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Qualitative and Quantitative Determination of the Residual Levels of Chemical Pesticides of the Shrimp Farms of Bangladesh

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Abstract

A survey was conducted in five different Unions of Bagerhat Upazila under Bagerhat District, Bangladesh to know the various types of chemical pesticides applied by the farmers to boast up agricultural productivity. Ten water and ten soil samples were collected from shrimp-cum-paddy farms, and analyzed the presence of organochlorine and organophosphorus pesticides. Liquid-Liquid Extraction (LLE) and Shaker Extraction (SE) method were used to extract the residual levels of pesticides from water and soil samples respectively. Qualitative and quantitative analysis of the residual levels of the notorious organochlorine pesticide, Dichloro-Diphenyl-Trichloroethane (DDT) and its hydrolytic degradation product, Dichloro-Diphenyl-Dichloroethane (DDD) as well as three different frequently used organophosphorous pesticides namely Chloropyriphos, Diazinon and Malathion were determined by the High Performance Liquid Chromatography (HPLC) method. Results revealed that none of the water and soil samples from the shrimp-cum-paddy farms of Bagerhat Upazila was contaminated with any of the pesticides examined. These results indicate that either these pesticides have not been indiscriminately applied at least in the shrimp-cum-paddy farms of this area or have degraded by the time the samples were collected.

Keywords: HPLC, DDT, chloropyriphos, diazinon, malathion.

Introduction

Bangladesh is a rural agrarian developing country; has only 0.31 percent of the total agricultural land in the world but 2.0 percent of total population of the globe[1]. Shrimp-cum-paddy farming is now one of the most important agricultural sectors of Bangladesh contributing to its economic growth since 1970 which mainly practiced in the Southern coastal regions of Bangladesh such as Khulna, Satkhira and Bagerhat districts. Shrimp farming in the coastal area has expanded extensively due to some additional advantage in the region such as salinity of water. A large amount of foreign currencies is earned every year by exporting shrimp to different countries such as America, England, and Belgium. In recent years, export of shrimp is decreasing due to presence of chemical pesticides in it.

Pest attack causes a great damage to agricultural production of Bangladesh every year. Insect pests are harmful for agriculture and fishery and as well as for our economy. Chemical pesticides are still considered a critical input to improve crop yields and to prevent crop losses before and after harvest[2]. Increasing interest and recognition are being shown by government and private sectors to the use of pesticides to increase the production of crops and fisheries. The application of pesticides has increased about 5 folds from 1989 to 1998[3]. Organochlorine compounds used as pesticides include DDT, DDD, DDE, Dicofol, Heptachlor, Lindane, Endrin, Chlordane, Chlorobenzilate, Chloropropylate, Methoxychlor, Aldrin, Dieldrin, Endosulfan, Isodrin, Isobenzan and Toxaphene. Commonly used insecticides containing organophosphorous compounds include Prathion, Dicapthon, Diazinon, Demeton, Bromophos, Endothion, Malathion, etc.

After applying chemical pesticides, firstly it was effective against pests but soon resistance appeared and became so widespread that many of them became ineffective. Although several public healths related hazards of chemical pesticides became apparent over time, however they are still seen as an essential and useful technology with the safe and effective management in place.

Now-a-days, the use of chlorinated hydrocarbons declines due to their long persistence, danger to aquatic and terrestrial lives and ecosystems. Pesticides may be entered into food chain either directly through the fishes or indirectly through plants which absorb those pesticides. Ultimately the pesticides can show their toxic effects in human, fish and other organisms of that area in where they are applied.

Safe and effective use of chemical pesticides is essential for avoiding the contamination of water and soil. The main objective of present investigation is to know and monitor the application of chemical pesticides such as organochlorine and organophosphorous pesticides in shrimp-cum-paddy farming areas of Bagerhat Upazila, Bangladesh.

Material and Methods

Bagerhat upazila under Bagerhat district was taken as the study area (figure-1) where lands are used predominantly for shrimp farming in paddy-cum-fish culture method. Rice and other vegetables are also cultivated in this area.

Water and soil samples were collected from different shrimp-cum-paddy farms of five different unions of Bagerhat Upazila to find whether any contamination and residual level of organochlorine (DDT, DDD) and organophosphorous (Chloropyriphos, Malathion and Diazinon) pesticides available in the study area. For the collection of water samples, 5-8 samples were collected from 5-8 spots of each farm and then mixed well and finally from that mixed sample, 1000 ml of water sample was collected. In the same process, 500 g of soil samples were collected. Water and soil samples were collected in sterilized plastic bottles and plastic bags respectively. All the water and soil samples were labeled by permanent marker and were kept under refrigeration at -20^{0}C and into cupboard at room temperature respectively to preclude the risk of hydrolysis and oxidation. Next samples were processed and preserved for subsequent experiments and necessary analyses at the Agrochemical and Environmental Research Division (AERD), Institute of Food and Radiation Biology (IFRB), Atomic Energy Research Establishment (AERE), Savar, Dhaka.

The samples were collected during January-February in 2009, which simply covered the post-monsoon rainy seasons. The sampling seasons were characterized by (a) heavy rainfall which washes topsoil and hence carry the agrochemical residues into the water bodies and the soil of the canals of shrimp farms and (b) all water bodies and soil of the canals of shrimp farm may entrap different types of pesticide residues. Water and soil contains a lot of organic matter and it is evident that more the organic matter in water and soil more the pesticide residues are entrapped.

For water sample preparation, Liquid-Liquid Extraction (LLE) and for soil sample preparation, Shaker Extraction (SE) method was applied. The overall procedure was provided by the laboratory where the samples were preserved and processed.

At first, 500 ml of water samples and 50 g of powdered soil samples were taken for extraction. Then, 100 ml of double distilled (DD) n-hexane was taken in a separating funnel and in a conical flask sequentially. DD n-hexane and water samples were shaken by mixing well for about 10 minutes and DD n-hexane and soil sample were allowed to mix well in a shaker for 8 hours. Then all the preparations kept standing for 10-15 minutes for settling down. Separation of water (lower layer) was done in a conical flask and hexane layer (upper layer) in another conical flask. Re-extraction of the aqueous layer was done by adding 50 ml of DD-hexane and then solvent layer was collected. Decanted followed by evaporated to dryness up to a volume of 2 ml using Rotary Vacuum Evaporator. Transferred the extract into a cleaned and rinsed vial and then cleaned-up of the extract over florisil column and eluted with 2% diethyl ether in DD n-hexane. Re-evaporation up to 2 ml by Rotary Vacuum Evaporator was done and transferred into another cleaned and rinsed vial. All of the cleaned extracts were collected in the vial and was dried up fully by N_2 blow from N_2 blower. Final volume was made up to 2 ml by adding acetonitrile prior to injection into HPLC column.

