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Chlorinated Pesticide Residue Status in Tomato, Potato and Carrot

M.T.I. Chowdhury*, M. A. Razzaque and M. S. I. Khan

Department of agricultural Chemistry, Sher-e-Bangla Agricultural University, Dhaka-1207, Bangladesh

ABSTRACT: A study was carried out to identify the bioaccumulation and the ascertain level of chlorinated pesticide residues in some vegetables collected from market baskets of New market, Dhaka, Bangladesh namely potato, tomato and carrot. The samples were randomly collected from different shops and analyzed by capillary column of Gas Chromatograph Mass Spectrometry (GCMS) with Electron Impact Ionization (EI) method for the detection of chlorinated pesticide. The results of the study revealed that collected samples of potato, tomato, red amaranth and spinach were contaminated with some chlorinated substances. But Indian spinach and carrot were free of contamination with organochlorine pesticide.

Key words: Pesticide residues, Environmental pollution, Toxicology, Vegetables, Health hazard

Introduction

Bangladesh is an agricultural country where more than 80% of the people depend on agriculture for their livelihood. Since there is no scope for horizontal expansion of land area, to achieve the targeted level of food production, the major emphasis has, therefore, been given on increasing the existing level of productivity of different crops through wider adoption of cost effective technologies, bringing more areas under high yielding varieties, hybrid and increasing the cropping intensity with the help of irrigation facility along with use of chemical fertilizers and pesticides (Mukhopadhay, 2005). Now-a-days the use of pesticides has become indispensable in increasing vegetable crop production because of its rapid effect, ease of application and availability.

The use of synthetic organic pesticides, DDT and other organochlorine compounds, began in this country in early 1950's for both agriculture and public health purposes. Bangladesh has been and still is, predominantly, an insecticide consuming country. Up to the present time pesticides belonging to organochlorines, organophosphates, organocarbamates and relevantly small volume of pyrethroid compounds have been used (Rahman , *et al.* 1995).

Over use of pesticides in crop fields has lead to decreased biodiversity of flora and fauna. Residues are present in all compartments of agro-ecosystems, but perhaps the most real risk of human is through consumption of residues in food as vegetables (Price, 2008). Reliable data are needed concerning the presence of pesticides outside the targets in order to set priorities for actions to remedy and prevent pollution and to follow the effect of action taken.

Farmers of Bangladesh in general use many types of pesticides to control harmful insects to minimize crop losses. As most of our people are illiterate they use pesticides indiscriminately. The indiscriminate use of pesticides against the pest cause several problems viz., insecticide resistance, toxic residues in vegetables, killing of natural enemies and ultimately pest resurgence. These harmful pesticides are dissolved in our water system and ultimately enter into the system of human, fishes and many other animals and cause severe damage to their health (Khandakar, 1990).

All pesticide compounds potentially pose environmental hazards as they are chemically tailored to be toxic. While causing lethal effect to target pests, these chemicals may evoke acute and chronic toxic effect to non - target organisms. An intensified use of pesticides can cause a serious public health hazard especially in the form of residues in food (Mansingh, *et al.*1996).

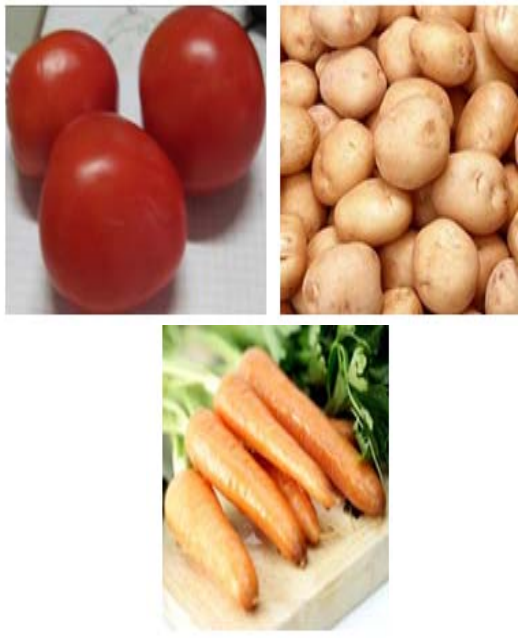
Vegetables are very important group of crops and they constitute major part of the human diet contributing nutrients and vitamins. Many farmers in the villages have taken up vegetable production on commercial basis and some grow them in home gardens. But in the urban areas people depend on the market for their vegetable requirements. These market vegetables mostly contain pesticide residue because of their over use in the field, which cause harmful effect for the human health. To assure safety of the consumers, many of the developed countries have set maximum residue limit (MRL) based on the acceptable daily intake (ADI) and potential daily intake (PDI) which should not be exceeded in food item. In Bangladesh context, since harvesting and selling of vegetables of economic importance are done without bothering for the postharvest interval of insecticide use, insecticide residue levels in in those vegetables would mostly go above MRL.

