proceedings

MDPI

Proceedings

Effects of glyphosate application on soil chemistry to control invasive plants in a Mediterranean ecosystem†

Jesús Jiménez-Ruiz [1,2] *, Juan Pablo del Monte [3] and María Inés Santín-Montanyá [4]

[1] Escuela Técnica Superior de Ingeniería Agronómica, Alimentaria y de Biosistemas (ETSIAAB), Universidad Politécnica de Madrid (UPM), Madrid, Spain.
[2] Unidad de Productos Fitosanitarios (UPF), Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA), Consejo Superior de Investigaciones Científicas (CSIC), Ministerio de Ciencia e Innovación, Madrid, Spain.
[3] Departamento de Producción Agraria, Área de Producción Vegetal, Escuela Técnica Superior de Ingeniería Agronómica, Alimentaria y de Biosistemas (ETSIAAB), Universidad Politécnica de Madrid (UPM), Madrid, Spain.
[4] Departamento de Medio Ambiente y Agronomía, Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA), Consejo Superior de Investigaciones Científicas (CSIC), Ministerio de Ciencia e Innovación, Madrid, Spain.
* Correspondence:
† Presented at the 1st International Electronic Conference on Agronomy, 3–17 May 2021;
Available online: https://sciforum.net/conference/IECAG2021

Abstract: Herbicides application in agriculture has increased over the last 30 years, triggered by the persistence and emerging new invasive weeds. Glyphosate, the most widely used herbicide in the world, is often used to control invasive weeds. In this study, we analyzed glyphosate effects on agricultural soil properties when it was applied to control the invasive grass giant reed (*Arundo donax* L.). The study was conducted in four areas in Spain. Glyphosate was applied at 10 L/ha. Preliminary sampling was conducted in order to determine the initial soil properties and six months after, soil samples were taken to determine the changes in the structural and chemical properties (mg HCO_3/kg, mg CO_3/kg, Kjeldahl nitrogen, organic and ammoniacal nitrogen, soil texture, pH, conductivity, dissolved oxygen and total K, Mg, Na, P), including glyphosate soil concentration. The results showed that there were not significant changes in the physical and chemical soil parameters which would influence the composition of these environments. However, it is necessary to study in deep other areas of the pesticide's evaluation, in order to safeguard that its application does not pose an unacceptable risk to human or animal health or the environment, as established in the European regulation for the authorization of plant protection products (Regulation (EC) nº 1107/2009) and the Directive of Sustainable Use of Pesticides (Directive 2009/128/EC).

Keywords: agroecosystems; herbicides; invasive plants; soil chemistry.

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Proceedings* **2021**, 68, x. https://doi.org/10.3390/xxxxx

Published: date

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Glyphosate is a derivative of the amino acid glycine, with phosphoric acid attached to the radical amino. It is an acid and is used in the form of salt (isopropylamine). It is a non-selective herbicide, wide spectrum, post-emerging nature (post birth). Glyphosate is absorbed by the foliage and from there it is translocated to the entire plant, roots and leaves. Its non-selective nature is due to the fact that most plants either metabolize it very slowly or do not degrade it [1]. It works by inhibiting the enzyme 3-enolpyruvyl-shechymate-5 phosphate synthetase (EPSPS), the psychic acid pathway, which causes the accumulation of psychic acid and its derivatives (only in plant cells). The inhibition of this enzyme also affects protein synthesis, affecting growth, resistance to diseases.

The inactivation of glyphosate in the soil is done in two ways, adsorption and mineralization. Mineralization is the main dissipation mechanism of the herbicide in the soil. Glyphosate is rapidly adsorbed to soil particles where its activity is limited, while free glyphosate is rapidly degraded by microorganisms.

The main breakdown metabolite of glyphosate is aminomethylphosphoric acid (AMPA) (Fig. 1). Once in the soil, the AMPA is adsorbed. Eventually AMPA breaks down to water, carbon dioxide, ammonium, and phosphate.

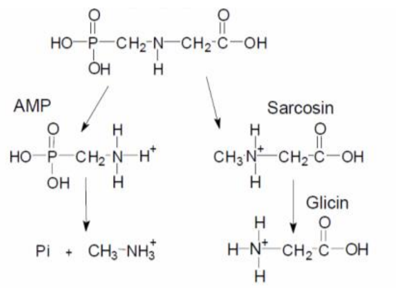

Figure 1. Glyphosate molecular structure and its main metabolites.

The following information regarding its persistence and degradability in the soil is extracted from the safety data sheet for glyphosate: 1. Microbial biodegradation is complete, forming natural compounds: CO_2, H_2O, N and phosphates, and 2. It is strongly adsorbed in the soil, so it does not leach, its half-life being more than 60 days.

