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Degradation dynamics of glyphosate in two types of soil from corn fields of the Philippines

Mercado, C. A.* **and Mactal, A. G.**

Department of Soil Science, College of Agriculture, Central Luzon State University, Science City of Munoz, Nueva Ecija, Philippines.

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Abstract Glyphosate degradation in two types of soils from corn fields in the Philippines was determined. The soils from two land mapping units showed different soil pH, CEC, soil organic matter and clay contents. These were planted with herbicide-ready corn variety for 16 years and are regularly applied with glyphosate. Initial analysis of soils in both LMU 1 and LMU 2 showed low level of glyphosate residue with a value of 0.01 mg/kg and is considered below the critical residue level for glyphosate of 0.1 mg/kg of soil. Glyphosate residue was analyzed at 1, 15 and 30 days after the application of 0.96 mg/kg of glyphosate in soils belonging to two LMUs. Results showed that glyphosate residue in the soil at 1 DAA decreased by 11.04 to 14.4 percent in LMU 1 and LMU 2 respectively. At 15 days after application, glyphosate residue continued to decline to 0.059 mg/kg for LMU 1 and 0.041 mg/kg for LMU 2. These values correspond to 93.85 to 95.73 % reduction from the initial level of 0.96 mg/kg. The amount of glyphosate at 30 DAA is detected below the limit of gas chromatography of 0.01 mg/kg. Glyphosate degradation for LMU 1 is represented by the equation y=-0.0329x+0.8488 with a correlation coefficient of 0.8391. On the other hand, glyphosate degradation for LMU 2 is represented by the equation y=-0.0324x+0.8299 with a correlation coefficient of 0.8254. Degradation was shown to be faster in soils with low organic matter, low clay content, low CEC and slightly alkaline (LMU 2). It showed that glyphosate is not as persistent as it is previously reported .

Keywords: Glyphosate degradation, Glyphosate residue, Glyphosate persistence

Introduction

The use of herbicides for weed control is important in modern agricultural development. The worldwide use of pesticides was approximately 5.2 billion pounds, according to the United States Environmental Protection Agency (EPA), of which herbicides accounted for the largest portion of total used (Donaldson *et al.,* 2011). Typically, at the beginning of the growing season, crops show greater vulnerability to weeds due to their slower growth and lower

* **Corresponding Author**: Mercado, C. A.; **Email:** catherinemaymercado@gmail.com

density during that time. Application of herbicides is therefore necessary (Bursić *et al.*, 2006). Herbicides are a group of organic compounds that possess far-reaching environmental consequences when persistent in the soil. When the herbicides are used scrupulously or constantly, a persistence issue arises; crop failure involves replanting; a prone crop follows a short-term crop that has obtained a persistent herbicide; and the decomposition of the applied herbicide continues very slowly (Sankaran *et al.*, 1993).

Glyphosate is a widely popular herbicide. About 6.1 billion kilograms of the herbicide glyphosate have been distributed globally throughout the last decade. Its popularity increased when genetically engineered crops also called “Roundup Ready” crops were introduced. However, in 2015, despite of its popularity, glyphosate was classified as' possibly carcinogenic to humans by the International Agency for Cancer Research, the World Health Organization's specialist cancer agency (https://www.soilassociation.org/media/7229/glyphosate-and-soil-health-a-summary1docx.pdf). Meanwhile, the effects of glyphosate on human health and ecological safety are still unclear. Because of its popularity, it is very important to understand its fate in soil and determine whether it leaves a considerable amount of residue in the soil as they may pose risks for the environment as well as on human health. The insufficient knowledge about glyphosate, the way it behaves in the natural environment, and its degradation has become a serious issue because of the possibility that it remains in the soil for years (Benbrook, 2016). The research aimed to determine the dynamics of the applied glyphosate in soils which devoted to glyphosate-ready corn variety.

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Materials and methods

This study was conducted at Brgy. Colubot, San Manuel, Tarlac. Digitized maps of the different agricultural areas in the barangay were acquired at the Department of Agriculture Provincial office of Tarlac. These maps served as a basis for the delineation of corn growing areas in Brgy. Colubot while the list of corn farmers was acquired from the Municipal Agriculture Office of San Manuel. Corn growing areas in the barangay were delineated using Garmin Oregon 650 and Orux Maps. The data gathered was plotted in Google Earth Pro and was exported in ArcGIS. Among 27 randomly selected corn farmers in the barangay, a survey interview was carried out. The interview focused on the cultivation practices during their production and the use of glyphosate-based herbicides in their farms. In addition, through the interview, yield data obtained from the Department of Agriculture Office at the Local Government Unit of San Manuel, Tarlac was verified.

