages are mentioned, such as the small analyte volume required, environmentally friendly, compactness, inexpensive, label-free and real-time detection. However, the system behavior is unknown in field samples since detection was performed only in ultrapure water.

Reporter spacer receptors (RSR), both colorimetric- and also luminescence-based systems, are the most widely used optical chemosensors (OC) (Roberts 1989). But, the sensor synthesis requirement is very expensive. To overcome this setback, Minami et al. (2014) developed an optical chemosensor named “Intramolecular Indicator Displacement

Assay (IIDA)" (OC-IIDA). In this sensor, an attached dye works as an anionic chromophore, which is bound to the receptor. The anionic analyte GLY competes for receptor binding leading to changes in photophysical properties of the dye. Besides the possibility of reusing it, one of the benchmarks of this work is the study of phosphate-type anions, e.g., phosphate (Pi), pyrophosphate (PPi), AMPA and phosphonate GLY in aqueous solutions with and without excess of NaCl as a competing electrolyte, which showed no differences (Minami et al. 2014).

Quantum dots (QDs) are also used to develop bioanalytical methods based on fluorescence resonance energy transfer (FRET) (Algar and Krull 2008). QDs act as donor fluorophore to a proximal ground-state acceptor (Guo et al. 2014). In this work, gold NPs stabilized with cysteamine (CS-AuNPs) were used as acceptors of fluorescence emission by QDs capped with thioglycolic acid (TGA-CdTe-QDs). The presence of GLY created electrostatic interactions with CS-AuNPs, promoting disaggregation between CS-AuNPs and TGA-CdTe-QDs, and consequently generating fluorescence.

#### Surface-enhanced Raman scattering

Surface-enhanced Raman scattering (SERS) can magnify molecular vibrations in a system. The enhancement factor can be as much $10^{14}$ or $10^{15}$, which is sufficient to allow even a single molecule to be detected. The enhancement takes place at a nanoscale roughness reflective metal surface where the molecules are adsorbed. Gold nanorod particles can be synthesized with controllable size and numerous surface functionalities, and due to its tunable optical properties, it can be used as SERS substrates. Therefore, GLY was detected in attomol levels through gold nanorods derivatized with 4-mercaptophenylboronic acid (Torul et al. 2010). At the range of $1–10^{-16}$ mM the SERS signal exhibited a linear dependence within the GLY. A disadvantage was that all solutions were prepared using deionized water, free of any organic matter, and considering the high complexity of organic compounds and metal ions interactions with GLY, studies should be performed to better understand and discriminate such complex profiles.

#### Surface plasmon resonance

Surface plasmon resonance (SPR) can be used as an optical biosensor that monitors the interactions between an analyte in a solution and a bioelement immobilized on the SPR sensor surface through special electromagnetic waves—surface plasmon polaritons. One of the advantages provided by SPR biosensors is its label-free real-time analytical technology in which the main application is to detect biological analytes through biomolecular interactions (Homola 2003). Using bacteriophages (SPR-pd), it has been developed a specific oligopeptide that presents good specificity against glycine, thiacloprid and imidacloprid (Ding and Yang 2013). SPR is much more sensitive than nuclear magnetic resonance spectroscopy (NMR); however, the immobilization of binding partners creates several undesirable issues. In particular, the molecular binding site may be near the surface and induce steric hindrances that could affect binding energy and/or kinetics, and the surface layers often exhibit decreased activity during the analysis (Ding and Yang 2013).

#### Nuclear magnetic resonance

NMR provides detailed information about the molecular structure through the exploration of magnetic properties of certain atomic nuclei. Using $^{31}$P NMR it was possible to determine GLY in blood, liver and urine in postmortem samples, reaching levels of 1 mg $mL^{-1}$ in less than a minute (Dickson et al. 1988). Using $^{31}$P and $^{1}$H NMR, GLY could be detected in biological fluids in between 10 and 20 min in a small sample size without any pretreatment (Cartigny et al. 2004). In fact, $^{31}$P NMR has been used to detect organophosphorus compounds as endogenous phosphorus metabolites present in plasma or urine. Interestingly, other components can be detected in the same NMR spectrum, e.g., the occurrence of metabolic acidosis in salicylate and alcohol/glycol poisonings (Cartigny et al. 2004). The main limitation of NMR analysis is the quantification analysis, particularly when therapeutic agents are administered, because several signals can overlap. However, in the clinical emergency context, the diagnostic problem is partially solved when only detection is needed, as is the case of monitoring the effectiveness of drug elimination. In an emergency clinical context, the diagnosis problem could be at least partly solved if a rapid identification procedure was available. The NMR method should be useful in rapidly confirming the diagnosis of poisoning and in evaluating the effectiveness of elimination procedures such as gastric lavage, forced diuresis or hemodialysis (Cartigny et al. 2004).

#### Chemiluminescence-molecular imprinting sensor

Chemiluminescence-molecular imprinting sensor (CL-MIS) can be made using small dimension microspheres (MIMs) as a molecular printer, reaching extremely high surface-to-volume ratio (Zhao et al. 2011). It was synthesized onto a molecularly imprinted polymer base, using precipitation polymerization with GLY as template. A circular glass sheet was used as a form to be coated by GLY-MIMs suspension. After, placing it into the well, the microplate is prepared as a recognition element, acting as a chemiluminescence (CL)-molecular imprinting (MI) sensor able to perform 96 sequentially independent measurements in just 10 min. Stability tests showed around 90% of its initial CL intensity for

3 months when stored in air at 4 °C. The authors pointed out that CL-MIS may become a useful and quick analytical technology for molecular recognition due to its excellent selectivity for GLY determination; however, they did not compare the GLY recognition sensor capacity with its derivatives as AMPA. Therefore, specificity was not considered.

## Electrochemical sensors

### Amperometric and voltammetric methods

To access a simple and fast way to determine GLY residue in soil samples, a single-sweep oscillo-polarographic method was developed (Sun et al. 2007). This is an adaptation of an old method (Brłnstad and Friestad 1976) that detected GLY in natural water by nitrosation, converting GLY in *N*-nitroso-*N*-(phosphonomethyl) glycine after derivatization with sodium nitrite, followed by detection with differential pulse polarography. This derivative showed a sensitive cathodic peak at − 0.81 V against saturated calomel electrode in pH 0.7 and resulted inefficient determination of GLY in formulations and soil samples. However, the presence of concomitant metal ions or organic compounds may have probably affected the analysis, and interference of any potential confounding effect should be further investigated to validate the proposed method for GLY quantification.

Glyphosate could be detected electrochemically in 20 min by its ability to bind to horseradish peroxidase (ES-HRP). Although the LOD of 1.70 ng $mL^{-1}$ achieved was very good, it is not known its applicability to real samples. Another ES-HRP with good reproducibility was also developed using a gold disk electrode. It is a sensitive, simple and low-cost method. Besides it can detect AMPA too. One interesting characteristic of this biosensor is the possibility to reuse it for up to three measurements before surface saturation (Songa et al. 2009a). Another proposed sensor also uses HRP electrostatically immobilized onto the surface of a rotating gold disk electrode modified with PDMA-PSS [poly(2,5-dimethoxyaniline)-poly(4-styrenesulfonic acid) nanoparticles for amperometric detection. Before the exposure of GLY onto the electrolyte solution the activity of the enzyme was measured with hydrogen peroxide. The stability of this enzymatic electrode was very good and could be used for over 60 measurements (Songa et al. 2009b).

Another electrochemical sensor study uses enzymatic inhibition method to determine GLY through a modified nanoclay that immobilizes atemoya peroxidase (ES-Atemoya). It is applicable to real water samples, stable for 8 weeks, and does not need pretreatment process. Unfortunately, there is no information regarding its portability and cross-reactivities with analogues (Oliveira et al. 2012).

Other two reports have been published on nanofilm-modified amperometric sensors. One used an electrogenerated NiAl-LDH ($Ni_1-Al_x(OH)_2NO_{3x}\cdot nH_2O$-layered double hydroxides) thin film by electrodeposition on the Pt electrode surface. The principle of detection is based on oxidation of amine group by Ni (III). The electrocatalytic efficiency and morphology of the obtained LDH film was strongly dependent on the electrodeposition time. It is important to note that this sensor could not properly work at strong alkaline pH (Khenifi et al. 2009). Despite these electroactive NiAl-LDH films easily electrodeposited, lower LODs could not be achieved. The second sensor was capable of detecting chemicals in soil, human serum samples and water simultaneously without cross-reaction. However, a derivatization by nitrosation is needed for GLY in order to distinguish herbicides, leading to an *N*-nitroso Glyphosate derivative (Prasad et al. 2014).

Toward a sensor fabrication, (*N*-methacryloyl-L-cysteine) monomers through S–Au bonds were used to immobilize a nanostructured polymer film that was grown directly onto the electrode surface. These molecules were polymerized in the presence of templates, cross-linker, initiator and carbon nanotubes as pre-polymer mixture. It reached limits as low as 0.35 ng $mL^{-1}$. Although it is clear there is no cross-reaction between GLY and GLU, there is no information about other possible cross-reactions among its metabolites. However, these procedures are generally very slow, need laboratory apparatus of high cost and are inadequate for on-site or in situ monitoring (Prasad et al. 2014).

A voltammetric electronic tongue (VET) was used in the determination of GLY. The VET consisted of three metallic electrodes of cobalt, copper and platinum, which produced a signal pattern when subjected to GLY in aqueous sample. Besides its simplicity, speed (2 s) and low cost, the electronic tongue was also capable of detecting this analyte, even in the presence of different concentrations of potential interferents, such as $Ca^{2+}$ and humic acids (Bataller et al. 2012). Another voltammetry-based detection system used rhodium, cobalt and copper electrodes coupled to a mathematical model to predicted GLY concentration, but despite the presence of fertilizers (ammonium nitrate) and organic substances, the system proved to be effective (Martínez Gil et al. 2013). Finally, voltammetric determination of GLY using a copper electrode in natural waters was performed in agreement with the green chemistry concept. The optimization showed ideal condition in neutral pH, reaching an LOD of 59 µg $L^{-1}$ (Garcia and Rollemberg 2007). Still with copper electrode, an electrochemical determination of the AMPA in drinking waters was demonstrated (Pintado et al. 2012). Electrochemical and spectroscopic investigations of GLY and AMPA were performed successfully on pure samples of GLY and commercial products (Habekost 2015). Electrochemical behavior of GLY on nickel and copper

electrode was measured in the development of a sensor by cyclic voltammetry (Sierra et al. 2008).

Interestingly, despite the success of several electrochemical sensors in the last decade, none of them has become a reality, and it is still questionable their reliability and reproducibility in real-time detection without controlled complex environments, especially because of variations and complexity of production of such electrodes, and also because of the complex interactions of GLY with other compounds. Although the proof of concepts were presented, one should be able to demonstrate the production cost-effectiveness, sensitivity and reproducibility in field detections for final validation.

