International Journal of Agriculture Innovations and Research
Volume 2, Issue 5, ISSN (Online) 2319-1473
Manuscript Processing Details (dd/mm/yyyy) :
Received : 14/04/2014 | Accepted on : 29/04/2014 | Published : 04/05/2014

Persistence of Atrazine and Oxyfluorfen in Soil Added with *Tithonia Diversifolia* and *Chromolena Odorata* Organic Matter

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Abstract – **The components of humic and fulvic acid of organic matter determine the effectiveness of herbicide adsorption in soil. The persistence of atrazine and oxyfluorfen in soils added with invasive weeds organic matter (*Tithonia diversifolia* and *Chromolena odorata*) was determined. The soils were treated with no organic matter (P0), *Chromolena odorata* compost (P1), *Chromolena odorata* compost (P2), *Chromolena odorata* green manure (P3) and *Tithonia diversifolia* green manure. All kinds of organic matter were added at a rate of 10 t ha^{-1}. Herbicide containing Atrazine (D_1) and Oxyfluorfen (D_2) were also applied to the soils. Highest persistence as shown by DT_{50} value of 46.20 d was found in the soil added with *Tithonia diversifolia* green manure. The persistence of atrazine and oxyfluorfen in the soils added with *Tithonia diversifolia* green manure were higher with DT_{50} value of 46 d and 37.46 d, respectively, than when added with *Chromolena odorata* green manure with DT_{50} values of 27.07 d and 17.20 d, respectively. These are related to the differences in fulvic and humic acids contained in both types organic matters. *Tithonia diversifolia* weed fiber contained higher fulvic and humic acids (28,24% and 8.28%, respectively) while *Chromolena odorata* were only 19.32% and 7.67%, respectively.**

Keywords – **Atrazine, *Chromolena Odorata,* Fulvic Acid, Humic Acid, Oxyfluorfen, *Tithonia Diversifolia*.**

I. Introduction

Weeds grown in Indonesia are mostly invasive. These weeds are predominantly foreign types and have increasingly attracted large attention due to their insidious behavior. They do not only disturb agricultural and water ecosystem but also threaten the natural ecosystem destroying its biodiversity and can prove to be **very costly** to control them. This problem has emotionally driven people to either destroy/control weeds or take advantage of their beneficial.

Tithonia diversifolia and *Chromolena odorata* are invasive alien species easily grown in any soil type and containing high N and K. These characteristics led them to be potential sources of organic matter as mulch, green manure and compost. *T. diversifolia* is an effective nutrient source as it contained 3.5% N, 0.37% P and 4.1% K which highly degradable and mixed with soil easily [6]. The chemical composition of *C. Odorata* were C 50.40%, N 2.42%, P 0.26%, K, 1.6 % Ca 2.02% dan Mg 0.78% [23].

Organic matter plays a very important role in herbicide adsorption in soils. The adsorption of herbicide influences its behaviors in soil such as biological activities, persistence, biodegradation, leaching and evaporation [21]. The behavior of herbicide under the influence of different organic matter determines herbicide effectiveness in suppressing weeds grown and its impact to environmental health.

The interaction between organic matter and herbicides has been reported by some researchers. Increasing organic matter content in soil might increased the rate of pesticide used [27]. Similarly, in soil with high organic matter content, herbicide persists longer [19]. Although, the influence of organic matter on herbicide persistence has been widely reported, information on the effect of specific parts of organic matter such as humic and fulvic acids on the active duration of herbicide in soil known as persistence is very limited. Therefore, the objectives of this research were to determine the effect of invasive weeds organic matter (*T. diversifolia* and *C. odorata*) on the persistence and effectiveness pattern of atrazine and oxyfluorfen.

