BEHAVIOR OF THE NON-SELECTIVE HERBICIDE GLYPHOSATE IN AGRICULTURAL SOIL

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ABSTRACT

Glyphosate \( [\text{N-phosphonomethyl}]\text{glycine} \) is a systematic, non-selective, organophosphorous herbicide used worldwide in agriculture and industrial zones. Following its application, residues of glyphosate can threaten soil or aquatic organisms in adjacent water. In this study, we followed the degradation, stabilization, remobilization and leaching of \(^{14}\text{C}-\text{glyphosate} \) in three agricultural soils in laboratory incubations and in lysimeters under field conditions. Glyphosate degradation was relatively rapid with a half-life of 14.5 days in the silt clay loam soil incubated at 20°C. Glyphosate’s degradation product, Aminomethylphosphonic Acid (AMPA), represented more than 85% of residues after 80 days of laboratory incubation. Leaching of glyphosate in lysimeters of three different investigated soils under outdoor conditions was very slow, less than 1% of the initial applied amount has been detected in the leachates after 100 days of experimentation. Glyphosate rapidly formed non-extractable residues after treatment. In summary, glyphosate was removed from soil very rapidly and its leaching seems to be very slow regardless the type of treated soil. On the other hand, the contamination risk of groundwater with its metabolite AMPA at long term is probably due to the release of the non-extractable residues.

Keywords: Glyphosate, AMPA, Soil, Persistence, Leaching

1. INTRODUCTION

Glyphosate \( [\text{N-phosphonomethyl}]\text{glycine} \) is a nonselective organophosphorous herbicide, the most used active ingredient worldwide in agricultural, silvicultural and industrial zones (Kryuchkova et al., 2014; Van Stempvoort et al., 2014; Moreno et al., 2013). Introducing the transgenic crops (maize, cotton, potatoes and soybean) resistant to glyphosate was an additional factor to increase dramatically its use worldwide (Aparicio et al., 2013; Panettieri et al., 2013; Imfeld et al., 2013; Abubakar et al., 2011; Wiatrak and Chen, 2011; Mercurio et al., 2014). Detection of glyphosate and its principal degradation product Aminomethylphosphonic Acid (AMPA) in water resources has been reported in several studies albeit at low concentrations (Coupe et al., 2012; Malaguerra et al., 2013). However, information on the residues dynamics of glyphosate and AMPA in agricultural soil is still scarce. Extraction and determination of glyphosate is an analytical challenge because of its high solubility (about 10.5 g L\(^{-1}\) in water) and its other physico-chemical properties: Log \( K_{oc} \) values (3.4-3.7), half-life varies from 6 to 10 weeks in water and from 1 to 9 weeks in soil (Botero-Coy et al., 2013; Coupe et al., 2012; Struger et al., 2008). After the application of glyphosate for weed control, a part of herbicide reaches the target plants and another part settles on the soil. Therefore, a part of glyphosate will be absorbed by the soil constituent and another part will still available in the soil solution (Guimont et al.,...
2005). The available residues of glyphosate in soil solution will be either mineralized or transferred to groundwater through the soil. The physicochemical properties of the soil, its biological activity and other chemical and biochemical reactions lead to the degradation of the herbicide (Al-Rajab et al., 2008).

Degradation of glyphosate is relatively rapid in the soil, which could be a limiting factor to contaminate the solution of soil and groundwater by glyphosate (Van Stempvoort et al., 2014). On the other hand, this rapid degradation could increase the risk of pollution by its metabolites: AMPA and sarcosine (Al-Rajab et al., 2008; Landry et al., 2005). Only the complete mineralization of a pesticide could eliminate its risk for a potential environmental pollution (Getenga, 2004). Glyphosate is strongly adsorbed to soil with Kd values between 16.6 and 34.5 (Coquet, 2003; Al-Rajab et al., 2008). The strong sorption of glyphosate to soil and the rapid formation of non-extractable residues increase the stabilization of compound in the soil and decrease the short term water pollution (Landry et al., 2005). These residues could be remobilized at long term and could reach the groundwater at low concentrations (Al-Rajab et al., 2010a; Coupe et al., 2012; Candelà et al., 2007).