A photoelectrochemical sensor (PEC) using a glassy carbon electrode (GCE) firstly modified with nanosheets graphitic carbon nitride g-$C_3N_4$ NSs (g-$C_3N_4$/GCE) and then self-assembled with $Ag^+$ onto the g-$C_3N_4$/GCE was performed (Li et al. 2016). The pyridine nitrogen units on g-$C_3N_4$ backbone could absorb chemically the $Ag^+$ and then photogenerated electrons would be used to reduce $Ag^+$/Ag, leading to the inhibition of electrons transfer and decrement of photocurrent. However, GLY can displace the Ag to form a very stable chelate, promoting an increase in current in a process called "Binding-induced internal-displacement of signal-on photoelectrochemical response." Response was given in 5–15 min. The PEC sensor possesses fine fabrication reproducibility, detection precision and excellent selectivity, even in the presence of the interferences, such as sulfluramid, glucose, vitamin B1, carbendazim, starch, sucrose and acetochlor. Even with excess of other interfering ions, such as $Ca^{2+}$, $Zn^{2+}$, $Al^{3+}$, $Pd^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Na^+$, $K^+$, $Cd^{2+}$, and all interferences mixed in $Ag^+$ solution, the photocurrent remained practically constant. Moreover, the mixture of the nine metal ions did not influence the signal response to $Ag^+$. The question that remains is—could $Ag^+$ of the electrode be strong enough to displace other chemicals that commonly bind GLY? This sensor still needs to be tested in the presence of humic acid. Some drawbacks of it are the pH- and time-dependent responses, besides losing its photocurrent response very quickly, even if stored in ideal conditions (dark sealed environment at 4 °C). Lastly, it is not known its behavior in the presence of GLY analogues main (Li et al. 2016).

## Capillary electrophoresis

Capillary electrophoresis (CE) is a common method to detect GLY or AMPA. This method requires derivatization for the same reasons cited before. CE is generally associated with UV–Vis (Cikalo et al. 1996; Chang and Wei 2005), fluorescence (Molina and Silva 2002) and MS (Goodwin et al. 2003) detectors, and in this latter method, derivatization is not required. A rapid and direct pre-concentration technique followed by CE was utilized, and detection was based on a capacitively coupled contactless conductivity system (CE-C(4)D). The method showed good reproducibility for GLY and its derivatives and analogues, AMPA and GLU, respectively (See et al. 2010). Comparing CE with LC, in samples of low to medium conductivity, the GLY concentration might be effectively determined, but there is the necessity to adjust the sample volume to the required sensitivity. Considering this and the fact that CE is much cheaper and less time-consuming than LC, CE should be the preferred method. On the other hand, in samples with high concentration of salts, AMPA is poorly extracted by the strong anion-exchange resin that was used to pre-concentrate both analytes in environmental aqueous samples (Corbera et al. 2005). Clikalo et al. (1996) used the same CE/UV procedure, however using tetradecyltrimethylammonium bromide (TTAB) as an electro-osmotic flow modifier and reached LOD with gains of 85 ng $mL^{-1}$ to GLY and 60 ng $mL^{-1}$ to AMPA in pure water samples in contrast, with 5000 ng $mL^{-1}$ for and 4000 ng $mL^{-1}$ reached by the previous report. Molina and Silva also reached even better LOD, from 0.06 to 0.16 ng $mL^{-1}$ (Molina and Silva 2002), by using a non-ionic surfactant MEKC-LIF as a selective agent, which was fast and sensitive tool for the determination of GLY, GLU and their metabolites. Besides, once it does not need a previous enrichment steps, it increases its potential for analysis of environmental samples. Chang and Liao (2002) also used indirect fluorescence as a detection method in commercial formulations and showed that this technique can be applied in routine analysis, but direct analysis of GLY in groundwater is still problematic. Finally, Goodwin et al. (2003) combined CE with MS for simultaneous determination of GLY, GLU and their metabolites using a simple microelectrospray interface (mESI). To drive separation and generate the electrospray, the interface uses the voltage applied to the CE capillary, thus avoiding sample dilution. Other advantage of mESI in relation an ESI is that it has no physical contact between the capillary outlet and the ground-state electrode because electrical contact is achieved by placing the capillary tip 1 mm away from the MS, that is, under these conditions the voltage generates the electrospray and promotes the necessary electrophoretic separation (Mazereeuw et al. 1997). This technique presents a hindrance, because only high resistivity background electrolytes (BGEs) can be used. Besides, if the BGE concentration is too high, interference may occur during detection due to electrical discharges. Some of the operational limitations of the "homemade" mESI used were the restricted range of acceptable sample matrices. On the other hand, when compared to the typical sheath liquid interface systems, it has the advantage that analyte

dilution is not required. The microchip electrophoresis system with laser-induced fluorescence (LIF) was also used as detection system for fast and sensitive analysis of GLY and GLU residues. In order to minimize the cost of the technology, a low-cost LIF detector with disposable cyclic olefin copolymer microchips was used (Mazereeuw et al. 1997); moreover, the technology is portable and user-friendly.

## Enzyme-linked immunosorbent assays

The enzyme-linked immunosorbent assay (ELISA) has been presented as an alternative approach to the drawbacks exposed in the other techniques, such as the requirement of derivatization procedures, hard sample pre-treatments, high-cost end equipments and reactions and time for analysis. Immunoassay offers some advantages over chemistry methods, since labeled antibodies can be used in competitive reactions to detect herbicides. It is also selective and sensitive to determine GLY and enables prompt environmental surveys. Besides, the ELISAs's LOD are higher than those typically achieved by LC/MS/MS, better than GC/MS methods, and even similar of those obtained by HPLC (Rubio et al. 2003). Two kinds of ELISA have been used to identify GLY. The first includes a derivatization step with acetic anhydride followed by detection with immobilized antibodies, resulting in an LOD equal to or less than 0.6 ng $mL^{-1}$ (Rubio et al. 2003). The second, an indirect ELISA (CI-ELISA) just needs water pretreatment. Moreover, it was found to be highly specific for GLY detection with cross-reactivity less than 0.1%, even in the presence of related compounds, e.g., AMPA and GLU (Clegg et al. 1999). A so-called linker-assisted enzyme-linked immunosorbent assay (L'ELISA) method that first derivatized GLY with succinic anhydride achieved LOD values as low as 0.1 ng $mL^{-1}$ (Lee et al. 2002). Additionally, González-Martínez et al. (2005) also improved the LOD to 0.021 ng $mL^{-1}$ by using a GLY ELISA sensor. In contrast, the drawback of ELISA methods is the high limits of AMPA detection, which under certain circumstances may be present in the absence of its parent pesticide (e.g., high use of GLY and vulnerable hydrogeological settings) (Scribner et al. 2007). Therefore, the quantification of AMPA through conventional analytical methods should be concurrently applied along with determination of GLY by ELISA (Sanchís et al. 2012). The difficulty of monitoring mixed herbicides is due to the requirement of specific antibodies, which are not always available, because generation of antibodies against poisonous chemicals cannot be produced by conventional methods. In conclusion, ELISA is the most cost-effective method for routine analysis, but the commercially available kits are still high relatively expensive (González-Martínez et al. 2005), and applications for soil samples in field conditions have not been demonstrated.

## Cell biosensor

A cyanobacterium sensor was developed based on the luciferase activity present in a modified *cyanobacterium Synechocystis* sp. cell. The results showed that the decrease in bioluminescence could be correlated with the herbicide concentration and with increasing incubation time. The reduction bioluminescence by 20% and 50% (EC20 and EC50) of the herbicide Glyphosate was determined at 6 h and 1 day, respectively. The EC20 at 6 h was $3.62 \times 10^3 \pm 0.79$ ng $L^{-1}$, and the EC50 at 1 day was $3.10 \times 10^3 \pm 0.17$ ng $L^{-1}$. One of the major restrictions of this method is its low selectivity, presenting cross-reactions with other herbicides as diuron, paraquat, mcpa, mecoprop, atrazine, propazine and simazine. Besides, the pH conditions must be optimized in order to obtain reproducible responses (Shao et al. 2002). The use of the green alga *Selenastrum capricornutum* demonstrated to be less sensitive to GLY when two parameters are considered: sensitivity and reaction time. The EC50 of 1050 ng $mL^{-1}$ could only be reached after 4 days (Abdel-Hamid 1996).

In comparison with other methods, such as the algal biosensor, chlorophyll fluorescence-based and isolated photosystem II (PSII) (Campanella et al. 2001; Frense et al. 1998; Koblizek et al. 1998), it is simpler, faster, economical and accurate. It is more suitable for prediction of long-term effects of chronic toxicity of pollutants, because of the longer doubling time of cyanobacteria. Unfortunately, to decrease the detection limit, it is necessary to increase the assay time (Schafer et al. 1994). Other cell biosensors preserve cell "physiological" functions by the utilization of an agarose gel matrix with immobilized cell components, to access electrophysiological interactions by measuring its potential. This method was called Bioelectric Recognition Assay (BERA). In a preliminary work it was able to specifically detect GLY in 3–5 min in concentrations lower than 0.1 ng $mL^{-1}$, even among other compounds with similar structure in water solution (Kintzios et al. 2001).

BERA biosensors can determine GLY in a fast and cost-efficient way without prior knowledge of the sample. Besides, it has kept its stability even after a 2-month storage in low temperature. This method responds differently to GLY and AMPA herbicides. Another characteristic of this sensor is that, rather than operating the biosensor electrode in direct contact with a single cell, BERA's electrodes are inserted into the matrix of a group of cells. It approaches the measurements made in natural tissues. It is expected that an evolution of this type of sensors should be made with

the interface of luminescent cells with optical transducers. Finally, the factors that can affect the biosensor response are, among others, gel density, cell density in the matrix, and cell size, because it has a direct correlation with gel porosity (Frense et al. 1998). However, it is not known how the biosensor will behave in field samples. An important drawback of this method is that the sensor depends on many careful and detailed steps, including cell culture.

### Cross-responses from multiple sensors

Different detection methods using data from conventional measurements of water quality have been published in numerous publications, which include artificial intelligence, statistical analyses and data mining. Cross-responses from multiple sensors (CRMS) are also a proposed method to detect some contaminants. An online water quality monitoring system can detect GLY from simultaneous and continuous measurements of eight parameters: UV-254, pH, temperature, conductivity, turbidity, oxidation–reduction potential (ORP), nitrate-nitrogen and phosphate, even if the contaminant in concentrations as low as 2000 ng $mL^{-1}$ had been introduced 1 min before (Che and Liu 2014). However, for each contaminant it is necessary to optimize the analytical parameters. Another drawback of such algorithm is the use of conventional parameters that are highly affected by other environmental factors, such as different soil compositions, different fertilizer formulations, among others.

## Discussion

Commercial glyphosate contains toxic agents called adjuvants (Mesnage et al. 2013). Most investigators have neglected the analysis of these toxic products. This is clear from analyzing Table 1 where basically only AMPA and GLU are the most common chemicals simultaneously analyzed with glyphosate. In clinical tests, immunosensors are usually more sensitive than ELISA; however, for GLY analysis, ELISA has shown to be more sensitive than most of the methods presented in this review. Among chromatographic methods, the most sensitive one for GLY detection is liquid chromatography using solid-phase extraction coupled to mass spectrometry with electrospray ionization (LC–SPE–ESI/MS/MS). However, SERS was much more sensitive reaching attomole levels of GLY using gold nanorods, far surpassing the other methods, although it is not yet applicable to field conditions. Recovery studies are a classical technique for validating the performance of an analytical method, mainly in the absence of a reliable comparison method. Average recovery analytes (ARA) showed superior performance for diffuse reflectance spectroscopy. The detection of Glyphosate in living tissues with high protein content appears to exhibit a systematic negative error. Studies with bluegill sunfish exposed to 14C-radiolabeled Glyphosate showed subsequent contamination in which the amount of radiolabeled extracted with EDTA was greater than the GLY content detected in these fish. After the digestion procedure of these samples with protein K and a new extraction with EDTA, a significant increase of radiolabeled occurred, suggesting that the GLY is strongly incorporated to the protein. Probably GLY is misleadingly replacing the amino acid coding for glycine during protein synthesis (Anthony and Stephanie 2017). Generally, the analytical chemistry is faced with problems in method development, reachable detection and quantification limits, for GLY (Huhn 2018).