High adsorption means low mobility and low persistence, the period of activity of glyphosate in the medium is relatively low. Its persistence in the soil, according to studies, is up to 60 days; in sediment it is somewhat older, about 120 days. Glyphosate is a highly polar herbicide, very soluble in water and insoluble in most organic solvents. Once in the soil, its degradation is essentially microbial. Between pH 7 and 9, the glyphosate molecule has two negative charges. It has a great capacity to form very stable complexes with trivalent metal ions such as ferric iron and aluminum, but also with divalent ions such as copper and zinc and to a lesser extent with calcium and magnesium.

The purpose of this study is to characterize the previous state of the soil in terms of the composition and the physico-chemical characteristics of those plots under study, where the chemical treatment with glyphosate has been applied to control the invasive plant *Arundo donax* L. (Giant reed) [2,3], as well as the characterization after its application with in order to study the possible short-term effects, establishing a pattern of behavior of the herbicide in the soil through the interactions that could occur between glyphosate with the elements present in it.

2. Materials and Methods

2.1. Samplig and Data collected:

Glyphosate was applied at 10 L/ha. Preliminary sampling was conducted in order to determine the initial soil properties and six months after, soil samples were taken to determine the changes in the structural and chemical properties (mg HCO_3/kg, mg CO_3/kg, Kjeldahl nitrogen, organic and ammoniacal nitrogen, soil texture, pH, conductivity, dissolved oxygen and total K, Mg, Na, P), including glyphosate soil concentration. Soil and sediment sampling was carried out according to the following guidelines and standards described in the Norma EN-ISO 5667-12 (1995). "GUIDANCE ON SAMPLING OF BOTTOM SEDIMENTS", ISO 5667-15 (1999): Guidance on preservation and handling of sludge and sediment samples, ISO/AWI 5667-15: Guidance on preservation and handling of sludge and sediment samples, Methods Manual for Bottom Sediment Sample Collection (Palmer:1985), Sediment sampling quality assurance. User's Guide (Barth and Starks: 1985) and EPA (1994): "COMPLIANCE INSPECTION MANUAL".

Soil and sediment data collected: Basic physical/chemical properties of soils and sediments: granulometry, pH and conductivity. Organic matter: the organic load of the soil / sediment were analyzed. Kjeldahl Nitrogen (NKT), Total Phosphorus (PT): basic forms of nutrients. Only on the soil: Sodium (Na), Potassium (K) and Magnesium (Mg): the basic ions for plant growth were analyzed, as they are micronutrients. Carbonates and bicarbonates were analyzed to know the hardness of the soil. Glyphosate was analyzed by Gas Chromatography and Mass Spectrometry (CG-MS). The Gas Chromatography - Mass Spectrometry (CG-MS) coupling is a powerful tool for the analysis of complex samples since it is based on the possibility of separating molecular species according to their mass.

2.2. Study area:

The study was conducted in four areas in Spain located in the East (Fig. 2), concretely in soils close to riparian zones due to the species *A. donax* invades mainly this kind of fluvial ecosystems.

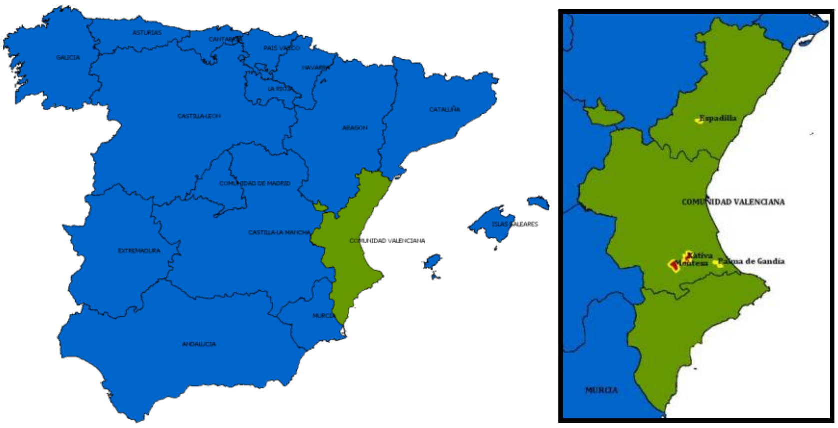

Figure 2. Location of the areas studied in the East of Spain.

3. Results

3.1. Characterization of the medium before the herbicide application

After analyzing the physical-chemical parameters stipulated according to the nature of the samples, whether soil or sediment, the results obtained in campaign 1 are presented below (Table 1):

Table 1. Results of the physic-chemical analyzes carried out on the soil and sediments of the studied sections, before the herbicide application.

