RESEARCHES CONCERNING THE INFLUENCE OF INORGANIC SUBSTRATUM OVER GLYPHOSATE MINERALIZATION CAPACITY IN SOIL

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Abstract. The object of this work was to study the dynamic of glyphosate mineralization in different agricultural soils characteristic to the west 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 2,2mCi/mmol. The experimental results indicated that the dynamic of glyphosate mineralization until the stage CO_2 in present of inorganic compounds is different for each soil, the mineralization of the herbicide is important in the first days of incubation and then decreases with time until the end of experimentation.

Keywords: 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 used both agriculturally and domestically. It has a high soil adsorption coefficient (Kd=61 g/cm^3) and a very low octanol/water coefficient (Kow=0.00033). These numbers suggest that glyphosate has low mobility and. Glyphosate's low octanol/water coefficient and low fat (lipids) solubility indicate that it has a low tendency to bioaccumulate. Glyphosate has only a slight tendency to leach in soil and is classified as very slightly mobile pesticide. In the soil environment, glyphosate is resistant to chemical degradation, is stable to sunlight, is relatively nonleachable, and has a low tendency to runoff (except as adsorbed to colloidal matter). The adsorbtion of glyphosate on the soil particles depend to the physical-chemical composition of soil [1, 2]. The scientific studies found that the prime factor in determining the amount of glyphosate adsorbed to soil particles is the soil phosphate level and that glyphosate is bound to soil through the phosphonic acid moiety. Glyphosate competes with inorganic phosphate for soil binding sites and the degree of binding depends on availability of unoccupied phosphate binding sites [5].

Glyphosate's primary route of decomposition in the environment is through microbial degradation in soil. 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. The biological degradation process is carried out under both aerobic and anaerobic conditions by soil microflora. Rates of decomposition depend on soil and microfloral population types [3].

In many countries, toxicology studies have been conducted to enable evaluation of the potential health risk. Recent studies have found that rats excreted 97.5% of an administered dose in their urine and feces. Other metabolism studies have found that glyphosate residues have minimal tissue retention and are rapidly eliminated from various animal species including mammals birds and fish [4].

In this paper has been studied the influence of inorganic substratum (ammonium nitrate) over mineralization capacity in four different soils (Black Chernozem, Typical Gleysol, Phaeozom and Slight Vertisol with moderate carbonatation).

MATERIALS AND METHODS

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

Four types of soils have been taken under study: Black Chernozem, Vertisol, Gleysol and Phaeozem with different characteristics.

GLEYSOL**:** dust <0.02 mm – 26.0%, clay < 0.01 mm – 37.1% , Sand – 36.7%, pH in H_2O - 8,05, Humus matter – 3.35 %, $CaCO_3$ – 0.16, Phosphorus – 30.5ppm, K – 249 ppm.

BLACK CHERNOZEM: Clay < 0.01 mm – 41.1%, Sand (0,2-0,02 mm) – 29.2%, Sand (0,2-2 mm) – 0.5%, dust (0.02-0.001 mm) – 29.2%, pH in H_2O- 6.45%, Humus matter (%) – 4.09, N total (%)- 0.136

P (ppm)- 28.8.

VERTISOL, LOW GLEIZATED, MODERATE CARBONATATION: Clay < 0.01 mm, 41.8%,

Sand (0.2-0.02 mm) – 30.5%, Sand (0.2-2 mm) – 0.5%, Dust (0.02-0.001 mm) – 27.2%, pH in H_2O- 6.51, P (ppm) – 51.81

PHAEOZEM: clay < 0.01 mm – 35.5%, Sand (0.2-0.02 mm) – 29.2%, Sand (0.2-2 mm) – 0.4%, dust (0.02-0.001 mm) – 35.3%, pH in H_2O – 5.60, Humus matter (%) – 2.60, P (ppm) – 17.4, K (ppm) – 149.

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

25 g soil samples in replicates of two were placed in biometer flasks after the air dried and homogenized soil was 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 non-labeled glyphosate and the initial radioactivity was

done by Glyphosate-phosphonomethyl-^{14}C-labeled with specific activity 2.2mCi/mmol. Liquid Scientillation Counter TRIATHLER was used for radio-assaying.

