# Balawan Joshua Mawrie, Dr. Dibyendu Paul

Department of Environmental Studies, North Eastern Hill University, Shillong- 793022, Meghalaya, India.

Corresponding Author: Balawan Joshua Mawrie

### ABSTRACT

Pesticides are used on a regular basis in the agricultural and health sectors to control pests and vector borne diseases. Although, pesticides have proved to be an important tool in the fight against pest infestation and spread of various diseases but at the same time these chemicals can pose a serious threat to human health, biodiversity and the environment as a whole. A certain group of pesticides which are categorized as organochlorines are known for their persistence in nature and have the ability to bio-accumulate. Some of these organochlorine pesticides are toxic and are even classified as probable and possible human carcinogens by the International Agency for Research in Cancer. It is for a number of reasons like these that several of them have been banned in many countries including India. The main objective of this study was to investigate whether the food that were sold in a market in Shillong City were contaminated or not by three banned organochlorine pesticides, namely, Dieldrin, Heptachlor and Endosulfan. In this study, samples of nine food products (apple, grapes, tomato, lettuce, potato, cabbage, wheat, rice and pulses) were collected from Iewduh Market and analysed for any contamination levels. The analysis was carried out by Gas Chromatography Mass Spectrometry using standard operating procedures. The results of this study revealed that the residual levels of the pesticides that were studied were Below Detectable Limit (<0.1 mg/kg) in all the samples of the food products that were chosen for the purpose of this study.

Keywords: Banned organochlorine pesticides, Dieldrin, Heptachlor and Endosulfan.

#### **INTRODUCTION**

For an agrarian nation like India, agricultural production is of utmost importance as it has to support a population of approximately 1.3 billion people. Agricultural production also plays a major role in maintaining the health of the economy. Sustaining production can be a major challenge and there are many hurdles that can be encountered. One of the key problems that decrease crop production is the losses faced due to pest infestation and diseases. Monetarily, India incurs crop losses to the tune of 36 billion U.S. dollars annually (Dhaliwal et al., 2015). <sup>[1]</sup> Globally, to tackle this menace the use of pesticides has been employed in a number of ways resulting in favourable outcomes to some extent. According to the World Health Organisation a pesticides are described as any chemical compounds that can be used to kill pests such as insects, rodents, fungi and disease carrying vectors and are required to be used and managed properly as they are potentially toxic to other organisms including human beings. <sup>[2]</sup> Pesticides use

dates back thousands of years when substances such as compounds of sulphur, mercury, arsenic were used to tackle pest by the Sumerians and Chinese. However, it was up until the 1940's that synthetic pesticides came into the picture and were began to use in a much wider scale to control pest in the agricultural and health (John sector Unsworth, 2010).<sup>[3]</sup> Pesticides have been classified in a number of ways, they can be classed as contact pesticides where they have to come in contact with the body of the pest for a desired reaction or as systemic pesticides where they get absorbed into the plant vascular system and exhibit their anti pest properties when the plant is ingested by a pest. Pesticides are also categorized based on their target groups, for example, insecticide. fungicide, rodenticide. herbicides molluscicides, bactericides, avicides, virucides, algicides acaricides and miticides (Zacharia, 2011).<sup>[4]</sup> Another form of pesticide classification is based on their chemical makeup and there are four main namely; organochlorines, groups organophosphates, carbamates and pyrethrin or pyrethroids (Garcia et al., 2012).<sup>[5]</sup> Pesticides have greatly reduced crop losses due to pests; however, it is a well known fact that they pose a major threat to biodiversity as well as human health due to their toxic nature. Of the four main groups of pesticides that have been mentioned, organochlorines are notoriously known for being highly persistent in nature and have the ability to bio-magnify as we go higher up the food chain. Roberts and Reigart (2013)revealed that ingestion of organochlorine pesticides can lead to severe health complications and affect the nervous system in particular and also stated that some organochlorines have the potential to be carcinogenic and interfere with endocrine receptors. <sup>[6]</sup> Even low level chronic exposure to organochlorines can impact the health and well being of human beings. It is this reason that a number for of organochlorine pesticides have been banned or restricted for use under the Indian law and the same have been enlisted by the