Selling of vegetables after 1-2 days of spraying pesticides has become a normal practice in most of the areas of Bangladesh. A few pesticides are available in Bangladesh whose retention period is less than 3-5 days. Macintyre *et al.*, (1989) reported that low level exposure of food products containing pesticides residue to consumers' products over time and again might cause cancer, teratogenesis, genetic damage and suppression of the immune system. So, it is very important to determine the pesticide residue level in different crops such as tomato, potato etc.

Modern pesticide residue analysis in develop countries is focusing more and more on subtle problems, such as looking for very low concentrations of pesticides in the environment. For this, complicated and expensive equipments like- gas chromatograph, high performance liquid chromatograph, mass spectrometer etc are being used.

Therefore, it is very clear that pesticide residue problem is becoming serious focused human health and environmental hazard due to indiscriminate pesticides application. The present study was therefore undertaken to determine the presence and concentration of persistent organic pollutants (PoPs) in some selected vegetables and to determine the presence and concentration of harmful organochlorinated pesticide residues in three selected vegetables.

Fig. 1. Collected vegetable samples



* *Corresponding Author, Email: mhzsauag@yahoo.com*

Materials and Methods

The research work was performed in the laboratory of the Analytical Research Division, Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh.

Experimental materials

Samples were collected from different vendors of vegetable market. About 1.0 kg each of three vegetables viz. tomato (*Lycopersicon esculentum*), potato (*Solanum melongena*) and carrot (*Daucus carrota*) were purchased from different vendors to prepare composite samples for detection of the presence of organochlorinated pesticides if any there in.

Analytical methods

For identification of organochlorine pesticides (OCP) and persistent organic pollutants (PoPs) in vegetables following analytical extraction methods were used proposed by Gohlki and Mclafferty (1993).

Exactly 250 g of each item of vegetable was taken for analysis. Each sample was sliced on chopping board and tissues were dissected from the vegetable. Chopped in small pieces and mixed thoroughly. Each sample was macerated in a mortar. Ground samples were taken in a conical flask. 250 mL of each solvent, n-Hexane and 95% ethyl alcohol was added and the mixture was shaken, preferably mechanically for 1 hour. 50 gm of anhydrous sodium sulfate was added before mixing to remove excess water (Gohlki and Mclafferty, 1993). The extract was filtered through the filter paper, until no solvent remained into the conical flask. The amount of extracted solution was about 100ml. The liquid phase was transfer to a large separating funnel and diluted with 250 mL of water, shaken for 10 minuets and allowed the phases to separate. In the first rinse, the aqueous phase contains about 30 percent alcohol, in which solvents such as hexane were soluble only to about 1 percent. The various insecticides distribute themselves in favor of the water insoluble phase, which contained only about 3 percent of alcohol. This small amount of alcohol was removed by the second rinse.

Fifty mL of the extract was transferred to a round bottom flask and the volume was reduced to about 5 ml with a rotary evaporator and water bath at 37°C. 5 g of fine sea sand was added to the flask and continue the evaporation with constant stirring to ensure that the plant extractives represent were left in a thin coat on the sand. 5 mL of acetonitrile was added to the beaker and placed on a hot plate. The mixture was heated and stirred to the boiling point. 6 ml of water was added to the hot solution immediately after boiling and then was allowed cooling. The entire volume was added to the column. The beaker was rinsed with hot 40 percent acetonitrile and was placed in the column. Above air pressure was applied to the column to the column to hasten the entry of the 60 percent acetonitrile and 40 percent distilled water solution of the extract. When the liquid level just reached the top of the granular packing the pressure was released and 100 mL of developing eluent was added. The pressure was applied again and the eluate was collected at a rate not exceeding 1 mL per minute. The eluate was placed into a 500mL separator funnel, 50 mL of water was added, shaken, 100mL of hexane was added, shaken thoroughly, and allowed to separate. The extraction was repeated with an additional 25 mL of hexane. The Hexane layer was combined to make up to a definite volume. This solution could be used for the chemical test.