Have been established, for each type of soil, 3 experimental variants: blank soil assay with glyphosate, soil with addition of 125 µL NH_4NO_3 0.1 M and soil with addition of 250 µL NH_4NO_3 0.1 M. The soils were incubated at 20^{0}C, 40 days. The mineralization curves of $^{14}CO_2$ accumulated were compared during of 40 days.

Carbon dioxide formed through glyphosate marked molecule degradation is trap in alkaline solution of NaOH 0.2 M, and measured with the help of Liquid Scientillator. For each sample the disintegration number are read for 5 minutes. Knowing the market pesticide quantity initial dosed we measure the mineralized pesticide percent between 2 samplings through reporting the read disintegration number of C14 to each sampling, to the initial disintegration number emanated by the glyphosate.

RESULTS

The experimental results indicate a high microbial degradation of the glyphosate herbicide. The $^{14}CO_2$ quantity accumulated as follow of glyphosate biodegradation under the microorganism action is shown in Figures 1 & 2.

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.

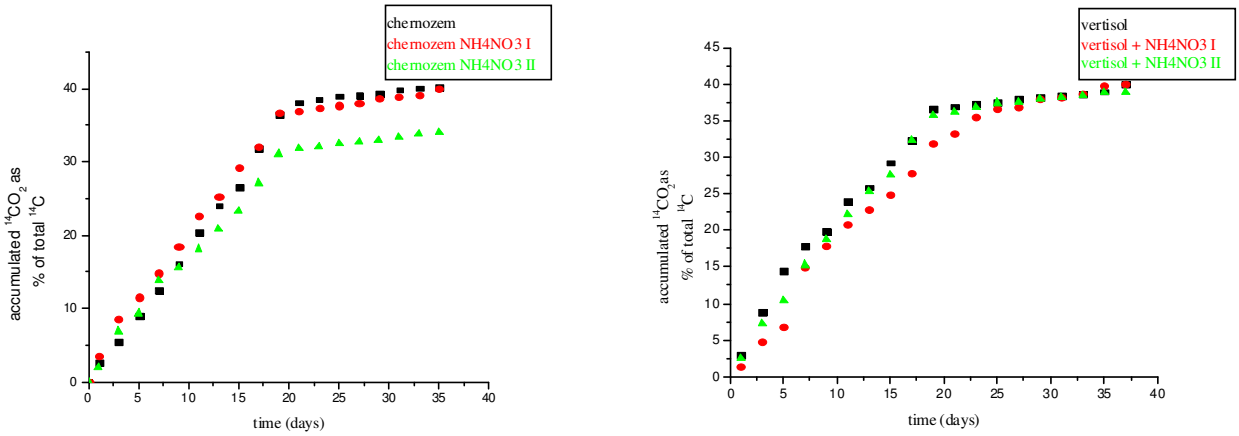

Figure 1. Glyphosate mineralization curves, in Chernozem and Vertisol, in the prezence of inorganic substratum

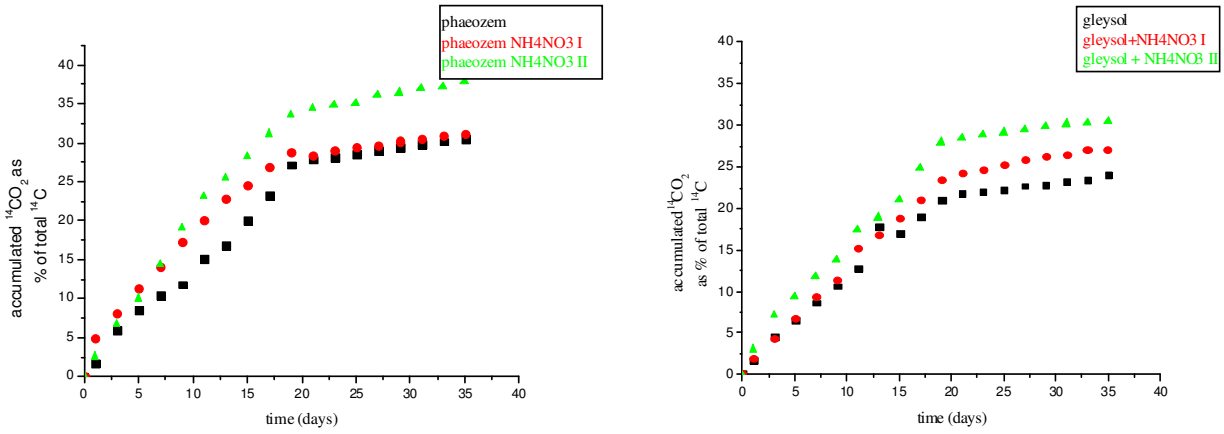

Figure 2. Glyphosate mineralization curves, in Phaeozem and Gleysol in the presence of inorganic substratum