Detection of glyphosate and its metabolite AMPA in water resources have been reported in France during the years 2003-2004 at concentrations higher than 0.1 µg L−1 which is the EC limit (Landry et al., 2005). The occurrence of glyphosate in the surface water in southern Ontario (Canada) has been reported in 2008 showing that the detected concentrations of glyphosate were <65 µg L−1 in a total of 502 samples collected during 2 years (Struger et al., 2008). Glyphosate and AMPA were detected in Canadian riparian groundwater samples collected in 2009 at maximum concentrations of 0.042 and 2.87 µg L−1 for glyphosate and AMPA respectively (Van Stempvoort et al., 2014). Also, detection of glyphosate has been reported in about 20 streams in midwestern states at concentration above 0.1 µg L−1 and 83% of streams had detectable concentrations of AMPA (Battaglin et al., 2005).

Information on residue dynamics of glyphosate in different types of soil is scarce. Within this context, our objectives in this study were to gather information concerning the persistence, dissipation pathways, leaching, stabilization and remobilization of glyphosate in soil.

2. MATERIALS AND METHODS

2.1. Chemicals

[Phosphonomethyl-14C]-glyphosate diluted, purity 99% was purchased from Cluzeau (CIL, Paris). Aminomethylphosphonic Acid (AMPA), 10 ng µL−1 in water, was purchased from (Dr. Ehrenstorfer GmbH, Germany). Sarcosine [N-methylglycine], purity 99% was purchased from Fluka (Germany). H2PO4, FMOC-chloride, Potassium hydroxyde and Sodium tetraborate decahydrate were purchased from Fluka (Germany). Methanol and acetonitrile (HPLC grade) were purchased from SDS (France).

2.2. Sampling

Soils used in this study were obtained from three different agricultural lands in Lorraine region (France). Therefore, based on information provided by the landowners, these soils were never exposed to direct agricultural application of glyphosate and their properties were as following: Sandy loam soil (sand:Silt:Clay (59:30:11), pH 5.1; % organic matter 0.82); silt clay loam soil (sand:Silt:Clay (16:53:31), pH 6.3; % organic matter 1.45); and clay loam soil (sand:Silt:Clay (35:30:35), pH 7.9; % organic matter 1.91).

In the laboratory studies, soils were air dried then sieved at 2 mm and stored in fridge at 4°C until treatment. Otherwise, in the outdoor leaching study, lysimeters were prepared in site using an undisturbed soil for each type of soil separately, a total of 7 columns of each soil were used in this study. Lysimeters were polyvinyl chloride pipes of 10 cm wide and 35 cm long. Therefore, the 21 lysimeters of the three selected soils were placed in the experimental field of ENSAIA (54500 Vandoeuvre-lès-Nancy, France) for 100 days.