Soil samples were collected from the corn growing areas in Brgy. Colubot, San Manuel, Tarlac. Soil samples were collected in predetermined points. Sampling points were stored in a Global Positioning System (GPS) to locate the collection point of the soil samples for analysis of some soil properties. In each sampling site, one composite surface soil sample from 10 location was collected from 0-30 cm depth. The collected soil samples were subjected to air-drying, pulverized, sieved into 2 mm mesh sieve and packed in a plastic bag and were brought to Regional Soils Laboratory at San Fernando, Pampanga and Central Laboratory, College of Agriculture, Central Luzon State University for the analysis of soil pH using 1:1 soil water ratio, soil texture through hydrometer method, cation exchange capacity through ammonium acetate method and organic matter content using Walkley-Black method. The results of analysis were plotted in Microsoft Excel and imported to ArcGIS 10.3.1 for mapping. The data for the soil properties were interpolated using Ordinary Gaussian Kriging.

Land mapping units were delineated which was based on the soil properties of corn growing areas in Brgy. Colubot. Soils with clay in texture, medium organic matter, high cation exchange capacity and soil pH of very slightly acidic were the areas represented by LMU 1. On the other hand, soils with clay loam in texture, low organic matter, low cation exchange capacity and soil pH of slightly alkaline were represented by LMU 2. Herbicide glyphosate was applied at land mapping units following the rate of one gallon per hectare. The date of application of herbicide was monitored for the collection of soil samples for residue analysis at different time intervals. Soil samples were collected from the corn growing areas of Brgy. Colubot before application, 1, 15, 30, and 90 days after application. Collected soil samples were stored at lower than room temperature before they were brought to the laboratory for the analysis of residue using gas chromatography.

Results

Study area

Brgy. Colubot has an area of 108 hectares that are devoted for corn farming. The land use map of Brgy. Colubot, San Manuel, Tarlac was shown in Figure 1. The soil belongs to San Manuel series, clay loam to clay texture with low (46.177 hectares) to medium (61.823 hectares) organic matter content, low to high CEC and pH ranging from slight acidic to slightly alkaline. Glyphosate ready corn have been planted since the year 2007. It is fertilized with inorganic fertilizers at an average rate of 134-42-42 kg N-P_2O_5-K_2O per hectare. Water pumps are used to irrigate the fields as there is no irrigation facility available in the area. The average yield of farmers based from 2016, 2017 and 2018 data ranged from 6.9 tons to 7.5 tons/ha.

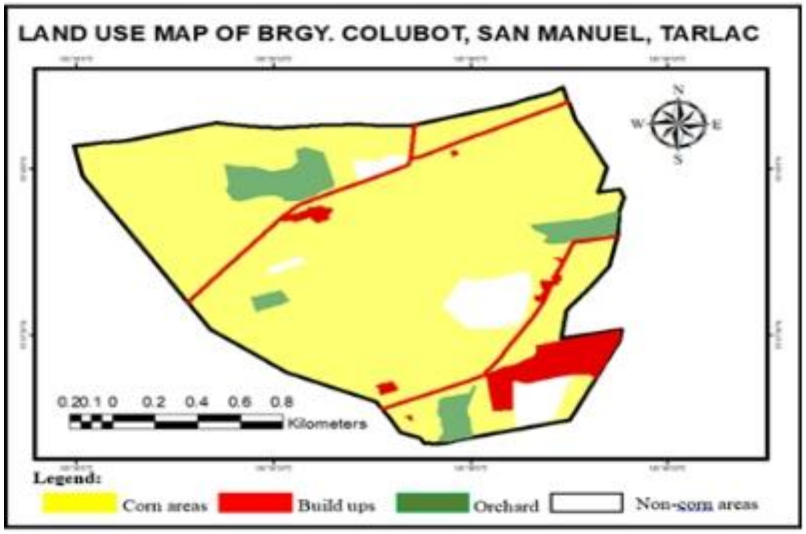

Figure 1. Land use map of Brgy. Colubot, San Manuel Tarlac, Philippines

Soil properties

Soil properties of the Land Mapping Units (LMU) is shown on Table 1***.*** LMU1 are clay soil, mdedium roganic matter, high CEC and very slightly acid while LMU2 is clay loam, low organic matter, high CEC and slightly alkaline.