DISCUSSIONS

$^{14}CO_2$ quantity accumulated, express as percents from total radioactivity, during first mineralization phase, between 1-20 days since the inorganic fertiliser administration, does not present significant differences of values in the presence of ammonium nitrogen to different concentration comparative with blank assay, in no one of the analysed type of soil. In Chernozem and Vertisol case, the presence of inorganic substratum lead to a slow decrease in biodegradation capacity of glyphosate. $^{14}CO_2$ quantity accumulated, express as percents from total radioactivity, is after 20 days, in the case of blank Chernozem 36.42%, de 36.0 % in the case of addition of 125 µL NH_4NO_3 0.1 M and decrease to 31.1% in the variant with 250 µL NH_4NO_3 0.1 M. Addition of the nitrogen leads to decrease of $^{14}CO_2$ quantity discharge through glyphosate bio-

degradation, respectively of the carbon source, as a result of micro-organisms attack over the available nitrogen source.

The initial higher content of inorganic substance from the two soils compete the ammonium nitrate addition, so as the bio-degradation curves register a slow increase of $^{14}CO_2$ quantity accumulated in the presence of small concentrations of inorganic compounds comparatively with blind sample. By doubling the ammonium nitrate quantity the carbon molecule bio-degradation capacity decreases.

Gleysol and Phaeozem presents similar profiles of the bio-degradation curves (Fig. 2), but different comparatively with Chernozem and Vertisol. Addition of NH_4NO_3 in sample of soil treated with glyphosate leads to growing of bio-degradation capacity of glyphosate. $^{14}CO_2$ quantity discharge grows once with the increase of ammonium nitrogen addition, both in initial quick bio-degradation phase and in the second slower phase. In the case of Phaeozem the $^{14}CO_2$ quantity discharge in blank sample, after 5 days since the treatment is 11.9% and grows through addition of ammonium nitrogen in concentration of 125 µL NH_4NO_3 0.1 M to 17.28%, respectively to 19.15 % in the case of doubling ammonium nitrogen quantity. Increasing tendency regarding $^{14}CO_2$ quantity discharge through glyphosate bio-degradation it maintain after 9 days since the treatment application when it ascertain an increase of 23.39% in the blank sample variant, to 26.91% in the case of variant with low ammonium nitrogen addition, respectively to 33.67% by doubling addition of ammonium nitrogen.

The same profile of mineralization curve and increase tendency of $^{14}CO_2$ quantity discharge through microbial degradation of glyphosate it ascertain also in the case of Gleysol (Fig. 2). In this case $^{14}CO_2$ quantity discharge through inorganic substrate addition is more accentuated in the second phase of mineralization curve. So, after 20 days since the treatment was discharged 21.03% $^{14}CO_2$ in blank sample, 23.44% $^{14}CO_2$ in sample with addition of 125 µL NH_4NO_3 0.1 M and 27.98% in sample with double addition of ammonium nitrogen. Explication of increase of bio-degradation capacity of glyphosate in the presence of inorganic substratum on the base of nitrogen in the case of Gleysol and Phaeozem came from different physical chemical characteristics of the two soils comparatively with Chernozem and Vertisol. Gleysol is characterized with a high pH (8.05) favouring micro-organisms activity, they have the possibility to access preferential the glyphosate leading to increase of $^{14}CO_2$ quantity in the presence of high concentrations of NH_4NO_3.

The experimental results indicated that the dynamic of glyphosate mineralization until the stage CO_2 is different for each soil.

In Chernozem and Vertisol soils, addition of inorganic substratum (ammonium nitrate in different doses), lead to a slow decrease of bio-degradation capacity of glyphosate as a result of micro-organisms attack over the nitrogen available source.

Physical-chemical characteristics of Gleysol and Phaeozem favour micro-organisms (actinomicets) activity, they have the possibility to access preferential the glyphosate leading to increase of $^{14}CO_2$ quantity in the presence of high concentrations of NH_4NO_3.

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