Investigation of Glyphosate and Propanil herbicide residues In Shamyia River

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Abstract

The result indicated that Propinal herbicide was higher than glyphosate herbicide in samples of Shamyia River the branched of the Euphrates river that taken specially in water and plant by using Hplc with standard solutions for each herbicide in the first site in april and june while glyphosate higher from Propinol in sediment .

Keyword: Glyphosate herbicide; Propinal herbicide; Shamyia River pollution

Introduction

Herbicide commonly known as a weed killer used to kill unwanted plants, selective herbicides kill specific targets while leaving the desired crop relatively unharmed (Yamamoto & Nakamura, 2003). Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non target species, air, water, bottom sediments and food (Miller, 2004).The glyphosate and propanil were mostly herbicide use in rice crops in AL-Shamyia city , the river passes through a branch of the Euphrates River called the AL-Shamyia River.

Study area

AL-Shamyia is one of the important city in the AL-Qadissiya province The river passes through a branch of the Euphrates River called the AL-Shamyia River(figure 1), city center of AL-Shamyia is 284 Km from Baghdad (AL-Mousawe, 2005).

Description of the Study Sites

Site One (Salahiya Town) (S1)

Located north of Shamyia city about 7 Km far from the city center. In AL-Salahyia town (agriculture town), the water was clear in this site.

Site two (Shamyia city) (S2)

Located near AL- Shamyia Bridge. Surface layer of water was covered by floated plastic bottles and municipal waste (Polluted area). It is affected by domestic wastewater and workshops from AL-Shamiya city which populated with about (200000) individuals.

Site three (Rice field) (S3)

It is situated about 3Km south from AL- Shamyia city. In this Irrigation area many of rice fields and agriculture are discharged all their water that contain with herbicide and fertilizer from AL- Shamyia River.

Materials and Methods

Sampling for HPLC Analysis

Water Samples Collection

Water samples were collected within a period of 12 months one liter every time, in a rice fields of AL-Shamyia area is situated sampling schedule comported three distinct periods of the spring of 2009: (1) during field preparation for rice seeding (26April); (2) during rice seedling (8July); and (3) when crop harvest (4 November) for residual of both herbicide in water. Each water sample a tightly sealed polyethylene (Bottle of 1 litter) , transported

with refrigeration and stored at 4 °C until to, the sample was filtration by Millipore filter unit(0.45 *M*m)then the sample was injected in HPLC to analysis it .

Sediments Samples Collection

Samples were taken by hand from the surface layer (0-10 cm) from the areas placed in plastic bags and keep in cool box, in laboratory placed in the refrigeraton(-18°C) until to analysis (AL-Helaly, 2010).

Aquatic Plant Samples Collection

The fresh ends of plant were taken by handabout 20 gram and washed with river water then placed in plastic bags, transported to the laboratory in a coole box and placed in the freezer(-8 °C) until analysis. The non-rooted-submerged hornwort aquatic plant *Ceratophyllum demeresum* belongs to the family Ceratophyllacae from Spermatophyta, Dicotyledones plants(Al-Saadi & Al-Mayah, 1983). it was dominant at all the study sites. Sample of sediment and plant collect in 17 June; 19 July and 17 August 2011.

Determination Residual of Herbicide

The samples were injected in the HPLC column using the chromatographic system as described. Residue peak was tentatively identified on the basis of retention time residue amount were determined by comparing peak heights to those obtained from known amount of glyphosate and propanil standard from white rose company . All Analytics processes were done at the Ministry o f Science and Technology, department of chemical and petrochemical.

HPLC – Operating Parameters

Water

LC-UV system Shimadzu (Tokyo, Japan).

1.	Column	C18 (50×4.6 mmi.d.; 3 mm)3um pati& size
2.	Mobile phase	THF(Tetra hydro furan)
3.	Flow rate	1ml/min

4.	Pressure	180bar
5.	UV-detector	UV-VIS SPD 2010 280nm
6.	Recorder	CR-6A Shimadzu

A 1000 ml injected in to HPLC column using Sepk-C18 (1cm ×0.46mm i.d) to detention the herbicide .add 5 ml from methanol to column, evapor the methanol by nitrogen gas to 1ml, injected 20 ml of concentrated solution on column for separation. The retention time for glyphosate is 2.65-2.7 and 3.1-3.2 for propnil.

Concentration of sample was calculated by this formula (Harborn, 1984):-

$$\text{Con. } \mu g/ml = \frac{\text{Area of sample}}{\text{Area of standard}} \times \text{Con. of standard (10 } \mu g/ml) \times \text{Concen.Factor } (10^{-3})$$

Sediment & Plant

LC-UV system Shimadzu10AV-LC (Tokyo, Japan).