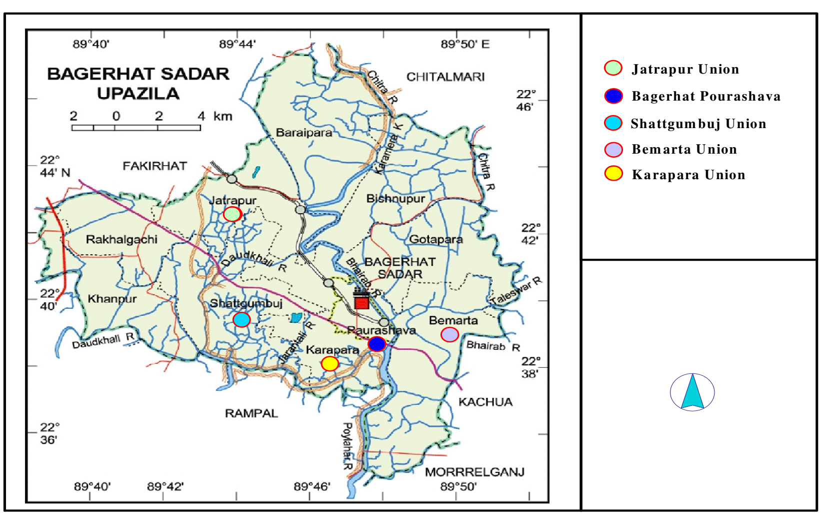

Figure-1
Map of Sampling Areas of Bagerhat Sadar Upazila under Bagerhat District, Bangladesh

For the analysis of pesticide residues, 20 µL aliquot was injected by micro-liter syringe into the HPLC column fitted with ultraviolet (UV) detector at the flow rate of 1.0 ml/min. The mobile phase was composed of 65 percent acetonitrile and 35 percent distilled water and the column was C18. Finally the absorbance was detected at 254 nm wavelength in which the chromatograms were found.

Results and Discussion

Water and soil samples collected from different shrimp-cum-paddy farms of the study area were not contaminated with any organochlorine pesticide residues. Figure-2 and figure-3 showing the standard chromatogram of acetonitrile (solvent) and DDT respectively; the absence of DDT in water and soil sample (figure-4 and figure-5); the standard chromatogram of DDD (figure-6) and the absence of DDD in water and soil sample (figure-7 and figure-8).

