Interactive Relationships Between Sorption and Decomposition of ^{14}C-Methyl Labeled Glyphosate [N-Phosphono Methyl) Glycine] in Soil : The Use of Non-Steady State Compartment Analysis(NSSCA) to Model the Behaviour of ^{14}C-Methyl Labeled Glyphosate in Soils*

Suwardji dan P.Eberbach

Department of Soil Science, Faculty of Agriculture, University of Mataram; Jalan Pendidikan 37, Mataram,NTB, Indonesia 83125;School of Agriculture, Charlest Sturt University NSW Australia
Contact person Phone/Fax. 0370-628143; Email :suwardji@unram.ac.id

ABSTRACT

Simple model of Non Steady State Compartment Analysis (NSSCA) is used to evaluate non-linear degradation curve characteristic of glyphosate in soil. The use of this technique is able to separate the non-linear curve degradation of glyphosate into two phases mainly soluble and sorbed phases. This model can also be used to numerically estimate the amount of glyphosate distributed into the soluble and sorbed phases.This result suggested that this technique can be used to study the influence of sorption on decomposition of glyphosate. Further, this finding showed that sorption of glyphosate is function of soil pH, clay content and exchangeable-Fe.

Key words: Compartment analysis, soluble and sorbed glyphosate, and sorption and decomposition of glyphosate.

1. INTRODUCTION

Degradation of pesticides in soil has been thought to follow first-order reaction kinetics. However, some efforts to linearize the apparent first order kinetic function using a logarithmic transformation of the decomposition product have frequently failed, suggesting for these cases the decomposition function is not first ordered. Several hypotheses to explain these phenomena have been offered and include; reaction kinetics of an order higher than one (Hamaker and Goring, 1976), processes of decomposition affecting the catabolism of the pesticide (Zimdahl and Gwynn, 1977), sorption processes influencing availability of the substrate for decomposition (Nomura and Hilton, 1977) and the heterogeneity or spatial variability of soils (Gustafson and Holden, 1990). Degradation of the herbicide glyphosate in soil frequently conforms to an apparent non first-order decay paradigm (Moshier and Penner, 1978; Nomura and Hilton, 1977; Torstensson and Stark, 1979, 1981; Torstensson, 1982). Nomura and Hilton (1977) suggested that the shape of the decomposition curve related to sorptive properties of the soil for glyphosate.

A new approach using non-steady state compartment analysis to explain the apparent non first-order catabolism of glyphosate and to quantify the processes affecting decomposition of glyphosate in soil. The objective of using this technique is to provide further information to assist in explaining the influence of sorptive processes on glyphosate decomposition.

2. THEORITICAL BACKGROUND

An appreciation of the dynamics of pesticides in the environment is not only useful for the purpose of predicting their fate in the environment, but also it is becoming a necessity for registration of chemicals in many countries. In order to understand the environmental dynamics

***Makalah Sebagai Key Note Speaker pada Seminar Nasional ASPIORA BATAN Jakarta 9/8/2018**

of a pesticide, it is prerequisite to understand the kinetics of degradation, which allow predictions to be made of disappearance times (i.e. Half-life). Additionally, using computer models to predict pesticide environmental fate estimation to increase precision of this estimation and enhances precision of the model. Villeneuve *et al* (1988) showed that a variation between 15-22% in the degradation parameter of PRZM led to a 100% uncertainty of the

simulation. Hence a greater appreciation of degradative behaviour increases simulation precision. Several theorems have been proposed to facilitate the understanding of the important processes involved.

2.1. First Order Decomposition Kinetics

The first order kinetic model is the most fundamental and the most commonly used model to quantify substrate degradation. This model considers chemical in soil in dimutative quantities relative to bulk soil. Therefore the rate of degradation would be affected only by quantify of the chemical. First order kinetics is frequently used to generate decomposition rate constants and decomposition parameters; particularly half-lives of herbicides in soil. These constants are frequently incorporated as degradation rate estimators in pesticide movement models, for example PRZM (Pesticide Root Zone Model).

The first order kinetic model is most commonly described as:

$$dC/dt = kC0 \qquad 1$$

The equation 1 exists is a time derivative model of concentration as function of *k,* the first order rate constant and the initial concentration (C0). By integrating (1) and transforming both sides logarithmically, the equation adopts its linear form

$$\ln C = \ln C0 + \ln kt \qquad 2$$

The equation 2 is a simple linear regression format where the ln C0 is intercept equates to the $\ln C0$ and *k* is the slope of the linear relationship between the natural log of the amount of chemical remaining and time. While many derivations of the first order decomposition theorem exist, such as orders greater or less than one, or square root function, these are empirically derived and have no conceptual foundation and only improve the fit of the data to the linear model (Gustafson and Holden, 1990).