2.3. Extraction of Glyphosate

The efficacy of different solvents for extraction of glyphosate from soil was evaluated as follows. A 5 g portion of each soil (in triplicate) was treated with a 0.5 mL solution of H2O (concentration of 19.4 Bq g−1) of [Phosphonomethyl-14C]-glyphosate and 0.1 µg g−1 of unlabelled glyphosate. Treated soil was placed into a 250 mL PPCO (Nalgene®, VWR, USA) centrifuge bottle and 25 mL of selected solvent were added. Five different solvents were tested separately for the glyphosate extraction efficacy: Ammonium oxalate monohydrate 0.1M; potassium dihydrogen phosphate (KH2PO4) 0.1M; a mixture of (NH4OH 0.5M+ KH2PO4 0.1M+H2PO4 0.5%); CaCl2 0.1M and distilled water. Bottles were rotary shaken for 2 h, then centrifuged at 5000 g for 20 min, the supernatant of each sample was recovered. Extraction of each sample as been repeated twice, the supernatants of the same sample were combined and a portion of 1 mL counted by Liquid Scintillation Counter.
NaOH was placed into each jar for trapping another plastic scintillation vial with 10 mL of 0.5 N NaOH was added to a Mason jars (1.5 L). At the same time, a plastic vial of 10 mL H₂O was added to each jar in order to maintain the humidity of soil (Al-Rajaj et al., 2009). Another plastic scintillation vial with 10 mL of 0.5 N NaOH was placed into each jar for trapping ¹⁴C. Jars were incubated at 20°C in the dark for 80 days. The radioactivity trapped in NaOH was calculated at each sampling time using a Liquid Scintillation Counter LSC Packard Tri-Carb 1900 CA (Packard, USA). 1 mL of NaOH was added to 10 mL of scintillation cocktail in a plastic scintillation vial to measure the radioactivity in the LSC during 10 min. After treatment, each sample was added to a plastic scintillation vial with 10 mL of 0.5 N NaOH was placed into each jar for trapping ¹⁴CO₂. Jars were incubated at 20°C in the dark for 80 days. The radioactivity trapped in NaOH was calculated at each sampling time using a Liquid Scintillation Counter LSC Packard Tri-Carb 1900 CA (Packard, USA). 1 mL of NaOH was added to 10 mL of scintillation cocktail in a plastic scintillation vial to measure the radioactivity in the LSC during 10 min. At each sampling date, the 25-g soil samples were extracted separately using KH₂PO₄ as described previously. Then, after the third and last extraction, soil samples were air-dried at the lab ambient temperature for 3 days. The remaining ¹⁴C-radioactivity in the samples after extraction was referred as (non-extractable residues) which was determined by combustion at 900°C using a 307 Packard Oxidiser (Packard, USA).

2.4. Laboratory Degradation Study

About 25-g soil samples were placed in glass jars (60 mm diameter×40 mm high). Samples of silt clay loam soil were prepared in triplicates for each sampling time. Each sample was amended by 0.51 mg of glyphosate and 45.1 kBq in water. Final soil moisture was 80% of the soil retention capacity. After treatment, each sample was added to a Mason jars (1.5 L). At the same time, a plastic vial of 10 mL H₂O was added to each jar in order to maintain the humidity of soil (Al-Rajaj et al., 2009). Another plastic scintillation vial with 10 mL of 0.5 N NaOH was placed into each jar for trapping ¹⁴CO₂. Jars were incubated at 20°C in the dark for 80 days. The radioactivity trapped in NaOH was calculated at each sampling time using a Liquid Scintillation Counter LSC Packard Tri-Carb 1900 CA (Packard, USA). 1 mL of NaOH was added to 10 mL of scintillation cocktail in a plastic scintillation vial to measure the radioactivity in the LSC during 10 min. At each sampling date, the 25-g soil samples were extracted separately using KH₂PO₄ as described previously. Then, after the third and last extraction, soil samples were air-dried at the lab ambient temperature for 3 days. The remaining ¹⁴C-radioactivity in the samples after extraction was referred as (non-extractable residues) which was determined by combustion at 900°C using a 307 Packard Oxidiser (Packard, USA).

2.5. Leaching Study

Lysimeters were prepared and placed in the experimental field of Lorraine University (France) 3 months before the treatment. During the experiment of 100 days, the average temperature was 10°C; total precipitation was 235 mm; in total 8 leachates samples were collected. Leached radioactivity from each lysimeter was determined directly after collection, Therefore, water samples were stored at -18°C until analysis.