Table 1. Soil properties of the Land Mapping Units (LMU)

SAMPLE NO.	SOIL TEXTURE	ORGANIC MATTER CONTENT	CATION EXCHANGE CAPACITY	SOIL pH
LMU 1	Clay	Medium	High	Very slightly acidic
LMU 2	Clay loam	Low	Low	Slightly alkaline

Glyphosate residue

Results showed that glyphosate residue in the soil at 1 day after application decreased rapidly at 15 days after application for the both LMU's. Glyphosate residue during collection of samples was 0.96 mg/kg. However, after one day of application residue was found to be 0.854 mg/kg for LMU 1 and 0.82 for LMU 2. On the other hand, glyphosate residue at 15 days after application was 0.059 mg/kg for LMU 1 and 0.041 mg/kg for LMU 2. For LMU 1, glyphosate degradation was presented by the equation y=-0.0329x+0.8488 with a correlation value of 0.8391 as shown in Figure 2. On the other hand, glyphosate degradation for LMU 2 was presented by the equation y=-0.0324x+0.8299 with a correlation value of 0.8254 shown in Figure 3. Results showed that glyphosate residue is negatively correlated with time.

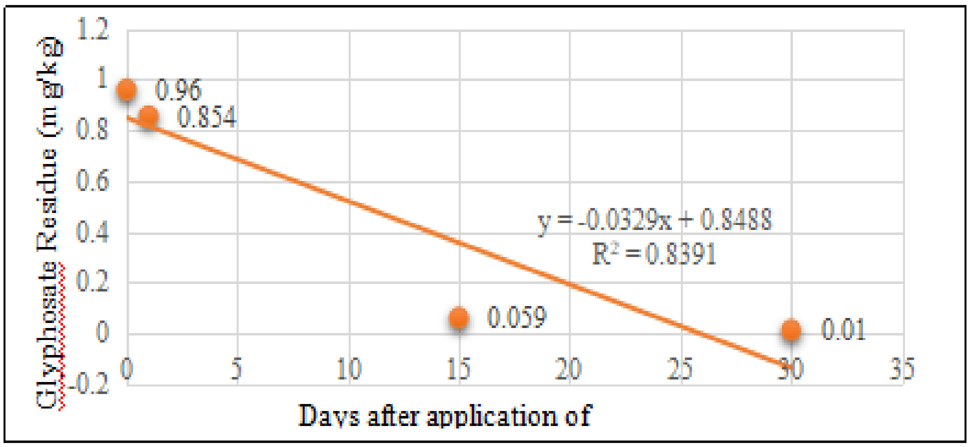

Figure 2. Glyphosate residue of soil in LMU 1, Brgy. Colubot, San Manuel, Tarlac

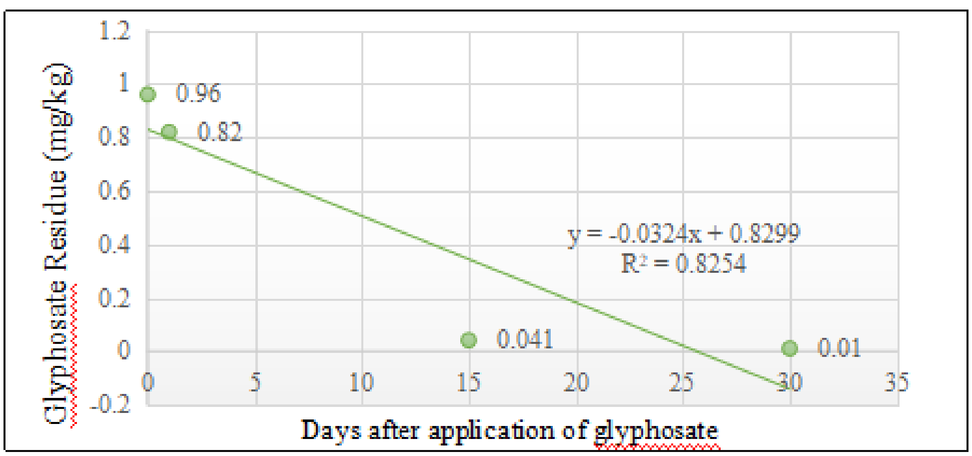

Figure 3. Glyphosate residue of soil in LMU 2, Brgy. Colubot, San Manuel, Tarlac

Table 2. Glyphosate residue of soil samples

DAYS OF SAMPLING	AMOUNT OF GLYPHOSATE RESIDUE (mg/kg)	
	LMU 1	LMU 2
Before application	<0.01	<0.01
At sampling	0.96	0.96
1 DAA	0.8544	0.82
15 DAA	0.059	0.041
30 DAA	<0.01	<0.01
90 DAA	<0.01	<0.01