## Conclusion

Nowadays, many kinds of glucometers are known as reference platforms for detection, due to their sensitivity, portability, reproducibility, fastness, specificity, selectivity, stability, low cost and easiness to operate. However, these characteristics cannot be found in Glyphosate detectors. There are three classes of security levels for food and potable water in which a detector can operate: below the 0.1 ng $mL^{-1}$ limit (EU), above 700 ng $mL^{-1}$ limit (US) and between both. Most of the sensors that reach EU values fail in other aspects as reproducibility, possible use in real samples, stability, portability or selectivity. It should be pointed out, however, that sometimes the method of choice should be cheaper and less time-consuming, instead of being highly sensitive. Sensors that do not need pre- or post-derivatization, or pretreatment of samples, are the most needed characteristic, and this is one of the drawbacks of the current methods. There is an urgent need to investigate residual applications of GLY directly in environmental samples on site, and for this, sensitivity, specificity, portability and speed are essential. Interestingly, such characteristics have been reported for GLY sensing using colorimetric or electrochemical biosensors, but these biosensors are difficult to prepare and maintain, due to the use of antibodies as probes, which require controlled conditions for optimal operation. In this sense, the major concern is the shelf life of such sensors, and solutions must search for greater stability prior to detection. Several authors have also claimed the development of low-cost methods to detect GLY, but none of them have published their costs or compared with other methods. Real-time detection at lower cost, faster, with good sensitivity is important issues, and at the moment no method can reach the required parameters for field tests with environmental samples.

Another important issue is that GLY is never used alone, which means that commercial formulations contain

**Table 1** Comparative analysis among glyphosate detection methods

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| HPLC | Pregnant women<br>Umbilical cord | Paraquat | 0.4 | 94.33–99.03% (ARA)<br>Fluorescence (detection) | Kongtip et al. (2017) |
| HPLC | General water | – | 0.02–6.25 × $10^3$ | – | Ding et al. (2013) |
| HPLC | Soils and sludges | – | 10 (< 15%) | 9-Fluorenyl methoxycarbonyl chloride (derivatization)<br>75–110% (ARA)<br>Fluorescence (detection) | Sun et al. (2017) |
| HPLC | Seawater | AMPA | 0.6 | 9-Fluorenyl methoxycarbonyl chloride (derivatization)<br>Borate buffer<br>Fluorescence (detection) | Wang et al. (2016b) |
| HPLC/MS (HILIC–MS/MS) | Olive oil and olives | Amitrol, cyromazine, diquat, paraquat, mepiquat, trimethylsulfonium, fosetyl aluminum | 50 | Liquid partitioning with methanol | Nortes-Méndez et al. (2016) |
| HPLC/MS | Milk and urine produced by lactating women | AMPA | 0.28 (urine) | The produtes aren't detectable in milk | Nortes-Méndez et al. (2016) |
| HPLC/MS/MS | Water matrices (drinking, surface and groundwater) | AMPA | 0.1 | No derivatization<br>85–113% (ARA) | Guo et al. (2016) |
| LC–ESI/MS/MS | Soybean | AMPA, GLU | 300 (5.3–13%) | 73.9–109.1% (ARA) | Martins-Júnior et al. (2009) |
| LC–ESI/MS/MS | Soybean | AMPA | 5 (5.3–13%) | 73.9–109.1% (ARA) | Martins-Júnior et al. (2011) |
| LC/FLD | Fatty matrix (rapeseed) | AMPA | 20 (12.8–14.7%) | 70.8–74.1% (ARA) | Kaczyński and Łozowicka (2015) |
| LC–SPE–ESI/MS/MS | General water | AMPA, GLU | 0.0002 (< 7%) | 91–107% (ARA) | Ibáñez et al. (2005, 2006), Vreeken et al. (1998) |
| LC–SPE–ESI/MS/MS | Surface, drinkable and waste water | AMPA, GLU | 0.03 (< 8.4%) | 50 samples (62 min $run^{-1}$) in a sequence (analysis time)<br>96% (ARA)<br>9-Fluorenyl methoxycarbonyl chloride (derivatization) | Vreeken et al. (1998) |
| LC/MS–ESI | Urine and serum | BIA, GLU, AMPA, 3-MPPA | 0.05 | – | Sato et al. (2009) |
| LC/MS/MS | Water | AMPA, GLU | 1.2 (6.3–10.2%) | 12 min (analysis time)<br>77.0–102% (ARA)<br>Metal ions, sample preservation, and storage time (interferents) | Hao et al. (2011) |
| LC/MS/MS | Water | AMPA | 0.025 (groundwater)<br>0.066 (surface water)<br>0.105 (WWTP effluent) | Fluorenylmethyl chloroformate (derivatization)<br>97.0–100% (ARA) | Poiger et al. (2017) |
| LC/MS/MS | Fatty matrix (rapeseed) | AMPA | 5 (6.9–9.2%) | 88.8–95.0% (ARA) | Kaczyński and Łozowicka (2015) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| LC/MS/MS | Serum | AMPA, GLU, BIA, AMPA, 3-MPPA | 30 (5.9%) | 30 min (analysis time)<br>94–108% (ARA)<br>Often observed (interferents)<br>Filter (pretreatment) | Yoshioka et al. (2011) |
| LC/MS/MS | Blood, urine and gastric content samples | Paraquat, diquat, GLU | 100 | pH (4–8) | Tsao et al. (2016) |
| LC–MS | Coffee leaves | AMPA | 41 | FMOC (derivatization) | Schrübbers et al. (2016) |
| LC–FLD + MS/MS | Water canals | AMPA | 0.058 | Lyophilization (3–4 days for 72 samples)<br>pH 9<br>FMOC-Cl (derivatization) | Ramirez et al. (2014) |
| LC–SPE | Tap, filtered and river water | AMPA | 200 | 8 min (analysis time)<br>67.1–104.0% (ARA) | Delmonico et al. (2014) |
| GC/CI/MS | Biological | Phosphonoglycine, phosphonosarcosine, phosphonoalanine, phosphono-*b*-alanine, phosphonohomoalanine, phosphono-gama-homoalanine, GLU | 1 | TFA–Gly $(OMe)_2$ (derivatization) | Kudzin et al. (2003) |
| GC/FID | Biological | Phosphonoglycine, phosphonosarcosine, phosphonoalanine, Phosphono-*b*-alanine, phosphonohomoalanine, phosphono-gama-homoalanine, GLU | 30 | TFA–Gly $(OMe)_2$ (derivatization) | Kudzin et al. (2003) |
| GC/FPD | Rice, soybean sprouts | GLU, AMPA, 3-MPPA | 20 | Trimethyl orthoacetate (TMOA) (derivatization) | Tseng et al. (2004) |
| GC/FPD | River water, soil, carrot | GLU, AMPA | 8,1 2 and 20 pg, respectively/injection | 20 min (analysis time)<br>91–106% (ARA)<br>*N*-isopropoxycarbonylmethyl (derivatization) | Kataoka et al. (1996) |
| GC/MS | Biological | Phosphonoglycine, phosphonosarcosine, phosphonoalanine, phosphono-*b*-alanine, phosphonohomoalanine, phosphono-gama-homoalanine, GLU | 1.5 | TFA–Gly $(OMe)_2$ (derivatization) | Kudzin et al. (2003) |
| GC/MS | Human serum | AMPA | 250 | *t*-BDMS (derivatization)<br>> 73% (ARA) | de Llasera et al. (2005) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| GC/MS | Groundwater | AMPA | 0.1 (10%) | 103% (ARA)<br>Trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) (derivatization) | Kudzin et al. (2002) |
| GC/MS | Soil | AMPA | 6 (23%) | 78% (ARA)<br>Trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) (derivatization) | Kudzin et al. (2002) |
| GC/MS/MS | Deionized water | – | 0.24 | Trifluoroacetic anhydride (TFAA) and 2,2,3,3,4,4,4-heptafluoro-1-butanol (HFB) (derivatization)<br>Nitrite nitroso ion and amylum and iodine (pretreatment) | Lou et al. (2001), Ding et al. (2015) and Pei and Lai (2004) |
| GC/IT–MS | GLY, GLU and bialaphos | GLU, BIA, their metabolises and nineteen amino acids | 10–20 | *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide in dimethylformamide (derivatization) | Tsunoda (1993) |
| IC | Water | Bentazone and picloram | 1.54 | 11.0–106.0% (ARA)<br>50 min per assay (analysis time) | Luo et al. (2015) |
| IC | Aquatic environment | Not informed | 0.04 (1.94%) | 96.4–103.2% (ARA)<br>inorganic ion and organic acids (no interferents) | Zhu et al. (1999) |
| IC/ICP–MS | Water | AMPA, polyphosphates | 0.7 ($\leq$ 7.4% for $n = 3$) | 97.1–107.0% (ARA)<br>500 µL (sample injection volume) | Guo et al. (2005) |
| IC/ICP–MS | Reservoir and treated water, and clean water reclaimed from waste water | GLU, fosamine, ethephon | 1.1–1.4 | 95–109% (ARA) | Guo et al. (2007) |
| FS-FPMs/DNA | Distilled water | – | 0.04 | Unknown (interferents) | Lee et al. (2013) |
| DRS | Commercial formulations, environmental and drinking waters | – | 7280 (4.6–5.4%) | 93.2–102.6% (ARA)<br>$Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$, $Mn^{2+}$ and $SO_4^{2-}$, $CO_3^{2-}$, $C_6H_5O_7^{3-}$, $PO_4^{3-}$, $NO_3^-$ (Interferents)<br>20 µL (sample volume) | da Silva et al. (2011) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| IS | Water | – | 0.021 | 25 min per assay (analysis time)<br>Automated (derivatization)<br>Occasionally (Pretreatment)<br>> 500 × (reusability)<br>500 µL (sample volume)<br>48 h (stability) | González-Martínez et al. (2005) |
| IS | Soil (min. 10 g) | – | 7.9 | 25 min (analysis time)<br>Automated (derivatization)<br>Occasionally (Pretreatment)<br>> 500 × (reusability)<br>48 h (stability) | González-Martínez et al. (2005) |
| IS | Pearl River water, tea and soil | – | 8 | 87.4–103.7% (ARA) | Wang et al. (2016a) |
| Spectrophotometric | Groundwater | Gibberellins | 0.82 | – | Zhang et al. (2015b) |
| Spectrophotometric | Commercial formulation in soil and water samples | – | 3380 (0.5–1.02%) | 60 s (analysis time)<br>90.3–96.5% (ARA)<br>Dithiocarbamate (derivatization) | Sharma et al. (2012) |
| Spectrophotometric | Soil | – | 1100 (2.7%) | 80.0–87.0% (ARA) | Jan et al. (2009) |
| Spectrophotometric | Wheat grain | – | 1100 (2.7%) | 95.0–102.0% (ARA) | Jan et al. (2009) |
| Spectrophotometric | Distilled water | – | 1100 (2.7%) | 92.0–5.0% (ARA) | Jan et al. (2009) |
| Spectrophotometric | Legume | – | 210 | 98.0–102.0% (ARA) | Çetin et al. (2017) |
| Fluorescence | Agricultural products | GLU | – | Laser-induced fluorescence<br>Microchip electrophoresis | Wei and Pu (2015) |
| Fluorescence | Water | – | 670 | Sensor synthesized by combining copper (II) oxide and multiwall carbonnano-tubes (MWCNTs)<br>96–107% (ARA) | Chang et al. (2016b) |
| Fluorescence | Milli-Q water | – | 12 | Fluorescence (CDs/AgNPs) | Wang et al. (2016c) |
| Fluorescence | Water, tea, soil | – | 8 | Carbon dot-labeled antibodies (CD-IgG)<br>Antigen and magnetics beads (GLY-$Fe_3O_4$)<br>87.4–103.7% (ARA) | Wang et al. (2016a) |
| UV–Vis spectroscopy | Aqueous media | – | 84 | 9-Fluorenylmethoxycarbonyl chloride (FMOC-Cl) (derivatization)<br>Organic matter (interferents) | Waiman et al. (2012) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| UV–Vis spectroscopy | Aqueous solution | – | 3200 | Tungsten halogen lamp coupled to the cuvette holder by a 500 µm core diameter optical fiber | De Góes et al. (2017) |
| FS-AU/DNA | Distilled water | Pesticides and target materials containing carboxyl groups | 10 | 2 h (analysis time) | Lee et al. (2010) |
| SERS | Tomato juice | – | $16.9 \times 10^{-12}$ (2.48) | 90% (ARA)<br>4-Mercaptophenylboronic acid (derivatization) | Torul et al. (2010) |
| SERS | Water<br>Spiked beer | – | 0.1 (water)<br>0.01 (spiled beer) | Thiocholine-induced aggregation of OsCO-Au NPS | Tan et al. (2017) |
| SERS | Aqueous solution | – | 900 | He–Ne laser 632.8 nm<br>Silver nanoparticles | De Góes et al. (2017) |
| SPR-pd | Buffer solution | – | 98 | Glycine, thiacloprid, and imidacloprid (no interferents) | Ding and Yang (2013) |
| NMR $^{31}P$ | Biological fluids and tissue digest | – | $1 \times 10^6$ | 1 min (analysis time)<br>Just an enzymic digestion of the liver (pretreatment) | Dickson et al. (1988) |
| NMR $^{1}H$–$^{31}P$ | Biological fluids | Salicylate, alcohol/glycol | 33,814 | 10–20 min (analysis time) | Cartigny et al. (2004) |
| Colorimetric assay | Water and food | – | 2.9 | 2-Mercapto-5-nitrobenzimidazole-capped silver nanoparticles adding $Mg^{2+}$ | Rawat et al. (2016) |
| Colorimetric sensor | Drinkable, lake and ground water | – | 169 | 20 min (analysis time)<br>$H_2PO_4^{2-}$, $HPO_4^{-}$, $SO_4^{2-}$, $C_2O_4^{2-}$, $CO_3^{2-}$, $F^-$, $Cl^-$, $NO_3^-$, chloride salts of ion $Na^+$, $K^+$, $Ca^{2+}$, $Ba^{2+}$ and $Mg^{2+}$, $KNO_3$, KBr, and $Pb(NO_3)_2$, dicamba, AMPA, acetochlor (at 4 µg $mL^{-1}$), atrazine (at 4 µg $mL^{-1}$) (not interferents)<br>Concentrations can be differentiated by naked eyes | Chang et al. (2016a) |
| Strip colorimetric cdPVA | Environmental water | – | 100 | 1–3 s (analysis time)<br>AMPA and glycine (no interferents)<br>30 µL (sample volume)<br>20 days (stability) | De Almeida et al. (2015) |
| Strip colorimetric test | River water | AChE inhibitors | 100 | 30–60 min (analysis time) | Liu et al. (2015) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| CS-AuNPs | Tap water with chloro | – | 1 | 0.1 mM of GLU, AMPA, dicamba, acetochlor, atrazine, and trifluralin (not interferents)<br>$SO4^{2-}$, Al(III) and Cu(II) (interferents) | Zheng et al. (2013) |
| TR-FRET | Water | – | 131.9 | Lanthanide ($Ln^{3+}$)-doped nanoparticles | Wang et al. (2016d) |
| FRET | Apple | – | $9.8 \times 10^{-3}$ | Vitamin C, Vitamin B2, AMPA and GLU (not interferents)<br>2–15 min (analysis time)<br>pH 7.0 | Guo et al. (2014) |
| OC-IIDA | Water, salted water | – | 200 | 12 simultaneous tests | Minami et al. (2014) |
| CL-MIS-MIMs | Foodstuff, water | – | 46 (4.68% for $n = 11$) | 96 independent measurements sequentially in 10 min (analysis time) | Zhao et al. (2011) |
| Oscillo-polarographic | Formulations and soil | – | 96 (1.7) | *N*-nitroso-*N*-(phosphonomethyl) glycine (derivatization) | Sun et al. (2007) |
| DPP (differential pulse polarography) | Crops, soil, and water | – | 500–1000 | > 60% (ARA) aminomethylphosphonic acid (not interferents) | Friestad and Brønstad (1985) |
| Amp-HRP | Corn | GLU | 0.1 | 60 × (reusability) | Songa et al. (2009c) |
| DIPN-GNPs-PGE | Water | GLU | 0.34 (0.13%) | 97.8–102.3% (ARA)<br>*N*-nitroso (derivatization)<br>20 × (reusability)<br>60 days (stability) | Prasad et al. (2014) |
| DIPN-GNPs-PGE | Soil | GLU | 0.35 (0.48%) | 98.6–102.8% (ARA)<br>*N*-nitroso (derivatization)<br>20 × (reusability)<br>60 days (stability) | Prasad et al. (2014) |
| DIPN-GNPs-PGE | Human serum | GLU | 0.35 (5.49%) | 98.1–110.2% (ARA)<br>*N*-nitroso (derivatization)<br>50-fold dilution (Pretreatment)<br>20 × (reusability)<br>60 days (stability) | Prasad et al. (2014) |
| ES-Atemoya | Environmental water | – | 30 (5.5%) | 94.9–108.9% (ARA)<br>8 weeks (Stability) | Oliveira et al. (2012) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| ES-HRP | Doubly distilled water | – | 1.7 | 20 min (analysis time)<br>Unknown (interferents) | Songa et al. (2009b) |
| ES-HRP | Phosphate buffer solution (0.1 M, pH 6.10) | AMPA | 0.16 | 20 min (analysis time)<br>Unknown (interferents)<br>3 × (reusability) | Songa et al. (2009b) |
| NiAl-LDH | Deionised water | GLU | 169 | 20 s (analysis time) | Khenifi et al. (2009) |
| VET | Aqueous environments | – | 16,905 | Humic acids and $Ca^{2+}$ (not interferents) | Bataller et al. (2012) |
| Spectroelectrochemical Electrochemical | Double-distilled water | AMPA | 16,905 | Screen-printed electrode (SPE)<br>Signal of $[Ru(bpy)_3]^{2+}$ (ECL) | Habekost (2017) |
| DPV (differential pulse voltammetry) | Nature water | – | 59 | Copper electrode<br>Phosphate buffer 0.05 mol $L^{-1}$ and pH 7.3 | Garcia and do Carmo Rollemberg (2007) |
| DPV | GLY 99.9% purediluted | – | 2.02 | Copper phthalocyanine/multiwalled carbon nanotube film-modified glassy carbon | Moraes et al. (2010) |
| SWV (square wave voltammetry) | GLY 99.9% purediluted | – | 25 | Mercury drop electrode<br>*N*-nitroso (derivatization) | Teófilo et al. (2004) |
| SWV | Soil | – | 25 | Carbon fiber microelectrode<br>Phosphate buffer 0.2 mol $L^{-1}$ and pH 5.3 (pretreatment)<br>88.5–102.3% (ARA) | Tapsoba et al. (2012) |
| PEC | Orange juice | – | 0.004 (2.9–3.6%) | 94.5–114.9% (ARA)<br>pH and time dependent (pretreatment)<br>Starch, carbendazim, PMG, vitamin B1, glucose, sulfluramid, blank, sucrose and acetochlor (not interferents) | Li et al. (2016) |
| CE | Marijuana | Paraquat and AMPA | 8000 | Indirect UV/VIS detection | Sharma et al. (2012) |
| CE | Natural waters | AMPA | 85 (< 6%) | 84–87% (ARA)<br>*p*-toluenesulfonyl chloride (derivatization)<br>Salts in water (interferents) | Corbera et al. (2005) |
| CE-C(4)D | Drinking water | GLU, AMPA | 0.1–2.2 (10%) | Not informed | See et al. (2010) |
| CE/LIF | River water, broccoli, soybean | GLU | 0.34 | 84.0–101.0% (ARA) | Wei et al. (2013) |
| CE/MS/mESI | Wheat | GLU, AMPA, 3-MPPA | 169.07 (1–2%) | – | Goodwin et al. (2003) |
| CE/UV–Vis | Ground and lake water | GLU, AMPA | 16.9 | 9-Fluorenylmethyl chloroformate (derivatization) | Chang and Wei (2005) |