2.6. Analytical Methods

¹⁴C-Radioactivity has been determined using a Liquid Scintillation Counter LSC. Glyphosate residues were determined using a Varian HPLC (USA) equipped with two detectors: A fluorescence detector and a β-radioactivity detector. A Lichrosorb (NH₃) column (4×250 mm, 5 μm) purchased from (CIL-Cluzeau, France) was used and thermostated at 30°C. Fluorescence detector was set at (λ 260 and 310 nm), while the flow rate of 1.2 mL min⁻¹ was adopted in the β-radioactivity detector with a counting cell of 500 μL. The mobile phase was a mixture of (KH₂PO₄ 0.05 mol L⁻¹, pH 5.7)/acetonitrile (70/30: V/V) at flow rate of 0.8 mL min⁻¹. The injected volume was 50 μL. Within these conditions, the retention times were 4.2, 6.6 and 13.3 for sarcosine, AMPA and glyphosate respectively. Determination of the non-extractable residues in soil has been effectuated by combustion of 0.5 g portions at 900°C using an oxidizer (Packard, USA).

Statistical analyses were conducted using Stat Box (Version 6.4, Grimmer Software, France).

3. RESULTS

3.1. Extraction of Glyphosate

Extraction recovery of glyphosate varied from 4 to 74% of the initial applied amount (Table 1). CaCl₂ (0.1 M) and water were the less effective solvents in glyphosate extraction in the three investigated soils. However, ammonium oxalate (0.1 M) was the most effective solvent with a recovery rate range from 60 to 74%. The only issue with the extraction with ammonium oxalate that the extracts were very dark and need an intensive clean up. On the other hand, potassium dihydrogen phosphate (KH₂PO₄ 0.1 M) was adopted as a suitable solvent since the extracts were clear and it showed an acceptable recovery rate varied from 45 to 49% in investigated soils (Table 1). Recovery rate with citric acid (20%) was not high enough (less than 37%) for the three investigated soils.

3.2. Dissipation of Glyphosate

Results showed an immediate and high degradation rate of glyphosate after its application on the soil (Fig. 1). Mineralization of glyphosate after 17 days of incubation reached 39.7% of the initial amount applied. Thereafter, the mineralization of glyphosate declined gradually. The half-life of glyphosate derived from the mineralization rates was 31 days for silt clay loam soil. However, the extraction curves are opposite to those of the mineralization (Fig. 2).

The percentage of extracted residues from the silt clay loam soil at T0 was only 56.9±0.7%. This availability to extraction decreased overtime, it reached 6.9% of the initial amount for silt clay loam soil. HPLC analysis showed the appearance of two degradation products of glyphosate AMPA and sarcosine. However, this analysis of glyphosate residues by HPLC did not allow us to measure the sarcosine because its retention time was too short and equal that of co-eluted and unlabelled organic compounds. The half-life of glyphosate extractable was 14.5.
Table 1. Extraction efficiency of glyphosate from the selected soils using different solvents

| Solvent                | Sandy loam (Mean±standard deviation: n = 3) | Silt clay loam (Mean±standard deviation: n = 3) | Clay loam (Mean±standard deviation: n = 3) |
|------------------------|---------------------------------------------|-----------------------------------------------|------------------------------------------|
| KH₂PO₄ (0.1M)          | 44.9 (±0.3)                                 | 48.8 (±0.7)                                   | 48 (±0.5)                                |
| Ammonium oxalate (0.1 M) | 59.9 (±0.7)                                 | 73.5 (±0.2)                                   | 61.1 (±0.1)                              |
| Citric acid (20%)      | 34.2 (±0.1)                                 | 36.4 (±0.2)                                   | 28.9 (±0.2)                              |
| CaCl₂ (0.1 M)          | 5.7 (±0.5)                                  | 3.6 (±0.9)                                    | 10.3 (±0.6)                              |
| H₂O                    | 14.3 (±0.2)                                 | 23.5 (±0.1)                                   | 31.7 (±0.1)                              |

Fig. 1. Residues evolution of glyphosate and AMPA in the extractable residues in silt clay loam soil during incubation at 20°C

Fig. 2. Evolution of different portions of ¹⁴C-glyphosate residues (extractable, mineralization as ¹⁴CO₂ and Non extractable) in silt clay loam soil during incubation at 20°C
3.3. Leaching of Glyphosate

Our study showed that the residues of glyphosate were detected in the first leachates samples of three soils, the cumulated precipitation was 85 mm. In the case of silt clay loam soil, the maximum residues concentration of 9.5±7 µg L⁻¹ has been reached after 2 months of application. Concentration of leached residues decreased dramatically after 2 months until the end of experiment (Fig. 3).