2.2. Compartmentation

Compartmentation is the theorem based on the partitioning of a chemical into various compartments or states in soil. Each compartment may reflect an index of chemical availability or physical location. Decomposition of the chemical in soil is still likely to follow first order reaction kinetics. But availability of the chemical for degradation could be anticipated to be an intrinsic rate of limiting factor. Hence, the slow down in rate of decomposition may reflect diminishing of the chemical availability.

The concept of compartmentation was first proposed by Hamaker and Goring (1976) who suggested that a chemical substance when it is introduced into soil is partitioned into two compartments or phases (Figure 1). Each compartment reflects a certain availability, or reactivity of the substrate. The labile phase contains the soluble and exchangeable fraction of pesticide, while the non-labile phase contains only materials, which are physically bound to soil

constituents. The model assumes that chemical in the labile phase is mobile and exchangeable with the soil solution. Chemically this transformable substrate and potentially phytotoxic; but material in the second compartment is only slowly exchangeable with the labile phase and it is bound as such that it is resistant to microbial and chemical decomposition and not phytotoxic. Prior to the chemical being introduced into the system, both compartments are empty, but following application, all of the chemical substances in soil are in the labile phase which then equilibrates readily with the non-labile phase. At the equilibrium condition, the partitioning between the two phases is presumed to be governed by particular soil properties, which reflect the strength of binding of a pesticide within a particular compartment. The two compartments and their interrelationship are defined in two sequential equations:

$$dC1/dt = -(k + k1)C1 + k\text{-}1C2 \quad 3$$

$$dC2/dt = k1C1 - k\text{-}1C2 \quad 4$$

where k is a first order reaction constant describing substrate decomposition rate and, $k1$ and $k\text{-}1$ are first-order rate constants describing movement between the labile and non-labile phases as a function of their respective phase concentrations, $C1$ and $C2$. Values for each of the rate constants can be derived through curve fitting procedures or by estimating values directly from using three measurements; the initial slope, steady-state slope and steady state intercept.

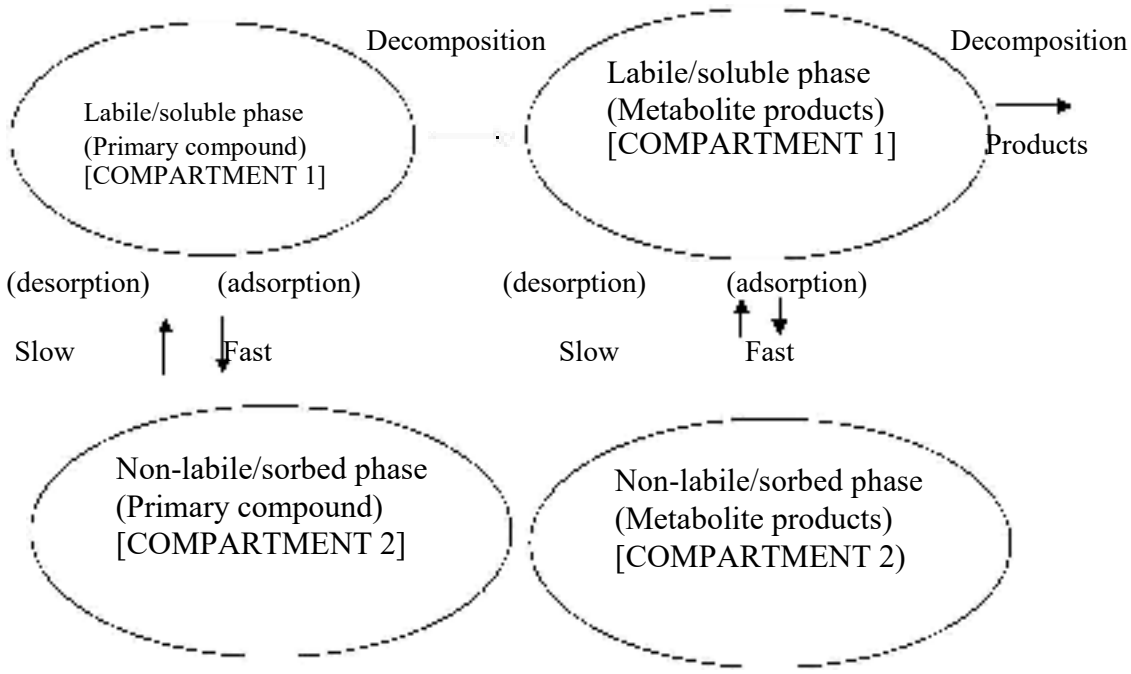

Figure 1. Two compartment model of Hamaker and Goring (1976)

2.3. Quantification of Herbicide Decomposition in Soil Using Indirect Compartment Analysis

Non-steady state compartment analysis is a model frequently used by cell physiologists to explain apparent non-linear substrate disappearance curves (Atkins, 1969). This technique is used to split or fractionate, substrate decomposition or the elution curve into the fundamental constituents or compartments from which it is comprised. In doing so, rate-limiting factors that influence the observation are quantified. For example, the rate of diffusion of a substrate across a semi-permeable membrane may be established and quantified relative to the rate of metabolism of the substrate once inside the cell. The technique is commonly used to measure the kinetics of substrate dynamics in cell biology studies in animal and plant physiology and is useful for estimating the flux of ions across membranes and can take into account the non-steady state of the system in question. Due to its ability to quantitatively split linear portions of apparent non-linear first order equations into their individual compartments, this technique shows particular suitability in explaining the of observed non-linear first order decay curve of a pesticide undergoing degradation in soil.