Extract 0.4 µL of sample in volume was taken with a micro syringe and injected into injection port of the Gas Chromatograph Mass Spectrometer capillary column, which was fitted with Electron Impact Ionization.

Detection of pesticides

For organochlorine pesticide detection E1 mode of Gas Chromatograph Mass Spectrometer was used. Identification of the suspected pesticide was carried out to retention time of the pure analytical standards. The function of Gas Chromatograph Mass Spectrometer is identification, quantification and analysis of a compound. Name, molecular formula, molecular structure, molecular weight and fragmentation pattern can also be detected by GCMS.

Results and Discussion

Status of chlorinated pesticides residue in potato, tomato and carrot were analyzed and detected by Gas chromatograph Mass spectrometer (GCMS) and their results are described in the following headings.

Chromatograph of tomato

The tomato (*Lycopersicon esculentum*) samples were analyzed and chlorinated pesticide residues were detected by GCMS for this study. The Chromatograph shows the presence of different organic compounds in vegetable samples. Detected peaks due to different organic compounds in tomato sample have been presented in Fig. 2. The major organic compounds present in tomato samples according to their peak were phytol; hexadecanoic acid, ethyl ester; phenol, 2,6-bis(1,1-dimethylethyl)-4 -(-1 –methyl -1 -phenylethyl); 2, 2-thiobis. [4-(1, 1, 3, 3-tetramethylbuthyl) phenol]; N-(1-benzyl- 3-chloro- 2- oxopropyl)- 4- iodobenzen sulfonamide; 1, 2–benzenedicardiearboxylic acid, diisooetyl ester; Di-n-oetyl phthalate; phthalic acid, diisooetyl ester; Aspidofractinine-3-methanol (2 alpha, 3-beta, 5-alpha); Cholest-5-en-3-ol, carbonochloridate; Dis (5-tert-butyl-6-methoxy-m-talyl) sultide; Cholesta-3,5-diene; (Z) 14-tricosenyl formale; Hexadecane acid dodeyl ester. Among the 14 compounds detected only Cholest-5-en-3-ol, carbonochloridate was found as chlorinated compound in tomato samples (Table 1)

Figure 2. Chromatogram of tomato in GCMS

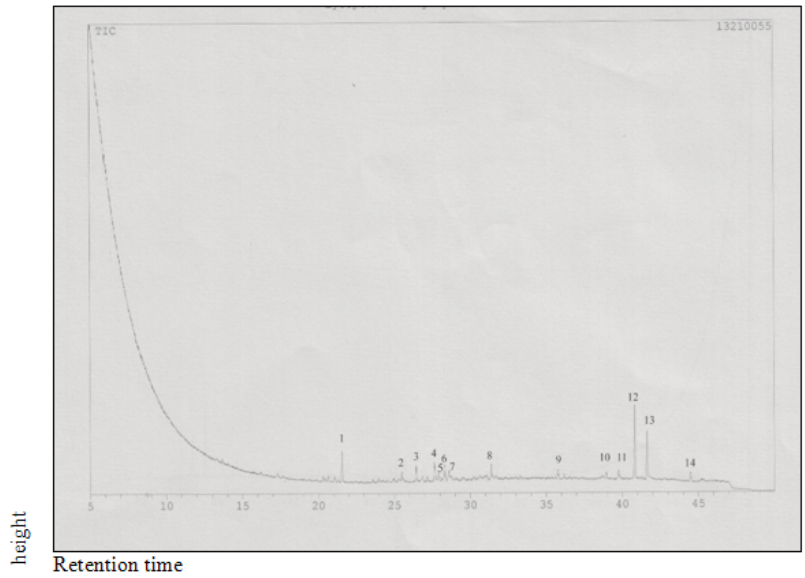


Table 1. List of detected organic compounds with chlorinated pesticides in Tomato (*Lycopersicon esculantum*) sample