4. DISCUSSION

4.1. Extraction of Glyphosate

Extraction and determination of glyphosate in agricultural soil is problematic due to its high solubility and its physic-chemical properties (Botero-Coy et al., 2013). In the present study, extraction recovery of glyphosate varied from 4 to 74% of the initial applied amount (Table 1). CaCl₂ (0.1 M) and water were the less effective solvents in glyphosate extraction in the three investigated soils. However, ammonium oxalate (0.1 M) was the most efficient solvent with a recovery rate ranged from 60 to 74%. The only issue with the extraction with ammonium oxalate that the extracts were very dark and need an intensive clean up. On the other hand, potassium dihydrogen phosphate (KH₂PO₄ 0.1 M) was adopted as a suitable solvent since the extracts were clear and it showed an acceptable recovery rate varied from 45 to 49% in investigated soils (Table 1), this rate was similar to that one reported by other studies (Cheah and Lum, 1998; Landry et al., 2005). Recovery rate with citric acid (20%) was not high enough (less than 37%) for the three investigated soils. Non-extractable residues of glyphosate in soil increase with the time; consequently, glyphosate will be less available for extraction or degradation.

4.2. Dissipation of Glyphosate

Monitoring of mineralization of glyphosate labelled on the phosphonomethyl group allows assessing both the loss of glyphosate and AMPA. We observed an immediate and high degradation rate of glyphosate after its application on the soil (Fig. 1). The absence of lag phase indicates that the microflora of soil already had an enzymatic system capable of degrading glyphosate and such did not need an adaptation period. Mineralization of glyphosate after 17 days of incubation reached 39.7% of the initial amount applied. Thereafter, the mineralization of glyphosate declined gradually. The fast mineralization of glyphosate in the soil appears due to its bioavailability. The half-life of glyphosate derived from the mineralization rates was 31 days for silt clay loam soil. On
the other hand, the effect of organic matter content in the soil on mineralization of glyphosate was not clear under the conditions of this study. The extraction rate of glyphosate is an indication of the accessibility of the residues for microbial degradation and/or their transfer to groundwater under natural conditions. The extraction curves are opposite to those of the mineralization (Fig. 2).

The percentage of extracted residues from the silt clay loam soil at T0 was only 56.9±0.7%. We can assume that the treatment in a dry soil may cause an entry of glyphosate into the microporosity of aggregates during the capillary invasion by the aqueous solution of treatment (Guimont et al., 2005; Al-Rajab et al., 2010b). The size of this compartment would be defined at the time of treatment and may depend on the physicochemical and physical properties and the moisture rate of soil at the application moment. This availability to extraction decreased overtime, it reached 6.9% of the initial amount for silt clay loam soil. The evolution of extraction rate with KH$_2$PO$_4$ over time in the soil is related to the mineralization of residues and the availability of non-extractable residues for mineralization or extraction. A similar behaviour of extractable residues of glyphosate over time was reported by (Getenga, 2004; Miles, 1998). HPLC analysis showed the appearance of two degradation products of glyphosate AMPA and sarcosine. However, this analysis of glyphosate residues by HPLC did not allow us to measure the sarcosine because its retention time was too short and equal that of co-eluted and unlabelled organic compounds.

The appearance of AMPA during the first days of incubation is due the fast mineralization of glyphosate in soil, reaching about 85.1% of residues after 80 days of treatment (Fig. 1). Our results are consistent, to some extent, with those obtained by (Cheah and Lum, 1998) who reported the rate of AMPA in the extracts of a sandy loam soil increased gradually over incubation time and reached 50% of residues after 45 days of treatment. The half-life of glyphosate extractable was 14.5, this value is in accord with the half-lives of 6 to 9 days reported in other study for glyphosate in four agricultural soils incubated at 25°C (Eberbach, 1998) as well as the 19.2 days half-life observed in a sandy loam soil by (Cheah and Lum, 1998). However, much longer half-lives have also been reported by (Getenga, 2004) whereby the half-life of glyphosate was 85.6 days in a clay soil.