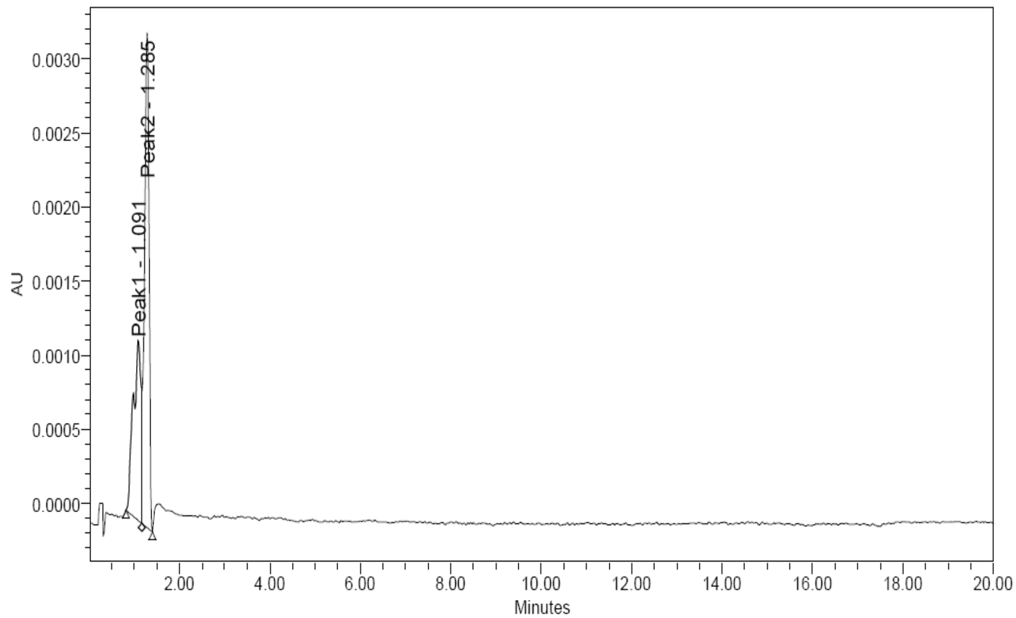

Figure-2
Standard Chromatogram of Acetonitrile

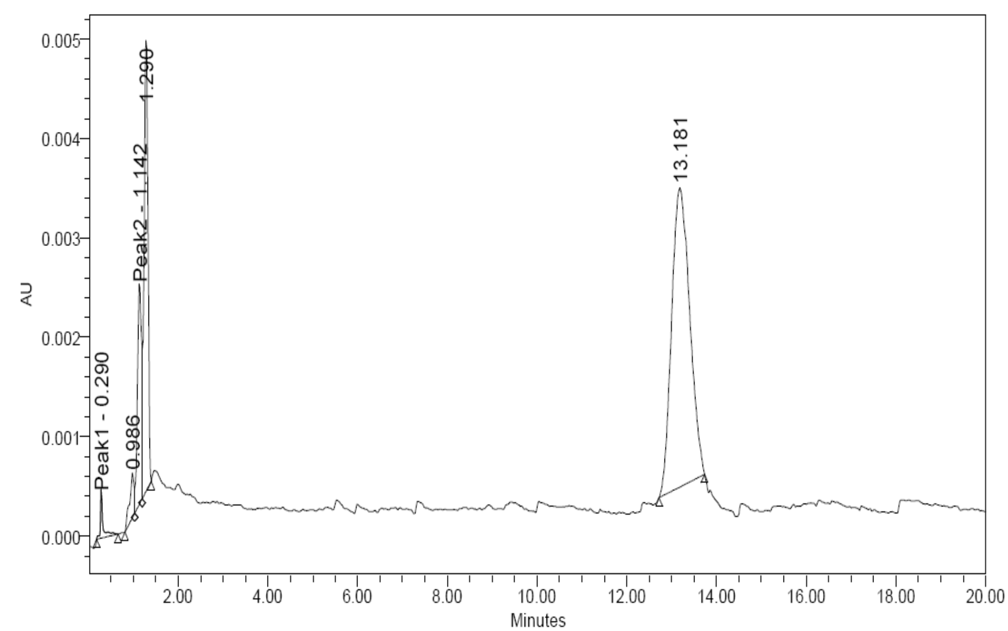

Figure-3
Standard Chromatogram of DDT

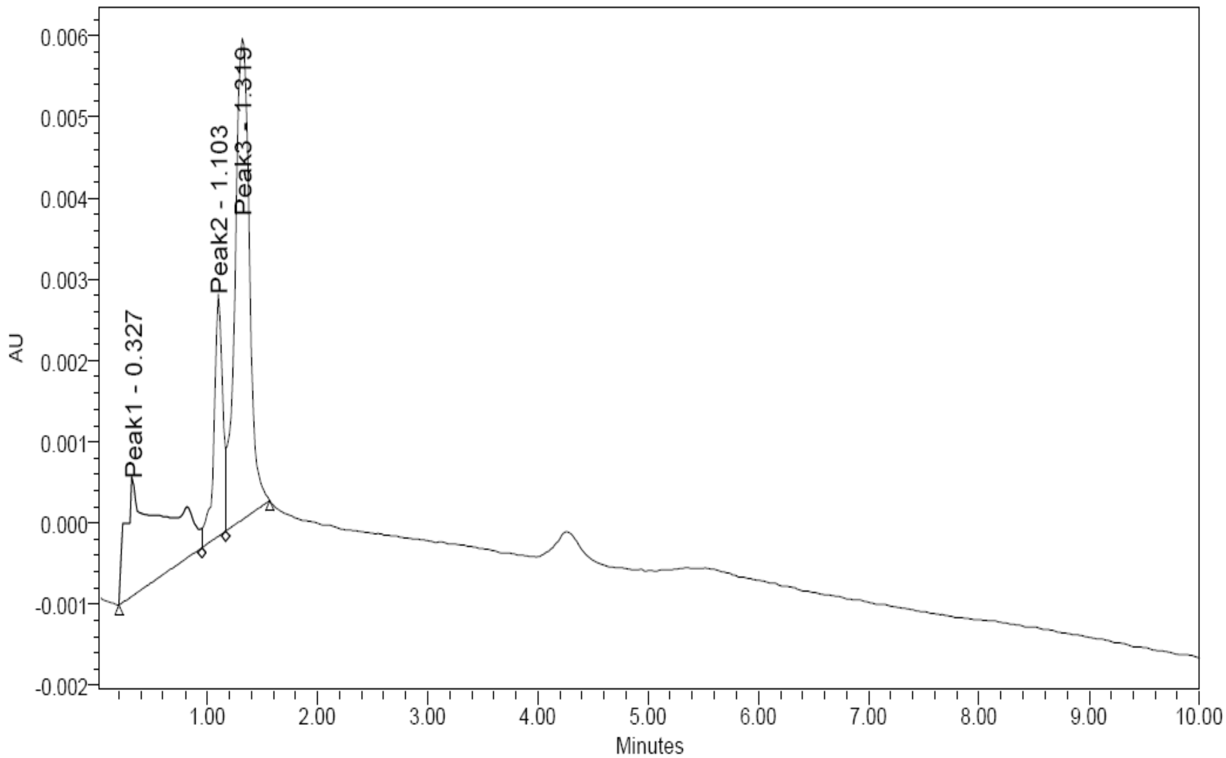

Figure-4
Chromatogram of Water Sample 01 Showing the Absence of DDT

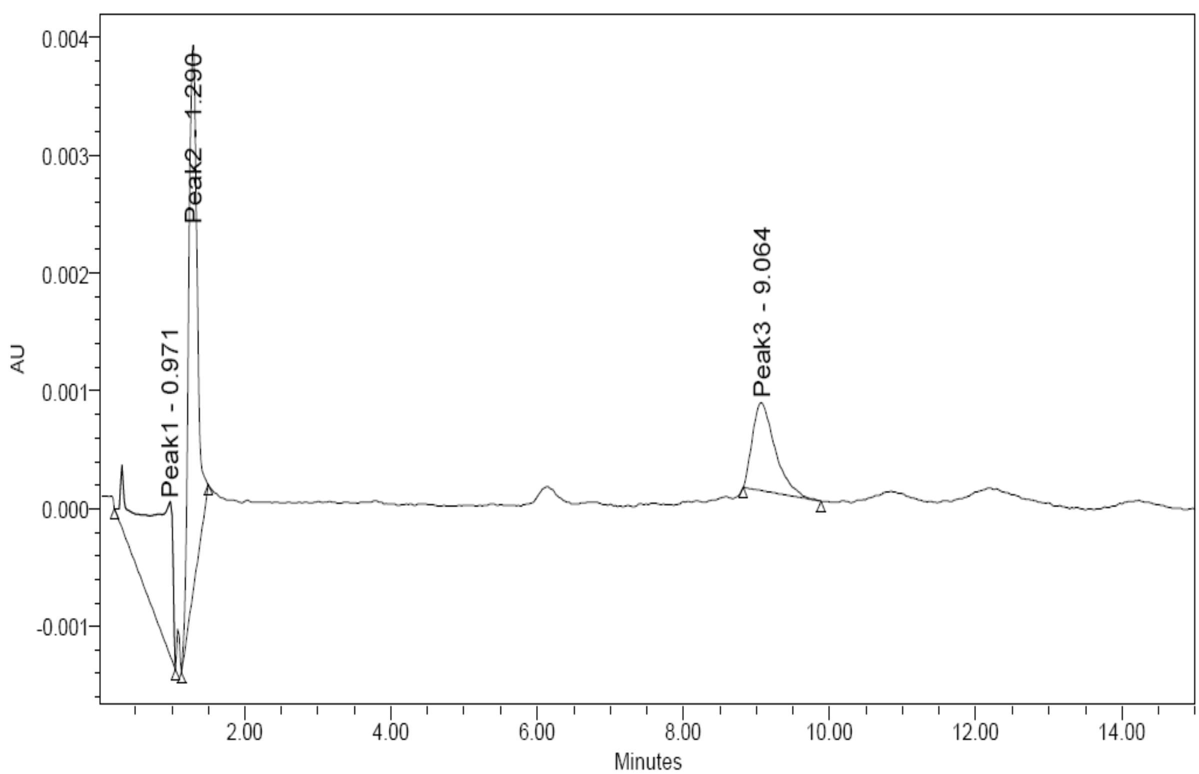

Figure-5
Chromatogram of Soil Sample 01 Showing the Absence of DDT

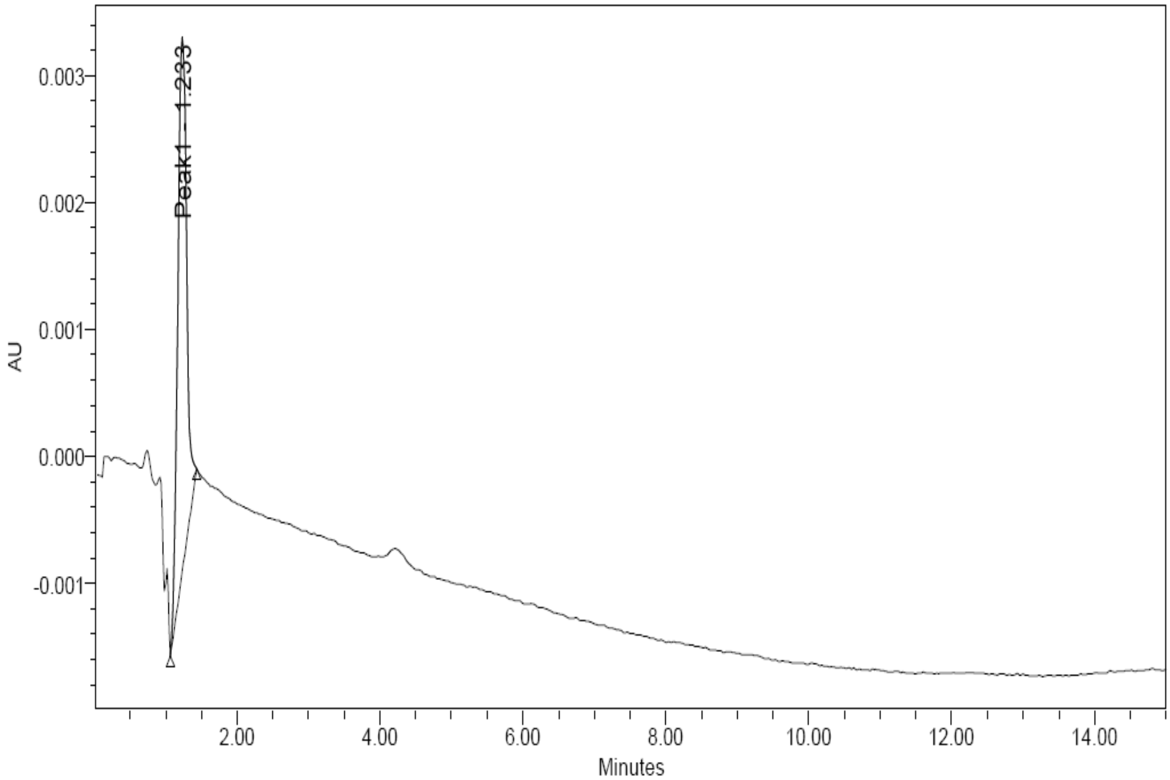

Figure-6
Standard Chromatogram of DDD

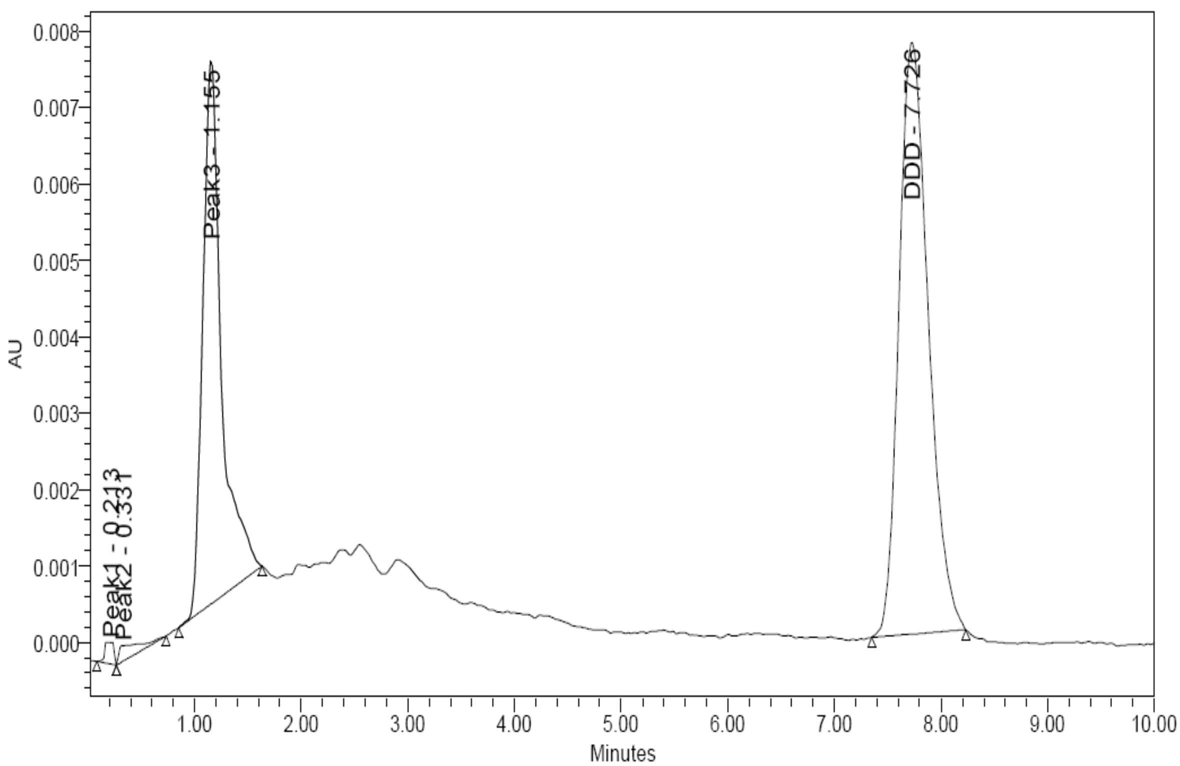

Figure-7
Chromatogram of Water Sample 02 Showing the Absence of DDD

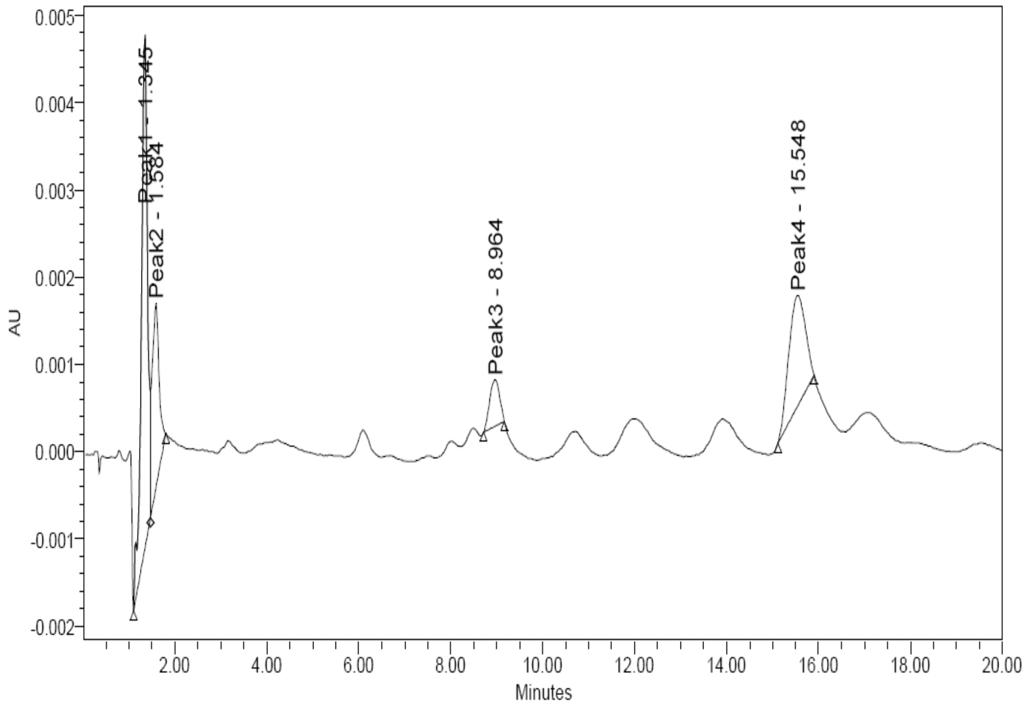

Figure-8
Chromatogram of Soil Sample 05 Showing the Absence of DDD

Figure-9 has been showing the standard chromatogram of Chloropyriphos; the absence of chloropyriphos in water and soil sample (figure-10 and figure-11) respectively; the standard chromatogram of Diazinon (figure-12) and the absence of Diazinon in water and soil sample (figure-13 and figure-14) respectively; the standard chromatogram of Malathion (figure-15) and the absence of Malathion in water and soil sample (figure-16 and figure-17) respectively. It is concluded that there were no Chloripyriphos, Diazinon and Malathion found in Water and Soil Samples of Shrimp-cum-Paddy Farms.

