DYNAMIC OF GLYPHOSATE MINERALIZATION IN DIFFERENT SOIL TYPES

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ABSTRACT

Glyphosate [N-(phosphonomethyl)-glycine] is a largely used broad-spectrum, non selective, systemic, post-emergence herbicide. The object of this work was to study the dynamic of glyphosate mineralization in different agricultural soils characteristic to the western part of Romania: black chernozem, typical gleysol, phaeozom and slight vertisol with moderate carbonatation. The degradation experiment was conducted under controlled laboratory conditions using glyphosate-phosphonomethyl-^{14}C-labeled with specific activity 2.2 mCi/mmol. The experimental results indicated that the dynamic of glyphosate mineralization until the CO_2 stage is different for each soil: the mineralization of the herbicide is rapid in the first days of incubation and then decreases with time until the end of experimentation. The mineralization curves for the soils had only two phases, the initial rapid phase, for about 20 days, followed by a slow final phase, when the curves attained plateaus. The initial rapid phase of degradation was attributed to microbial action on the free glyphosate while the slower phase was due to the subsequent attack on the adsorbed glyphosate.

Key words: mineralization, soil, glyphosate-phosphonomethyl-^{14}C-labeled, chernozem, typical, gleysol, phaeozom and slight vertisol.

INTRODUCTION

Glyphosate [N-(phosphonomethyl)-glycine] is a broad-spectrum, non selective, systemic, post-emergence herbicide. Glyphosate based herbicides are among the most widely used broad spectrum herbicides in the world because they are highly efficacious cost effective, practically non-toxic and degrade readily in the environment. Glyphosate is moderately persistent in soil. It is strongly adsorbed to most soils and therefore has a low potential for runoff except when adsorbed to suspended matter which can be washed off into water (Alexa et al., 2008). Any element in the soil, capable of forming complexes with glyphosate, has been shown to affect the adsorption of glyphosate (Getenga and Kengara, 2004). Soil microflora quickly biodegraded glyphosate into AMPA and CO_2. The herbicide is inactivated and biodegraded by soil microbes at rates of degradation related to microbial activity in the soil and factors that affect this activity. Glyphosate degradation rates vary considerably across a wide variety of soil types and microfloral population types.

The herbicide is highly soluble in water and is resistant to hydrolysis. But the low mobility of glyphosate in soil implies minimal potential for the contamination of drinking water from ground-water (Alexa et al., 2006). The physical-chemical characteristics of water (conductivity and ionic concentration) influence the rate of glyphosate extraction from water samples, which decrease with the increasing of conductivity and ionic concentration (Alexa et al., 2007, 2008).

The object of this work was to study the dynamic of glyphosate mineralization in four different agricultural soils characteristic to the western part of Romania: black chernozem, typical gleysol, phaeozom and slight vertisol with moderate carbonatation.

MATERIAL AND METHODS

The degradation experiment was conducted under controlled laboratory conditions using a TRIATHLER Liquid Scintillation Counter and, Glyphosate-phosphonomethyl-^{14}C-labeled with specific activity 2.2 mCi/mmol.

Four types of soils were taken under study: black chernozem, vertisol, gleysol and phaeozom with different characteristics.

The description of the analyzed soils is presented in table 1.

The samples of analyzed soils were taken from horizon A, from a depth of 10 cm. In order to obtain a representative sample, the samples were taken from different points by splitting the surface in quarters, diagonally and on rows, through the carrots.

Twenty five grams soil samples in replicates of two were placed in biometer flasks after the air dried and homogenized soil was

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conditioned by being moistened to 85% of the field water capacity. Glyphosate solution (both labeled and non-labeled) in distilled water was added in the soils samples. The added concentration was 2 ppm, respectively 4 ppm non-labeled glyphosate and the initial radioactivity was done by Glyphosate-phosphonomethyl-^{14}C-labeled with specific activity 2.2 mCi/mmol. Liquid Scintillation Counter TRIATHLER was used for radio-assaying. The soils were incubated at 20°C, for 40 days. The mineralization curves of $^{14}CO_2$ accumulated were compared during 40 days.

