

# Sorption and Decomposition of Glyphosate in Soils Under four Temperature Regimes\*

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## Abstract

Decomposition behaviour of glyphosate in 8 Australian soils was investigated under four temperature regimes using non steady state compartmental analysis (NSSCA). Temperature had a significant influence on partitioning glyphosate into the soluble and sorbed phases as well as half life of this substrate in both phases. At 5 C, only small amount of glyphosate was partitioned into soluble phase, ranged from (1.4-9.1 %) in 8 soil investigated, but as temperature increased the amount of glyphosate partitioned into soluble phase increased substantially such that at 28° C ranged from (1.4-53%). While half life of the soluble phase was in the similar order (1-2 weeks) between 8 soils investigated, half life of the sorbed phase varied widely (73-4950 days). This suggested that different strengths of binding existed within the sorbed phase in 8 soils tested. The rate of glyphosate desorbed from the sorbed phase was dependent on soil type and temperature. Glyphosate was shown to be more strongly held in the acidic soil than in alkaline soil and its sorption was correlated with the soil pH, the amount of exchangeable Fe and Al and incubation temperature. The regression equation was:  $D_{\text{sorp}} = -0.0918 - 0.0001543 \text{ pH} + 0.02772 \text{ pH}^2 + 0.0000713 \text{ Exch (Fe + Al)} - 0.0918 \text{ Temp}$ ,  $R^2 = 0.63$

**Key words :** Soluble and sorbed glyphosate, decomposition and sorption behaviour of glyphosate, non steady state compartmental analysis.

## Introduction

Glyphosate, *N*-(phosphonomethyl) glycine, an active ingredient of herbicide Roundup is extensively used in agriculture to control a wide range of annual and perennial weeds. It is reported to be rapidly inactivated in soil (Sprankle *et al.* 1975a). Rapid inactivation of this compound in soil has been ascribed to rapid binding to soil constituents, and not necessarily due to rapid microbial degradation (Sprankle *et al.* 1975b). However, its inactivation appears not to be permanent, since residual activity of this 3compound has been reported to injure certain plant species (Salazar and Appleby 1982).

Glyphosate and phosphate may be bound by clay particle in a similar manner. Hance (1976) reported that adsorption of glyphosate showed some correlation with un-occupied phosphate adsorption sites. Since adsorption of phosphate has been shown to vary with temperature (Barrow 1979), the adsorption of glyphosate may also be influenced by temperature.

The decomposition rate of glyphosate varies greatly in different soil types and its half life ranges from few weeks to several years (Sprankle *et al.* 1975b; Nomura and Hilton 1977; Tortensson and Stark 1981). As microbial cometabolism is the main pathway of glyphosate disappearance (Torstensson 1985), the variations in decomposition rate of glyphosate may be due to either differences in the strength of ilthe differences in the level of microbial activity among soils (Torstensson 1985).

The objectives of this study reported in this paper were to investigate the influence of temperature on partitioning glyphosate into the soluble and sorbed pools, rate of decomposition and sorption kinetics of glyphosate in eight soils with wide range of physical and chemical properties using non steady-state compartmental analysis (Eberbach 1998).1

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## Materials and methods

Soil samples were collected in the surface layer (0-5 cm) of soil. Eight soil types were selected from South East Australia. These soils were chosen for their wide range of physical and chemical properties and their importance in crop production. After sampling, soils were mixed thoroughly and carefully sieved pass through 2 mm diameter and then stored in a cool room (4 ° C) prior to use. Physical and chemical properties of soils used in this study are presented at Table 1.

Table 1. Physical and chemical properties of soils used in this study

<i>Soil</i>	Water content (75% of -33kPa)	pH H <sub>2</sub> O (1:5)	Clay content (%)	OM (%)	Exh-Fe (ppm)	Ox-Fe (%)	Cit-Dit-Fe (ppm)	Exh-Al (%)	Ox-Al (%)	Cit-Dit-Al (%)
Alluvium	20.70	8.30	27	0.74	4.5	0.08	0.37	nd	0.15	0.10
Renzina	40.08	8.14	21	3.46	3.1	0.17	1.87	nd	0.30	0.18
Black earth	25.97	7.62	28	3.03	6.5	0.26	1.24	nd	0.18	0.11
Terra rossa	25.75	7.60	44	1.67	7.2	0.22	2.48	nd	0.23	0.30
Sandy loam	1.70	6.41	7	0.66	7.7	0.02	0.13	nd	0.0044	0.003
Red podzolic	13.41	5.30	17	1.96	7.0	0.08	1.48	23.9	0.05	0.11
Acid sand	20.56	4.90	12	2.68	41.7	0.13	0.34	62.7	0.03	0.03
Yellow podzolic	18.22	4.60	16	2.56	76	0.23	0.54	114.3	0.04	0.04

Methods used : Clay content (Gee and Bauder 1986) , Organic matter (Heanes 1984), Exchangeable Fe and Al (Gilman *et al.* 1979) , Oxalate extractable Fe and Al (Rayment and Higginson 1991), Citrate-dithionite extractable Fe and Al (Holmgren 1967), nd : not detected.