The technique ascribes the linear or steady state portion of a logarithmic herbicide decomposition curve as being attributed to the slowest exchanging compartment; in this instance the decomposition of desorbed material. After removing or 'stripping' the influence of material derived from this compartment from the raw data, the kinetics of the remaining material can be determined, and where necessary, further stripped (Figure 2).

3. MATERIALS AND METHODS

3.1 Soils

Four soils from different regions of southeast Australia were selected for use in this study.These soils were chosen because of their wide range of physical and chemical properties and their importance in crop production. Only surface soils (0-5 cm) were used in this study. After collection, soils were mixed thoroughly, placed in plastic bags and stored in a cool room (4°C). When required, soils were spread out in thin layer on a plastic sheet and dried at room temperature overnight. After drying soils were carefully sieved to pass through 2 mm in diameter. Sub-samples of soil were taken to determine the air-dry soil moisture content. Soil samples to be used for physical and chemical analysis were then ground and sieved to pass through a 0.15 mm in diameter.

Some physico-chemical properties of soils used in this study are presented in Table 1. Water content at -33 k Pa was determined using the pressure plate apparatus. Particle size distribution was determined using the hydrometer method (Gee and Bouder 1986). Soil pH in water was determined using a glass electrode. Organic carbon was determined by spectrometric method (Haines 1984) after chromic digestion. Sesquioxides of Fe and Al was estimated using two extractants mainly acid oxalate extractant (Rayment and Higginson 1991) and citrate-dithionite extractant (Homgren 1967). The amount of Fe and Al was quantified using atomic absorption spectrophotometer (Rayment and Hingginson 1992).

3.2. Glyphosate

Labeled ^{14}C-methyl glyphosate (specific activity 37 kBq with radiochemical purity of 95.6%: Amersham) was diluted with unlabelled analytical grade glyphosate in deionized water to give a concentration of specific activity of 7.348µCi µmol^{-1}

3.3. Degradation of ^{14}C-glyphosate in soil.

A decomposition study was carried out using a flow through apparatus similar to Goswami and Koch (1976) with modifications which was previously described by Eberbach (1998). Air dried soil samples (10 g) were placed in a 125mL side inlet incubation vessel and replicated four times. Soil moisture was raised by adding deionised water. When 1 mL of ^{14}C-glyphosate solution was added to the soil, soil moisture content should be 75% of field capacity (-33 k Pa). The incubation vessels were then sealed with aluminum foil. To allow moisture to evenly distribute throughout the soil, these incubation vessels were incubated at 22°C ±1°C for 24 hours. Then 1mL solution of glyphosate containing (^{14}C-glyphosate with specific activity 37 kBq and non-labeled glyphosate, 99.5% purity) in deionised water was added into the soil and the final concentration of glyphosate was 2800 ng g^{-1} air dry soil. The incubation vessels were then immediately connected to the flow through system and placed in the prescribed incubation temperature in the incubator.

The $^{14}CO2$ evolved from the decomposed ^{14}C-glyphosate was flushed with a moist carbon dioxide-free air (100 mL $vessel^{-1}$ min^{-1}) for 15 minutes every 3 hours. $^{14-}$C-carbon dioxide was trapped in a 4-mL of trapping solution [(ethylene glycol monomethyl ether: ethanolamine (3:1 v/v)].

The traps were removed and 1 mL of $^{14}CO2$ containing trapping solution was transferred into a 6 mL scintillation vial. Four mL of scintillation cocktail (toluene :ethylene glycol monoether, 2:1 v/v) (Jeffay and Alvarez 1961) were added to the vials and samples were counted in Packard Liquid Scintillation Analyser Model T 1600 for 20 minutes or until the equivalent of 10,000 counts were reached. During the initial stage of the incubation period, the trapping solution was removed every 24 hours for 4 days and after which the traps were removed at 3 days intervals for a total of about 60 days.