Parameter	Unit	Location Río Bernisa-Palma deGandia		Location Río Cañoles - Montesa		Location Río Cañoles-Xàtiva		Location Río Mijares-Espadilla	
		Soil	Sediment	Soil	Sediment	Soil	Sediment	Soil	Sediment
Bicarbonate	**mg HCO3/Kg**	500	-	51320	-	33230	-	1630	1340
Carbonate	**mg CO3/Kg**	1300	-	255000	-	198000	-	3000	2000
Conductivity 25ºC	**microS/cm**	115	210	186	689	222	242	413	506
Total phosphorus	**mg/Kg**	8127	5030	285	415	231	257	422	141
Total magnesium	**mg/Kg**	26080	-	19740	-	22160	-	15480	10170
Organic material	**%**	3,1	3,8	5,9	8,4	5,0	3,8	3,3	1,3
Kjeldahl Nitrogen	**mgN/Kg**	500	703	2023	2067	1781	903	1525	31114
pH	**ud. pH**	8,8	8,0	7,6	8,4	8,5	8,6	7,4	9,5

Total potassium	mg/Kg	4982	-	7323	-	9097	-	7542	2458
Total sodium	mg/Kg	905	-	923	-	703	-	831	421

Results obtained for the physical-chemical parameters analyzed for each of the points studied before (C1) and after glyphosate application (C3), as well as the percentage of variation between campaigns:

Table 2. Results of the physic-chemical analyzes carried out on the soil and sediments on Río Bernisa-Palma de Gandia.

Parameters	Units	Location: Río Bernisa-Palma de Gandia					
		Soil			Sediment		
		C1	C3	% variation	C1	C3	% variation
Bicarbonate	**gHCO3/Kg**	0,5	38,4	>100	-	-	
Carbonate	**gCO3/Kg**	1,3	175	>100	-	-	
Conductivity 25ºC	**mS/cm**	0,115	1,29	>100	0,21	1,14	>100
Total phosphorus	**g/Kg**	8,127	0,239	-97,1	5,03	0,227	-95,5
Total magnesium	%	3,1	4	29,0	3,8	12,5	>100
Organic material	**gN/Kg**	0,5	4,195	>100	0,703	7,324	>100
Kjeldahl Nitrogen	**ud. pH**	8,8	7,0	-20,5	8,0	7,5	-6,3
pH	**mg/Kg**	4982	4892	-1,8	-	-	
Total potassium	**mg/Kg**	905	546	-39,7	-	-	
Total sodium	**mg/Kg**	26080	25260	-3,1	-	-	

Table 3. Results of the physic-chemical analyzes carried out on the soil and sediments on Cañoles - Montesa.

Parameters	Units	Location: Cañoles - Montesa					
		Soil			Sediment		
		C1	C3	% variation	C1	C3	% variation
Bicarbonate	**g HCO3/Kg**	51,32	52,1	1,5	-	-	
Carbonate	**g CO3/Kg**	255	166	-34,9	-	-	
Conductivity 25ºC	**mS/cm**	0,186	1,758	>100	0,689	1,449	>100
Total phosphorus	**g/Kg**	0,285	0,168	-41,1	0,415	0,289	-30,4
Organic material	%	5,9	2,8	-52,5	8,4	3,4	-59,5
Kjeldahl Nitrogen	**gN/Kg**	2,023	3,412	68,7	2,067	7,59	>100
pH	**ud. pH**	7,6	7,3	-3,9	8,4	7,6	-9,5
Total potassium	**mg/Kg**	7323	3358	-54,1	-	-	
Total sodium	**mg/Kg**	923	556	-39,8	-	-	
Total magnesium	**mg/Kg**	19740	19330	-2,1	-	-	

Table 4. Results of the physic-chemical analyzes carried out on the soil and sediments on Cañoles - Xátiva.

Parameters	Units	Location: Cañoles- Xàtiva					
		Soil			Sediment		
		C1	C3	% variation	C1	C3	% variation
Bicarbonate	**g HCO3/Kg**	33,23	42,5	27,9	-	-	
Carbonate	**g CO3/Kg**	198	182	-8,1	-	-	
Conductivity 25ºC	**mS/cm**	0,222	1,625	632,0	0,242	1,15	375,2
Total phosphorus	**g/Kg**	0,231	0,337	45,9	0,257	0,28	8,9
Organic material	%	5,0	3,8	-24,0	3,8	< 2	-
Kjeldahl Nitrogen	**gN/Kg**	1,781	3,921	120,2	0,903	5,95	558,9

pH	**ud. pH**	8,5	6,8	-20,0	8,6	7,2	-16,3
Total potassium	**mg/Kg**	9097	8039	-11,6	-	-	
Total sodium	**mg/Kg**	703	657	-6,5	-	-	
Total magnesium	**mg/Kg**	22160	19930	-10,1	-	-	

Table 5. Results of the physic-chemical analyzes carried out on the soil and sediments on Río Mijares-Espadilla.

