

THE IMPACT OF THE HERBICIDE GLYPHOSATE ON WATER SOURCES: A REVIEW

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ABSTRACT. Glyphosate is one of the most used herbicides worldwide. Its efficiency for weed control and cost make it a seemingly perfect choice in the agricultural area. Studies and monitoring reports show divergent results in what concerns the impact of glyphosate on water sources. Because of its nature the herbicide is prone to be found more in sediment and particulate matter than in water. Different compositions of the herbicide were found to pose certain negative impacts on species of amphibians, soil microbes and induce abnormalities in the activity of some enzymes in pregnant rats. In this review we will assess the literature in the last five years regarding this topic and portray the different findings.

Key words: *glyphosate, herbicide, review, water*

INTRODUCTION

The interest in assessing the negative effects of pesticides has been present since the 1960s. One of the forerunners of this environmental movement was Rachel Carson. The results of her research were published in a book titled *Silent Spring*, which have prompted policy changes regarding pesticide use. Along with the development of analytical techniques the ability to analyze complex matrices contaminated with pesticides has risen constantly (Ramos, 2012; Vuckovic et al., 2010).

Two of the major groups pertaining to pesticides are insecticides and herbicides. Glyphosate (figure1) is a nonselective, postemergent herbicide that first appeared on the market in 1971, studies revealing ecological risks associated with the aforementioned chemical (Solomon and Thompson, 2003). Although the mode of action of this herbicide is by inhibiting the activity of an enzyme important in the synthesis of proteins only in plants, deleterious effects on aquatic and terrestrial species have been confirmed (Contardo-Jara et al., 2009; Paganelli et al., 2010).

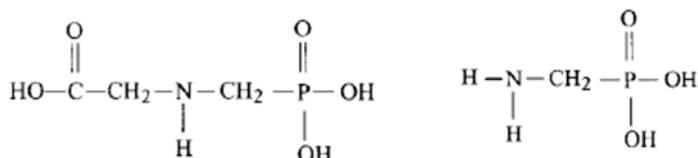


Fig. 1. Structural forms of glyphosate and its metabolite AMPA (after Williams et al., 2000)

In pure form the herbicide appears as a crystalline powder and is soluble in water, and due to its low vapor pressure it does not volatilize easily. Its toxicity is given by its persistence in the environment. The rate of degradation in soil and water differ. Depending on the types of soil the half-life can range between 4-19 days (Al-Rajab and Schiavon, 2010), whereas in the aquatic environment the range varies between 2.5-32 days (Mallat and Barcelo, 1998). Glyphosate can reach water sources through various ways, such as runoff - occurring during periods of rainfall, leaching - carrying the herbicide toward groundwater, and drift - settling after improper application of the herbicide on unintended areas of use (Zhou et al., 2010; Arronson et al, 2011). During degradation glyphosate transforms into aminomethyl phosphonic acid (AMPA), studies showing that both this metabolite and the herbicide itself can be more present in sediments than in water, being detected in almost 88.5% of samples from stream sediments (Aparicio et al., 2013). Furthermore, research has shown that the toxicity of the targeted compound is more deleterious when it pertains to glyphosate-based formulations, than stand-alone glyphosate, even though the adjuvants from formulations are said to be inert (Tsui and Chu, 2004; Benachour and Seralini, 2009; Lipok et al, 2010).

In the following chapters we will try to underline the major research results regarding the impact of glyphosate on water sources, focusing on the detrimental effects on aquatic living organisms, the different methods used for such studies and their limitations.

MATERIAL AND METHODS

High performance liquid chromatography (HPLC)

Scanning through the literature we can easily observe that the most often employed techniques for the analysis of glyphosate are the chromatographic techniques such as high performance liquid chromatography (HPLC). In older studies, high performance liquid chromatography-electrospray ionization mass spectrometry (HPLC-ESI MS MS) was employed and showed satisfying detection levels in the range of 0.05 to 3 µg/L (Vreeken et al, 1998). HPLC has also been used in recent studies coupled with ultraviolet (UV) detection and on C18 columns having an analysis time of 15 minutes, but extra steps are needed to remove reagents used in the derivatization process, thus hampering a more swift analytical approach (Qian et al, 2009). While both UV detectors and fluorescence detectors are used to quantify glyphosate, the sensitivity of the fluorescence detector has proved to be superior

(Sundaram and Curry, 1997). In addition to the aforementioned detectors, HPLC is also coupled with a spectrophotometric module, which enables a faster detection (Kim et al., 2007).