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

Soil	Water Content (75% of -33kPa)	pH H_2O (1:5)	Clay content (%)	Organic Carbon (%)	Exchange-able Fe (mg/kg)	Oxalate-Fe (%)	Citrate-Dithionite - Fe (%)	Exchange - Able Al (%)	Oxalate-Al (%)	Citrate-dithionite Al (%)
Alfisol	40.08	8.14	31	3.46	3.1	0.17	1.87	Nd	0.30	0.18
Vertisol	25.97	7.62	28	3.03	4.5	0.26	1.24	Nd	0.18	0.11
Oxisol	25.75	5.30	44	1.67	7.2	0.22	2.48	Nd	0.23	0.30
Inceptisol	13.41	7.30	17	1.96	5.0	0.08	1.48	23.9	0.05	0.11

The incubation vessels were flushed with moist, of $CO2$-free air flowing at 100 ml $vessel^{-1}$ min^{-1} for 15 minutes automatically every 3 hours. The $^{14}CO2$ evolved from the decomposing glyphosate was trapped in 4 ml of ethylene glycol monomethyl ether:ethanolamine (3:1 v/v) in scintillation vials covered with laboratory film. The traps were removed and 1 ml of $^{14}CO2$ containing trapping solution was transferred into a 6 ml scintillation vial. Four ml of scintillation cocktail (toluene :ethylene glycol monoether, 2:1 v/v) (Jeffay and Alvarez 1961) were added to the vials and samples were counted in Packard Liquid Scintillation Analyser Model T 1600 for 20 minutes or until the equivalent of 10,000 counts were reached. In this experiment, traps were removed from the apparatus and counts were made every 24 hours for 4 days, and then at 2 to 3 day intervals for a total of 60 days

3.4. Data handling

Cumulative decomposition of ^{14}C-glyphosate was calculated for each soil by measuring the $^{14}CO_2$ evolved from the soil over a particular time interval and adding this value to the amounts of glyphosate previously evolved. Subtracting the cumulative value from the amount of glyphosate initially added allows for a relationship between the amount of glyphosate remaining in soil and time to be established.

At the completion of the experimental period, the amount of glyphosate remaining for each time interval were transformed logarithmically to determine if decomposition were first ordered (Figure 2b). For most soils this transformation did not linearize the entire decomposition curve, hence data analysis using non steady state compartment analysis (Atkin, 1969) was attempted. This involves dividing of the transformed curve into its two components; the initial curvi-linear phase and the final linear (steady state) phase. The final linear phase represents elution of glyphosate derived from the most slowly available source or compartment (Figure 2b). The regression of this relationship (equation 2c) yields *k*, which describes the rate of release of glyphosate derived from this source while the y-intercept ($C0$) estimates the amount of glyphosate initially partitioned into this compartment. Assuming the sorption of glyphosate, when applied to soil occurs rapidly, and that the desorption of glyphosate from this phase commences immediately following adsorption (see Figure 1), then the influence of glyphosate derived from the adsorbed (non-labile) phase can be separated numerically from the glyphosate partitioned in the labile phase. This involves using the regression describing glyphosate desorption from the non-labile phase (Figure 2c), to predict the amount of glyphosate desorbed for each time interval during the curvi-linear phase. This value is converted from the logarithmic form, and subtracted from the original curve (stripping). The resultant values represents the concentration of glyphosate eluted from all other compartments which exchange glyphosate at a rate faster than the rate of desorption from that non-labile compartment for that given moment in time . These values are then transformed logarithmically and if the plot of the transformed data over time is linear(Figure 2d), no further stripping is required, however, if the plot is curvi-linear, the stripping process is repeated. In this study, only one strip of the data set was required.

3.5. Statistical Analysis

All data were tested for homogeneity of variance using Bartlett test (Sokal and Rohlf, 1969) and were found to be homogeneous. Logarithmic transformation was used to linearize the shape of the decomposition curves so that the kinetics of the decomposition could be determined. The slopes of the regression lines were compared following the procedure for two independent slopes as described in Howell (1982).

4. RESULTS AND DISCUSSION

Decomposition of ^{14}C-glyphosate in the four soils tested varied as shown in Figure 3a. For each soil, rapid decomposition of the herbicide occurred during the first day. This was followed by a gradual reduction in the rate of decomposition occurring over the next twenty to thirty days until an apparent steady rate of decomposition was achieved, which continued until the termination of the experiment on day 60. The pattern of decomposition reported here is similar to patterns observed in other reports (Moshier and Penner, 1978; Nomura and Hilton,1977;Torstensson and Stark, 1979, 1981; Torstensson, 1982). However, the establishment of a steady state took considerably longer in this study than has been observed by

others (Lönsjö *et al.*, 1980; Moshier and Penner, 1978; Nomura and Hilton,1977; Torstensson and Stark, 1981).