Parameters	Units	Location: Río Mijares- Espadilla					
		Soil			Sediment		
		C1	C3	% variation	C1	C3	% variation
Bicarbonate	**g HCO3/Kg**	1,63	0,91	-44,2	1340	-	-
Carbonate	**g CO3/Kg**	3	281	9266,7	2000	-	-
Conductivity 25ºC	**mS/cm**	0,413	0,101	-75,5	0,506	0,1018	-79,9
Total phosphorus	**g/Kg**	0,422	0,212	-49,8	0,141	0,109	-22,7
Organic material	**%**	3,3	4	21,2	1,3	<2	-
Kjeldahl Nitrogen	**gN/Kg**	1,525	3,425	124,6	31,114	0,72	-97,7
pH	**ud. pH**	7,4	7,1	-4,1	9,5	6,8	-28,4
Total potassium	**mg/Kg**	7542	4873	-35,4	2458	-	-
Total sodium	**mg/Kg**	831	510	-38,6	421	-	-
Total magnesium	**mg/Kg**	15480	9080	-41,3	10170	-	-

Regarding the concentration of glyphosate present in the soil and sediment, after 6 months of the application, the results obtained are presented in the table 6. Glyphosate concentration was the same before and after pesticide application.

Table 6. Results of the analysis of glyphosate concentration in soils and sediments.

Before glyphosate application		After glyphosate application	
Soil	Sediment	Soil	Sediment
Glyphosate concentration (mg/Kg)	Glyphosate concentration (mg/Kg)	Glyphosate concentration (mg/Kg)	Glyphosate concentration (mg/Kg)
< 0,025	< 0,025	< 0,025	< 0,025

4. Discussion and conclusions

We can conclude that both in the soil and sediment, values of glyphosate were below the detection limit. Regarding the magnitude of the effect on the glyphosate application, no considerable changes were observed that could imply an affection or a variation in the structural characteristics and the physical-chemical properties on soils or sediments analyzed. It has been found that the trend of the results obtained between the two campaigns (before and after pesticide application) is consistent with the theoretical principles in reference to the properties of glyphosate [1,4]. Expected variations of the analyzed parameters have occurred in terms of the physical-chemical changes that occurred in response to the application of glyphosate in the medium due to its high adsorption attracted by the electrical charges of the soil particles. As explained, glyphosate has a high solubility in water. In the case of reaching the river water with sediments, it will be easily adsorbed by these and degraded by microbial action. This solubility in water makes it very sensitive to washing by rain, so the absence of precipitation in the

12-24 hours following the treatment is essential to ensure its effectiveness and avoid the occurrence of a washing by leaching into the soil, precaution that must be taken into account considering the composition of the sampled soils and their behavior: mainly sandy soils that do not retain water. Despite this, it has been found 6 months after the application presence of glyphosate in the soil or sediment is practically absent.

Author Contributions: Conceptualization, J.J-R.; methodology, J.J-R.; formal analysis, J.J-R.; investigation, J.J-R.; resources, J.J-R.; data curation, J.J-R.; writing-original draft preparation, J.J-R.; supervision, JP.dM. and MI.S-M.

Funding: This research was funded by the Ministry of Environment, General Directorate for Water (DGA).

Conflicts of Interest: authors declare no conflict of interest.

References

1. Calderon, M.J.; Quintana, MA.; López-Piñeiro, A.; Hermosín, MC.; Cornejo, J.; Estudio preliminar sobre el comportamiento del herbicida glifosato en dos suelos de Extremadura. Estudios de la zona no saturada del Suelo Vol. VII.; **2005;** ISBN 84-9749-171-8, pp. 23-28.
2. Jiménez-Ruiz, J.; Hardion, L.; Del Monte, JP.; Vilan, B.; Santín-Montanyá, MI.; Monographs of the invasive plant in Europe Nº 4: *Arundo donax* L. *Bot Letters* **2021**, *168:1*, 131-151 DOI: 10.1080/23818107.2020.1864470
3. Jiménez-Ruiz, J.; Santín-Montanyá, MI. An approach to the integrated management of exotic invasive weeds in riparian zones. In *Riparian zones: characteristics, management practices and ecological impacts*.; O S Pokrovsky., Ed.; Publisher: Nova Science Publishers: Environmental Research Advances, Hauppauge (NY), **2016,** pp. 99-142.
4. Menéndez, J.; González, J.; de Prado, R.; Factores que afectan a la eficacia del glifosato. *Agricultura: Revista* agropecuaria y ganadera **1999**, 799:146-149.