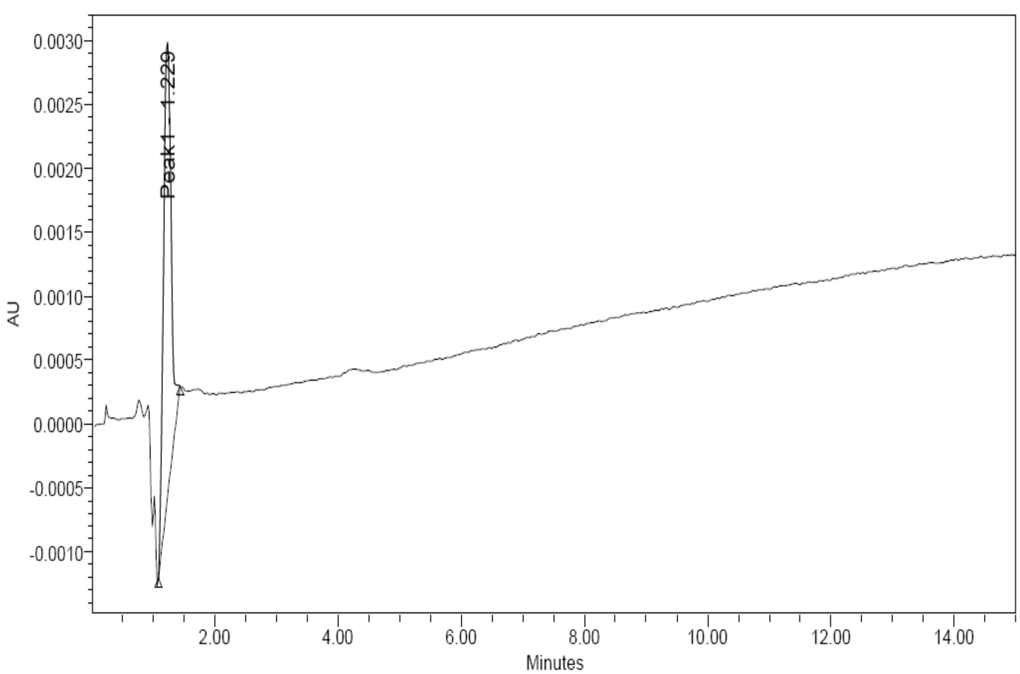

Figure-9
Standard Chromatogram of Chloropyriphos

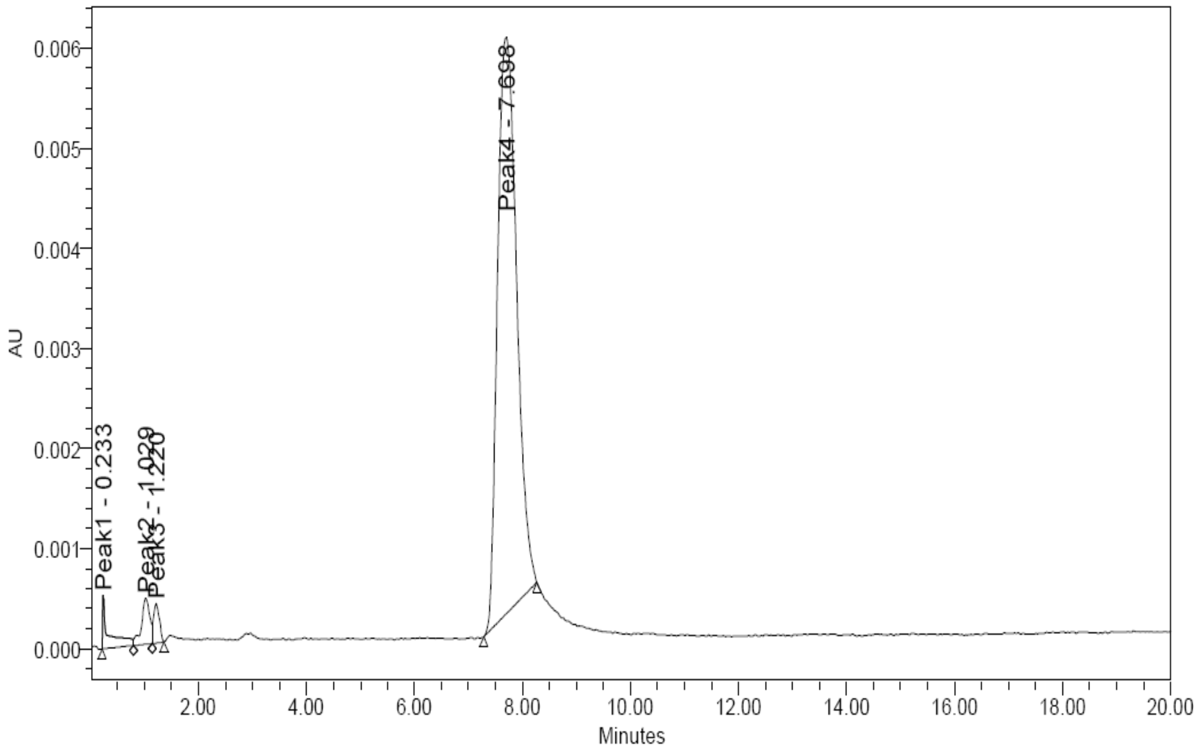

Figure-10
Chromatogram of Water Sample 03 Showing the Absence of Chloropyriphos

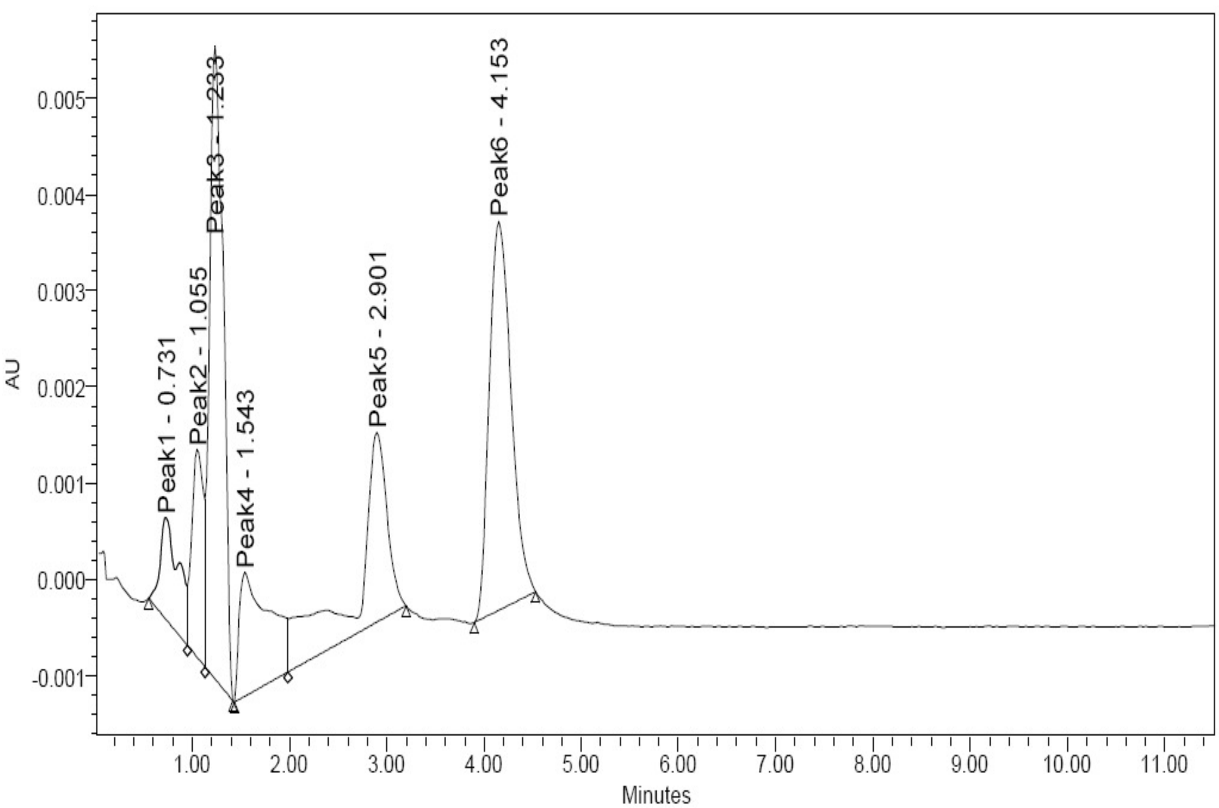

Figure-11
Chromatogram of Soil Sample 03 Showing the absence of Chloropyriphos

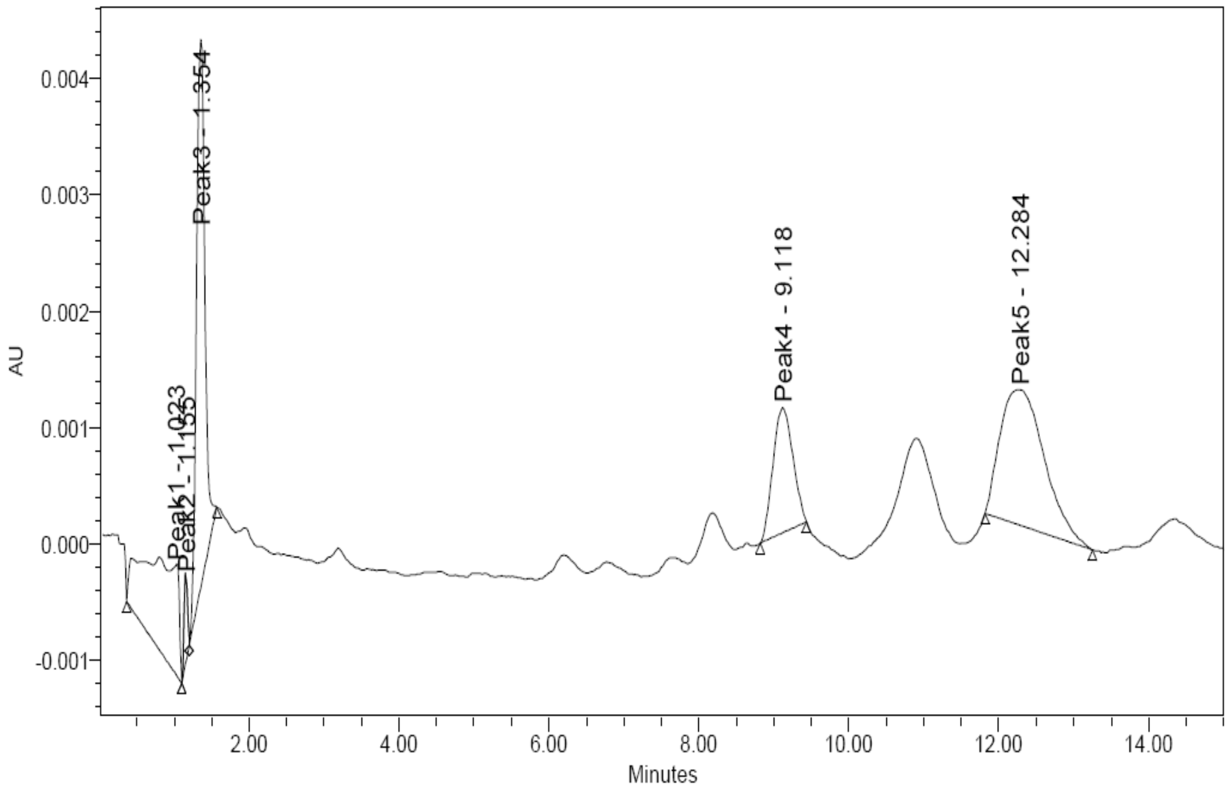

Figure-12
Standard Chromatogram of Diazinon

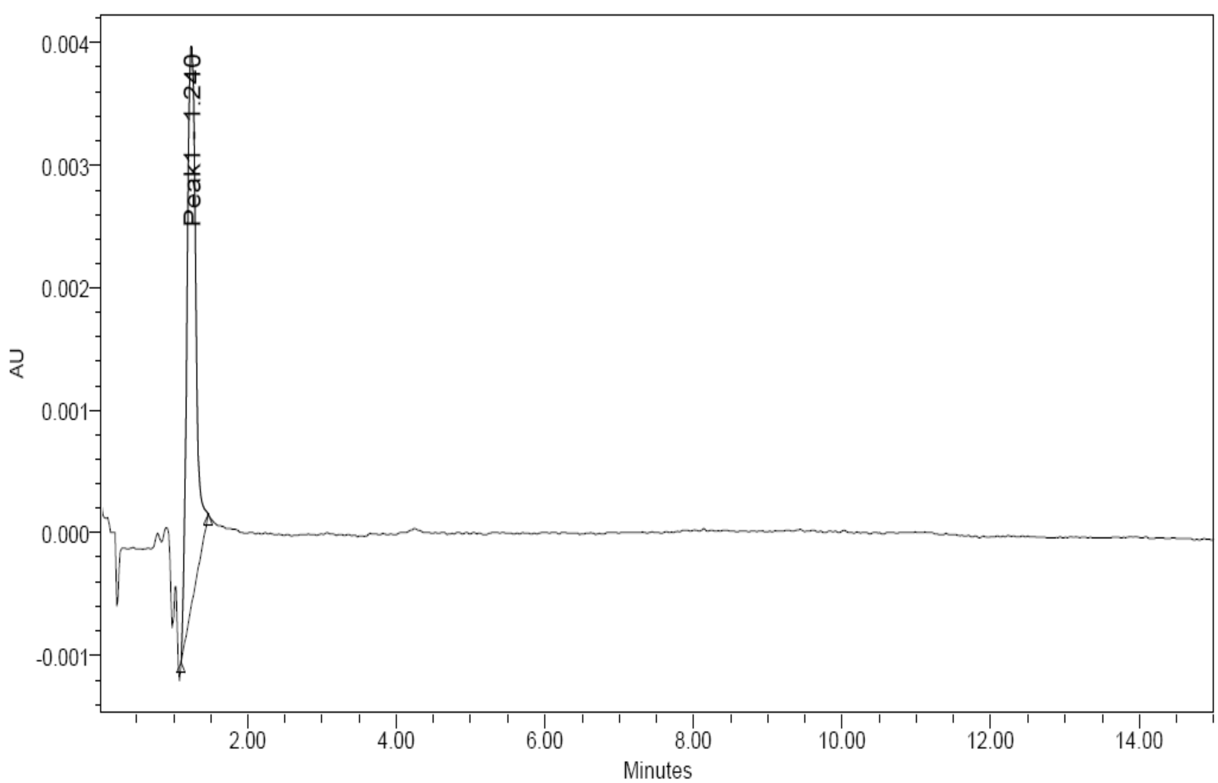

Figure-13
Chromatogram of Water Sample 04 Showing the Absence of Diazinon

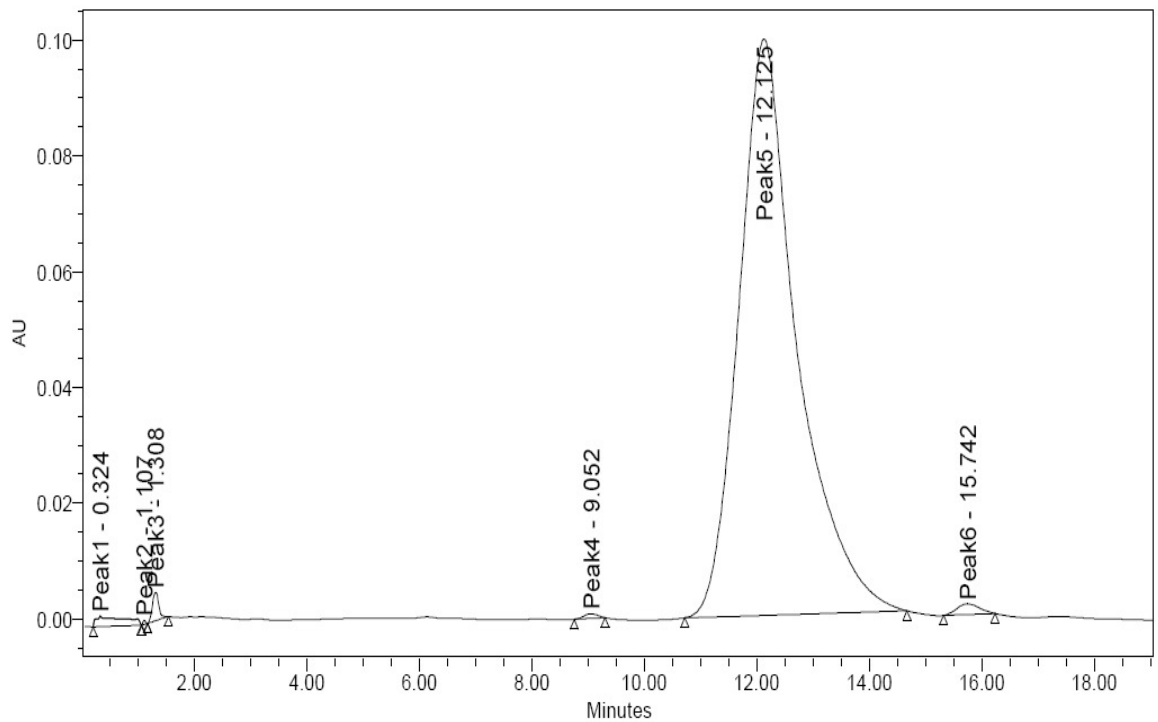

Figure-14
Chromatogram of Soil Sample 04 Showing the Absence of Diazinon

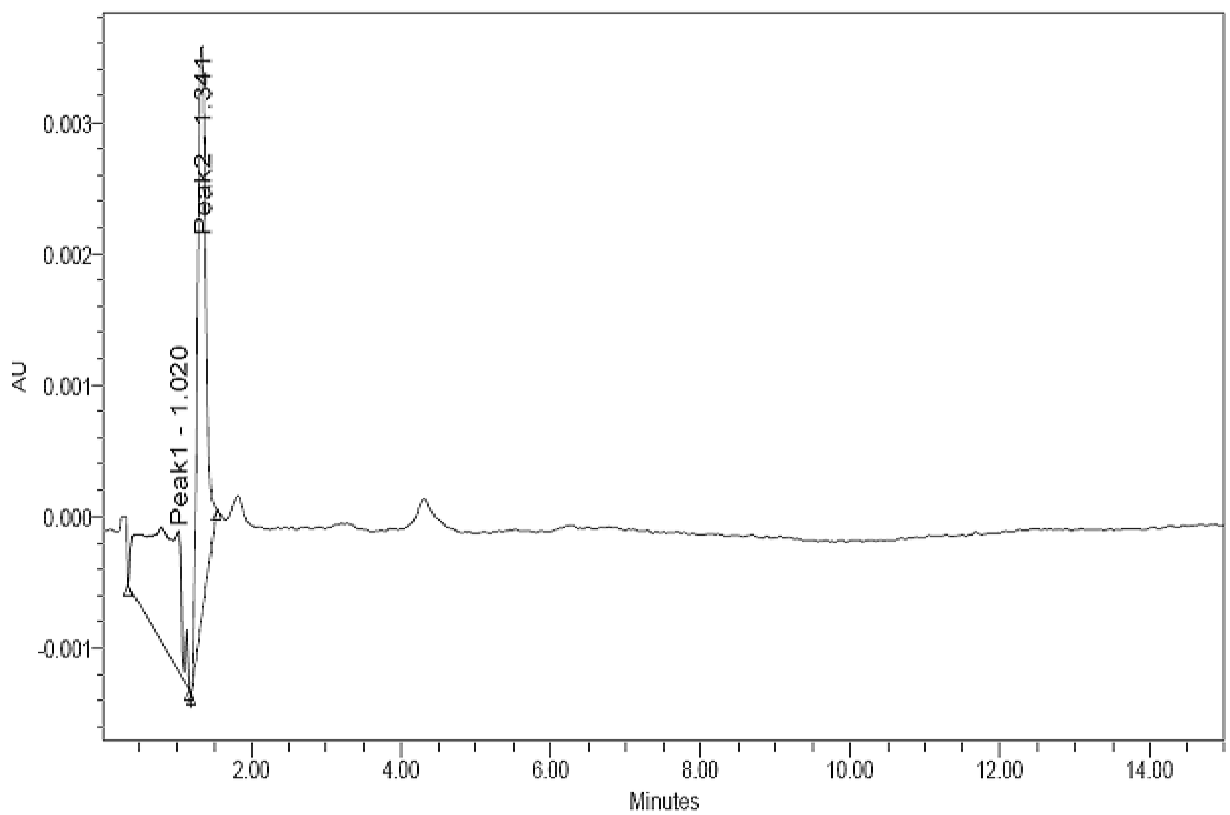

Figure-15
Standard Chromatogram of Malathion

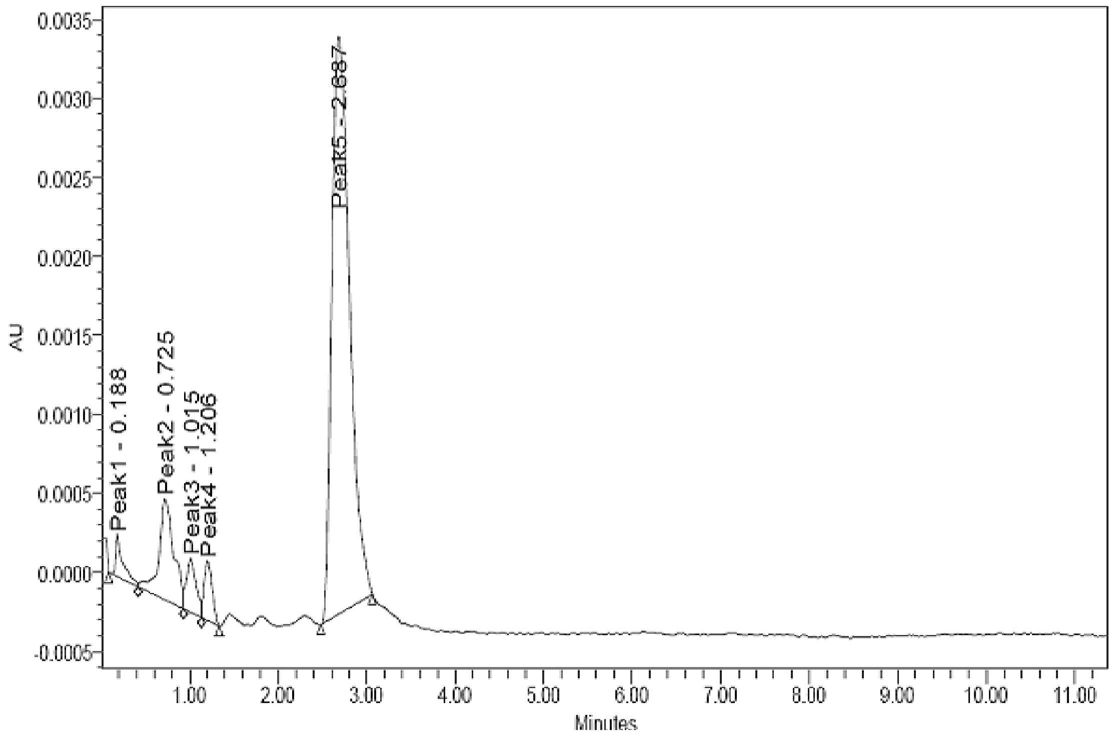

Figure-16
Chromatogram of Water Sample 10 Showing the Absence of Malathion

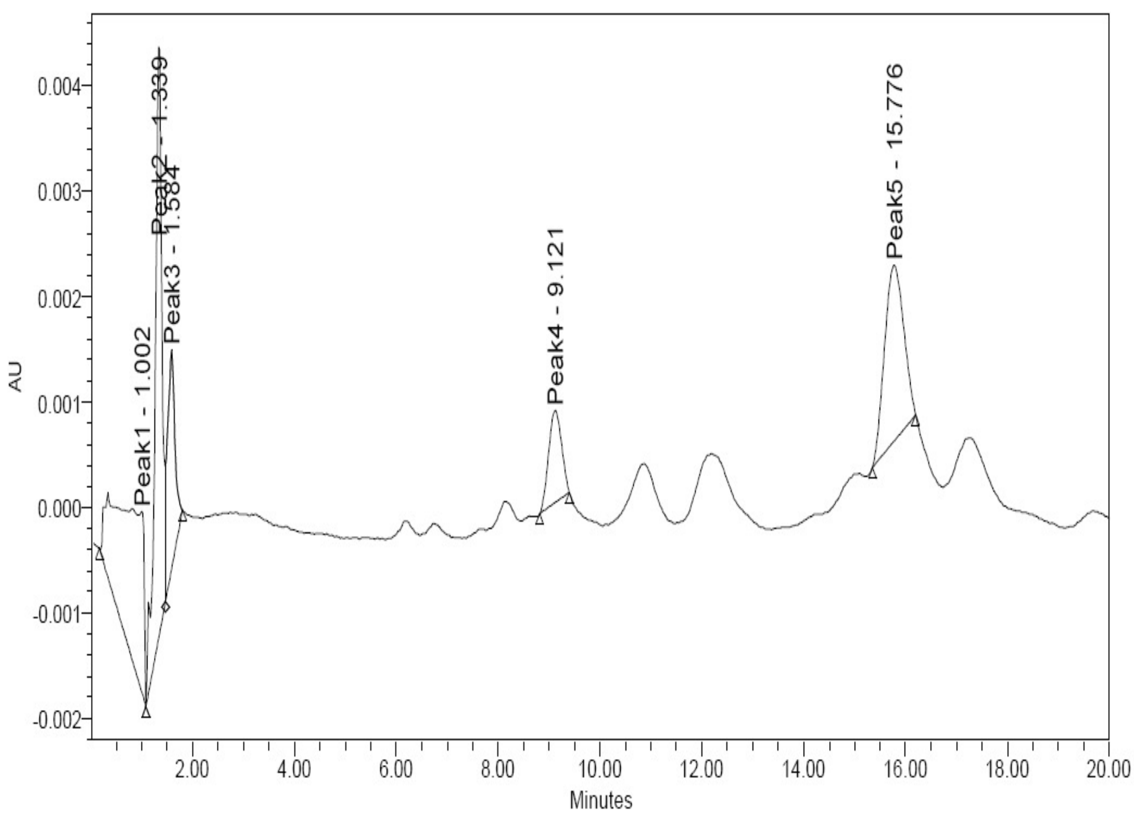

Figure-17
Chromatogram of Soil Sample 10 Showing the Absence of Malathion

Discussion: The present study indicates that no organochlorine pesticides but only organophosphorous pesticides have been applied by the farmers in the shrimp-cum-paddy farming areas of Bagerhat Upazila, Bangladesh. The water and soil samples were collected from this place. Actually, most of the farmers in the study area did not have enough knowledge about the types of pesticides they have been used. They were not aware of the adverse effects of pesticides on environment and exposure effects of pesticides on public health.