**Table 1** (continued)

| Method | Samples | Simultaneous identification | LOD ng $mL^{-1}$ or ng $g^{-1}$ (RSD) | Other analytical characteristics | References |
|---|---|---|---|---|---|
| CI-ELISA | Water | – | 76 | Glyphosine, AMPA (interferents) | Clegg et al. (1999) |
| L'ELISA | Surface and ground waters | – | 0.1 (0.2%) | Succinic anhydride (derivatization) | Lee et al. (2002) |
| Cyan-sensor | Water, soil, environmental | – | 450 | Minutes till some days (analysis time)<br>Other herbicides, heavy metals copper and zinc and a representative volatile organic 3,5-DCP (interferents) | Shao et al. (2002) |
| BERA | Distilled water | – | 0.1 | 3–5 min (analysis time) | Kintzios et al. (2001) |
| CRMS | Water for treatment | Atrazine, lead nitrate, cadmium nitrate | 2000 | 1 min (analysis time) | Che and Liu (2014) |

*LOD* lower detection limit, *RSD* relative standard deviations

adjuvants as additional toxic agents. They are used to increase Glyphosate toxicity by allowing its penetration into plants and in some cases are more toxic than GLY, but they are never included in GLY long-term toxicity tests and are considered to be inert. They constitute a "black hole" in pesticide toxicology, because they are often kept secret by companies, and are never measured in the environment, and so, they are not included in the establishment of pesticide acceptable daily intakes. So, pure GLY purchased from chemical companies is not the commercial form used, and the pure form is the one used for the development of sensors. Therefore, the true need is the ability to quantify GLY in real environmental complex matrices and not as a pure GLY form dissolved in ultrapure water. The ability to quantify GLY bound to metal ions and cations ($Ca^{2+}$) in soil or in water in a fast, simple and sensitive way using a stable portable device is still a challenge.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

## References

Abdel-Hamid MI (1996) Development and application of a simple procedure for toxicity testing using immobilized algae. Water Sci Technol 33:129–138

Alferness PL, Iwata Y (1994) Determination of glyphosate and (aminomethyl)phosphonic acid in soil, plant and animal matrixes, and water by capillary gas chromatography with mass-selective detection. J Agric Food Chem 42:2751–2759

Algar WR, Krull UJ (2008) Quantum dots as donors in fluorescence resonance energy transfer for the bioanalysis of nucleic acids, proteins, and other biological molecules. Anal Bioanal Chem 391:1609–1618

Allinson G, Allinson M, Bui A et al (2016) Pesticide and trace metals in surface waters and sediments of rivers entering the Corner Inlet Marine National Park, Victoria, Australia. Environ Sci Pollut Res Int 23:5881–5891

Anthony S, Stephanie S (2017) Glyphosate pathways to modern diseases VI: prions, amyloidosis and autoimmune neurological diseases. J Biol Phys Chem 17:8–32

Antoniou M, Habib M, Howard CV et al (2012) Teratogenic effects of glyphosate-based herbicides: divergence of regulatory decisions from scientific evidence. J Environ Anal Toxicol S4:006