Central Insecticide Board and Registration Committee, Ministry of Agriculture and Farmer Welfare. <sup>[7]</sup> Although, stringent measures are in place to check the use of banned pesticides, but it is of utmost importance that monitoring studies are carried on a regular basis. One such investigation is to analyse the level of pesticide residues in food products in order to assess the risk faced by the general exposure population of to banned organochlorines which may still be illegally used in the agricultural sector. For the purpose of this study sample of three fruit products: apple, grapes and tomato; three vegetable products: cabbage, lettuce and potato; and three cereals and pulses food products: wheat, rice and pulses were collected from a local market in Shillong City and were analysed for any possible contamination by three organochlorine pesticides which are banned or restricted for use in India. The four pesticides in question are as follows:

*Dieldrin:* Scientifically, it is known as; 1,2,3,4,10,10-hexachloro-6,7-

epoxy1,4,4α,5,6,7,8,8α-octahydro-1,4-

endo,exo-5,8-dimethanonaphthalene. It is use as a pesticide itself, but it is also a break down product of aldrin. It poses a threat as it is persistent in nature and has been classed as a probable human carcinogen by the U.S. Environmental Protection Agency.<sup>[8]</sup>

*Heptachlor:* as per the toxicological profile provided by the Agency for Toxic Substances and Disease Registry (2007), Heptachlor is a breakdown product of chlordane and technical heptachlor itself is used as a pesticide. In nature heptachlor is broken down into heptachlor epoxide. It is classified as a possible human carcinogen by both the International Agency for Research on Cancer and Environmental Protection Agency.<sup>[9]</sup>

*Endosulfan:* It is a broad spectrum contact insecticide used for the control of pest in several fruits, vegetables and grains. It is persistent in nature and can have adverse effects with children being more vulnerable to health impacts associated with exposure

to endosulfan such as mental retardation, deformities. congenital anomalies and reported cerebral palsy as bv the Government of Kerala through the Department of Health and Family Welfare in 2011. <sup>[10]</sup>

The Central insecticide Board and Registration Committee have listed Dieldrin and Heptachlor under the banned category whereas Endosulfan was listed under the category of restricted for use.<sup>[7]</sup> However in an ad interim order which came out on May, 2011 the Honourable Supreme Court of India has banned the production sale and use of Endosulfan in the country.<sup>[11]</sup> This study is important to reveal if there is any contamination of several food products with the above mentioned organochlorine pesticide as they can prove to be a serious threat to the health of the general population of Shillong.

### **Study Area:**

This study was conducted in Shillong City which is the state capital of Meghalaya, a state within the Indian

Territory and located in its North Eastern Region. Though small in size, Shillong is a bustling city with a population of around 0.14 million people (2011 census). [12]Within this city there is one main market locally called Iewduh or Bara Bazar where a majority of food products come in from various parts of the country for sale. Many local framers also bring their produce to trade in this market. Iewduh serves as a common platform which supplies the rest of the smaller markets within the city with the bulk of the food products. In turn, a major part of the population of Shillong City relies on this market to meet their daily food needs. This market provides for a very suitable sampling area for any food product related study. Therefore, using this market as an area for collecting food samples for the purpose of this study can significantly suggest the level of risk faced by the population of this city from any possible contamination of food with organochlorine pesticide residues.



Plate 1: Vegetable selling Section of the Market

## **METHODOLOGY**

Sampling: one kilogram of each of the food products were collected from 5 random areas of the market totaling to 5 kilograms for each of the food products. These are then taken to the laboratory and a five hundred gram composite sample was then segregated and analysed for any possible contamination with the pesticide residues.

Chromatography-Mass Analysis: Gas Spectrometry (GC-MS) is analytical method that has been used to carry out a number of



Plate 2: Fruits being sold at the Market

pesticide based studies. <sup>[13-15]</sup> Analysis of the sample was conducted at the Institute of Pesticide Formulation Technology, New Delhi. The samples were analysed using Gas Chromatography-Mass Spectrometry (GC-MS) following standard operating procedures. GC-MS is a technique that is widely applied in the field of pesticide residue study.

Sample preparation: Before introducing the sample into the GC-MS it needs to undergo sample preparation and this can be

achieved by a number of methods such as QuEChERs, <sup>[16-18]</sup> Soxhlet Extraction, <sup>[19-21]</sup> Solid Phase Micro-Extraction, <sup>[22-24]</sup> amongst many others.