1.	Column	C18 (50×4.6 mmi.d.; 3 mm)3um pati& size
2.	Mobile phase	acetonitrile :THF(Tetra hydro furan)(20:80)V/V
3.	Flow rate	1.2 ml/min
4.	Pressure	180bar
5.	UV-detector	UV-VIS SPD 2010 254nm
6.	Recorder	CR-6A Shimadzu

100 grams of material was added to 250 ml of Tetra hydro furan and then shaker for 15 minutes in ultrasound to ensure that the descent of the components of the material and then left the solution for one hour to stability , filtering the solution to isolate gravel, sand and fiber was then concentrated of the solution 250 ml by pass in SPEAK-C-18 Cartridge column length 5 cm to concentrated ,the detention of all herbicide on the column and down herbicide

retained on the column by passing 5 ml of methanol. Concentration of sample was calculated by this formula (Harborn , 1984) .

$$\text{Con. } \mu g/ml = \frac{\text{Area of sample}}{\text{Area of standard}} \times \text{Con. of standard (10 } \mu g/ml) \times \text{Concen.Factor } (2\times10^{-1})$$

Result

Water

The residual concentration of glyphosate showed that the minimum value in non detected by HPLC in November 2009 HPLC at site 1,2 and 3. The same values recorded at site 3 in July .Maximum value 0.0004 ppm was recorded at site 1, 2 in July 2009, and recorded at site 3 0.00.2ppm in April 2009.On the other hand The residual concentration of Propanil showed that maximum value was 3.121 ppm at site 1 in April 2009 .While Minimum value recorded in November 2009 was 0.00094 ppm at site 2 and 3.

(Table 1). Table (1): The residual concentration of herbicides in AL-Shamyia River (Water).

Sites	Site 1			Site 2			Site 3		
Month / Herbicide	April 2009	July 2009	Nov 2009	April 2009	July 2009	Nov 2009	April 2009	July 2009	Nov 2009
Glyphosate ppm	0.0002	0.000488	----	0.0002	0.000433	----	0.0002	---	---
Propnil ppm	3.121	0.1764	0.0098	2.267	0.0483	0.00094	2.156	0.051	0.0094

Sediment

The residual concentration of glyphosate in sediment of AL-Shamyia River showed the minimum non detected value was in the August in site 1, June , July in site 2 and August in site 3 (Table 2) .Higher value was in July in site 3. The residual concentration of Propanil in sediment of AL-Shamyia River showed that maximum value was in June in site 1,While the minium non detected in June in site 2,3.

Table (2): The residual concentration of herbicides in AL-Shamyia River (Sediment).

Sites	Site 1			Site 2			Site 3		
Month / Herbicide	June 2011	July 2011	August 2011	June 2011	July 2011	August 2011	June 2011	July 2011	August 2011
Glyphosate ppm	0.0083	0.0217	---	---	---	0.006	0.0115	0.0308	---
Propnil ppm	0.0124	0.00412	0.0046	---	0.00038	0.00562	---	0.00210	0.00269

Plant (*Ceratophyllum demeresum*)

The residual concentration of glyphosate in plant of AL-Shamyia River showed that the minimum value was in August at site 1 .while in site 2 was in June, July , and August ,while the higher value was recorded in August in site 3.for Propinal the minium value was in June and August in site 2(Table 3). The maxium value was in June in site 1.

Table (3): The residual concentration of herbicides in AL-Shamyia River (Plant)

Sites	Site 1			Site 2			Site 3		
Month / Herbicide	June 2011	July 2011	August 2011	June 2011	July 2011	August 2011	June 2011	July 2011	August 2011
Glyphosate ppm	0.003471	0.015090	---	---	---	---	0.00539	0.00578	0.0152
Propnil ppm	0.024134	0.02119	0.00243	---	0.002515	---	0.01351	0.01046	0.01252

Discussion

Water

Chromatographic method by HPLC had been used for the direct and simultaneous separation and determination of two herbicide glyphosate and propanil herbicide. The analysis result showed the residue of propanil was higher in the water of AL-Shamyia River than glyphosate ,many farmers in this area may be used propanil more than glyphosate, especially post emergence, when the glyphoste was used before release the unsafe herbs. Cabras (1983)studied herbicides bentazone, 2,4-D, MCPA, propanil, molinate, and tiocarbazil also the insecticide phenthoate were applied to rice fields in Sardinia at rate that were rates equivalent to maximum aqueous concentrations of 0.4-2.8 mg kg^{-1}, assuming the water to be 20 cm deep. The pesticides paraquat water can be reach including rivers, ponds, and be harmful for the ecosystem, but reduced in several ways, including absorption, adsorption and decomposition of life biodegradation and photolysis (AL-Jobbry, 2001).

Sediment

The present study indicated that the minimum value of glyphosate was in August at site 1, June , July in site 2 and August in site 3 , there was no record (non detected) by HPLC. Higher value was in July at site 3. The residual concentration of propanil in sediment showed that maximum value was in June at site 1.While the minimum value was in June at site 2,3. Sprankle *et al.* (1975) found that the prime factor in determining the amount of glyphosate adsorbed to soil particles is the soil phosphate level and that glyphosate is bound to soil through the phosphonic acid moiety, glyphosate is resistant to chemical degradation, stable to sunlight, relatively non leachable and has a low tendency to runoff (except as adsorbed to colloidal matter).