II. Materials and Methods

The research was conducted in the Green House of Faculty of Agriculture Tadulako University from January to March 2014. Entisols was used along with *T. diversifolia* and *C. odorata* organic matters in the form of compost and green manure. Herbicide with active substance of atrazine and oxyfluorfen was also added to the soil. The experiment was conducted in two phases: 1) compost and green manure production, and 2) soil incubation. The organic matters were taken by trimming *C. odorata* and *T. diversifolia* during their vegetative stage which grown uniformly on a field. Some of the cuttings were made to produce compost while the remaining was left as green manure. Both forms of organic matters were then analyzed for their chemical components. The compost and green manure at a rate of 20 g each were mixed with 5 kg soil and placed in a pot. The soils were then sprayed with either atrazine oxyfluorfen herbicides at a rate of 3.9 mg pot^{-1} after diluting it five times. Each combination of the organic matter type and herbicide type treatment was replicated thrice resulting in 30 experimental units. The treated soils were then incubated for 90 d.

The total concentration of herbicide in soil was determined using spectrophotometer analysis. The preparation of soil sample for herbicide determination was as followed [13;20] : (1) soil sample of 10 g was mixed with 20 ml hexane solution; (2) the mixture was then stirred manually for 10 minutes to form suspension; (3) the suspension was centrifuged for 5 minutes at a rate of 200 rpm to produce supernatant; (4) the supernatant then was concentrated by flowing nitrogen gas into it resulting in 1 ml concentrated supernatant; (5) the concentrated supernatant was then applied into oxide silica chromatography plate with a mixture of hexane and diethyl ether solvent (85:15); (6) the spots formed in the chromatography plate was then illuminated with ultra violet ray and the spots identified were scraped; (7) the scraped spots were dissolved with 3 ml acetonitrile and analyzed for atrazine at wavelength of 230 nm and for oxyfluorfen at 250 nm; (8) the oxyfluorfen and atrazine content in the soil were calculated according to the following equation:

$$\text{Active substance} = (\text{sample absorbant}/\text{standard absorbant}) \times \text{Standard concentration} \quad (1)$$

Prior to incubation, the soil was analyzed for C-organic, N-total, C/N ratio, CEC, Al-exchangeable, P, K, Ca, Mg contents and pH whilst the organic matters for C-organic, N-total, C/N ratio, contents of P, K, Ca, Mg, humic acid and fulvic acid. pH was evaluated using pH meter (glass electrode), C-organic using Walkley and Black method, P-inorganic using H_2S0_4 0.5 M extractant, P-total using H_2S0_4 0.5 M extractant after the soil was heated to 550^0C, P-organic using the difference between P-total and P-inorganic, available P using Bray II method, CEC using NH_4-OAC 1 M pH 7 extractant and Al-exchangeable using 1 N KCl extractant. After 0, 30, 60 and 90 d of the incubation, the total concentration of herbicide in soil was determined. The persistence of herbicide in soil was calculated based on their half time. The model for the herbicide persistence was approached using the following equation [7; 25]:

$$C = C_0e^{-kt} \quad (2)$$

Where, C = the concentration of herbicide in soil at time t
C_0 = herbicide concentration at t = 0
K = herbicide degradation constant

The result of the above regression analysis is used to estimate the half time (DT_{50}) of the herbicide according to the following equation [12]:

$$DT_{50} = 0.639/k \quad (3)$$

Where, k =degradation rate constant of the herbicide.

The relationship between the herbicide at each rate of the organic matters was analyzed using parallel and coincident line regression tests, while the effect of the organic matters using orthogonal contrast test.

III. Results and Discussion

Chemical Composition of Compost and Green Manure

The chemical composition of both *T. diversifolia*and*C. Odorata* green manure sisdepicted in Table 1.

The content of C-organic was slightly higher in *T. diversifolia* than in *C. odorata* while N contents are similar. However, N content in both types of organic matters are still above the critical value for mineralization to occur. The critical content of N was between 1.9 – 1.1%, if the N content is under the critical level then the N will be immobilized [10].

Table 1: Chemical Composition of T. diversifolia and C. odorata Green Manure

Parameter	unit	Analysis Result	
		T. diversifolia	*C. odorata*
C-organic	%	25,53	29,65
N-total	%	2,71	2,60
C/N		9,42	11,40
P	%	0,44	0,59
Ca	%	2,38	3,72
Mg	%	0,61	0,73
K	%	5,12	3,73
Humic Acid	C %	28,24	19,32
Fulvic Acid	C %	8,28	7,67

Source: Laboratory of Environment and Natural Resources, Faculty of Agriculture, Tadulako University (2013).