Gas chromatography (GC)

Due to the herbicide's low volatilization analysis through gas chromatography (GC) is not as often employed as HPLC (Sánchez-Bayo et al., 2010). A landmark study has researched the mobility and adsorption characteristics of glyphosate, concluding that it can bind to soil in a similar way as organophosphates compounds (Sprankle et al., 1975). Therefore, numerous studies assess glyphosate in soil, due to its ability to easily bind to soil particles coupled with different detectors, such as a nitrogen-phosphorus detector (NPD) (Druart et al., 2011; Hu et al., 2008). In a case of glyphosate poisoning, human serum was analysed by GC and coupled with mass-spectrometry (MS) the method being validated for both the herbicide and its metabolite AMPA with good recoveries >73% (Megumi et al., 2008).

Admittedly, there are also other techniques employed for the analysis of glyphosate, such as capillary electrophoresis (CE), immunoassays (ELISA), ion chromatography (IC), which start to become more and more prevalent (Lee et al., 2013; Guo et al., 2005, Marques et al., 2009

Derivatization

Analyses are complicated by the fact that glyphosate usually needs to be derivatized due to its lack of chromophores, therefore reagents are needed in order to enable fluorescence, so they can be detected. Derivatization accomplishes the following objectives:

- Enhancement of the detectability of non-absorbing or non-fluorescent analytes;
- Sensitivity enhancement of "problematic" analytical techniques such as, capillary electrophoresis, while, in some cases, derivatization has been reported to improve the sensitivity even in mass spectrometric detection;
- Stabilization of samples after collection, with low molecular weight;
- Alteration of the properties of the analytes to ensure compatibility with selected analytical techniques such as, separation of derivatized polar amino acids with reversed phase liquid chromatography or of non-volatile compounds by gas chromatography (Zacharis and Tzanavaras, 2013).

The most commonly used reagents in the derivatization process are 9-fluorenylmethylchloroformiate (FMOC), Trifluorethanol (TFE) and Trifluoroacetic anhydride (TFAA) (Alexa et al., 2008; Freuze et al., 2007; Waiman et al., 2012).

IMPACT ON WATER SOURCES

Although soils are prone to its contamination, due to its ability to bind, water sources can also get contaminated through different processes such as leaching, runoff and discharge of sewage systems.

The main source of herbicides in the water matrix is usually agriculture, but recent studies have indicated that urban sources are also significant, the herbicide being used on roads or railways (Coupe et al., 2012; Botta et al., 2009). Even though the E.U. has a maximum residue level (MLR) set at 0.1 ng/ml in drinking water regarding glyphosate in what concerns concentrations in groundwater there is a lack of policy, but the issue is being recently reviewed. In urban areas concentrations of glyphosate were found to be ranging between 75-90 µg/L, while in agricultural basins ranging between 0.5- 4 µg/L (Botta et al., 2009; Aparicio et al., 2013). In table 1 we can observe the concentrations of glyphosate through Europe.

Table 1. Concentrations of glyphosate in surface waters in European countries (Horth and Blackmore, 2009)

Country / Substance	Date	No. sites	No. samples	Detected (samples)		Samples $\geq 0.1 \mu\text{g l}^{-1}$		Max. Conc. $\mu\text{g l}^{-1}$	LoQ (LoD) $\mu\text{g l}^{-1}$
				No.	%	No.	%		
Austria									
AMPA	2001-02	?	345	≥ 90	≥ 26	90	26	3.4	?
Belgium									
Glyphosate (Flanders)	2006	105	≥ 1260 ≤ 2520	83 (s)	79 (s)	?	?	<10	?
Glyphosate (Wallonia)	2001-06	26	531	≥ 429	≥ 81	429	81	1.3	≤ 0.1
AMPA (Flanders)	2006	105	≥ 1260 ≤ 2520	97 (s)	92 (s)	?	?	<10	?
Finland									
Glyphosate	2002-09	3	26	3	11.5	2	7.7	0.46	0.1
AMPA	2002-09	3	26	3	11.5	1	3.8	0.22	0.05
France									
Glyphosate	97-06	2493	39166	12680	32	10495	27	50	0.05-0.2
AMPA	98-06	2217	28963	15983	55	14583	50	48.9	0.05-0.1
Germany (Baden-Württemberg, Rheinland-Pfalz, Thüringen & River Rhine combined)									
Glyphosate	1997-08	104	1176	264	22	96	8	4.7	0.02-1.5
AMPA	1997-08	65	660	449	68	392	59	3.6	0.05-0.5
Ireland									
Glyphosate	2007-09	256	1700	98	5.8	≥ 1	≥ 0.06	1.8	(0.08)
Italy (Lombardia Region)									
Glyphosate	2005-07	150	714	142	20	13	1.8	11.0	(0.1)
Norway									
Glyphosate	97-06	11	80	74	92.5	≤ 57	≤ 71	0.93	(0.01)
AMPA	97-06	11	80	74	92.5	≤ 48	≤ 60	0.54	(0.01)
Slovak Republic									
Glyphosate	2006-08	40	330	105	31.8	49	14.8	3.6	(0.05)
Spain *									
Glyphosate	2006-08	115	748	96	7.4	80	11	15.3	0.003-0.1
Sweden									
Gly	2000-08	≥ 21	881	218	24.7	≥ 8	≥ 0.9	13.0	<0.1
AMPA	2000-08	≥ 21	868	118	13.6	≥ 7	≥ 0.8	4.0	<0.1
The Netherlands									
Glyphosate	2006	300	1384	215 (s)	72 (s)	109 (s)	36 (s)	>1.0	<0.1
AMPA	2006	305	1410	305 (s)	100 (s)	≥ 50 (s)	≥ 16 (s)	>8.0	?
UK									
Glyphosate	93-07	≥ 92	2809	297	10.6	297	10.6	8.8	0.1
Total									
Glyphosate	93-09	≥ 3716	≥ 50805	≥ 14704	~ 29	≥ 11700	~ 23	50	0.003-0.2
AMPA	97-09	≥ 2728	≥ 33612	≥ 17119	~ 50	≥ 15172	~ 45	48.9	0.05-0.5