During DDT and DDD analysis, the specific peaks found in individual chromatogram obtained from each of the water and soil samples revealed that none of the samples resembled the standard chromatogram peaks specific for them. In some of the soil samples, chromatograms showed some peaks but those were non-specific for DDT and DDD. This might be either due to the presence of unknown chemical pesticides used or unknown contaminants. The unknown contaminants may arise either from the injection syringe or vial or any other source. Thus the results of water and soil sample analysis indicate that possibly DDT was not applied in the study area. This might be the reason of the absence of organochlorine pesticides residues in the water and soil samples of the shrimp farms of Bagerhat upazilla.

Previous studies reported that in Bangladesh, the presence of DDT and DDD in some surface water samples of the irrigated crop fields at Gaibanda and water samples from Begumganj irrigated crop field recorded DDT residues at 19 g/L which is much higher than the WHO guideline value of 2 µg/L[4]. It was found that water samples from the rivers under "Meghna-Dhanogoda Irrigation Project" in Bangladesh contained organochlorine residues at levels of 1.82, 1.91, and 2.39 ng/ml and ranged from 0.2 to 6.75 ng/ml in water samples collected from the irrigation canals respectively. Maximum 5.7 ng/ml of DDT was found in the water samples of this project[5]. A study on water quality aspects related to possible ground water contamination by pesticide residues at Gangachara upazilla under Rangpur District was conducted. Samples were analyzed for the presence of organochlorine pesticides at the Institute of Food and Radiation Biology (IFRB) under Atomic Energy Research Establishment (AERE), Savar but none of the samples contained such