The C/N ratio of T. diversifolia was 9.42 lower than *C. odorata* which was 11.40. This condition can lead to N mineralization as N content is larger than 1.73% and the C/N ratio less than 25 [5].

Table 1 also shows that the content of humic and fulvic acids of *T. diversifolia* is 28.24% and 8.28%, respectively, higher than that of *C. odorata* which is 19.32% and 7.67%, respectively. Those humic and fulvic acid contained in *T. diversifolia* and *C. odorata* will influence the chemical properties of soil which then affect the adsorption of herbicide applied. Humic and fulvic acids have the capability to break the bond between phosphor and aluminum or iron in soil reducing the solubility of aluminum [1]. Organic acids such as humic, fulvic, acetate, oxalate, butyrate, lactate, and citrate are substances with high capability in forming chelate with Al, Fe, and Mn, and reduce P adsorption [18]. Humic and fulvic acid are organic colloids, forming through humification, affecting the effectiveness of pesticide adsorption [9]. Humic acid has high affinity to herbicide [21].

The chemical composition of *T. diversifolia* and *C. odorata* composts is depicted in Table 2. It shows that the chemical composition of the fiber of both weeds was different from that before composting process.

In general, the chemical composition of both *T. diversifolia* and *C. odorata* composts was higher than the green manure. The percentage of all chemical characteristic except organic acids (humic and fulvic acids) has increased.

Table 2: Chemical composition of T. diversifoliaand C. odorata Composts

Parameter	Unit	Result of Analysis	
		T. diversifolia	*C. odorata*
C-organik	%	28,45	34,52
N-total	%	3,2	3,0
C/N		8,89	11,51
P	%	0,75	0,83
Ca	%	3,58	4,67
Mg	%	1,21	1,35
K	%	7,58	6,05
Humic Acid	C %	25,10	15,97
Fulvic Acid	C %	5,40	4,62

Source: Laboratory of Environment and Natural Resources, Faculty of Agriculture, Tadulako University (2013).

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Herbicide Concentration in Soil

The concentration of atrazine and oxyfluorfen herbicides in the soil over four periods in which each period covers 30 days was depicted in Figure 1 and 2, respectively. The degradation rate of atrazine and oxyfluorfen herbicides decreases with time irrespective of the types of organic matters added. Fast decreasing rate occur initially after application then the degradation rate was slower toward the end of incubation showing exponential pattern [16].

Based on the analysis of variance of the parallel and coincident line regression, it is shown that the concentration of both atrazine and oxyfluorfen in soil with no organic matter added was higher than that with organic matters added. This phenomenon indicates that organic matter added to the soil will change the behavior of herbicide depending upon the type of herbicides. Many factors in soil affect the behavior of herbicides in which the most determinant factors are soil, climate and herbicide properties [8].

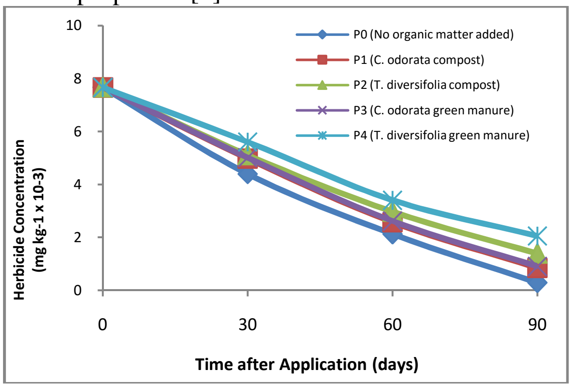

Fig.1. Atrazine concentration in incubated soil with and with no organic matter application