Peak	Name of Compound	Mol wt.	Mol From	Chlorinated Compound
1.	Phytol	296	C_{20} $H_{40}0$	–
2.	Hexadecanoic acid ethyl ester	284	C_{18} $H_{36}0_2$	–
3.	Phenol, 2,6-bis (1,1-dimethylethyl)-4-(-1-methyl-1-phenylethyl)	324	$C_{23}H_{32}0$	–
4.	2,2-Thiobis. [4-(1,1,3,3-tetramethylbuthyl) phenol]	384	$C_{28}H_{42}O_2S$	–
5.	N-(1-Benzyl-3-chloro-2-oxopropyl)-4-iodobenzen sulfonamide.	463	$C_{16}H_{15}ClNO_3S$	–
6.	1,2–Benzenedicardiearboxylic acid, diisooetyl ester	390	$C_{24}H_{38}O_4$	–
7.	Di-n-oetyl phthalate	390	$C_{24}H_{38}O_4$	–
8.	Phthalic acid, diisooetyl ester	390	$C_{24}H_{38}0_4$	–
9.	Aspidofractinine-3-methanol (2 alpha, 3-beta, 5-alpha)	310	$C_{20}H_{26}N_2O$	–
10.	Cholest-5-en-3-ol carbonochloridate	448	$C_{28}H_{45}Cl_2$	√
11.	Dis (5-tert-butyl-6-methoxy-m-talyl) sultide	386	$C_{24}H_{34}O_2S$	–
12.	Cholesta-3,5-diene	368	$C_{27}H_{44}$	
13.	(Z) 14-tricosenyl formale	366	$C_{24}H_{46}O_2$	–
14.	Hexadecane acid dodeyl ester	424	$C_{28}H_{56}O_2$	–

Chromatogram of potato

The potato (*Solanum tuberosum*) samples collected were analyzed to detect chlorinated pesticide residues if any there in. The chromatograph of the samples extract shows the presence of 10 organic compounds in (Fig 3). The major organic compounds found in potato sample were 1,16-cyclocorynan –17- oic acid, 19,20-didchydro methyl ester-SS;1,3-propanediol, 22-diethyl –SS; n-hexadecanoic acid; hexadecanoic acid, ethyl esters; 9-octadecenoic acid (z)- hexylester-SS; nonadecanoic acid, ethyl ester-SS; 1,2-benzenedicarboxylic acid, disooctylester; di-n–octyl phthalate; heptocosane.1-chloro-SS; chloromethyl-5-chloroundecanoate. Among the 10 compounds heptocosane 1-chloro-SS and chloromethyl-5-chloroundecanoate were detected to be chlorinated compound contained in potato samples (Table 2)

Figure 3. Chromatogram of Potato in GCMS

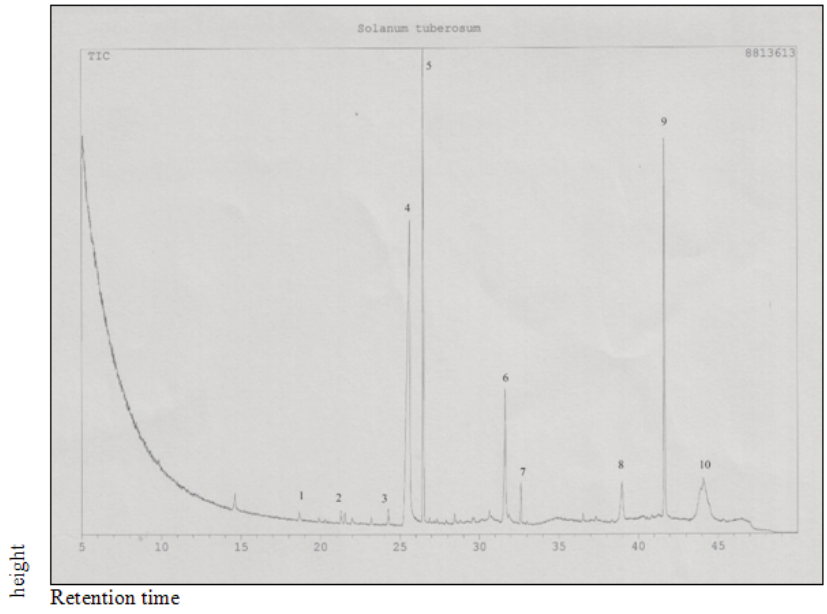


Table 2. List of detected organic compounds with chlorinated pesticides in potato (*Solanum tuberosum)* sample