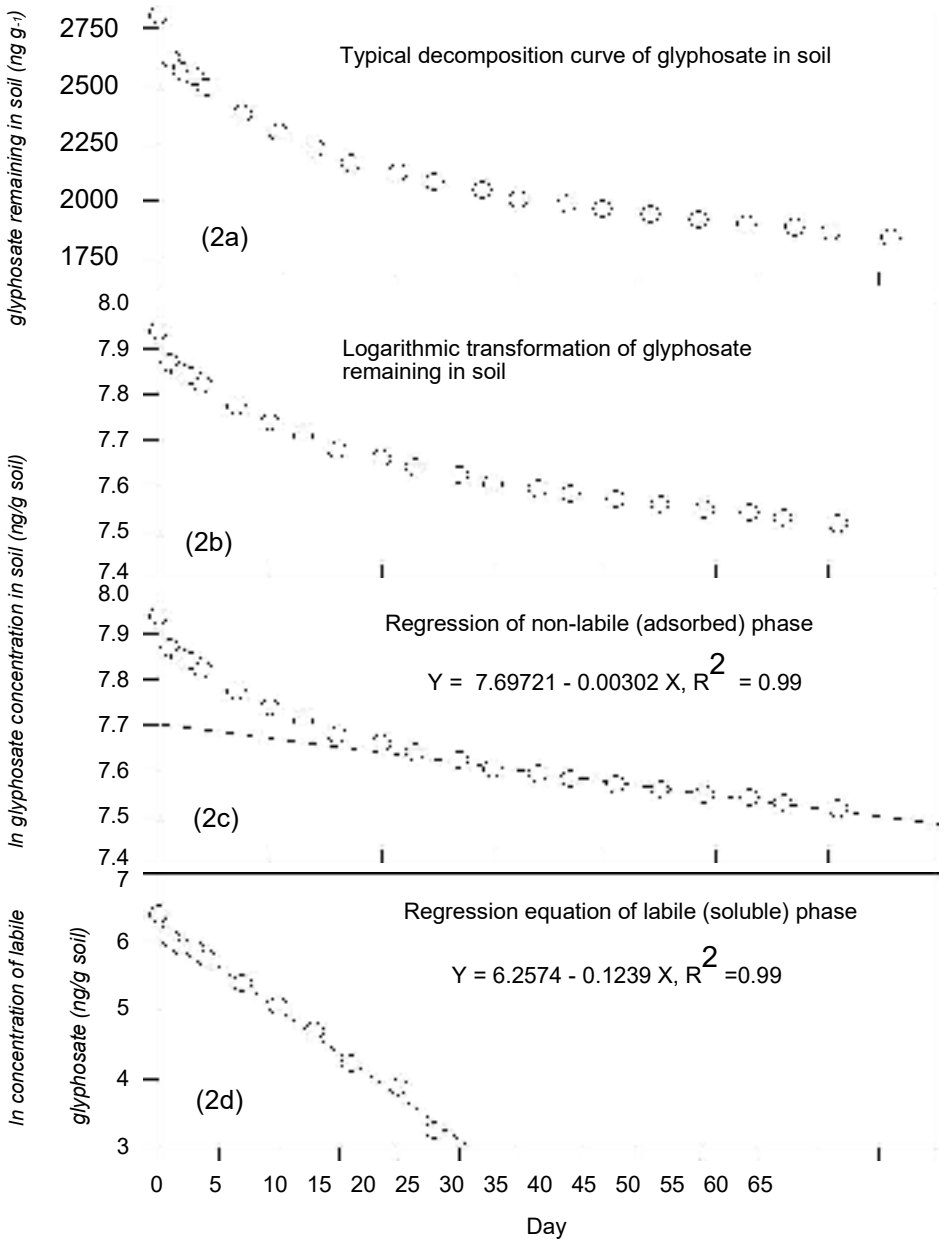

Figure 2. Partitioning glyphosate into labile and non-labile form using Non Steady State Compartmental Analysis (Atkins, 1969)

Various authors have ascribed this gradual reduction in the rate of glyphosate decomposition to be due in the early stages to decomposition of relatively soluble glyphosate while in the latter stages, due to decomposition of strongly bound (adsorbed) glyphosate (Nomura and Hilton, 1977). This apparent two-stage pattern of decomposition has under particular conditions been reported for some other herbicides in soil including trifluralin (Zimdahl and Gwynn, 1977), and for sulphonylureas (Thirunarayanan *et al*., 1985).

Transforming logarithmically the cumulative amount of glyphosate decomposed as a function of time did not linearize the decomposition curve (Figure 3b), indicating that decomposition of glyphosate at 22°C did not follow simple first order reaction kinetics. However, this transformation did improve the linearity of the steady state portion of the curve. The improved linearity of the steady state portion of the curve suggested that glyphosate was being released for decomposition from the non-labile compartment according to first order kinetics. Assuming this to be true, then this observation suggests that the glyphosate decomposing prior to the onset of steady state is derived simultaneously from more than one source; from the source of maximum adsorption strength (non-labile phase) as well as from another source where the glyphosate is less strongly held (labile phase). This concept agrees in principle with the two compartment model as proposed by Hamaker and Goring (1976)(Figure 1); where for this herbicide the model suggests that prior to the onset of steady state the glyphosate available for decomposition was derived simultaneously from two different sources; soluble or exchangeable glyphosate (Compartment 1) and adsorbed glyphosate (Compartment 2). Using non-steady state compartment analysis (Atkins, 1969) the influence of decomposition of glyphosate derived from the non-labile phase was removed from the pre-steady state portion of the curve; revealing characteristics of glyphosate derived from a less strongly held source (labile phase). Logarithmic transformations of this data when plotted against time were linear which suggested that decomposition of glyphosate released from the labile phase, like that from non-labile phase (compartment 2) followed first order reaction kinetics. Hence for all soils, the curvi-linear nature of the logarithmic transformed glyphosate decomposition curve were in fact the superimposing of two glyphosate desorption-decomposition curves: one over the top of the other. One curve illustrated the decomposition of weakly held glyphosate while the other represented decomposition of strongly adsorbed glyphosate, with the latter only becoming apparent once all of the weakly held glyphosate had been decomposed (Figure 2c and 2d).