The fraction of non-extractable residues represent the residues which cannot be extracted from the soil by the series of KH$_2$PO$_4$ extractions (exhaustive extraction) (Fig. 2). The formation of the non-extractable residues NER in the silt clay loam soil reached 43% of the initial applied amount at T0 and 49.4% at T1. The rate stayed stable until T2 after which it decreased to 30.9% by the end of experiment. The rate of non-extractable residues decreased over time unlike other pesticides such as atrazine where the rate of non-extractable residues increases gradually over dozens of days (Winkelman, 1991). The rate of non-extractable residues is probably dependent on the properties and physical aspects of the soils including the size of the microporpal compartment. This rapid formation of non-extractable residues immediately after treatment is very specific for glyphosate. The treatment of herbicide on a dry soil promotes the capillary invasion and the rapid transport of the solution of treatment in the microporosity intra aggregate, subsequently making the herbicide inaccessible for extraction (Guimont et al., 2005). We also reported that the initiation of the degradation of glyphosate did not affect the evolution of extractable residues rate. The very slow decrease of non-extractable residues showed that these residues can return by diffusion and under the effect of a concentration gradient, to areas accessible to microorganisms to subsequently undergo mineralization.

4.3. Leaching of Glyphosate

This study showed that water circulation in the soil might has an important role in contamination of groundwater with glyphosate. The diminution of soil macroporosity on the surface layer (where most residues usually present) with the time slows the water infiltration and might encourage the desorption of glyphosate residues. The circulation of glyphosate residues in soil could be due to a preferential water flow regarding the presence of its residues in the 1st collected leachates (Fig. 3). In disaccord with results reported by (Dousset et al., 2004), our study showed that the residues of glyphosate were detected in the first leachates samples of three soils, the cumulated precipitation was 85 mm. Detection of glyphosate residues in the 1st leachates was due to the preferential flow (Laitinen et al., 2006). In the case of silt clay loam soil, the maximum residues concentration of 9.5±7 µg L$^{-1}$ has been reached after 2 months of application. However, (De Jonge and Jacobsen, 2000) have reported residues concentration of glyphosate much higher than what was obtained from the current study.

Concentration of leached residues decreased dramatically after 2 months until the end of experiment (Fig. 3). Our findings were in accord with results reported by (De Jonge and Jacobsen, 2000; Landry et al., 2005) who detected the glyphosate residues in the soil
leachates after 3 months of application. Overall, the total residues (extractable and non-extractable) of glyphosate in the soil should be considered to evaluate its persistence in the soil, not only the extractable residues.

5. CONCLUSION

The present study monitored the residue dynamics of glyphosate in agricultural soil in controlled and outdoor conditions. Results obtained for the fate study suggest that the water pollution with this herbicide is closely related to the adsorption and the formation of non-extractable residues, which are themselves dependent on soil texture and its moisture condition at the time of treatment. In case of rain following treatment, the risk of groundwater pollution by glyphosate will be low but may continue to be present for a long time since the mineralization is slow. The silt clay loam soil could be less favourable for water pollution since it showed a formation of large amount of non-extractable residues. In the semi-field lysimeters study, leaching of glyphosate was limited, but its metabolite AMPA seems to be the main potential pollutant of the groundwater. The water circulation mode in the soil was preferential flow which facilitate a fast leaching of residues to reach the groundwater.

In summary, these results suggest that the organophosphorus herbicide glyphosate is rapidly degradable in the agricultural soil. Leaching of glyphosate seems to be very slow regardless the type of the soil. Release of the non-extractable residues of glyphosate probably increases the risk of groundwater pollution with its metabolite AMPA at long term. More investigations are requested for a better understanding of the effect of soil content of organic carbon and soil microflora on environmental behavior of glyphosate.