Peak	Name of Compound	Mol wt.	Mol From	Chlorinated Compound
01.	1,16-cyclocorynan-17-oic Acid, 19,20- didchydro methyl ester-SS	322	$C_{20}H_{22}N_2O_2$	-
02.	1,3-propanediol, 22-diethyl-SS	132	$C_7H_{16}O_2$	-
03.	n-hexadecanoic acid	256	$C_{16}H_{32}O_2$	-
04.	Hexadecanoic acid, ethyl ester-SS	284	$C_{18}H_{36}O_2$	-
05.	9-octadecenoic acid (z)- hexylester-SS	366	$C_{24}H_{46}O_2$	-
06.	Nonadecanoic acid, ethyl ester-SS	326	$C_{21}H_{42}O_2$	-
07.	1,2-benzenedicarboxylic acid, disooctylester	390	$C_{24}H_{38}O_4$	-
08.	Di-n–octyl phthalate	390	$C_{24}H_{38}O_4$	-
09.	Heptocosane.1-chloro-SS	414	$C_{27}H_{55}Cl$	√
10.	Chloromethyl-5-chloroundecanoate	268	$C_{12}H_{22}Cl_2O_2$	√

Chromatogram of carrot

The carrot (*Daucus carota*) samples were analyzed and chlorinated pesticide residues were detected by GCMS for this study. The chromatograph shows the presence of different organic compounds in vegetable samples. Detected peaks due to different organic compounds present in spinach sample have been presented in Fig 4. The major organic compounds found in carrot sample were caryophyllene; bicyclo(3,1,1) hept-2-ene-2,6-dimethyl -6 - (4-methyl- 3- pentenyl) -SS; phytol; hexadecanoic acid, ethyl ester-SS ; phenol, 2,4-bis (1-phenylethyl)-SS; phenol-,2,6-bis (1,1-dimethylethyl)-4-(1methyl-1-phenylethyl)-SS; phytal; linoleic acid, ethyl ester; 2,4–bis (dimethyl benzyl)-6-butyl phenol-SS; 1,2–benzencdicarboxylic acid, diisooetyl ester; di-n-octyl phthalate. Among the 11 organic compounds present in carrot samples no one was found as chlorinated (Table 3).

Figure 4. Chromatogram of carrot in GCMS

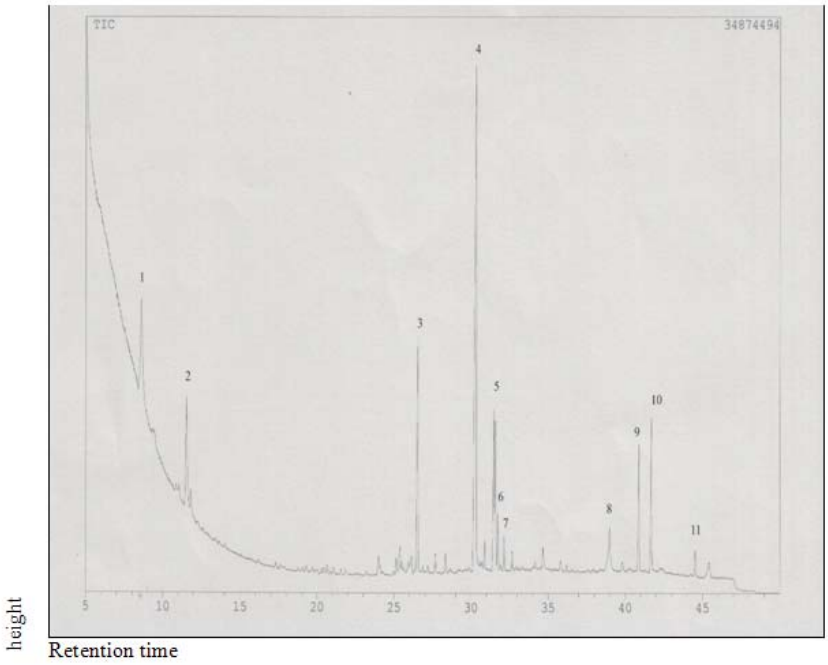


Table 3. List of detected organic compounds with chlorinated pesticides in carrot (*Daucus corota*) sample