LOD - limit of detection, **LoQ** - limit of quantification, ? - no information, (s) - sites (number of samples not known), - not relevant, * data from sites with known quality problems

There can be noted a gap, a scarcity of studies regarding leaching of glyphosate in groundwater, even though there are a few researches that signal its presence (Van Stempvoort et al., 2014; Crowe et al., 2011). Data can be also contradictory and controversial, mentioning that it has a low potential to leach into groundwater, also not responding well to photodegradation (Manassero et al., 2010; NPIC, Glyphosate Technical Factsheet). Studies have proved that glyphosate can pose risks toward an array of aquatic organisms, ranging from benthic algae to bivalves and amphibians (Edge et al., 2013; Mottier et al., 2013). Moreover, the literature indicates cases in which adjuvants in the glyphosate based formulations are more toxic than glyphosate itself, causing distress to algal strains (Lipok et al., 2010; Sihtmaa et al., 2013).

Studies have been numerous and at times divergent. Vendrell et al (2009), established that glyphosate does not pose risks for the algae from a Spanish lake due to low concentrations, while Perez et al (2011) has concluded that even at concentrations ranging from >0.1 mg/L and <1 mg/L, algae and aquatic plants can be affected. Negative effects may be not only due to the singular impact of this agent, studies showing how the toxicity of glyphosate and AMPA can act as an additional stressor. Amphibians are an especially sensitive species because they can absorb water borne chemicals through their skin. Relyea (2005) conducted a study in which he exposed species of anurans to direct overspray observing lethal effects on a high percentage of the exposed individuals. Edge and his team (2013) concluded that Roundup WeatherMax (a glyphosate formulation used in agriculture) does not cause negative effect on juvenile amphibians under field exposure.

Binding on sediments, glyphosate can also pose risks to the periphyton communities from streams. Numerous studies indicate this divergent nature between field and laboratory studies. While in the laboratory, single concentrations of glyphosate may not pose significant deleterious effects, in real exposure studies, due to multiple stressors benthic communities can suffer significantly (Magbanua et al, 2013).

CONCLUSIONS

Glyphosate has a high polarity and as said previously said high water solubility, which has made its analysis extremely difficult. Even though GC can offer good selectivity, sensitivity and it is economical the tedious process of derivatization counterbalances the aforementioned benefits. Most methods require pre-column or post-column derivatization and are not fast and selective enough in a market where the demand for fast and easy analysis is constantly rising. Unlike another herbicide of interest named atrazine, studies that reveal the occurrence of glyphosate in the environment are just recently becoming higher in number.

Even though the use of glyphosate generates benefits, recent studies draw attention on new aspects that should continue to be constantly monitored by the newest analytical methods available. In addition, glyphosate based formulations are diverse encompassing different adjuvants, continuous studies being required in order to fully assess their deleterious impact.

The results pointed out that although laboratory experiments are a significant starting point, in order to completely understand the deleterious effects on water source and aquatic ecosystems of glyphosate studies must be undertaken in natural systems, as well.

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