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7. REFERENCES

Abubakar, M.S., D. Ahmad, O. Jamarei, S. Samsuddin and M. Norhisam, 2011. Evaluation of a dual-purpose chemical applicator for paddy fields. Am. J. Applied Sci., 8: 362-367. DOI: 10.3844/ajassp.2011.362.367

AL-Rajab, A.J., L. Sabourin, A. Scott, D.R. Lapen and E. Topp, 2009. Impact of biosolids on the persistence and dissipation pathways of triclosan and triclocarban in an agricultural soil. Sci. Total Environ., 407: 5978-5985. DOI: 10.1016/j.scitotenv.2009.08.003

AL-Rajab, A.J., L. Sabourin, D.R. Lapen and E. Topp, 2010b. The non-steroidal anti-inflammatory drug diclofenac is readily biodegradable in agricultural soils. Sci. Total Environ., 409: 78-82. DOI: 10.1016/j.scitotenv.2010.07.074

AL-Rajab, A.J., S. Amellal and M. Schiavon, 2008. Sorption and leaching of 14C-glyphosate in agricultural soils. Agronomy Sustainable Dev., 28: 419-428. DOI: 10.1051/ago:2008014

Aparicio, V.C., E. De Geronimo, D. Marino, J. Primost and P. Carriquiriborde et al., 2013. Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins. Chemosphere, 93: 1866-73. DOI: 10.1016/j.chemosphere.2013.06.041, PMID: 23849835

Battaglin, W.A., D.W. Kolpin, E.A. Scribner, K.M. Kuvila and M.W. Sandstrom, 2005. Glyphosate, other herbicides and transformation products in midwestern streams. J. Am. Water Resources Assoc., 41: 323-332. DOI: 10.1111/j.1752-1688.2005.tb03738.x

Botero-Coy, A.M., M. IBañEZ, J.V. Sancho and F. Hernández, 2013. Improvements in the analytical methodology for the residue determination of the herbicide glyphosate in soils by liquid chromatography coupled to mass spectrometry. J. Chromatography A, 1292: 132-141. DOI: 10.1016/j.chroma.2012.12.007

Candela, L., J. Álvarez-Benítez, M.T. Conde and P.S.C. Rao, 2007. Laboratory studies on glyphosate transport in soils of the maresme area near barcelona, Spain: Transport model parameter estimation. Geoderma, 140: 8-16. DOI: 10.1016/j.geoderma.2007.02.013

Cheah, U.B.K.R.C. and K.Y. Lum, 1998. Degradation of four commonly used pesticides in malaysian agricultural soils. J. Agric. Food Chem., 46: 1217-1223. DOI: 10.1021/jf970579t

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Coquet, Y., 2003. Variation of pesticide sorption isotherm in soil at the catchment scale. Pest. Manage. Sci., 58: 69-78. PMID: 12558101

Coupe, R.H., S.J. Kalkhoff, P.D. Capel and C. Gregoire, 2012. Fate and transport of glyphosate and aminomethylphosphonic acid in surface waters of agricultural basins. Pest. Manage. Sci., 68: 16-30. DOI: 10.1002/ps.2212

De Jonge, H.D. J. L. W. and O.H. Jacobsen, 2000. [14C] Glyphosate transport in undisturbed topsoil columns. Pest. Manage. Sci., 56: 909-915.

Dousset, S., C.C. Durlet and M. Thevenot, 2004. Transport of hexazinone and glyphosate through undisturbed soil columns in soils under Christmas tree cultivation. Chemosphere, 57: 265-272. DOI: 10.1016/j.chemosphere.2004.06.007

Eberbach, P., 1998. Applying non-steady-state compartmental analysis to investigate the simultaneous degradation of soluble and sorbed glyphosate (N-(phosphonomethyl)glycine) in four soils. Pesticide Sci., 52: 229-240.