Arroyave JM, Waiman CC, Zanini GP, Avena MJ (2016) Effect of humic acid on the adsorption/desorption behavior of glyphosate on goethite. Isotherms and kinetics. Chemosphere 145:34–41

Barcelo D (2000) Sample handling and trace analysis of pollutants. Techniques, applications and quality assurance, vol 21, 1st edn. Elsevier, Amsterdam

Barrett KA, McBride MB (2005) Oxidative degradation of glyphosate and aminomethylphosphonate by manganese oxide. Environ Sci Technol 39:9223–9228

Bataller R, Campos I, Laguarda-Miro N et al (2012) Glyphosate detection by means of a voltammetric electronic tongue and discrimination of potential interferents. Sensors 12:17553–17568

Beecham JE, Seneff S (2015) The possible link between autism and glyphosate acting as glycine mimetic—a review of evidence from the literature with analysis. J Mol Genet Med. https://doi.org/10.4172/1747-0862.1000187

Benachour N, Séralini G-E (2009) Glyphosate formulations induce apoptosis and necrosis in human umbilical, embryonic, and placental cells. Chem Res Toxicol 22:97–105

Börjesson E, Torstensson L (2000) New methods for determination of glyphosate and (aminomethyl)phosphonic acid in water and soil. J Chromatogr A 886:207–216

Bradley PM, Journey CA, Romanok KM et al (2017) Expanded target-chemical analysis reveals extensive mixed-organic-contaminant exposure in U.S. streams. Environ Sci Technol 51:4792–4802

Brłnstad JO, Friestad HO (1976) Method for determination of glyphosate residues in natural waters based on polarography of the *N*-nitroso derivative. Analyst 101:820–824

Byer JD, Struger J, Klawunn P et al (2008) Low cost monitoring of glyphosate in surface waters using the ELISA method: an evaluation. Environ Sci Technol 42:6052–6057

Campanella L, Cubadda F, Sammartino MP, Saoncella A (2001) An algal biosensor for the monitoring of water toxicity in estuarine environments. Water Res 35:69–76

Candela L, Caballero J, Ronen D (2010) Glyphosate transport through weathered granite soils under irrigated and non-irrigated conditions—Barcelona, Spain. Sci Total Environ 408:2509–2516

Cartigny B, Azaroual N, Imbenotte M et al (2004) Determination of glyphosate in biological fluids by 1H and 31P NMR spectroscopy. Forensic Sci Int 143:141–145

Castle LA, Siehl DL, Gorton R et al (2004) Discovery and directed evolution of a glyphosate tolerance gene. Science 304:1151–1154

Cattani D, de Liz Oliveira Cavalli VL, Heinz Rieg CE et al (2014) Mechanisms underlying the neurotoxicity induced by glyphosate-based herbicide in immature rat hippocampus: involvement of glutamate excitotoxicity. Toxicology 320:34–45

Cavalcante DGSM, Martinez CBR, Sofia SH (2008) Genotoxic effects of Roundup® on the fish *Prochilodus lineatus*. Mutat Res Genet Toxicol Environ Mutagen 655:41–46

Cavaş T, Könen S (2007) Detection of cytogenetic and DNA damage in peripheral erythrocytes of goldfish (*Carassius auratus*) exposed to a glyphosate formulation using the micronucleus test and the comet assay. Mutagenesis 22:263–268

Çetin E, Şahan S, Ülgen A, Şahin U (2017) DLLME-spectrophotometric determination of glyphosate residue in legumes. Food Chem 230:567–571

Chalubinski M, Kowalski ML (2006) Endocrine disrupters–potential modulators of the immune system and allergic response. Allergy 61:1326–1335

Chang SY, Liao C-H (2002) Analysis of glyphosate, glufosinate and aminomethylphosphonic acid by capillary electrophoresis with indirect fluorescence detection. J Chromatogr A 959:309–315

Chang SY, Wei M-Y (2005) Simultaneous determination of glyphosate, glufosinate, and minomethylphosphonic acid by capillary electrophoresis after 9-fluorenylmethyl chloroformate derivatization. J Chin Chem Soc 52:785–792

Chang Y, Zhang Z, Hao J et al (2016a) A simple label free colorimetric method for glyphosate detection based on the inhibition of peroxidase-like activity of Cu(II). Sens Actuators B Chem 228:410–415

Chang Y-C, Lin Y-S, Xiao G-T et al (2016b) A highly selective and sensitive nanosensor for the detection of glyphosate. Talanta 161:94–98

Chaufan G, Coalova I, Ríos de Molina MDC (2014) Glyphosate commercial formulation causes cytotoxicity, oxidative effects, and apoptosis on human cells: differences with its active ingredient. Int J Toxicol 33:29–38

Che H, Liu S (2014) Contaminant detection using multiple conventional water quality sensors in an early warning system. Proc Eng 89:479–487

Chenier PJ (2002) Sulfuric acid and its derivatives. In: Chenier PJ (ed) Survey of industrial chemistry. Springer, Boston, pp 23–40

Cikalo MG, Goodall DM, Matthews W (1996) Analysis of glyphosate using capillary electrophoresis with indirect detection. J Chromatogr A 745:189–200

Clegg BS, Stephenson GR, Hall JC (1999) Development of an enzyme-linked immunosorbent assay for the detection of glyphosate. J Agric Food Chem 47:5031–5037

Corbera M, Hidalgo M, Salvadó V, Wieczorek PP (2005) Determination of glyphosate and aminomethylphosphonic acid in natural water using the capillary electrophoresis combined with enrichment step. Anal Chim Acta 540:3–7

Coutinho CFB, Mazo LH (2005) Complexos metálicos com o herbicida glifosato: revisão. Quim Nova 28:1038

Coutinho CFB, Coutinho LFM, Mazo LH et al (2007) Direct determination of glyphosate using hydrophilic interaction chromatography with coulometric detection at copper microelectrode. Anal Chim Acta 592:30–35

da Silva AS, Fernandes FCB, Tognolli JO et al (2011) A simple and green analytical method for determination of glyphosate in commercial formulations and water by diffuse reflectance spectroscopy. Spectrochim Acta A Mol Biomol Spectrosc 79:1881–1885

Dai H, Sang M, Wang Y et al (2014) Determination of trace glyphosate in water with a prism coupling optical waveguide configuration. Sens Actuators A Phys 218:88–93

De Almeida LKS, Chigome S, Torto N et al (2015) A novel colorimetric sensor strip for the detection of glyphosate in water. Sens Actuators B Chem 206:357–363

De Góes RE, Muller M, Fabris JL (2017) Spectroscopic detection of glyphosate in water assisted by laser-ablated silver nanoparticles. Sensors 17(954):1–15

de Llasera MPG, Gómez-Almaraz L, Vera-Avila LE, Peña-Alvarez A (2005) Matrix solid-phase dispersion extraction and determination by high-performance liquid chromatography with fluorescence detection of residues of glyphosate and aminomethylphosphonic acid in tomato fruit. J Chromatogr A 1093:139–146

Delmonico EL, Bertozzi J, Evelázio de Souza N, Celestino Oliveira C (2014) Determination of glyphosate and aminomethylphosphonic acid for assessing the quality tap water using SPE and HPLC. Acta Sci Technol 36:513–519

DeLorenzo ME, Lauth J, Pennington PL et al (1999) Atrazine effects on the microbial food web in tidal creek mesocosms. Aquat Toxicol 46:241–251

Dickson SJ, Meinhold RH, Beer ID, Koelmeyer TD (1988) Rapid determination of glyphosate in postmortem specimens using 31P NMR. J Anal Toxicol 12:284–286

Ding X, Yang K-L (2013) Development of an oligopeptide functionalized surface plasmon resonance biosensor for online detection of glyphosate. Anal Chem 85:5727–5733

Ding J, Guo H, Liu W-W et al (2013) Current progress on the detection of glyphosate in environmental samples. J Sci Appl Biomed 2014:2015

Ding J, Guo H, Liu W-W, Zhang W-W, Wang J-W (2015) Current progress on the detection of glyphosate in environmental samples. J Sci Appl Biomed 3(6):88–95

do Carmo Langiano CV, Martinez CBR (2008) Toxicity and effects of a glyphosate-based herbicide on the Neotropical fish *Prochilodus lineatus*. Comp Biochem Physiol C Toxicol Pharmacol 147:222–231

Ejaz S, Akram W, Lim CW et al (2004) Endocrine disrupting pesticides: a leading cause of cancer among rural people in Pakistan. Exp Oncol 26:98–105

El-Gendy KS, Aly NM, El-Sebae AH (1998) Effects of edifenphos and glyphosate on the immune response and protein biosynthesis of bolti fish (*Tilapia nilotica*). J Environ Sci Health B 33:135–149

European Commission (2002) Review report for the active substance glyphosate. European Commission 6511/VI/99-final. https://big.assets.huffingtonpost.com/ec.2002.pdf. Accessed 20 April 2018

Fang F, Xu H, Wei RQ et al (2011) Determination of glyphosate by high performance liquid chromatography with *o*-nitrobenzenesulfonyl chloride as derivatization reagent. Fenxi Ceshi Xuebao 30:683–686

Fang F, Wei RQ et al (2014) Determination of glyphosate by HPLC with a novel pre-column derivatization reagent. Chin J Bioprocess Eng 12(3):69–73

Forlani G, Mangiagalli A, Nielsen E, Suardi CM (1999) Degradation of the phosphonate herbicide glyphosate in soil: evidence for a possible involvement of unculturable microorganisms. Soil Biol Biochem 31:991–997

Franz JE, Mao MK, Sikorski JA (1997) Glyphosate: a unique global herbicide. ACS Monograph 189

Frense D, Müller A, Beckmann D (1998) Detection of environmental pollutants using optical biosensor with immobilized algae cells. Sens Actuators B Chem 51:256–260

Friestad HO, Brønstad JO (1985) Improved polarographic method for determination of glyphosate herbicide in crops, soil, and water. J Assoc Off Anal Chem 68:76–79

Garcia AF, do Carmo Rollemberg M (2007) Determinação voltamétrica do herbicida glifosato em águas naturais utilizando eletrodo de cobre. Quim Nova 30(7):1592–1596

Garcia AF, Rollemberg MC (2007) Voltammetric determination of glyphosate in natural waters with a copper electrode. Quím Nova 30:1592–1596

Garry VF, Harkins ME, Erickson LL et al (2002) Birth defects, season of conception, and sex of children born to pesticide applicators living in the Red River Valley of Minnesota, USA. Environ Health Perspect 110(Suppl 3):441–449

Gasnier C, Dumont C, Benachour N et al (2009) Glyphosate-based herbicides are toxic and endocrine disruptors in human cell lines. Toxicology 262:184–191

Giesy JP, Dobson S, Solomon KR (2000) Ecotoxicological risk assessment for roundup® herbicide. In: Ware GW (ed) Reviews of environmental contamination and toxicology. Springer, New York, pp 35–120

Glass RL (1981) Colorimetric determination of glyphosate in water after oxidation to orthophosphate. Anal Chem 53:921–923

Glass RL (1984) Metal complex formation by glyphosate. J Agric Food Chem 32:1249–1253

Glusczak L, dos Santos Miron D, Crestani M et al (2006) Effect of glyphosate herbicide on acetylcholinesterase activity and metabolic and hematological parameters in piava (*Leporinus obtusidens*). Ecotoxicol Environ Saf 65:237–241

