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Distribution and Dissipation of pesticide after the first application of double of the recommended dose of chlorpyrifos

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***Abstract*—A study was designed to determine the residual chlorpyrifos in rice cultivation after the application of double of the recommended dose (2 L/ha) of pesticides in the experimental fields of Bangladesh Rice Research Institute (BRRI). Water samples were collected from the experimental fields at 0, 1th, 3th, 5th, 7th, 10th and 14 th days after the application of chlorpyrifos In this project water sample of 7th, 10th and 14th days were analysed to residual amount of chlorpyrifos. Samples were extracted with dichloromethane and evaporated into small volume and then reconstituted by n-hexane in 1 mL. The n-hexane extract was analysed by GC-ECD. A calibration curve was prepared with 5 different concentration (0.016, 0.032, 0.063, 0.125 and 0.250 ppm) of standard chlorpyrifos using Microsoft office excel. The curve followed linear relationship with correlation coefficients, R^2=0.996. The detection limit of chlorpyrifos was 0.004 ppm and the limit of quantification was 0.0132 ppm. The result for the analysis of the rice field water samples of 7th, 10thand 14th days shows that concentration of chlorpyrifos after 7 days was below dectection limit. This finding indicates that the chlorpyrifos degrade 7 days after the application of double of the recommended dose in rice field.**

Keywords— Pesticide, Chlorpyrifos, Water, Detection limit, BRRI, Calibration curve, Parameter, etc.

I. INTRODUCTION

In the early years the chemicals used as pesticides are generally inorganic and organochlorine compounds (e.g. DDT, DDE etc). They had some severe disadvantages e.g. they were often highly toxic, very persistent, posing a threat to the environment, or they damaged the crops they were meant to protect. Pesticide safety knowledge and pesticide applicator regulation are designed to protect the public from the misuse of pesticide, but do not eliminate all misuse. Reducing the use of pesticides and choosing less toxic pesticides may reduce risks placed on society and the environment

Chlorpyrifos is a broad spectrum insecticide, a chemical used to kill a wide variety of insects. It Wasintroduced in 1965 [1]. Chlorpyrifos is effective in controlling a variety of insects, including cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice [2]. It is used as an insecticide on grain, cotton, field, fruit, nut and vegetable crops, and well as on lawns and ornamental plants [3].Trade and other nameof chlorpyrifosare Brodan, Detmol UA, Dowco 179, Dursban, Eradex, Lorsban, Piridane, Stipend [4].Chlorpyrifos is moderately toxic to humans [5]. Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system, and the respiratory system [6]. A low blood cholinesterase level can sometimes persist from two to six weeks with long-term exposure to chlorpyrifos [6]. It is also a skin and eye irritant . An influenza-like condition with headache, nausea, weakness, loss of appetite, and malaise has also been reported [7]. The acute dermal LD_{50} for chlorpyrifos in male and female rats is greater than 2,000 mg/kg [8]. In some animal species, chlorpyrifos may produce neurotoxicity, or harm to nerve tissue [9].EPA has determined that chlorpyrifos does not adversely affect reproduction [10]. In two studies reviewed by the EPA, no effects were seen in the animals tested at dose levels up to 1.2 mg/kg/day [10].

In humans, chlorpyrifos and its principal metabolites are eliminated relatively rapidly following

a single dose [11]. It is readily absorbed into the bloodstream through the gastrointestinal tract if it is ingested, through the lungs if it is inhaled, or through the skin if there is dermal exposure [10]. After a single oral dose, its half-life in the blood appears to be about one day [12]. The US EPA requires precautionary language on chlorpyrifos product labels, warning of the hazard that this insecticide poses to birds, wildlife and aquatic organisms. It should not be applied directly to water. Drift and runoff from treated areas may be hazardous to aquatic organisms in adjacent aquatic sites [13].Chlorpyrifos is very highly toxic to birds, freshwater fish, aquatic invertebrates and estuarine and marine organisms [5]. Its oral LD_{50} in pheasants is 8.41 mg/kg, 112 mg/kg in mallard ducks.Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system, and the respiratory system. It is also a skin and eye irritant.Chlorpyrifos may bioconcentrate at very low levels in ecological systems (BCF = 2.50 to 3.54) [14].In water, chlorpyrifos readily adsorbs to suspended sediment and bottom materials. Volatilization is probably the primary route of loss of chlorpyrifos from water. Research suggests that this insecticide is unstable in water, and the rate at which it is hydrolyzed increases with temperature, decreasing by 2.5 to 3-fold with each 10^0C drop in temperature. The rate of hydrolysis is constant in acidic to neutral waters, but increases in alkaline waters. In water at pH 7.0 and 25 degrees C, it had a half-life of 35 to 78 days . The half-life of chlorpyrifos in water of an unknown pH was about 80-100 days.