Discussion

Glyphosate formulations are used as a broad-spectrum systemic herbicide that have been widely used in agriculture, raising growing concerns about increasing toxic residues in soils. Today, in agronomic crops and orchards, glyphosate formulations are broad-spectrum systemic herbicide that have been widely used, and making it as the world's largest selling herbicide in 2013 (Stephen and Stephen, 2008).

The research determined the degradation dynamics of glyphosate in two types of soil from corn fields in the Philippines. Residue analysis was taken from 10 sampling sites in corn growing areas in Brgy. Colubot, San Manuel, Tarlac showed that residue before application, 30 days and 90 days after application were below the detection limit of gas chromatography of 0.01 mg/kg. For this reason, another set of soil samples were collected on corn growing areas in Brgy. Colubot. Glyphosate residue was analyzed from soils sprayed with 0.96 mg/kg of glyphosate at 0, 1, 15 and 30 days after application (DAA) from the delineated land mapping units.

Glyphosate residue in the soil at 1 DAA decreased by 11.04 to 14.4 percent in LMU 1 and LMU 2 respectively. At 15 days after application, glyphosate residue continued to decline to 0.059 mg/kg for LMU 1 and 0.041 mg/kg for LMU 2. These values were corresponded to 93.85 to 95.73 % reduction from the initial level of 0.96 mg/kg. The amount of glyphosate at 30 DAA had already belowed the detection limit of gas chromatography of 0.01 mg/kg. Glyphosate degradation for LMU 1 is represented by the equation $y=-0.0329x+0.8488$ with a correlation coefficient of 0.8391 while in LMU 2, degradation is represented by the equation $y=-0.0324x+0.8299$ with a correlation coefficient of 0.8254. Degradation was observed to be faster in soils with low organic matter, low clay content, low CEC and slightly alkaline (LMU

2). The results of the study conducted by *Zhang et al.* (2015) showed that with the increase in time after application of glyphosate formulations, the amount of glyphosate and its degradation product aminomethylphosphonic acid (AMPA) in soils decreased. Furthermore, the results of glyphosate residue analysis indicated that there was a rapid degradation of glyphosate for tropical soils compared to temperate soils.

The length of time herbicides persist is determined by many factors. Soil quality, soil chemistry, and microbial activity are variables that influence the persistence of herbicides (Curran, 1999). In this study, soil texture, soil organic matter, cation exchange capacity and soil pH were the soil properties that influenced degradation. LMU 1 showed a medium organic matter content, high cation exchange capacity and pH value classified as very slightly acidic. The amount of glyphosate residues in LMU 1 is relatively higher than in LMU 2 at 1 DAA and 15 DAA.

The extent of pesticide sorption in soils may have caused the difference in the quantity of glyphosate residue observed from the soils taken from the two land mapping units. Pesticide sorption is governed by the pesticide's molecular properties and the soil adsorbent surface characteristics, which determine the type of interactions between pesticide molecules and soil adsorbent surfaces (Cuervo and Fuentes, 2014). Adsorption is a process of accumulation at an interface and is contrasted with absorption, or passage through an interface (Zimdhal, 2007). In addition, the content of organic matter and the quantity and composition of the clays are very much linked to adsorption. Soils rich in oxides and metallic hydroxides are also strongly adsorbed by ion pesticides, while cationic pesticides are adsorbed by soils with a high content of clays (mainly montmorillonite and vermiculite) and organic matter (Cuervo and Fuentes, 2014). Adsorption influences soil movement and availability and the degradation rate (Zimdhal, 2007).

Therefore, soils high in clay, organic matter, or both were decreased the loss of herbicide through leaching and volatilization. Furthermore, high levels of organic matter and clay adsorbed herbicides and residues persist longer than in sandy soils (Curran, 1999). However, when the pH increases, the proportion of ionizable molecules also increases, and there is electrostatic repulsion. The ionic property of glyphosate having zwitterion (positive and negative ion) makes it less adsorptive to soil in different land mapping units making it less persistent in soils from Barangay Colubot.

Acknowledgements

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