Decomposition studies was carried out using flow through apparatus similar to that used by Goswami and Koch (1976). The method used in this study was described in Eberbach (1998) with some modifications. In this study, the <sup>14</sup>CO<sub>2</sub> was trapped in 4 ml of ethylene glycol monomethyl ether : ethanolamine (3:1 v/v) solution. The traps were removed and 1 ml of <sup>14</sup>CO<sub>2</sub> trapping solution was transferred into a 6 ml scintillation vial. Four ml of toluence:ethylene glycol monoether (2:1 v/v) scintillation cocktail (Jeffay and Alvarez 1961) was added to the vial and samples were counted in Packard Liquid Scintillation Analyser Model T 1600 for a period of 20 minutes or until the equivalent of 10.000 counts were reached. At the start of the incubation, <sup>14</sup>CO<sub>2</sub> released was determined every 24 hours for 4 days and then at 3-4 days interval for a total of about 60 days. Incubation temperatures used in this study were 5°, 12°, 22° and 28° C ± 1° C.

At the end of the experiment, soil moisture content was determined. Statistical analysis showed that soil moisture content at the beginning and completion of the experiment was not significantly different (P < 0.01). Therefore any differences occurring in the rate of degradation in each soil tested were presumed to be due to incubation temperatures and not due to variability in soil moisture content during the incubation period.

The glyphosate remaining in each soil was calculated by measuring the evolution of <sup>14</sup>CO<sub>2</sub>, subtracting the cumulative <sup>14</sup>CO<sub>2</sub> evolved from the soil over time from the amount of <sup>14</sup>C-glyphosate initially added. Non-steady state compartmental analysis was used to discriminate between soluble and sorbed fraction in each soil and temperature combination using the technique described in Eberbach (1998).

## Statistical Analysis

Homogeneity of variance of the original data set was tested using Bartlett's test (Sokal and Rohlf 1981) and found to be heterogeneous. Data was only transformed logarithmically to the base 2 in an attempt to linearise the data for the function of estimating reaction kinetics. Statistical analysis was done using all transformed data. The data of regression lines were analyzed using analysis of co-variance, and the significant differences among the coefficient of slope were further tested using Gabriel test (GT-2) at  $P < 0.05$  (Sokal and Rohlf 1981). Comparison between degradation of soluble glyphosate and degradation of sorbed glyphosate were regressed against several key soil properties (Table 1) using multiple regression analysis (Genstat Release 5.2 1992).

## Results and discussion

An assumption has been made in this paper, that the measured evolution of  $^{14}\text{CO}_2$  reflects the decomposition rate of  $^{14}\text{C}$ -glyphosate. This assumption is made based on previous work by Eberbach (1989), which showed that the loss of extractable glyphosate (using triethylamine as an extractant) at  $25^\circ\text{C}$  occurred at the same rate as did the evolution of  $^{14}\text{CO}_2$ . In support of this assumption, other work showed that aminomethylphosphonic acid (AMPA) is only a transitory intermediate of glyphosate metabolism (Eberbach and Bownmer 1995). This infers then that once catabolism of glyphosate occurs, it is decomposed rapidly and completely.

Decomposition of  $^{14}\text{C}$ -glyphosate in the 8 soils at each of the four incubation temperatures varied widely as shown in Figure 1. In each soil, regardless of temperature, glyphosate decomposition was more rapid in the first few days, slowing with time to a steady rate of decomposition. This pattern of decay has been commonly reported in the literature for numerous herbicides ((Nomura and Hilton 1977; Moshier and Penner 1978 ; Torstensson and Stark 1982; Thirunarayanan *et al* 1985; Zimdahl and Gwynn 1977). Nomura and Hilton (1977) speculated that the initial steep part of the curve represents the degradation of soluble glyphosate, while the final steady state section of the curve reflects decomposition of bound herbicide. Eberbach (1998) using non steady state compartmental analysis (NSSCA), resolved this curve into its two compartments, and showed that the initial rapid decomposition was due to decomposition of weakly held glyphosate while the slower steady state section of the curve was due to decomposition of bounded glyphosate. Further this technique allowed for the kinetics of each phase, to be resolved, and hence this technique was adopted for use in the present study to determine how temperature influences kinetic of sorption and decomposition of glyphosate.