The logarithmic transformed data for each soil representing glyphosate obtained from the labile phase and the non-labile phase were regressed over time using simple linear regression analysis. In each case the regressions were highly significant ($P<0.001$) and the regression equations and relevant statistics are presented in Table 2. From the regression equations for the labile and non-labile phases for each soil, the half-life of glyphosate in each phase and the amount of glyphosate in each phase ($C0$) were calculated and are presented in Table 2.

The partitioning of glyphosate between the soluble and sorbed phase in each of the soils examined was similar ranging from 5.52 to 36.17% of the material decomposed coming from the soluble phase and the remaining material coming from the sorbed phsae for the Alfisol, Vertisol, Oxisol and Inceptisol soils. The distribution of glyphosate between the labile and non-labile phase as reported here is consistent with the data of Nomura and Hilton (1977) where, in each soil they examined, more than half of the glyphosate remained after the onset of a steady state

rate of decomposition. Similarly, more glyphosate appeared to be allocated to the sorbed than the soluble phase in a variety of forest soils (Torstensson and Stark, 1981).

The half-lives of glyphosate from each phase were calculated from the rate constants for decomposition of glyphosate derived from each compartment and were within the same order of magnitude for each of the soils examined. Half-lives for glyphosate in the soluble phase were similar between the four soils studied (6 to 10 days), however half-lives for glyphosate in the sorbed phase varied widely ranging from 109 to 333 days(Table 2). This suggested that different mechanisms of binding existed within the sorbed phase for each of the four soils investigated. This being the case, then the strength of binding of non-labile glyphosate decreased according to the following order: Oxisol > Inceptisol > Vertisol > Alfisol. The decrease in order of binding strength in the current study compares favorably with the calculated decrease in amounts adsorbed by these soils as shown in a previous study (Suwardji, 1998).

Adsorption of glyphosate has been shown to be influenced by amount of clay (Glass, 1987; Hance, 1976; Hensley *et al.*, 1978; McConnell and Hossner, 1985; Sprankle *et al.*, 1975) soil pH (Suwardji, 1998; McConnell and Hossner, 1985), amount of montmorillonite (Suwardji, 1999; Glass, 1987; Hensley *et al.*, 1978; McConnell and Hossner, 1985; Shoval and Yariv, 1979) and exchangeable Fe (Glass, 1987; Hensley *et al*., 1978). The substantially longer half-life of the sorbed glyphosate in the Oxisol relative to the three alkaline soils (Alfisol, Vertisol and Inceptisol) may be attributed to the low pH, high amounts of clay content and exchangeable Fe in this soil.

The relationship between decomposition of soluble glyphosate and time are linear for each of the four soils and regressions for these relationships are presented in Table. Statistical comparisons of the slopes of these lines showed that no significant ($P<0.05$) difference between the Alfisol, Vertisol and Inceptisol soils. But there was significantly ($P< 0.05$) different between those three soils and Oxisol soil. The difference in rates of decomposition suggested that there may be a fundamental difference regarding the mechanism of glyphosate sorption between three soils (Alfisol, Vertisol and Inceptisol) and Oxisol that this difference may also be related to the amount of exchangeable Fe in each of the soils. High concentrations of Fe in soil have been demonstrated to significantly reduce the herbicidal activity of acropetally imbibed glyphosate (Sprankle *et al.*, 1975; Hensley *et al.*, 1978) and as potentially phytotoxic glyphosate is derived from the soluble phase, exchangeable Fe was assumed to have some effect on the behaviour of glyphosate within this phase. In this instance, the soils with the higher exchangeable Fe content (Oxisol) had lesser amounts of glyphosate relegated to the first compartments and a smaller half-life for glyphosate. From these results the amount of exchangeable Fe in each of the soils was thought to influence the proportioning of glyphosate into each of the compartments and also may have some influence on the reaction order regarding release of material from the first compartment for decomposition.