Plant (*Ceratophyllum demeresum*)

The result showed that the minimum value of glyphosate was in the August at site 1,2 and June,July in site 2 .while the higher value was in August at site 3.for propinal the minium in

June and August at site 2. The maxium in June at site 1.also may be related with agriculture procees in this area. The duration of both steps was dependent on a number of factors, including species, age, environmental conditions, concentration of glyphosate, and concentration of the surfactant (Franz *etal*, 1997). Green *et al.* (1992) demonstrated that foliar absorption of glyphosate was slow in both red maple and white oak with only 37 to 38% absorbed over a period of days and no significant increase in absorption thereafter. Green *et. al*., (1992) and D'Anieri *et al*. (1990) suggested that differential foliar absorption played an important role in hardwood tolerance.Propanil is moved from the leaves to the growing shoots, then back to other leaves, crop plants such as rice completely metabolize propanil(WSSA,1989). Carryover of herbicidal activity to subsequent crops is not likely, and the use of propanil with other pesticides such as the organophosphorous compounds can kill even desirable plants because these plants can no longer metabolize the propanil(Casarett,1980).

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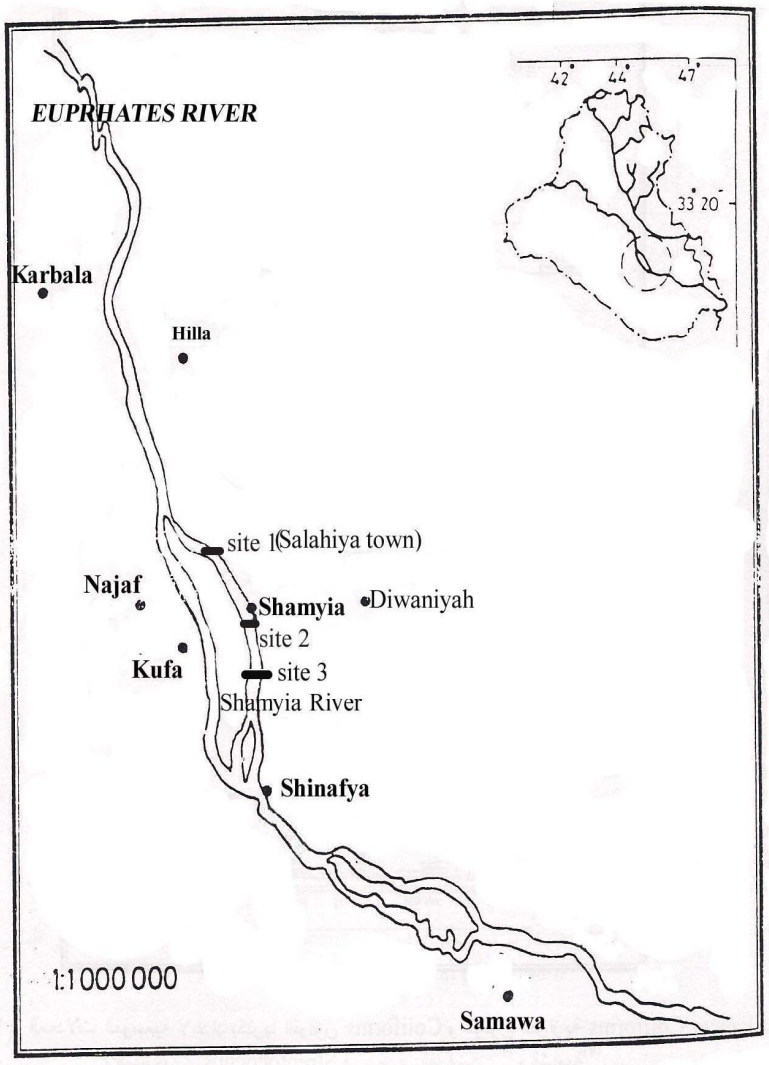

Figure (1): Map of AL-Shamyia River with sample site.

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التحري عن متبقيات مبيدي البروبانيل والكلايفوسيت في نهر الشامية

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الخلاصة

اشارت النتائج الى ان بقايا تراكيز مبيد البروبانيل كانت اعلى من بقايا تراكيز الكلايفوسيت في العينات الماخوذة من نهر الشامية المتفرع من نهر الفرات وخاصة عينات المياه ونبات الشمبلان عند استخدام جهاز الكروماتوغرافي الغازي السائل فائق الضغط HPLC مع المحاليل القياسية لكل مبيد وخاصة في الموقع الاول في شهري نيسان وتموز ، بينما كانت تراكيزمبيد الكلايفوسيت هي الاعلى في الرواسب .