Glusczak L, dos Santos Miron D, Moraes BS et al (2007) Acute effects of glyphosate herbicide on metabolic and enzymatic parameters of silver catfish (*Rhamdia quelen*). Comp Biochem Physiol C Toxicol Pharmacol 146:519–524

González-Martínez MA, Brun EM, Puchades R et al (2005) Glyphosate immunosensor. Application for water and soil analysis. Anal Chem 77:4219–4227

Goodwin L, Startin JR, Keely BJ, Goodall DM (2003) Analysis of glyphosate and glufosinate by capillary electrophoresis–mass spectrometry utilising a sheathless microelectrospray interface. J Chromatogr A 1004:107–119

Govindarajulu PP (2008) Literature review of impacts of glyphosate herbicide on amphibians: what risks can the silvicultural use of this herbicide pose for amphibians in B.C.? B.C. Ministry of Environment, Victoria, BC. Wildlife Report No. R-28

Grisolia CK (2002) A comparison between mouse and fish micronucleus test using cyclophosphamide, mitomycin C and various pesticides. Mutat Res 518:145–150

Gui Y-X, Fan X-N, Wang H-M et al (2012) Glyphosate induced cell death through apoptotic and autophagic mechanisms. Neurotoxicol Teratol 34:344–349

Guo Z-X, Cai Q, Yang Z (2005) Determination of glyphosate and phosphate in water by ion chromatography–inductively coupled plasma mass spectrometry detection. J Chromatogr A 1100:160–167

Guo Z-X, Cai Q, Yang Z (2007) Ion chromatography/inductively coupled plasma mass spectrometry for simultaneous determination of glyphosate, glufosinate, fosamine and ethephon at nanogram levels in water. Rapid Commun Mass Spectrom 21:1606–1612

Guo J, Zhang Y, Luo Y et al (2014) Efficient fluorescence resonance energy transfer between oppositely charged CdTe quantum dots and gold nanoparticles for turn-on fluorescence detection of glyphosate. Talanta 125:385–392

Guo H, Riter LS, Wujcik CE, Armstrong DW (2016) Direct and sensitive determination of glyphosate and aminomethylphosphonic acid in environmental water samples by high performance liquid chromatography coupled to electrospray tandem mass spectrometry. J Chromatogr A 1443:93–100

Habekost A (2015) Spectroscopic and electrochemical investigations of *N*-(phosphonomethyl)glycine (glyphosate) and (aminomethyl) phosphonic acid (AMPA). World J Chem Educ 3(6):134–140

Habekost A (2017) Rapid and sensitive spectroelectrochemical and electrochemical detection of glyphosate and AMPA with screen-printed electrodes. Talanta 162:583–588

Hance RJ (1976) Herbicide usage and soil properties. Plant Soil 45:291–293

Hanke I, Singer H, Hollender J (2008) Ultratrace-level determination of glyphosate, aminomethylphosphonic acid and glufosinate in natural waters by solid-phase extraction followed by liquid chromatography–tandem mass spectrometry: performance tuning of derivatization, enrichment and detection. Anal Bioanal Chem 391:2265–2276

Hao Chunyan, Morse David, Morra Franca, Zhao Xiaoming, Yang Paul, Nunn Brian (2011) Direct aqueous determination of glyphosate and related compounds by liquid chromatography/tandem mass spectrometry using reversed-phase and weak anion-exchange mixed-mode column. J Chromatogr A 1218(33):5638–5643

Heras-Mendaza F, Casado-Fariñas I, Paredes-Gascón M, Conde-Salazar L (2008) Erythema multiforme-like eruption due to an irritant contact dermatitis from a glyphosate pesticide. Contact Dermat 59:54–56

Hidalgo C, Rios C, Hidalgo M et al (2004) Improved coupled-column liquid chromatographic method for the determination of glyphosate and aminomethylphosphonic acid residues in environmental waters. J Chromatogr A 1035:153–157

Ho MW, Cherry B (2010) Glyphosate tolerant crops bring diseases and death. Sci Soc 47:12–15

Hogendoorn EA, Ossendrijver FM, Dijkman E, Baumann RA (1999) Rapid determination of glyphosate in cereal samples by means of pre-column derivatisation with 9-fluorenylmethyl chloroformate

and coupled-column liquid chromatography with fluorescence detection. J Chromatogr A 833:67–73
Hokanson R, Fudge R, Chowdhary R, Busbee D (2007) Alteration of estrogen-regulated gene expression in human cells induced by the agricultural and horticultural herbicide glyphosate. Hum Exp Toxicol 26:747–752
Homola J (2003) Present and future of surface plasmon resonance biosensors. Anal Bioanal Chem 377:528–539
Hu J-Y, Zhao D-Y, Ning J et al (2007) Determination of glyphosate residues in soil and apple by capillary gas chromatography with nitrogen-phosphorus detection. Chin J Pestic Sci 3:016
Hu J-Y, Chen C-L, Li J-Z (2008) A simple method for the determination of glyphosate residues in soil by capillary gas chromatography with nitrogen phosphorus. J Anal Chem 63:371–375
Huang Y, Reddy KN, Thomson SJ, Yao H (2015) Assessment of soybean injury from glyphosate using airborne multispectral remote sensing. Pest Manag Sci 71:545–552
Huhn C (2018) More and enhanced glyphosate analysis is needed. Anal Bioanal Chem 410:3041–3045
Humphries D, Anderson A-M, Byrtus G (2005) Glyphosate residues in Alberta's atmospheric deposition, soils and surface waters. Alberta Environment no. T/806
Ibáñez M, Pozo ÓJ, Sancho JV et al (2005) Residue determination of glyphosate, glufosinate and aminomethylphosphonic acid in water and soil samples by liquid chromatography coupled to electrospray tandem mass spectrometry. J Chromatogr A 1081:145–155
Ibáñez M, Pozo OJ, Sancho JV et al (2006) Re-evaluation of glyphosate determination in water by liquid chromatography coupled to electrospray tandem mass spectrometry. J Chromatogr A 1134:51–55
Jan MR, Shah J, Muhammad M, Ara B (2009) Glyphosate herbicide residue determination in samples of environmental importance using spectrophotometric method. J Hazard Mater 169:742–745
Jayasumana C, Gunatilake S, Senanayake P (2014) Glyphosate, hard water and nephrotoxic metals: are they the culprits behind the epidemic of chronic kidney disease of unknown etiology in Sri Lanka? Int J Environ Res Public Health 11:2125–2147
Jayasumana C, Gunatilake S, Siribaddana S (2015) Simultaneous exposure to multiple heavy metals and glyphosate may contribute to Sri Lankan agricultural nephropathy. BMC Nephrol 16:103
Jiraungkoorskul W, Upatham ES, Kruatrachue M et al (2003) Biochemical and histopathological effects of glyphosate herbicide on Nile tilapia (*Oreochromis niloticus*). Environ Toxicol 18:260–267
Johal GS, Huber DM (2009) Glyphosate effects on diseases of plants. Eur J Agron 31:144–152
Kaczyński P, Łozowicka B (2015) Liquid chromatographic determination of glyphosate and aminomethylphosphonic acid residues in rapeseed with MS/MS detection or derivatization/fluorescence detection. Open Chem 13:1011–1019
Kataoka H, Ryu S, Sakiyama N, Makita M (1996) Simple and rapid determination of the herbicides glyphosate and glufosinate in river water, soil and carrot samples by gas chromatography with flame photometric detection. J Chromatogr A 726:253–258
Kawai S, Uno B, Tomita M (1991) Determination of glyphosate and its major metabolite aminomethylphosphonic acid by high-performance liquid chromatography after derivatization with *p*-toluenesulphonyl chloride. J Chromatogr A 540:411–415
Khenifi A, Derriche Z, Forano C et al (2009) Glyphosate and glufosinate detection at electrogenerated NiAl-LDH thin films. Anal Chim Acta 654:97–102
Khrolenko MV, Wieczorek PP (2005) Determination of glyphosate and its metabolite aminomethylphosphonic acid in fruit juices using supported-liquid membrane preconcentration method with high-performance liquid chromatography and UV detection after derivatization with p-toluenesulphonyl chloride. J Chromatogr A 1093:111–117
Kintzios S, Pistola E, Panagiotopoulos P et al (2001) Bioelectric recognition assay (BERA). Biosens Bioelectron 16:325–336
Koblizek M, Masojidek J, Komenda J et al (1998) A sensitive photosystem II-based biosensor for detection of a class of herbicides. Biotechnol Bioeng 60:664–669
Kongtip P, Nankongnab N, Phupancharoensuk R et al (2017) Glyphosate and Paraquat in maternal and fetal serums in Thai women. J Agromed 22:282–289
Koskinen WC, Marek LJ, Hall KE (2016) Analysis of glyphosate and aminomethylphosphonic acid in water, plant materials and soil. Pest Manag Sci 72:423–432
Kudzin ZH, Gralak DK, Drabowicz J, Luczak J (2002) Novel approach for the simultaneous analysis of glyphosate and its metabolites. J Chromatogr A 947:129–141
Kudzin ZH, Gralak DK, Andrijewski G et al (2003) Simultaneous analysis of biologically active aminoalkanephosphonic acids. J Chromatogr A 998:183–199
Laitinen P, Rämö S, Nikunen U et al (2009) Glyphosate and phosphorus leaching and residues in boreal sandy soil. Plant Soil 323:267–283
Lee EA, Zimmerman LR, Bhullar BS, Thurman EM (2002) Linker-assisted immunoassay and liquid chromatography/mass spectrometry for the analysis of glyphosate. Anal Chem 74:4937–4943
Lee HU, Shin HY, Lee JY et al (2010) Quantitative detection of glyphosate by simultaneous analysis of UV spectroscopy and fluorescence using DNA-labeled gold nanoparticles. J Agric Food Chem 58:12096–12100
Lee HU, Jung DU, Lee JH et al (2013) Detection of glyphosate by quantitative analysis of fluorescence and single DNA using DNA-labeled fluorescent magnetic core–shell nanoparticles. Sens Actuators B Chem 177:879–886
Li X, Xu J, Jiang Y et al (2009) Hydrophilic-interaction liquid chromatography (HILIC) with dad and mass spectroscopic detection for direct analysis of glyphosate and glufosinate residues and for product quality control. Acta Chromatogr 21:559–576
Li Y, Zhang S, Zhang Q et al (2016) Binding-induced internal-displacement of signal-on photoelectrochemical response: a glyphosate detection platform based on graphitic carbon nitride. Sens Actuators B Chem 224:798–804
Liao Y, Berthiona J-M, Coleta I et al (2018) Validation and application of analytical method for glyphosate and glufosinate in foods by liquid chromatography–tandem mass spectrometry. J Chromatogr A 1549:31–38
Liu Q, Jiang X, Zhang Y et al (2015) A novel test strip for organophosphorus detection. Sens Actuators B Chem 210:803–810
Lou ZY, Zhu GN, Wu HM (2001) Study on the detection method of glyphosate in pond water. Chin J Ningbo Acad 13(Suppl):142–145
Luo X, Chen L, Zhao Y (2015) Simultaneous determination of three chloroacetic acids, three herbicides, and 12 anions in water by ion chromatography. J Sep Sci 38:3096–3102
Lushchak OV, Kubrak OI, Storey JM et al (2009) Low toxic herbicide Roundup induces mild oxidative stress in goldfish tissues. Chemosphere 76:932–937
Mallat E, Barceló D (1998) Analysis and degradation study of glyphosate and of aminomethylphosphonic acid in natural waters by means of polymeric and ion-exchange solid-phase extraction columns followed by ion chromatography-post-column derivatization with fluorescence detection. J Chromatogr A 823:129–136
Marc J, Mulner-Lorillon O, Bellé R (2004) Glyphosate-based pesticides affect cell cycle regulation. Biol Cell 96:245–249
Martínez Gil P, Laguarda-Miro N, Camino JS, Peris RM (2013) Glyphosate detection with ammonium nitrate and humic acids