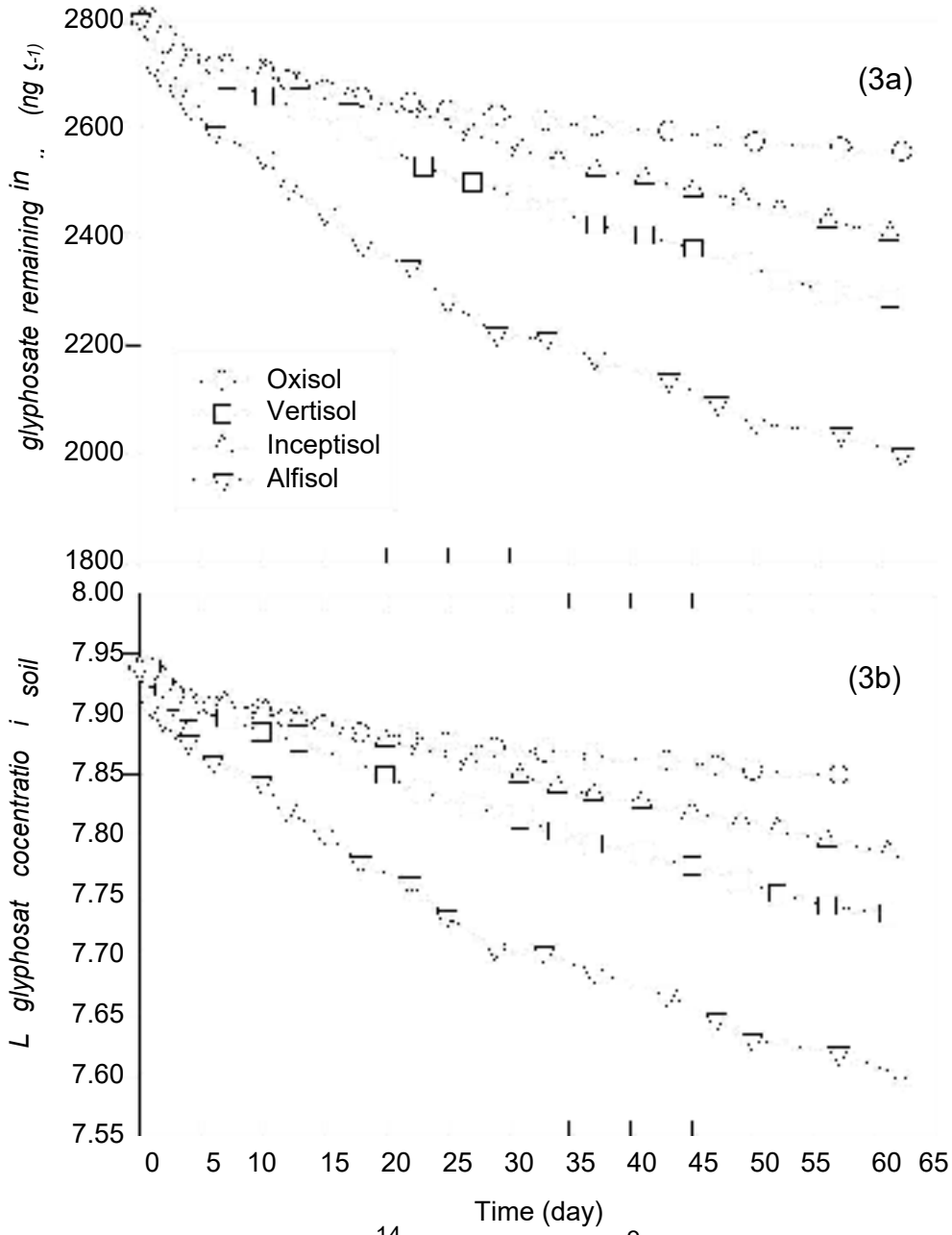

Figure 3. Decomposition of ^{14}C-glyphosate at 22^{o}C in four soils (3a)
and logarithmic transformation of glyphosate remaining in soil versus time (3b)

Table 2. Regression equation, adjusted R^2, rate constant, pool size and half live of the soluble and sorbed phase at incubation temperature 22°C(Analyzed using non steady state compartment analysis)

Soil Type	Phase	Regression equation[1]	R^2	Rate constant (ng/day)	Pool[3] size (%)	Half life (days)
Alfisol	Soluble	Ln y = 6.692056-0.09895X	0.99***	-0.09895	36.17	7
	Sorbed	Ln y =7.50027-0.00639 X	0.99***	-0.00639	64.59	109
Vertisol	Soluble	Ln y = 6.57099-0.10976X	0.99***	-0.10976	25.74	6
	Sorbed	Ln y = 7.66237-0.00482X	0.99***	-0.00482	75.95	144
Oxisol	Soluble	Ln y= 5.06425- 0.069119X	0.96***	-0.06911	5.52	10
	Sorbed	Ln y = 7.86592-0.00208X	0.99***	-0.00208	93.10	333
Inceptisol	Soluble	Ln y = 6.47649-0.09457X	0.99***	-0.09457	23.20	7
	Sorbed	Ln y = 7.64628 - .00380X	0.99***	-0.00380	74.74	182

[1]Regression equation in the form of ln y = a + bx, where y is the loss of glyphosate from particular compartment; a is intercept or pool size; b is the slope of regression or rate constant; and x is time in day. [2]*** significant at a P <0.001

[3]Pool size is the amount partitioned into each compartment (soluble and sorbed compartment) and expressed as a percentage of the glyphosate initially added.