Using the technique of NSSCA, temperature was shown to have a strong influence on the partitioning of glyphosate into the soluble and sorbed phases as well as on the half life of this substrate in both phases (Table 1 and 2). For most soil and temperature combinations, regression analysis of the curve products were highly significant ( $P < 0.001$ ). Incubation temperature significantly affected the partitioning of glyphosate into the soluble and sorbed phases. At  $5^\circ\text{C}$ , generally, only small amount of glyphosate

partitioned into the soluble phase in 8 soils investigated, ranging from (1.4-9.1%). As the incubation temperature increased, the amount of glyphosate partitioned into the soluble phase increased substantially such that at 28 °C ranged from (1.4 - 53 %) (Table 1 and 2).

The residence time of glyphosate in each of phase varied also between soils; While the half life of the soluble phase was relatively similar between 8 soils and ranged from 1-2 weeks, the half life of glyphosate in the sorbed phase was estimated to vary widely (73-4950 days). This suggests the soluble glyphosate decomposed readily but differences in the strength of binding existed within the sorbed phase the 8 soils investigated, which affected the availability of glyphosate to be decomposed. Assuming estimates of half life reflect binding strength, the strength of binding of sorbed glyphosate in 8 soils investigated decreased in the following order : yellow podzolic > acid sand > sandy soil > terra rosa > alluvium > black earth > red podzolic.

The rate of glyphosate desorbed from the sorbed was dependent on soil type and temperature. Glyphosate appeared to be more strongly bound in acid soil than in alkaline soil. Multiple regression analysis showed that sorption of glyphosate was correlated with the soil pH, the amount of exchangeable Fe and Al, and incubation temperature. The regression describing desorption was :

$$D_{\text{sorp}} = -0.0918 - 0.0001543 \text{ pH} + 0.02772 \text{ pH}^2 + 0.0000713 \text{ Ex (Fe+Al)} - 0.0918 \text{ temp}, R^2 = 0.93$$

Previous studies have reported that sorption of glyphosate is influenced by soil pH and the amount of exchangeable Fe in soil (McConnell and Hossner, 1985; Glass, 1987) as well as the amount of clay and monmorillonite (McConnell and Hossner, 1985; Shoval and Yariv (1978). Our results support these findings. As glyphosate is a zwitterion, the sorption of this compound may be dependent on soil pH. Sprankle (1975b) showed that as the soil pH decreased, glyphosate becomes progressively less negatively charged. In acid soils below the dissociation constant of glyphosate (pKa 5.6), a substantial proportion of glyphosate is in the monovalent anionic form compared with in the divalent anionic form as in alkaline soils. We postulate that the differences in the charge of molecule as a result of soil pH may influence the strength of adsorption in acid soil relative to neutral-alkaline soils. Recent work with glyphosate and other herbicides agree with this assertion (Eberbach 1998; Stougaard *et al.* 1990). However, an exception may apply in the case of red podzolic soil as used here. Eventhough this soil had a pH beneath the dissociation constant of glyphosate, glyphosate dissolved rapidly from this soil. The reason for this is not fully understood. The lowest strength of adsorption in this soil may be due to the low amounts of exchangeable Fe and Al as well as a low amount of monmorillonite, both which are recognized as having important in the sorption of glyphosate in soil. Further investigation is required to confirm this assertion.

In the present study, for each soil desorption was slow at 5 °C and as the temperature increased the rate of desorption increased and achieving a maximal rate at 28 °C. This suggests that sorption of glyphosate is an exothermic reaction. The result reported here is thermodynamically consistent with sorption behaviour of many herbicides, i.e. for picloram (Farmer and Aochi 1974), various dinitroanilines (Harvey

1974) and chlorsulfuron (Thirunarayanan *et al.* 1985). Thirunarayanan *et al.* (1985) suggested that this phenomenon may be explained on the basis of free energy of the solute and adsorbed molecule. They hypothesized that an increase in temperature may increase the internal energy of the molecule which resulted in less electrostatic attraction between the herbicide and the soil sorbent, hence decreasing the adsorption of the compound in soil. While this explanation was appropriate for seven soils used in the present study ( 5 alkaline soils and 2 acid soils) this explanation is not appropriate for the acid yellow podzolic soil. Desorption in this soil remained relatively constant as temperature increase. In very acid soils with a pH below the dissociation constant for glyphosate (pKa 5.6), the charge of glyphosate is predominantly -1 relative to -2 as in alkaline conditions. Differences in the charge on the molecule as a result of soil pH may influence the manner in which the compound is adsorbed or the strength of adsorption in acid relative to neutral-alkaline soils. Further work needs to be directed to study sorption dynamics of glyphosate in acid soil.

The results in the present study showed that glyphosate to be more strongly bound in alkaline soils at low temperature was in contrast with the finding of Eberbach (1998). He reported that at low temperature glyphosate is weakly bound in alkaline soil. In the present study, we used a more extensive soils and more of incubation temperatures. Since Eberbach (1998) used only two alkaline soils and two temperature incubation, we believe that his results may reflect an artefact peculiar to those soil used.