Table 1. Chemical and physical characteristics of analyzed soils

Horizon	Ap	Am
Depth, cm	0-25	25-45
Gleysol		
Dust <0.02 mm	26.0	27.0
Clay < 0.01 mm	37.1	36.5
Sand (0.2-0.02 mm)	36.7	36.0
Sand (0.2-2 mm)	0.2	0.5
pH in H_2O	8.05	8.05
Humic matter (%)	3.35	3.78
$CaCO_3$	0.16	0.16
P (ppm)	30,5	24,8
K (ppm)	249	266
Black chernozem		
Clay < 0.01 mm	41.1	44.5
Sand (0.2-0.02 mm)	29.2	27.7
Sand (0.2-2 mm)	0.5	0.5
Dust (0.02-0.001 mm)	29.2	27.3
pH in H_2O	6.45	6.74
Humic matter (%)	4.09	3.97
N total (%)	0.136	0.157
P (ppm)	28.8	12.1
Vertisol, low gleizated, moderate carbonatation		
Clay < 0.01 mm	41.8	42
Sand (0.2-0.02 mm)	30.5	32.7
Sand (0.2-2 mm)	0.5	0.3
Dust (0.02-0.001 mm)	27.2	25.0
pH in H_2O	6.51	7.15
P (ppm)	51.81	51.82
Phaeozom		
Clay < 0.01 mm	35.5	29.5
Sand (0.2-0.02 mm)	29.2	27.8
Sand (0.2-2 mm)	0.4	0.3
Dust (0.02-0.001 mm)	35.3	42.4
pH in H_2O	5.60	6.30
Humic matter (%)	2.60	2.36
P (ppm)	17.4	18.3
K (ppm)	149	137

The experimental model (Figure 1) for soil incubation is made of a 500 ml recipient, ermetically closed. In its interior are placed:

- a plastic vial in which we introduced 25 g radioactive soil according to experimental treatment;
- a plastic vial containing 10 ml distillate water, which assures atmosphere saturation with water vapor;
- a plastic vial of liquid scintillated type, containing 5 ml NaOH 0.2 M, which takes over the emanated $^{14}CO_2$ and which is periodically changed.

Figure 1. ^{14}C experimental model

The principle of this test consists in the fact that the soil microorganisms which metabolize the herbicide emanate the CO_2, the phenomenon intensity being directly proportionate with the quantity of CO_2 produced. Through addition of a small quantity of radioactively marked herbicide in mixture with the standard herbicide (cold) the evolution of the pesticide in soil can be followed with the help of the Liquid Scintillation Counter.

The radiation emanated by the ^{14}C in solution is transformed, with the help of solvents and organic receivers mixture (scintillating liquid) in photons which are measured with a photo-multiplier. The measurement of radioactivity with Scintillation Counter allows the estimation of the desintegration number in the soil sample.

Carbon dioxide formed through glyphosate marked molecule degradation is trapped in alkaline solution of NaOH 0.2 M, and measured with the help of the liquid Scintillation Counter. The dosage is realized on 5 ml solution NaOH whereon we add 10 ml scintillant mixture. For each sample the desintegration number are read for 5 minutes. Knowing the standard pesticide quantity initially dosed, we measure the mineralized pesticide percent between 2 samplings through reporting the read desintegration number of ^{14}C to each sampling, to the initial desintegration number emanated by the glyphosate. We calculate also the degradation velocity by reporting the percent mineralization of herbicide to the time taken in study. Through obtained percents addition we obtain the total quantity of glyphosate mineralization taking into account the time.

RESULTS AND DISCUSSION

The experimental results indicate a high microbial degradation of the glyphosate herbicide. The $^{14}CO_2$ quantity accumulated following glyphosate biodegradation under the microorganism action is higher in all 4 analyzed soils, comparing with blind sample (untreated soil).

Figure 2 shows the results of mineralization of glyphosate for different soils. The soil mineralization curves indicate the same profile. The mineralization curves for the soils had only two phases, the initial rapid phase followed by a slow final phase, when the curves attained plateaus. The rapid phase lasted for about 20 days.

In the first days, the quantity of accumulated $^{14}CO_2$ is similar for all soils and the values are between 1.68% for gleysol and 2.81% for vertisol. After 5 days, the quantity of $^{14}CO_2$, expressed in % from total radioactivity, grows to 14.34% in the case of vertisol, to 8.92% in chernozem, 8.57% in phaeozom and 6.42% in gleysol.

The quantity of $^{14}CO_2$ accumulated after 20 days, expressed in % from total radioactivity is 36.42% for chernozem, 36.04% for vertisol, 21.30% for gleysol and 27.27% for phaeozom (Figure 2).

The soil characteristics influence the degradation capacity of glyphosate in the presence of microorganisms. In the case of chernozem soil with high content of humic matter (4.09%), the quantity of $^{14}CO_2$, expressed in % from total radioactivity, after 20 days, is higher than in gleysol (3.35%).