The objective of the present work was to determine the degradation and dissipation pattern of chlorpyrifos in water sample collected from experimental rice fields. Bangladesh Rice Research Institute(BRRI), Gazipur where Chlorpyrifos was sprayed on rice field at recommended dose and double of the recommended doses. After application of chlorpyrifos the sample water, soil and rice seedlings were collected. All the samples were collected after pesticide application at 0, 1th, 3th, 5th, 7th, 10th and 14thdays. In this project the water sample of 7, 10 and 14 day after at double of the recommended doses were analysed to see residual amount of chlorpyrifos.

II. EXPERIMENTAL

A. Materials and Methods

A1. Chemical and Reagents

Analytical or reagent grade solvents purchased from Sigma, E. Merck or BDH were used to carry out the experiments. Analytical grade dichloromethane (DCM) was used in the experiment. DCM was distilled using glass distillation set before use. Extra pure n-hexane was used to prepare final sample to inject in GC.Anhydrous sodium sulfate was made free from any interfering organic substances and moisture by heating at 250^{0}C for at least three hours.Sodium chloride (NaCl) was used saturated sodium chloride solution.

A2. Glass apparatus& Instruments

Separating funnel, round bottom flask , funnel and GC vial were used as glass apparatus. During the experiment a rotary vacuum evaporator (model-R-210, company BUCHI, Switzerland), a recipro shaker (model-RS -1, company – AUTONICS , Japan), an oven (model-NDO-600 ND , company-EYELA) and a GC -2010 (Shimadzu) with ECD were used as essential instruments.

A3. Sampling

Bangladesh Rice research Institute(BRRI), Gazipur to see the distribution and dissipationpattern of modern pesticides (e.g. Diazinon, Chloropyrifosetc) after application during rice cultivation.Experimental field were design in BRRI on 23th January, 2010 where rice seedlings were planted. Chlorpyrifos was sprayed in the fields at the double of the recommended dose on 18th February,2010.The sample water, soil and rice seedlings were collected from the rice field. All the samples werecollected after application at 0, 1st, 3rd, 5th, 7th, 10th and 14th day. In this project the water sample of 7th, 10th and 14th day after at double of the recommended doses were analysed to see residual amount of chlorpyrifos.

Table 1: *Information about the samples collection*

No of days.	Samlpe ID	Dose.(L/ha)
7th	WT_5R_2 (71)	blank
	WT4R1 (71)	2
	WT4R2 (71)	
	W T4R3 (71)	
10th	WT_5R_2(101)	blank
	WT4R1 (101)	2
	WT4R2 (101)	
	W T4R3 (101)	
14th	WT_5R_2(141)	blank
	WT4R1 (141)	2
	WT4R2 (141)	
	W T4R3 (141)	

A4. Method of extraction

500 ml of water sample was taken into a 1000 mL separating funnel and added 50 mL saturated NaCl (brine), 60 mL distilled DCM . The mixture wasshaked by hand consciously about 1 minute at 220 rpr. Then the mixture was shaked by recipro shaker about 2 minutes. The mixture was allowed to separate into two organic layers and the extraction was repeated with another 60 mL DCM . 20 g anhydrous sodium sulphate was taken into the funnel to filter it. The combined organic layer was filtered through a filter paper (Whatman no 1) containing anhydrous Na_2SO_4 of 20 g. The filtrate was evaporated to dryness and reconstituted with 1 mL of n- hexane and transferred to a GC vial . The extract was ready to inject into gas chromatograph.

A5. Preparation of standard stock solution

Primary standards of chlorpyrifos of the highest available purity (99.5 % purity) were used. A known amount (0.01005 g) of the analytical grade chlorpyrifos was dissolved in a definite volume of n-hexane (100 mL) and the concentration of the standard was calculated (100 ppm). All the solutions were kept and preserved in screw cap test tubes leveled with proper marking by permanent ink and stored in a refrigerator. The working standard solutions of 0.016, 0.032, 0.063, 0.125 and 0.250 ppm were prepared by serial dilution of primary standard solution with n-hexane.

A6. Calibration curve for the determination of unknown concentration of chlorpyrifos

Working standard solutions of 0.016, 0.032, 0.063, 0.125 and 0.250 ppm were injected into GC. A calibration curve was made by plotting area versus concentration and the straight line was obtained.