as potential interfering substances by pulsed voltammetry technique. Talanta 115:702–705
Martins-Júnior HA, Lebre DT, Wang AY et al (2009) An alternative and fast method for determination of glyphosate and aminomethylphosphonic acid (AMPA) residues in soybean using liquid chromatography coupled with tandem mass spectrometry. Rapid Commun Mass Spectrom 23:1029–1034
Martins-Júnior HA, Lebre DT, Wang AY et al (2011) Residue analysis of glyphosate and aminomethylphosphonic acid (AMPA) in Soybean using liquid chromatography coupled with tandem mass spectrometry. In: Ng T-B (ed) Soybean - biochemistry, chemistry and physiology. InTech. https://www.intechopen.com/books/soybean-biochemistry-chemistry-and-physiology/residue-analysis-of-glyphosate-and-aminomethylphosphonic-acid-ampa-in-soybean-using-liquid-chromatog
Mazereeuw M, Hofte AJP, Tjaden UR, van der Greef J (1997) A novel sheathless and electrodeless microelectrospray interface for the on-line coupling of capillary zone electrophoresis to mass spectrometry. Rapid Commun Mass Spectrom 11:981–986
Merás ID, Díaz TG, Franco MA (2005) Simultaneous fluorimetric determination of glyphosate and its metabolite, aminomethylphosphonic acid, in water, previous derivatization with NBD-Cl and by partial least squares calibration (PLS). Talanta 65:7–14
Mesnage R, Bernay B, Séralini G-E (2013) Ethoxylated adjuvants of glyphosate-based herbicides are active principles of human cell toxicity. Toxicology 313:122–128
Metzger JO (1997) Green Chemistry. Designing Chemistry for the Environment. Herausgegeben von PT Anastas und TS Williamson. American Chemical Society, Wahington, DC, 1996. 251 S., geb. 89.95£.-ISBN 0-8412-3399-3. Angew Chem Int Ed Engl 109:812–813
Minami T, Liu Y, Akdeniz A et al (2014) Intramolecular indicator displacement assay for anions: supramolecular sensor for glyphosate. J Am Chem Soc 136:11396–11401
Mol HGJ, van Dam RCJ (2014) Rapid detection of pesticides not amenable to multi-residue methods by flow injection–tandem mass spectrometry. Anal Bioanal Chem 406:6817–6825
Molina M, Silva M (2002) Analytical potential of fluorescein analogues for ultrasensitive determinations of phosphorus-containing amino acid herbicides by micellar electrokinetic chromatography with laser-induced fluorescence detection. Electrophoresis 23:1096–1103
Moraes FC, Mascaro LH, Machado SAS, Brett CMA (2010) Direct electrochemical determination of glyphosate at copper phthalocyanine/multiwalled carbon nanotube film electrodes. Electroanalysis 22:1586–1591
Napoli M, Cecchi S, Zanchi CA, Orlandini S (2015) Leaching of glyphosate and aminomethylphosphonic acid through silty clay soil columns under outdoor conditions. J Environ Qual 44:1667–1673
Nedelkoska TV, Low GK-C (2004) High-performance liquid chromatographic determination of glyphosate in water and plant material after pre-column derivatisation with 9-fluorenylmethyl chloroformate. Anal Chim Acta 511:145–153
Nešković NK, Poleksić V, Elezović I et al (1996) Biochemical and histopathological effects of glyphosate on carp, *Cyprinus carpio* L. Bull Environ Contam Toxicol 56:295–302
Nielsen JB, Nielsen F, Sørensen JA (2007) Defense against dermal exposures is only skin deep: significantly increased penetration through slightly damaged skin. Arch Dermatol Res 299:423–431
Nortes-Méndez R, Robles-Molina J, López-Blanco R et al (2016) Determination of polar pesticides in olive oil and olives by hydrophilic interaction liquid chromatography coupled to tandem mass spectrometry and high resolution mass spectrometry. Talanta 158:222–228
Okada E, Pérez D, De Gerónimo E et al (2018) Non-point source pollution of glyphosate and AMPA in a rural basin from the southeast Pampas, Argentina. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-018-1734-7
Oliveira GC, Moccelini SK, Castilho M et al (2012) Biosensor based on atemoya peroxidase immobilised on modified nanoclay for glyphosate biomonitoring. Talanta 98:130–136
Paganelli A, Gnazzo V, Acosta H et al (2010) Glyphosate-based herbicides produce teratogenic effects on vertebrates by impairing retinoic acid signaling. Chem Res Toxicol 23:1586–1595
Patsias J, Papadopoulou A, Papadopoulou-Mourkidou E (2001) Automated trace level determination of glyphosate and aminomethyl phosphonic acid in water by on-line anion-exchange solid-phase extraction followed by cation-exchange liquid chromatography and post-column derivatization. J Chromatogr A 932:83–90
Pei MQ, Lai J (2004) Qualitative and quantitative analysis of glyphosate. Chin J Guangdong Police Sci Technol 1:14–15
Pintado S, Amaro RR, Mayén M, Mellado JMR (2012) Electrochemical determination of the glyphosate metabolite aminomethylphosphonic acid (AMPA) in drinking waters with an electrodeposited copper electrode. Int J Electrochem Sci 7:305–312
Pipke R, Amrhein N (1988) Isolation and characterization of a mutant of Arthrobacter sp. Strain GLP-1 which utilizes the herbicide glyphosate as its sole source of phosphorus and nitrogen. Appl Environ Microbiol 54:2868–2870
Poiger T, Buerge IJ, Bächli A et al (2017) Occurrence of the herbicide glyphosate and its metabolite AMPA in surface waters in Switzerland determined with on-line solid phase extraction LC-MS/MS. Environ Sci Pollut Res Int 24:1588–1596
Poletta GL, Larriera A, Kleinsorge E, Mudry M (2009) Genotoxicity of the herbicide formulation Roundup® (glyphosate) in broad-snouted caiman (*Caiman latirostris*) evidenced by the Comet assay and the Micronucleus test. Mutat Res Genet Toxicol Environ Mutagen 672:95–102
Pollegioni L, Schonbrunn E, Siehl D (2011) Molecular basis of glyphosate resistance–different approaches through protein engineering. FEBS J 278:2753–2766
Poulsen ME, Christensen HB, Herrmann SS (2009) Proficiency test on incurred and spiked pesticide residues in cereals. Accredit Qual Assur 14:477–485
Prasad BB, Jauhari D, Tiwari MP (2014) Doubly imprinted polymer nanofilm-modified electrochemical sensor for ultra-trace simultaneous analysis of glyphosate and glufosinate. Biosens Bioelectron 59:81–88
Ramirez CE, Bellmund S, Gardinali PR (2014) A simple method for routine monitoring of glyphosate and its main metabolite in surface waters using lyophilization and LC–FLD + MS/MS. Case study: canals with influence on Biscayne National Park. Sci Total Environ 496:389–401
Rawat KA, Majithiya RP, Rohit JV et al (2016) $Mg^{2+}$ ion as a tuner for colorimetric sensing of glyphosate with improved sensitivity via the aggregation of 2-mercapto-5-nitrobenzimidazole capped silver nanoparticles. RSC Adv 6:47741–47752
Relyea RA (2012) New effects of Roundup on amphibians: predators reduce herbicide mortality; herbicides induce antipredator morphology. Ecol Appl 22:634–647
Richard S, Moslemi S, Sipahutar H et al (2005) Differential effects of glyphosate and roundup on human placental cells and aromatase. Environ Health Perspect 113:716–720
Ridlen JS, Klopf GJ, Nieman TA (1997) Determination of glyphosate and related compounds using HPLC with tris(2,2′-bipyridyl) ruthenium(II) electrogenerated chemiluminescence detection. Anal Chim Acta 341:195–204

Roberts SM (1989) Molecular recognition: chemical and biochemical problems: the proceedings of an International Symposium, University of Exeter, April 1989. CRC PressI Llc

Royer A, Beguin S, Tabet JC et al (2000) Determination of glyphosate and aminomethylphosphonic acid residues in water by gas chromatography with tandem mass spectrometry after exchange ion resin purification and derivatization. Application on vegetable matrixes. Anal Chem 72:3826–3832

Rubio F, Veldhuis LJ, Clegg BS et al (2003) Comparison of a direct ELISA and an HPLC method for glyphosate determinations in water. J Agric Food Chem 51:691–696

Rueppel ML, Brightwell BB, Schaefer J, Marvel JT (1977) Metabolism and degradation of glyphosate in soil and water. J Agric Food Chem 25:517–528

Rull RP (2004) Neural tube defects and maternal residential proximity to agricultural pesticide applications and crops. Am J Epidemiol 163:743–753

Sadi B, Vonderheide AP, Caruso JA (2004) Analysis of phosphorus herbicides by ion-pairing reversed-phase liquid chromatography coupled to inductively coupled plasma mass spectrometry with octapole reaction cell. J Chromatogr A 1050:95–101

Samsel A, Seneff S (2013a) Glyphosate's suppression of cytochrome P450 enzymes and amino acid biosynthesis by the gut microbiome: pathways to modern diseases. Entropy 15:1416–1463

Samsel A, Seneff S (2013b) Glyphosate, pathways to modern diseases II: celiac sprue and gluten intolerance. Interdiscip Toxicol 6:159–184

Sanchís J, Kantiani L, Llorca M et al (2012) Determination of glyphosate in groundwater samples using an ultrasensitive immunoassay and confirmation by on-line solid-phase extraction followed by liquid chromatography coupled to tandem mass spectrometry. Anal Bioanal Chem 402:2335–2345

Sancho JV, Hernández F, López FJ et al (1996) Rapid determination of glufosinate, glyphosate and aminomethylphosphonic acid in environmental water samples using precolumn fluorogenic labeling and coupled-column liquid chromatography. J Chromatogr A 737:75–83

Sato K, Jin JY, Takeuchi T et al (2001) Integrated pulsed amperometric detection of glufosinate, bialaphos and glyphosate at gold electrodes in anion-exchange chromatography. J Chromatogr A 919:313–320

Sato M, Yamashita A, Kikuchi M et al (2009) Simultaneous analysis of phosphorus-containing amino acid type herbicides and their metabolites in human samples using *N*-acetyl, *O*-methyl derivatives by LC/MS. Jpn J Forensic Sci Tech 14:35–43

Schafer H, Hettler H, Fritsche U et al (1994) Biotests using unicellular algae and ciliates for predicting long-term effects of toxicants. Ecotoxicol Environ Saf 27:64–81

Schrübbers LC, Masís-Mora M, Rojas EC et al (2016) Analysis of glyphosate and aminomethylphosphonic acid in leaves from *Coffea arabica* using high performance liquid chromatography with quadrupole mass spectrometry detection. Talanta 146:609–620

Schuette J (1998) Environmental fate of glyphosate. Published by Environmental Monitoring & Pest Management. Department of Pesticide Regulation Sacramento, California ISSN 95824–95624

Scribner EA, Battaglin WA, Gilliom RJ, Meyer MT (2007) Concentrations of glyphosate, its degradation product, aminomethylphosphonic acid, and glufosinate in ground-and surface-water, rainfall, and soil samples collected in the United States, 2001–06. Geological Survey (US). https://pubs.usgs.gov/sir/2007/5122/pdf/SIR2007-5122.pdf