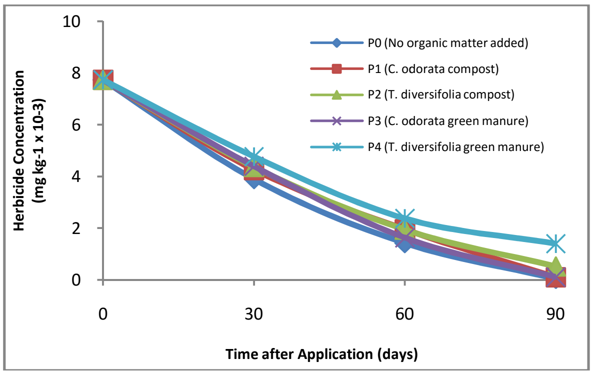

Fig.2. Oxyfluorfen concentration in incubated soil with and with no organic matter application

The concentration of atrazine is higher at any rate of organic matter added than that of oxyfluorfen (Table 3). This indicates that the adsorption of atrazine by soil colloid is higher than that of oxyfluorfen when the soil was added with organic matters. Humus in soil as the product of organic matter decomposition is a source of soil negative charge generated from its carboxyl (-COOH) and phenolic (-OH) functional groups [3]. Under alkaline condition (high pH), soil solution contains high amount of OH^- resulting in H^+ release from its organic functional groups and leading to negative charges ($-COO^-$, and $-O^-$) increase. Increasing negative charges due to organic matter addition can increase the adsorption of herbicide by soil colloids and decrease the concentration of herbicides in soil solution. Similarly, triazine a weak base herbicide was protonized in acid soil and in such way the triazine is adsorbed by soil colloids with negative charges and as a consequent its concentration decrease in soil solution [2; 26].

The results of the orthogonal contrast test showed that the concentration of the herbicides in the soil varied with different weeds and organic matters types added to the soil.

Table 3 shows that the average concentration of herbicide in soils added with no organic matter addition is much lower than that in soils added with various organic matter types. It indicates that the addition of organic matter lead to decreasing amount of herbicides loss from the soil. Organic fraction in soil has the potency to non-biologically reduces pesticide in soil through colloid adsorption mechanism. One particular factor affecting the adsorption of pesticide is soil characteristics such as organic matter content, content and types of clay, pH, cation exchangeable capacity, moisture, and soil temperature [22]. The amount of organic matter present in soil strongly affects the concentration of herbicide in soil environment because its adsorption of the herbicide prevents such processes as diffusion, leaching and volatilization of the herbicide in the soil [17].

The use of *T. diversifolia* as a source of organic matter shows lower herbicide concentration in soil than that of *C. odorata* (Table 3).

Table 3: The average concentration of Atrazine and Oxyfluorfen (mg kg^{-1}) in soil added with different types of organic matters

Types of organic matters	Atrazine	Oxyfluorfen
No organic matter adde (P0)	0,000287	0,0000420
C. odorata compost (P1)	0,000850	0,0000956
T. diversifolia compost (P2)	0,001390	0,0001945
C. odorata green manure (P3)	0,000900	0,0001040
T.diversifolia green manure (P4)	0,002050	0,0013950

The research also shows that the concentration of atrazine and oxyfluorfen in soil is higher when the organic matter was added in the form of green manure instead of compost. It indicates that the addition of *T. diversifolia* green manure could improve the adsorption of herbicide in the soil. Based on Table 1, it is shown that *T. diversifolia* in the form of green manure contains more humic and fulvic acids than that of compost leading to higher adsorption and higher concentration of atrazine and oxyfluorfen in the soil.

Herbicide Persistence

Based on the first order exponential kinetic model, the average of atrazine degradation rate constant with the addition of *T. diversifolia* and *C. odorata* both in the forms of green manure and compost is lower than that of oxyfluorfen (Table 5). The average of atrazine degradation rate constants in soil with no organic matter added, with *C. odorata* compost, with *T. diversifolia* compost, with *C. odorata* green manure, and with *T. diversifolia* green manure were 0.0332, 0.0274, 0.0187, 0.0256, and 0.0150, respectively, whereas the average of oxyfluorfen degradation rate constants were 0.0500, 0.0412, 0.0427, 0.0403 and 0.0185, respectively. These phenomena indicate that in soils with no organic matter addition, the rate of herbicide degradation was less as compared to those with organic matters. The degradation of herbicide in soils added with organic matters was determined by the role of organic matters in its adsorption which influence the dynamic of herbicide persistence [24].