5. CONCLUSSION

The use of NSSSCA to investigate the influence of sorption characteristic on the degradation behaviour of glyphosate has been evaluated. The NSSCA has shown its applicability in explaining the dependence of glyphosate degradation on sorption characteristic of soil. This technique is useful in studying the sorption mechanism *in situ*.

Glyphosate decomposition at 22°C was shown to be influenced by the strength of binding of the substrate within the adsorbed state. Two different pools of adsorbed glyphosate, each with different binding strengths, were identified. The labile compartment contained only the weakly bound glyphosate and it was from here that glyphosate for degradation was obtained. The second or non-labile compartment contained strongly-bound glyphosate that was desorbed slowly into the labile pool. The half-lives of glyphosate from the labile compartment in the four soils at 22°C were similar but the half-lives of glyphosate from the non-labile compartment varied widely between soils. The variation in half-life for release of glyphosate from the second compartment was thought to be a function of soil pH, clay content and exchangeable-Fe.

6. ACKNOWLEDGEMENTS

The author sincerely thank to Mr. Ir. Mahrup for reviewing this article. Thank is also extended to Dr. Ir. Sri Tejowulan, M.Sc. for proof reading of this manuscript.

7. REFERENCES

Gee, G.W. and Bauder, J.W. (1986). Particle-size analysis. In Method of soil analysis Part 1. Physical and mineralogical analysis (Ed. A.Klute) pp. 383-411. American Society of Agronomy Inc and Soil Science Society of America Inc, Madison, Wisconsin, USA.

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}-C labelled pesticides in soil. *Soil Biology and Biochemistry* 8, 527-528.

Gustafson, D.I. and Holden, L.R. (1990). Non-liear pesticide disipation in soil: A new model based on spatial variability. Environmental Science and Technology, 24: 1032-7.

Hamaker, J.W. and Goring, C.A.I. (1976). Turnover of pesticide residues in soil, In. Bound and Conjugated Pesticide Residue, Eds, D. Kaufman et al. ACS. Symposium Series, 29: 219-243.

Hance, R.J. (1976). Adsorption of glyphosate by soils. *Pesticide Science* 7, 363-366. Haines, D.L. (1984). Determination of total organic-C on soils by an improved chromic acid digestion and spectrophotometric procedure. *Communication of Soil Science and Plant Analysis* 15(10), 1191-1213.

Hensley, D.L., Beuerman, D.S.N. and Carpenter, P.L. (1978). The inactivation of glyphosate by various soils and metal salts. Weed Res., 18:287-91.

Holmgren, G.G.S. (1967). A rapid citrate-dithionite extractable iron procedure. *Soil Science Society of America Proceeding* 31, 210-211.

Howell, D.C. (1982). Statistical methods for psychology. Ducbury Press, Boston. Pp. 95-7.

Jeffay, H. and Alvarez, J. (1961). Liquid scintillation counting of carbon-14. Use of ethanolamine-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. (1978). Factors influencing microbial degradation of glyphosate ^{14}-C to $^{14}CO_2$ 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.

Rayment, G. E. and Higginson, F.R. (1992). Australian laboratory handbook of soil and water chemical methods. Ikata Press. Melbourne.

Shoval, S. and Yariv, S. (1979). The interaction between Roundup (glyphosate) and montmorillonite. Part 1. Infrared study on the sorption of glyphosate by montmorillonite. *Clay and Clay Mineral* 27, 19-28.

Sokal, R.R. and Rohlf, F.J. (1981). Biometry. Freemand and Co. San Francisco. 589p.

Sprankle, P. Meggitt, W.F. and Penner, D. (1975). Adsorption, mobility and microbial degradation of glyphosate in the soil. *Weed Science* 23, 229-234.

Suwardji, P.L. Eberbach and A.S. Black (1998).Sorption and decomposition of glyphosate in soils under four temperature regimes. Australian Soil Science Conference, Brisbane 27-29 April 1998, Oral paper. Pp.218-224.

Thirudarayanan, K, Zimdahl, L and Smika, D. (1985). Chlorsulfuron adsorption and degradation in soil. *Weed Science* 33, 558-563.

Torstensson, N.T.L. and Stark, J. (1981). Decomposition of ^{14}-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.

Torstensson, L.(1985). Behaviour of icideglyphosate i Glyphosate'. (Eds. Grossbard-150.Butterworths,andLondon. Atkinson) pp.

Torstensson, N.T.L. and Stark, J. (1979). Persistence of glyphosate in forest soils. Weed and Weed Control-20th Swedish Weed Conference, pp. 145-9.

Villeneuve, J.P. et al. (1988). A sensitivity analysis of adsorption and degradation parameters in the modelling of pesticide transport in soil. J. Contam. Hydrol., 3: 77-96.

Zimdahl, R.L. and Gwynn, S.M. (1977). Soil degradation of three dinitroanilines. *Weed Science* 25, 247-251.