Peak	Name of Compound	Mol wgt	Mol From	Chlorinated Compound
1.	Caryophyllene	204	$C_{15}H_{24}$	-
2.	Bicyclo(3,1,1)hept-2-ene-2,6-dimethyl -6-(4-methyl-3-pentenyl)-SS	204	$C_{15}H_{24}$	-
3.	Phytol	296	$C_{20}H_{40}O$	-
4.	Hexadecanoic acid, ethyl ester SS	284	$C_{18}H_{36}O_2$	-
5.	Phenol, 2,4-bis (1-phenylethyl)-SS	302	$C_{22}H_{22}O$	-
6.	Phenol-,2,6-bis (1,1-dimethylethyl)-4-(1methyl-1-phenylethyl)-SS	324	$C_{23}H_{32}0$	-
7.	Phytal	296	$C_{20}H_{40}O$	-
8.	Linoleic acid, ethyl ester	308	$C_{20}H_{36}O_2$	-
9.	2,4–bis (dimethyl benzyl)-6—butyl phenol SS	386	$C_{28}H_{34}O$	-
10.	1,2–benzencdicarboxylic acid, diisooetyl ester	390	$C_{24}H_{38}O_4$	-
11.	Di-n-octyl phthalate	390	$C_{24}H_{38}O_4$	-

The present study was undertaken for measuring the pesticide residue and persistent organic pollutants (PoPs) in potato, tomato and carrot. These vegetables were collected from different vegetable sellers of New Market, Dhaka. The collected vegetable samples contained some chlorinated hydrocarbons, as have been detected through gas chromatograph and mass spectrometer.

From the study of chromatograph of tomato (*Solanum melongena*) samples (Fig. 2) it is evident that a tomato sample contains 14 organic compounds of which 1 (one) compound (Cholest-5-en-3-ol, carbonochloridate) was marked as chlorinated compound (Table 1). This chlorinated hydrocarbone damage and eventually depletes the serotomn in the central nervous system (EHP, 2006). Singh and Karla (1992) observed 0.73 mg/kg of chlorinated compound after 8 sprays @ 50g/kg a.i/ha, which declined to 0.61 mg/kg one day after treatment and then became 0.08 mg/kg after 10 days. Dethe *et al.* (1995) found detectable levels of residues of 33.3% in tomatoes. Tejada and Columpang (1995) in market surveys found residue of chlorinated pesticide in tomato by 20-90%. They recommended that a pre-harvest interval of 5-7 days would be safe in tomato that degraded pesticide residues. Ahuja *et al.* (1998) observed tomatoes for residues of HCH and reported that the residues of monocrotophos on tomatoes persisted over the prescribed maximum residue limit values.

The chromatogram of collected potato (*Solanum melongena*) samples indicated the presence of 10 organic compounds of which 2 samples contained chlorinated compounds (Chloromethyl-5-chloroundecanoate and Chloromethyl-5-chloroundecanoate) (Fig. 3 and Table 2). According to EHP (2006) this two compounds are carcinogenic to human, used as an intermediate in making insecticide, herbicide, pharmaceuticals, food flavorings, dyes, rubber chemicals, adhesives, paints, explosives and disinfectants. Adeyeye and Osibanjo (1999) estimated residue levels of organochlorine pesticides in raw tubers from markets. Aldrin+dieldrin, total HCH, and total DDT detected were 98, 79 and 49% respectively in all tuber samples. Other pesticides were below their detection limits. The average levels were generally low and none were above the FAOs maximum residue limits.

It appears from the chromatograph of carrot (*Daucus carota*) samples that there were as much as 11 organic compounds present there in Fig. 4 and Table 3. But there were no chlorinated compounds detected, some of the compounds were fat and some were byproducts of enzymes. Gao *et al.* (2005) found bioaccumulation of organochlorine pesticides (OCPs) in carrot. These authors maintained that carrot was used as reference matrices for the recovery assay. DDT and its metabolites DDE and DDD gave better recoveries in carrot than HCH and HCB. Most of the OCPs gave recoveries between 80 and 120%, their relative standard deviation ranged from 3 to 15% while the recoveries of dieldrin and endrin were only between 20 and 50%. The total OCPs residual level in carrot was more than 100 mg/g. The ratios of gamma / alpha - HCH and DDT/DDE in the vegetables ranged from 1.0 to 2.5 and 1.0 to 4.2, respectively.

Pesticide residues have a relation with lipid content of vegetables. Lipids and fats act as a storage depot of organic toxic compounds (Doull *et al.* 1975). Pesticides may enter into vegetables through the initial stage of food chain. The presence of pesticide residues in fresh vegetables is an important factor for pesticide residues content in vegetable (Reinert, 1970) and different parts of the plants contain

different amount of pesticide residues (Elzorgani *et al.* 1979); But presence of pesticides in vegetables depends on the biodegradation of pesticide in the agricultural lands.