pesticides[6]. The ground water samples of Nayarhat (hand tube well) were also found to be apparently free from residues. In most cases residue levels were found to be within WHO guideline values for drinking water quality[7]. Thus the results obtained in our study are not similar with the results of some previous studies for the investigation on organochlorine pesticides conducted in different parts of Bangladesh.

However, organophosphorous pesticides are highly toxic to fresh water invertebrates and therefore pollution with these compounds may adversely affect the natural ecosystems. They are degraded and lost from the environment in various ways. In case of Chloropyriphos, Diazinon and Malathion, analysis of the specific peaks found in individual chromatogram obtained from each of the water and soil samples revealed that none of the samples resembled the standard chromatogram peaks specific for them. In some of the soil samples, chromatograms showed peaks in specific location; however they were non-specific for the organophosphorous compounds. This might be either due to the presence of other organophosphorous pesticides used or unknown contaminants. The unknown contaminants may arise either from the injection syringe or vial or any other source. Thus the results of water and soil sample analysis indicate that although the Chloropyriphos, Diazinon and Malathion organophosphorous pesticides were applied in the study area could not be detected perhaps owing to their limited persistency in the natural environment[8]. The organophosphorous degrades rapidly in soil, oxidation to the corresponding sulfoxide and sulfone and hydrolysis are two