Plate 3: Tomatoes collected for composite sample

Separation and Quantification: After the process of sample preparation the sample is then introduced into the GC-MS where it undergoes a series of processes. The different steps involved in this procedure includes injection of the sample through the injection port where it volatilizes after which the mixture is carried by a carrier gas which represents the mobile phase through the Gas Chromatography Column that is packed with materials such as silica which represent the stationery phase. Depending on the behaviour of the mixture passing through the stationery phase, it gets separated into its various components. The separated compounds of the sample then enter the Mass Spectrometer where they are ionised and quantification takes place. One important factor to note is the instrument conditions. Analysis of different substances requires different GC-MS conditions. The instrument conditions for analysis of pesticides using this technique as described by Goodman (2012) of Perkin Elmer include GC-column of 30m x 0.25mm x 0.25µm dimensions, helium as the carrier gas, injector temperature of 275°C, split less injection type and oven temperature program of 80°C hold time of 0 minutes at the rate of 20°C/min then 290 °C hold time of 4.75 minutes. As for the Mass Spectrometer the conditions that were explained include GC Inlet Line Temperature of 275 °C, Ion Source Temperature of 275 °C, SIFI (selected ion full ion) function type, scan range of m/z 40-450, scan time of 0.2 seconds and Inter Scan Delay of 0.1 seconds.<sup>[25]</sup> **RESULT** 

The analysis of the food samples collected from Iewduh Market in Shillong for pesticide residues of three organochlorine pesticides, namely; dieldrin, heptachlor and endosulfan which are banned in India yielded desired results. The GC-MS analysis showed that the samples of all the food products chosen for the purpose of the study revealed that the pesticide residues were Below Detectable Limit (<0.1 mg/kg). This anticipated outcome of the study conducted is given in the table below.

Table	1: Pe	sticid	e res	idue	(mg	(kg)	In Fi	ruit	Samples.	
	a		-		-					

Sl. No.	Sample	Pesticide Residues (mg/kg)			
		Dieldrin	Heptachlor	Endosulfan	
1.	Apple	< 0.1	< 0.1	< 0.1	
2.	Grapes	< 0.1	< 0.1	< 0.1	
3.	Tomato	< 0.1	< 0.1	< 0.1	

 Sl. No.
 Sample
 Pesticide Residues (mg/kg)

51. INO.	Sample	Pesticide Residues (Ing/kg)				
		Dieldrin	Heptachlor	Endosulfan		
1	Lettuce	< 0.1	< 0.1	< 0.1		
2.	Potato	< 0.1	< 0.1	< 0.1		
3.	Cabbage	< 0.1	< 0.1	< 0.1		

Table 3: Pesticide Residues (mg/kg) In cereal and pulses Samples.

Sl. No.	Sample	Pesticide Residues (mg/kg)				
		Dieldrin	Heptachlor	Endosulfan		
1.	Wheat	< 0.1	< 0.1	< 0.1		
2.	Rice	< 0.1	< 0.1	< 0.1		
3.	Pulses	< 0.1	< 0.1	< 0.1		

The result of the study shows that the samples of the food products that were selected for the analysis (apple, grapes, tomato, lettuce, potato, cabbage, wheat, rice and pulses) were free from any harmful levels of contamination by the banned organochlorine pesticides (dieldrin, heptachlor and endosulfan) that were opted for examination.

#### DICUSSION

This study whose main aim was to monitor any form of contamination of various food products with three banned