Table 2: *Concentrations and observed areas for standard chlorpyrifos solutions.*

Concentration (ppm)	Area
0.016	52886
0.032	100039
0.063	179639
0.125	310214
0.250	559727

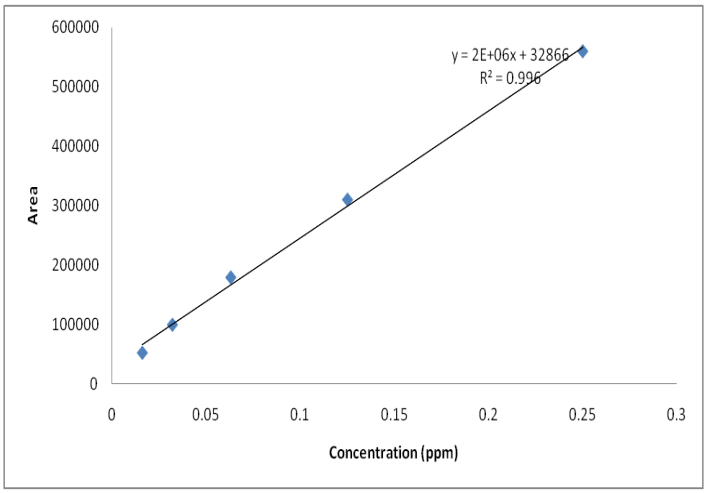

Figure: *Calibration curve of Chlorpyrifos obtained with chromatograms of different concentrations*

A7. Limit of detection (LOD) and Limit of quantification (LOQ)

In order to find the limit of detection, dilute solution ofChlorpyrifos were injected to the GC and peak height was considered when it was three times higher than the noise level. Analyzing the peak area, the detection limit was found to be 0.004 ppm. LOQ was determined by considering the peak height ten times higher than the noise level. Analyzing the peak area, the quantification limit was found to be 0.0132 ppm.

A8. Control sample

A blank experiment was done with water sample collected from the field in which chlorpyrifos was not sprayed and was analysed no chlorpyrifos was detected in the control sample.

A9. Retention time

The standard solution of chlorpyrifos was injected to GC-ECD and the retention time of chlorpyrifos was detected 12.143 minutes.

III. RESULT AND DISCUSSION

Table 03: *Using standard calibration curve calculated concentration of chlorpyrifos in water samples are given below*

No. of days	Sample ID	Dose(L/ha)	Concentration of chlorpyrifos (ppm)
7th	$WT_5R_2(71)$	blank	nd
	$WT_4R_1(71)$	2	bdl
	$WT_4R_2(71)$		bdl
	$WT_4R_3(71)$		bdl
10th	WT_5R_2 (101)	blank	nd
	$WT_4R_1(101)$	2	bdl
	$WT_4R_2(101)$		bdl
	$WT_4R_3(101)$		bdl
14th	WT_5R_2 (141)	blank	nd
	$WT_4R_1(141)$	2	bdl
	$WT_4R_2(141)$		bdl
	$WT_4R_3(141)$		bdl

- Bdl = below detection limit
- nd = not detected

In modern day agricultural practices, the use of pesticides provides unquestionable benefits byincreasing the production of crops. However, it has the drawback of pesticide residues which remain on the vegetables, constituting potential health risks to consumers. This leads on the one hand to the establishment of legal directives to control their level sthrough the maximum residue levels (MRLs) and on the other to continue search for pesticides, which are less persistent and less toxic for human beings. But the over dose of pesticides makes the residue problem,which might pollute our food and be harmful for our health. It has been reported that some of the pesticides are being used in the country where no pre-harvest time frame after application is maintained. There are areas where pesticides are used in excessive quantities,in such situation make monitoring and assessment of pesticides contamination difficult. Therefore, pesticides residue is becoming a major food safety concern of consumers and government. Analytical instrument are needed to determine, quantify and confirm pesticide residues in rice field for both research and regulatory purposes. According to World Health Organization (WHO), the MRL value of chlorpyrifos is 0.1 ppm**.** Bangladesh Rice Research Institute(BRRI), Gazipur to see the distribution and dissipation pattern of modern pesticides (e.g. Diazinon, Chloropyrifos, etc) after application during rice cultivation.The sample water, soil and rice seedlings were collected from the rice field. All the samples were collected after application at 0, 1st, 3rd, 5th, 7th, 10th and 14th day. In this report the water sample of 7th, 10th and 14th day after at double of the recommended doses (2 L/ha) were analyzed to see residual amount of chlorpyrifos. After analysis the concentration of chlorpyrifos was found below the detection limit. This means that the chlorpyrifos degraded before 7 days. So, it is necessary to see the residual level in rice grain, seedlings and soil samples after pesticide application which will give the idea about the distribution of chlorpyrifos in the rice field. But as rice grain is normally harvested after 3 months of seedlings, it would be safe to use chlorpyrifos in rice cultivation if the final application of chlorpyrifos is done 7 days before harvesting. But if it is applied on vegetable production like eggplant, tomato, ladiesfinger, cucumber etc. which are being harvested everyday. In those cases application should be done 7 days before harvesting.

IV. CONCLUSION

Farmers of our country do not have adequate knowledge to apply pesticides in crops and vegetables. Perennial use of pesticides gives pest resistance. In most of the cases farmers use pesticides more than the recommended dose not considering the affect of the chemicals or their amount. If the pesticide companies add more active ingredient than the written amount that will produce even more harmful effect in the human health and environment.

V. ACKNOWLEDGEMENTS

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