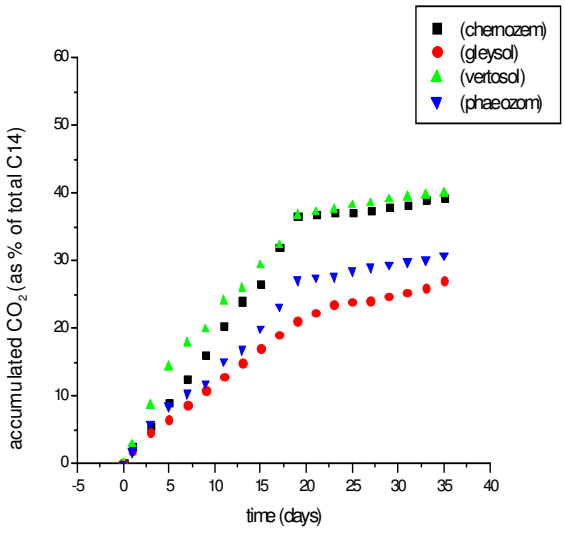

Figure 2. The mineralization of ^{14}C-glyphosate in different soils

The glyphosate biodegradation capacity in the presence of microorganisms grows in the following order: gleysol, phaeozom, chernozem and vertisol.

Regarding the herbicide quantity addition, we found that the free glyphosate from soil is directly and quickly desintegrated by microorganisms, even at higher applied concentration, double comparing with the quantity used in field (Figure 3).

The degradation velocity expressed as $^{14}CO_2$ accumulated per unit of time is presented in figure 4. The experimental results show that the rate of glyphosate degradation in time is higher in the firsts 5 days, than the velocity decreases until the curves attained plateaus.

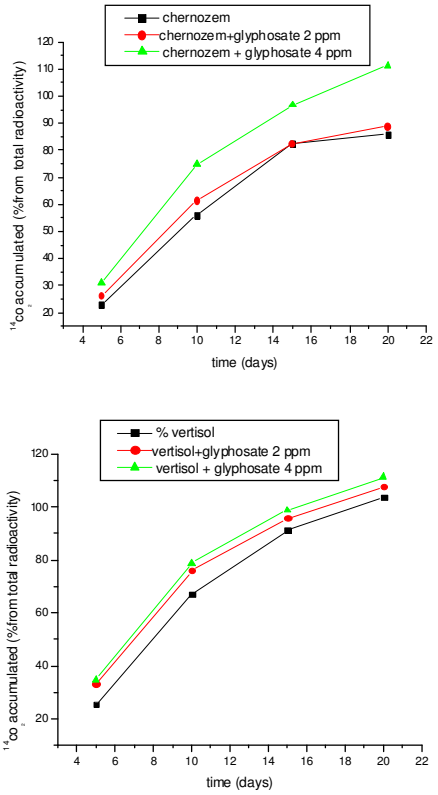

Figure 3. The mineralization of ^{14}C-glyphosate at different glyphosat concentrations

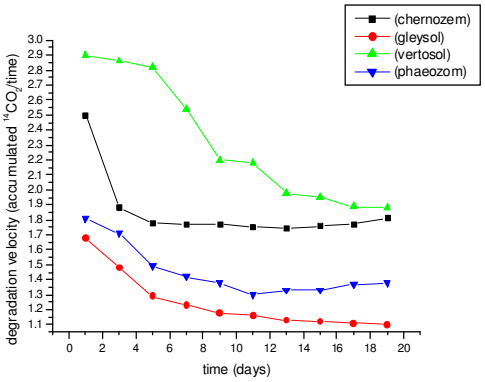

Figure 4. Glyphosate degradation velocity (accumulated $^{14}CO_2$ / time) in different soils

CONCLUSIONS

The experimental results indicated that the dynamic of glyphosate mineralization until the stage CO_2 is different for each soil and decreases in order: vertisol, black chernozem, phaeozom, gleysol.

The free glyphosate from soil is quickly and directly desintegrated by microorganisms, even at high applied concentrations, double comparing with quantity used in field.

The soil characteristics influence the degradation capacity of glyphosate in microorganisms presence. In soils like chernozem and vertisol the biodegradation capacity of the glyphosate is higher comparing with soils like gleysol and phaeozom.

The mineralization curves for the soils had only two phases, the initial rapid phase, for about 20 days, followed by a slow final phase, when the curves attained plateaus. The initial rapid phase of degradation was attributed to microbial action on the free glyphosate while the slower phase was due to the subsequent attack on the adsorbed glyphosate.

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