## **Conclusion**

This study showed that sorption of glyphosate is exothermic reaction and kinetic decomposition of this compound is dependent on the sorption characteristic of this compound in soil. The extent of sorption of this compound has some correlation with soil pH, the amount of exchangeable (Fe and Al) and temperature.

## **References**

- Barrow, N.J. (1979). Three effects of temperature on the reactions between inorganic phosphate and soils. *Journal of Soil Science* **30**, 271-279.
- Eberbach, P (1989). The activity of glyphosate and other herbicides in soil. Ph.D. Thesis, University of Melbourne.
- 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 Science*.(in press).
- Eberbach, P and Bowmer, K.H. (1995). Loss of <sup>14</sup>C-glyphosate from Alligatorweed by conversion to carbon dioxide. *Journal of Aquatic Plant Management* **33**, 27-29.
- Farmer, W.J, and Aochi, Y. (1974). Picloram sorption by soils. *Soil Science Society of America Proceeding* **38**, 418-423.

- Glass, R.L. (1987). Adsorption of glyphosate by soils and clay minerals. *Journal of Agriculture and Food Chemistry* **35**, 497-500.
- Goswami, K.P. and Koch, B.L. (1976). A simple apparatus for measuring degradation of  $^{14}\text{C}$  labelled pesticides in soil. *Soil Biology and Biochemistry* **8**, 527-528.
- Hance, R.J. (1976). Adsorption of glyphosate by soils. *Pesticide Science* **7**, 363-366.
- Harvey, R.G. (1974). Adsorption and volatility of dinitroaniline herbicides. *Weed Science* **22**, 120-124.
- Jeffay, H. and Alvarez, J. (1961). Liquid scintillation counting of carbon-14. Use of ethanalamine-ethylene glycol monomethyl ether-toluene. *Analytical Chemistry* **33**, 612-615.
- McConnell, J.S. and Hossner, R.L. (1985). pH dependent adsorption isotherm of glyphosate. *Journal of Agriculture and Food Chemistry* **33**, 1075-1078.
- Moshier, L.J. and Penner, D. (1978b). Factors influencing microbial degradation of  $^{14}\text{C}$  glyphosate to  $^{14}\text{CO}_2$  in soil. *Weed Science* **26**, 686-691.
- Nomura, N.S. and Hilton, H.W. (1977). The adsorption and degradation of glyphosate in five Hawaiian sugarcane soils. *Weed Research* **17**, 113-121.
- Salazar, L.C. and Appleby, A.P. (1982). Herbicidal activity of glyphosate in soil. *Weed Science* **30**, 463-466.
- Scheunert, I (1992). Physical and physico-chemical processes governing the residue behaviour of pesticide in terrestrial ecosystems. In 'Terrestrial Behaviour of Pesticide'. (Eds. Scheunert, I. and Parlar, H.). *Chemistry of Plant Protection Science* **8**, Springer-Verlag, New York.
- Sokal, R.R. and Rohlf, F.J. (1981). Biometry. Freeman and Co. San Francisco. 589p.
- Sprankle, P. Meggitt, W.F. and Penner, D. (1975a). Rapid inactivation of glyphosate in the soil. *Weed Science* **23**, 224-228.
- Sprankle, P. Meggitt, W.F. and Penner, D. (1975b). Adsorption, mobility and microbial degradation of glyphosate in the soil. *Weed Science* **23**, 229-234.
- Statistics Department, Rothamsted Experimental Station (1992). Genstat release 5.2. Reference Manual. Oxford Science Publication, London.
- Stougaard, R.N., Shea, P.J. and Martin, A.R. (1990). Effect of soil type and pH on adsorption, mobility and efficacy of imazaquin and imazethapyr. *Weed Science* **38**, 67-73.
- Torstensson, N.T. L.(1985). Behaviour of glyphosate in soils and its degradation. In 'The Herbicide Glyphosate'. (Eds. Grossbard and Atkinson ) pp. 137-150. Butterworths, London.
- Torstensson, N.T.L. and Stark, J. (1981). Decomposition of  $^{14}\text{C}$  labelled glyphosate in Swedish forest soils. Proceedings of the EWRS Symposium on Theory and Practice of the Use of Soil applied Herbicide. pp 72-79. EWRS Publication.
- Thirudarayanan, K, Zimdahl, L and Smika, D. (1985). Chlorsulfuron adsorption and degradation in soil. *Weed Science* **33**, 558-563.
- Zimdahl, R.L. and Gwynn, S.M. (1977). Soil degradation of three dinitroanilines. *Weed Science* **25**, 247-251.