Getenga, Z.M.K.F.O., 2004. Mineralization of glyphosate in compost-amended soil under controlled conditions. Bull. Environ. Contaminat. Toxicol., 72: 266-275. DOI: 10.1007/s00128-003-9004-9

Guimont, S., P.G.C. Real and B.M. Schiavon, 2005. Effects of soil moisture and treatment volume on bentazon mobility in soil. Agronomy Sustainable Dev., 25: 323-329. DOI: 10.1051/agro:2005012

Imfeld, G., M. Lefrancq, E. Maillard and S. Payraudeau, 2013. Transport and attenuation of dissolved glyphosate and AMPA in a stormwater wetland. Chemosphere, 90: 1333-1339. DOI: 10.1016/j.chemosphere.2012.04.054

Kryuchkova, Y.V., G.L. Burygin, N.E. Gogoleva, Y.V. Gogolev and M.P. Chernyshova et al., 2014. Isolation and characterization of a glyphosate-degrading rhizosphere strain, Enterobacter cloacae K7. Microbiol. Res., 169: 99-105. DOI: 10.1016/j.micres.2013.03.002

Laitinen, P., S.K. Ernon L. Ramo, S. Welling an d L. Ononen et al., 2006. Fate of the herbicide glyphosate, glufosinate-ammonium, phenmedipham, ethofumesate and metamitron in two Finnish arable soils. Pest. Manage. Sci., 62: 473-491. DOI: 10.1002/ps.1186

Landry, D., S. Dousset, J.C. Fournier and F. Andreux, 2005. Leaching of glyphosate and AMPA under two soil management practices in Burgundy vineyards (Vosne-Romanée, 21-France). Environ. Pollut., 138: 191-200. DOI: 10.1016/j.envpol.2005.04.007

Malaguerra, F., H.J. Albrechtsen and P.J. Binning, 2013. Assessment of the contamination of drinking water supply wells by pesticides from surface water resources using a finite element reactive transport model and global sensitivity analysis techniques. J. Hydrol., 476: 321-331. DOI: 10.1016/j.jhydrol.2012.11.010

Mercurio, P., F. Flores, J.F. Mueller, S. Carter and A.P. Negri, 2014. Glyphosate persistence in seawater. Mar Pollut Bull. DOI: 10.1016/j.marpolbul.2014.01.021

Miles, C.J.M.H.A., 1998. Extraction of glyphosate herbicide from soil and clay minerals and determination of residues in soils. J. Agric. Food Chem., 36: 486-491. DOI: 10.1021/jf00081a020

Moreno, N.C., S.H. Sofia and C.B. Martínez, 2013. Genotoxic effects of the herbicide Roundup Transorb and its active ingredient glyphosate on the fish prochilodorus lineatus. Environ. Toxicol. Pharmacol., 37: 448-454. DOI: 10.1016/j.etap.2013.12.012

Panettieri, M., L. Lazaro, R. López-Garrido, J.M. Murillo and E. Madejón, 2013. Glyphosate effect on soil biochemical properties under conservation tillage. Soil Tillage Res., 133: 16-24. DOI: 10.1016/j.still.2013.05.007

Struger, J., D. Thompson, B. Staznik, P. Martin and T. McDaniel et al., 2008. Occurrence of glyphosate in surface waters of southern ontario. Bull. Environ. Contaminat. Toxicol., 80: 378-84. DOI: 10.1007/s00128-008-9373-1

Van Stempvoort, D.R., J.W. Roy, S.J. Brown and G. Bickerton, 2014. Residues of the herbicide glyphosate in riparian groundwater in urban catchments. Chemosphere, 95: 455-63. DOI: 10.1016/j.chemosphere.2013.09.095

Wiatrak, P. and G. Chen, 2011. Influence of seeding rate on weed density in soybean planting system for southeastern coastal plains. Am. J. Agric. Biol. Sci., 6: 180-184. DOI: 10.3844/ajabssp.2011.180.184

Winkelmann, D.A.K.S.J., 1991. Degradation and bound residues formation of atrazine in a western tennessee soil. Environ. Toxicol. Chem., 10: 335-345. DOI: 10.1002/etc.5620100306