organochlorine pesticides that have the ability to compromise the health of the general population revealed a favourable outcome. The residual levels of Dieldrin, Heptachlor and Endosulfan in all the food samples of apple, grapes, tomato, lettuce, potato, cabbage, wheat, rice and pulses were all Below Detectable Limit which indicates that these food products may be free from being contaminated by at least these three banned organochlorine pesticides. This may imply that a majority of the food products that are available at the Iewduh Market may from banned organochlorine be free pesticides. However, to ensure the certainty that the food products are free from banned pesticides, further such pesticide based studies are required. This study also puts into light that when it comes to the three pesticides that were studied, the Government has been successful in implementing the banned on them and protecting the general population of the City of Shillong from the negative impacts of ingesting these pesticides along with the food that they eat. Although, this study showed the desired results, there are still a number of other banned pesticides that might be still used in the field of agriculture that can pose a serious threat to the well being of the people. Apart from the banned pesticides, there are a numerous number of other pesticides and chemicals which may prove detrimental to the health of the population that are still legally used up to this day. This is evident even in India where numerous pesticides that are banned elsewhere are still permitted for use in the country at various capacities. <sup>[26]</sup> Therefore, more concrete efforts from all sectors of society are required to ensure that the food we eat is safe. A move towards sustainable organic farming practices and proper implementation of food safety rules and regulations will be helpful in the step to attain food products free from harmful synthetic chemicals.

## CONCLUSION

This study provides much needed information regarding the status about whether the food products that have been collected from Iewduh Market are contaminated by banned Dieldrin. Heptachlor and Endosulfan or not. It also reflects on the successfulness of the banned that have been implemented on various organochlorine pesticides including these three. The results of this investigation reveals that the population of Shillong City are not subjected to any health risk with regard to their food being contaminated by Dieldrin, Heptachlor and Endosulfan. However, there are several chemicals that can contaminate our food and potentially compromise our health. Therefore, it is essential that monitoring studies for food contaminants are conducted on a regular basis to ensure that the general public are not consuming toxic substances with their food. Such studies are also necessary to add further information to the database relating to food being contaminated by harmful chemicals, especially for regions or cities where there is limited or no information with this regard.

#### **ACKNOWLEDGEMENTS**

We would like to express our gratitude to the Institute of Pesticide Formulation Technology for helping us with the analytical portion of the study. We also convey our heartiest thanks to the farmers, dealers and retailers who were at Iewduh Market for their cooperation in making this study possible. I would also like to extend my appreciation to Dr. D Paul for all the financial help with regard to the study.

#### **REFERENCES**

- 1. Dhaliwal GS, Vikas Jindal, Bharathi Mohindru. Crop Losses Due To Insect Pest: Global and Indian Scenario. Indian Journal of Entomology. 2015; 77(2): 165.
- 2. http://www.who.int/topics/pesticides/en/ (Retrieved on 18/3/2018).
- 3. Unsworth John. History of Pesticide. International Union of Pure and Applied Chemistry. 2010. Available from

http://agrochemicals.iupac.org/index.ph p?option=com\_sobi2&sobi2Task=sobi2 Details&catid=3&sobi2Id=31. (Retrieved on 18/3/2018).

- Zacharia, James Tano. Identity, Physical and Chemical Properties of Pesticides, Pesticides in the Modern World -Trends in Pesticides Analysis, Dr. Margarita Stoytcheva(Ed.), InTech. 2011. Available from http://www.intechopen.com/books/pesti cides-in-the-modern-world-trendsinpesticidesanalysis/identity-physicaland-chemical-properties-of-pesticides. (Retrived on 20/3/2018).
- 5. Garcai PF, Ascencio CY, Sandra, Ovarzun GCJ. Hernandez CA. V P. Alavarado Pesticides: classification. uses toxicity. and Measures of exposure and genotoxic Journal of Research risks. in Environmental Science and Toxicology (ISSN: 2315-5698). 2012; 1(11): 281-282.
- Roberts R. James, Reigart Routt J. Recognition And Management of Pesticide Poisonings. 6<sup>th</sup> ed. Office of Pesticide programs. U.S. Environmental Protection Agency. 2013. 63-64.
- http://cibrc.nic.in/list\_pest\_bann.html. (Retrieve on 20/3/2018).
- 8. U.S. Department of Health and Human Services. Toxicological Profile for Aldrin and Dieldrin. Atlanta: Agency for Toxic Substances and Disease Registry. September 2002. 1-4.
- 9. U.S. Department of Health and Human Services. Public Health Statement Heptachlor and Heptachlor Epoxide. Atlanta: Agency for Toxic Substances and Disease Registry. 2007. 1-3.
- Department of Health and Family Welfare, Government of Kerala. Report on Health Effects of Endosulfan and Progress of Rehabilitation Activities in Kerala: Endosulfan The Kerela Story. Kerela; 20<sup>th</sup> April 2011. 64p.
- 11. Press Information Bureau. Ban on Endosulphan. Ministry of Health and Family Welfare, Government of India. 2014.