major degradation routes of certain alkyl and aryl esters[9]. Another pathway involves reduction to degrade pesticides[10]. Hydrolysis appears to be the major mechanism of Diazinon degradation[11]. The organophosphorous pesticides might have been lost from the water and soil due to exposure to sunlight. During the time of exportation, preservation and sample processing they may also be lost. Adsorption of organophosphorous pesticides by soil has been mostly highly related to the organic matter and clay fractions of soil[12,13]. This group of pesticides is readily absorbed by plants[14]. The rate of degradation of organophosphorous pesticides increases with increased soil moisture content, temperature and acidity[9,15-18]. These factors, all together or individually may enhance the loss of insecticidal activity of organophophorous pesticides by microbial activity. All these mechanisms might be the reason for which the absence of the organophophorous pesticide residues examined in the water and soil samples of the shrimp farms of Bagerhat upazila.

Conclusion

The absence of pesticides in the water and soil samples of the study area may be because sampling was carried out at the end of the shrimp-cum-paddy farming seasons. The pesticides may be incorporated in to the rice and shrimp through food chain and may cause several public health hazards. Due to their fat soluble nature pesticides may be stored in the fatty tissues of shrimp and other fishes. A further study is needed to monitor the pesticide residues in the rice, shrimp and other fishes in the area to assess the risks of public health.

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