Based on the constants of degradation rate of herbicide, the degradation rate was highest in soils with no organic matter added followed by *C. odorata*, and *T. diversifolia* composts. Organic matter in the form of compost degrades herbicide more rapidly than that of green manure.

Table 4: The half time and degradation rate constant of atrazine and oxyfluorfen herbicides in soils added with various organic matters

Treatment		Constant	DT_{50}
Organic Matter	**Herbicide**		
No organic matter	Atrazine	0,0332	20,87
added (P0)	Oxyfluorfen	0,0500	13,86
C. odorata	Atrazine	0,0274	25,29
compost (P1)	Oxyfluorfen	0,0412	16,82
T. diversifolia	Atrazine	0,0187	37,06
compost (P2)	Oxyfluorfen	0,0427	16,23
C. odorata green	Atrazine	0,0256	27,07
manure (P3)	Oxyfluorfen	0,0403	17,20
T. diversifolia	Atrazine	0,0150	46,20
green manure (P4)	Oxyfluorfen	0,0185	37,46

Table 4 depicts the half time and constant rate of atrazine and oxyfluorfen degradation with various organic matter additions. It shows that the half time of oxyfluorfen was always lower than atrazine. Moreover, organic matter in the form of green manure reduces the half time of both herbicides compares to that compost. Similarly, the half time of herbicides was lower in soils with *C. odorata* added than that with *T. diversifolia*. Highest persistence of atrazine and oxyfluorfen was found in soils with *T. diversifolia* green manure with the half time of 46.20 d and 37.46 d, respectively. The $\mathbf{DT_{50}}$ average of atrazine persistence in soils with and without organic matter added is 31.29 d higher than that of oxyfluorfen (20.31 d). Atrazine was known as a very high resistance herbicide in soil and its persistence increases with increasing content of organic matter in soils [15].

Organic matter with high content of C-organic will increase the persistence of herbicide [19]. However, this research showed that although *T. diversifolia* had higher C-organic content than its counterpart, the persistence of herbicide was last longer in the first than in the latter. Therefore, it is suggested that the persistence of herbicide is not only determine by the amount of C-organic per se but more by the amount of humic acid. *T. diversifolia* contains higher humic (humic acid and fulvic acid) than its counterpart. This condition shows the role of humic acids is much more important in determining the behavior of herbicide in soils increasing the adsorption and influencing the active time of the herbicides. The reactivity of organic matters in herbicide adsorption is dependent upon the number and kind of functional groups. Various functional groups of humic acids (humic and fulvic acids) are organic colloids produced from the process of humification and they can determine the effectiveness of pesticide adsorption [11]. Other organic substance components such as fat, protein and polysaccharide have low herbicide adsorption affinity [4] while humic acid has high affinity [21]. The mechanism of atrazine adsorption by humic acid is due to hydrogen bond [14;28].

Conclusion

The content of humic and fulvic acid of *T.diversifolia* (48.24% and 8.28%, respectively) is higher than that of *C. odorata* (19.32% and 7.67%, respectively) and the Green manure of *T.diversifolia* and *C. odorata* contains more humic and fulvic acids than their compost form. While the highest persistence of herbicide was found in soils with *T. diversifolia* green manure addition with the DT_{50} value of 46.20 d for atrazine and of 37.46 d for oxyfluorfen, the persistence of atrazine and oxyfluorfen herbicide was higher in soils added with *T. diversifolia* green manure (46.20 d and 37.46 d, respectively) than with *C. odorata* green manure (27.07 d dan 17.20 d, respectively), and the humic and fulvic acid in organic matters had an important role in increasing the persistence of herbicide in soils.

Acknowledgment

Sincere thanks to the Rector of Tadulako University Prof. Muhammad Basir for his endless support and help, Professor Mahfudz and Professor Faturrahman for supervision and guidance.

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