http://pib.nic.in/newsite/PrintRelease.as px?relid=107462. (Retrived on 19/3/2018)

- 12. http://www.census2011.co.in/census/cit y/187-shillong.html. (Retrived on 20/3/2017)
- Baheer Chanbasha, Lee Kee Hian, Obbard Philip Jeffrey. Determination of organochlorine pesticide in sea water using liquid-phase hollo fibre membrane microextraction and gas chromatography-mass spectrometry. Journal of Chromatography A. 2002; 968, 191-199.
- 14. Nguyen Dong Thanh, Yu Eun Ji, Lee Myung Dae, Lee Gae-Ho. A multiresidue method for the determination of 107 pesticides in cabbage and radish using QuEChERS sample preparation method and gas chromatography mass spectrometry. Food Chemistry. 2008; 110, 207-213.
- Ozcan Cemile. Determination of Organochlorine Pesticides in Some Vegetable Samples Using GC-MS. Pol. J. Environ. Stud. 2016; 25(3), 1141-1147.
- 16. Cieslik Ewa, Sadowska-Rociek Anna, Ruiz Molina Manuel Juan, Surma-Zadora Magdalena. Evaluation of QuEChERS method for the determination of organochlorine pesticide residues in selected groups of fruits. Food Chemistry. 2011; 125, 773-778.
- 17. Wilkowska Angelika, Biziuk Marek. Determination of pesticide residues in food matrices using the QuEChERS methodology. Food Chemistry. 2011; 125, 805-812.
- Ravikumar Ch, Srinivas P, Seshaiah K. Determination of organochlorine residues in rice by gas chromatogramphy tandem mass spectrometry. Journal of Chemical and Pharmaceutical Research, 2013; 5(1): 361-366.
- Barriada-Pereia M, Concha-Grana E, Gonzalez-Castro JM, Muniategui-Lorenzo S, Lopez-Mahia P, Prada-Rodriguez, Fernandez-Fernandez E. Microwave-assisted extraction versus Soxhlet extraction in the analysis of 21 organochlorine pesticides in plants. Journal of Chromatography A. 2003; 1008, 115-122.
- 20. Ahmed EF. Analysis of pesticides and their metabolites in food and drinks.

Trends in Analytical Chemistry. 2001; 20(11), 649-659.

- Kannan Kurunthachalam, Tanabe Shinsuke, Ramesh Aramandla, Subramanian Annamalai, Tatsukawa Ryo. Persistent Organochlorine Residues in Foodstuffs from India and Their Implications on Human Dietary Ecposure. J. Agric. Food Chem. 1992; 40, 518-524.
- 22. Hu Renwei, Hennion Bernard, Urruty Louise, Montury Michel. Solid phase microextraction of pesticide residues from strawberries. Food Additives and Contaminants. 1999; 16(3), 111-117.
- 23. Hernandez Felix, Beltran Joaquim, Lopez J Francisco, Gaspar V Jose. Use of Solid-Phase Microextraction for the Quantitative Determination of Herbicides in Soil and Water Samples.

Analytical Chemistry. 2000; 72, 2313-2322.

- 24. CDS Silveira, Carasek E. Determination of organochlorine pesticide in leather by solid-phase microextraction and gas chromatography- mass spectrometry. Scientia Chromatographica. 2015; 7(2), 117-123.
- 25. Goodman William. The Application of GC/MS to the Analysis of Pesticides in Foodstuffs. Perkin Elmer. 2012
- 26. Press Trust of India. Use of pesticides elsewhere allowed in India, Business Lines, The Hindu. 7<sup>th</sup> December 2016. p 1. (Retrieved on 13/10/2017). http://www.thehindubusinessline.com/e conomy/agri-business/use-of-51pesticides-banned-elsewhere-allowedin-india-centre-tells-highcourt/article9416251.ece

How to cite this article: Mawrie BJ, Paul D. Monitoring of banned organochlorine pesticide residues in several food products from a market in Shillong city, India using gas chromatography - mass spectrometry. Int J Health Sci Res. 2018; 8(5):265-271.

\*\*\*\*\*\*\*\*