See HH, Hauser PC, Ibrahim WAW, Sanagi MM (2010) Rapid and direct determination of glyphosate, glufosinate, and aminophosphonic acid by online preconcentration CE with contactless conductivity detection. Electrophoresis 31:575–582

Seneff S, Swanson N, Li C (2015) Aluminum and glyphosate can synergistically induce pineal gland pathology: connection to gut dysbiosis and neurological disease. Agric Sci China 6:42

Shao CY, Howe CJ, Porter AJR, Glover LA (2002) Novel cyanobacterial biosensor for detection of herbicides. Appl Environ Microbiol 68(10):5026–5033

Sharma DK, Gupta A, Kashyap R, Kumar N (2012) Spectrophotometric method for the determination of Glyphosate in relation to its environmental and toxicological analysis. Arch Environ Sci 6:42–49

Shehata AA, Schrödl W, Aldin AA et al (2013) The effect of glyphosate on potential pathogens and beneficial members of poultry microbiota in vitro. Curr Microbiol 66:350–358

Shim YK, Mlynarek SP, van Wijngaarden E (2009) Parental exposure to pesticides and childhood brain cancer: U.S. Atlantic coast childhood brain cancer study. Environ Health Perspect 117:1002–1006

Si YB, Sang ZY, Cheng FX et al (2009) Determination of glyphosate in soil by high performance liquid chromatography after derivatization with *p*-toluenesulphonyl chloride. J Anhui Agric Univ 36:136–139

Sierra EV, Méndez MA, Sarria VM, Cortés MT (2008) Electrooxidación de glifosato sobre electrodos de níquel y cobre. Quim Nova 31:220–226

Simonetti E, Cartaud G, Quinn RM et al (2015) An interlaboratory comparative study on the quantitative determination of glyphosate at low levels in wheat flour. J AOAC Int 98:1760–1768

Singh BK (1998) Plant amino acids: biochemistry and biotechnology. CRC Press, Boca Raton

Skeff W, Recknagel C, Schulz-Bull DE (2016) The influence of salt matrices on the reversed-phase liquid chromatography behavior and electrospray ionization tandem mass spectrometry detection of glyphosate, glufosinate, aminomethylphosphonic acid and 2-aminoethylphosphonic acid in water. J Chromatogr A 1475:64–73

Slager RE, Simpson SL, Levan TD et al (2010) Rhinitis associated with pesticide use among private pesticide applicators in the agricultural health study. J Toxicol Environ Health A 73:1382–1393

Songa EA, Waryo T, Jahed N et al (2009a) Electrochemical nanobiosensor for glyphosate herbicide and its metabolite. Electroanalysis 21:671–674

Songa EA, Arotiba OA, Owino JHO et al (2009b) Electrochemical detection of glyphosate herbicide using horseradish peroxidase immobilized on sulfonated polymer matrix. Bioelectrochemistry 75:117–123

Songa EA, Somerset VS, Waryo T, Baker PG, Iwuoha EI (2009c) Amperometric nanobiosensor for quantitative determination of glyphosate and glufosinate residues in corn samples. J Macromol Sci Part A Pure Appl Chem 81:123–139

Stachowskihaberkorn S, Becker B, Marie D et al (2008) Impact of Roundup on the marine microbial community, as shown by an in situ microcosm experiment. Aquat Toxicol 89:232–241

Sun N, Hu B-X, Mo W-M (2007) Single sweep oscillopolarographic technique for the determination of glyphosate after derivatization with sodium nitrite. PESTICIDES-SHENYANG 46:609

Sun L, Kong D, Gu W et al (2017) Determination of glyphosate in soil/sludge by high performance liquid chromatography. J Chromatogr A 1502:8–13

Szarek J, Siwicki A, Andrzejewska A et al (2000) Effects of the herbicide Roundup™ on the ultrastructural pattern of hepatocytes in carp (*Cyprinus carpio*). Mar Environ Res 50:263–266

Tadeo JL, Sánchez-Brunete C, Pérez RA, Fernández MD (2000) Analysis of herbicide residues in cereals, fruits and vegetables. J Chromatogr A 882:175–191

Tan MJ, Hong Z-Y, Chang M-H et al (2017) Metal carbonyl-gold nanoparticle conjugates for highly sensitive SERS detection of organophosphorus pesticides. Biosens Bioelectron 96:167–172
Tapsoba I, Paré S, Toé AM et al (2012) SWV determination of glyphosate in Burkina Faso soils using carbon fiber microelectrode. Int J Biol Chem Sci 6:2211–2220
Teófilo RF, Reis EL, Reis C et al (2004) Experimental design employed to square wave voltammetry response optimization for the glyphosate determination. J Braz Chem Soc 15:865–871
Thompson DG, Cowell JE, Daniels RJ et al (1989) Liquid chromatographic method for quantitation of glyphosate and metabolite residues in organic and mineral soils, stream sediments, and hardwood foliage. J Assoc Off Anal Chem 72:355–360
Thongprakaisang S, Thiantanawat A, Rangkadilok N et al (2013) Glyphosate induces human breast cancer cells growth via estrogen receptors. Food Chem Toxicol 59:129–136
Tierney KB, Singh CR, Ross PS, Kennedy CJ (2007) Relating olfactory neurotoxicity to altered olfactory-mediated behaviors in rainbow trout exposed to three currently-used pesticides. Aquat Toxicol 81:55–64
Torul H, Boyaci İH, Tamer U (2010) Attomole detection of glyphosate by surface-enhanced Raman spectroscopy using gold nanorods. FABAD J Pharm Sci 35:179–184
Tsao Y-C, Lai Y-C, Liu H-C et al (2016) Simultaneous determination and quantitation of paraquat, diquat, glufosinate and glyphosate in postmortem blood and urine by LC–MS–MS. J Anal Toxicol 40:427–436
Tseng S-H, Lo Y-W, Chang P-C et al (2004) Simultaneous quantification of glyphosate, glufosinate, and their major metabolites in rice and soybean sprouts by gas chromatography with pulsed flame photometric detector. J Agric Food Chem 52:4057–4063
Tsui MTK, Chu LM (2003) Aquatic toxicity of glyphosate-based formulations: comparison between different organisms and the effects of environmental factors. Chemosphere 52:1189–1197
Tsui MTK, Chu LM (2008) Environmental fate and non-target impact of glyphosate-based herbicide (Roundup®) in a subtropical wetland. Chemosphere 71:439–446
Tsui MTK, Wang W-X, Chu LM (2005) Influence of glyphosate and its formulation (Roundup®) on the toxicity and bioavailability of metals to *Ceriodaphnia dubia*. Environ Pollut 138:59–68
Tsunoda N (1993) Simultaneous determination of the herbicides glyphosate, glufosinate and bialaphos and their metabolites by capillary gas chromatography—ion-trap mass spectrometry. J Chromatogr A 637:167–173
Tuesca D, Puricelli E (2007) Effect of tillage systems and herbicide treatments on weed abundance and diversity in a glyphosate resistant crop rotation. Crop Prot 26:1765–1770
Vass A, Robles-Molina J, Pérez-Ortega P et al (2016) Study of different HILIC, mixed-mode, and other aqueous normal-phase approaches for the liquid chromatography/mass spectrometry-based determination of challenging polar pesticides. Anal Bioanal Chem 408:4857–4869
Vreeken RJ, Speksnijder P, Bobeldijk-Pastorova I, Noij TH (1998) Selective analysis of the herbicides glyphosate and aminomethylphosphonic acid in water by on-line solid-phase extraction–high-performance liquid chromatography–electrospray ionization mass spectrometry. J Chromatogr A 794:187–199
Waiman CV, Avena MJ, Garrido M et al (2012) A simple and rapid spectrophotometric method to quantify the herbicide glyphosate in aqueous media. Application to adsorption isotherms on soils and goethite. Geoderma 170:154–158
Wang D, Lin B, Cao Y et al (2016a) A highly selective and sensitive fluorescence detection method of glyphosate based on an immune reaction strategy of carbon dot labeled antibody and antigen magnetic beads. J Agric Food Chem 64:6042–6050
Wang S, Liu B, Yuan D, Ma J (2016b) A simple method for the determination of glyphosate and aminomethylphosphonic acid in seawater matrix with high performance liquid chromatography and fluorescence detection. Talanta 161:700–706
Wang L, Bi Y, Hou J et al (2016c) Facile, green and clean one-step synthesis of carbon dots from wool: application as a sensor for glyphosate detection based on the inner filter effect. Talanta 160:268–275
Wang M, Ye H, You L, Chen X (2016d) A supramolecular sensor array using lanthanide-doped nanoparticles for sensitive detection of glyphosate and proteins. ACS Appl Mater Interfaces 8:574–581
Watts M (2009) Glyphosate, monograph, Pesticide Action Network Asia and the Pacific, Penang, Malaysia. Available via PAN ASIA PACIFIC. http://www.panap.net/sites/default/files/attachments/monograph_glyphosate.pdf. Accessed 13 March 16
Wei X, Pu Q (2015) Microchip electrophoresis for fast and interference-free determination of trace amounts of glyphosate and glufosinate residues in agricultural products. Methods Mol Biol 1274:21–29
Wei X, Gao X, Zhao L et al (2013) Fast and interference-free determination of glyphosate and glufosinate residues through electrophoresis in disposable microfluidic chips. J Chromatogr A 1281:148–154
Williams GM, Kroes R, Munro IC (2000) Safety evaluation and risk assessment of the herbicide Roundup and its active ingredient, glyphosate, for humans. Regul Toxicol Pharmacol 31:117–165
Winfield TW (1990) Determination of glyphosate in drinking water by direct-aqueous-injection HPLC, post-column derivatization, and fluorescence detection: test method 547. U.S. Environmental Protection Agency. https://www.o2si.com/docs/epa-method-547.pdf
Woodburn AT (2000) Glyphosate: production, pricing and use worldwide. Pest Manag Sci 56:309–312
World Health Organization et al (1994) Glyphosate environmental health criteria no. 159. WHO, Geneva
Yoshioka N, Asano M, Kuse A et al (2011) Rapid determination of glyphosate, glufosinate, bialaphos, and their major metabolites in serum by liquid chromatography–tandem mass spectrometry using hydrophilic interaction chromatography. J Chromatogr A 1218:3675–3680
Zelenkova NF, Vinokurova NG (2008) Determination of glyphosate and its biodegradation products by chromatographic methods. J Anal Chem 63:871–874
Zhang C, Hu X, Luo J et al (2015a) Degradation dynamics of glyphosate in different types of citrus orchard soils in China. Molecules 20:1161–1175
Zhang L, Chen L, Liu F (2015b) Mutual effect on determination of gibberellins and glyphosate in groundwater by spectrophotometry. Guang Pu Xue Yu Guang Pu Fen Xi 35:966–970
Zhao P, Yan M, Zhang C et al (2011) Determination of glyphosate in foodstuff by one novel chemiluminescence-molecular imprinting sensor. Spectrochim Acta A Mol Biomol Spectrosc 78:1482–1486
Zheng J, Zhang H, Qu J et al (2013) Visual detection of glyphosate in environmental water samples using cysteamine-stabilized gold nanoparticles as colorimetric probe. Anal Methods 5:917–924
Zheng J, Wang Y, Feng Z et al (2015) Preparation of cationic starch microspheres and study on their absorption to anionic-type substance. Water Sci Technol 71:1545–1553
Zhou Y-M, Li N, Niu S et al (2007) Detection glyphosate residues in water by LC. China Meas Technol 3:036
Zhu Y, Zhang F, Tong C, Liu W (1999) Determination of glyphosate by ion chromatography. J Chromatogr A 850:297–301

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