Conclusion

There is a public concern through out the country that farmers use different harmful pesticides in their crops for higher yield and more profit. A few samples were studied within limited time which is not focused overall status of persistent organic pollutants. The study revealed that the vegetables available in the market contained some organic compounds and some have been identified as chlorinated compounds whether they were originated from any pesticide if were applied could not be ascertained. Since use of chlorinated compounds in agriculture is banded / restricted in Bangladesh like elsewhere due to several reasons, the sources and the quantity of the detected chlorinated compounds need to be search out with emphasis. Persistent organic pollutants (POPs) such as chlorinated pesticides are of global concern due to their wide spread occurrence, persistence, bioaccumulation and toxicity to human and animals. So for the betterment of the world and food safety the sources of organic pollutant should be identified and eliminated.

References

Adeyeye, A. and Osibanjo, O. (1999) Residues of organochlorine pesticides in fruits, vegetables and tubers from Nigerian markets. Science of the Total Environment. 231(2/3): 227-233

Ahuja, A. K.; Soudamini, M., Debi, S., Awasthi, M. D., Mohapatra, S., Sharma, D., Reddy, P. P., Kumar N. K. K. and Verghese, A. (1998) Monitoring of vegetables of insecticide residue contamination at harvest. Advances in IPM for horticultural crops. Proceeding of the First National Symposium on Pest Management in Horticultural Crops: Environmental implications and thrusts, Bangalore, India, 15-17 October 1997, 243-246.

Dethe, M. D., Kale, V.D and Rane, S.D. (1995) Insecticide residues in/on farm gate samples of vegetables. Pest management in Horticultural Ecosystem. 1 (1): 49-53.

Doull, J., Klaassen. C.D. and AMDUR- M.O. (1975) Toxicology: The Basic
Science of Poison. 2nd ed. Macmillan publishing Co. Inc. New York.

EHP, (2006) Comparative Metabolism of Chloroacetamide Herbicides and Selected Metabolites in Human and Rat Liver Microsomes. Environmental Health Perspectives. Environmental and Occupational Toxicology Division- Bureau of Chemical Hazards, Environmental Health Directorate, Department of National Health Canada, Environmental Health Centre, Room B35, Tunnev's Pasture. Ottawa. Ontario KIA OL2. Canada. EHP 12(108). January 2006.

Elzorgani, G.A., Abdullah, A.M. and Ali, M.E.T. (1979) Residues of organochlorine insecticides in fish in Lake Nubia Bull. Environ. Contam. Taxicol. 22:44.

Gao, H. J; Jiang, X; Wang, F; Wang, D. Z; Bian, Y R. (2005) Residual levels and bioaccumulation of chlorinated persistent organic pollutants (POPs) in vegetables from suburb of Nanjing, People's Republic of China. Bulletin of Environmental Contamination and Toxicology. 74(4): 673-680

Gohlki, R. S. and Mclafferty, F. K. (1993) Early gas chromatography/mass spectrometry. Journal of the American Society for Mass Spectrometry 4 (5): 367-371.

Khandakar, K. (1990) Population, Agriculture And Environmental Degradation. An article published in the daily "The Bangladesh Observer" July 28, 1990.

MacIntyre, A.N.N., Allison, N. and Penman, D.R. (1989) Insecticides issues and options for New Zealand Ministry of the Environment, Wellington, New Zealand.

Mansingh, A. Robinson, D.E, Walker N. and Thomas, C. (1996) Distribution, fate and effects of pesticides in tropical Marine environment, presented at he third IAEA-MEL Res. Coordination meeting Heredia, Costa Rica, 9-13 September.

Mukhopadhay. K., Bera. R. and Roy, R. (2005) Modern agriculture and environmental pollution. Everyman 's Science (XL) 3: pp. 186.

Price. C. (2008) Implications of Pesticide residues in intep-rated ditch-duke farminL), systems. Central Thailand. Aauaculture News 32: nn. 23.

Rahman, M.S. Malek, M.A., and Matin, M.A (1995) Trend of pesticide usage in Bangladesh. Sci. Total Environ. 156, 33-35

Reinert, R. W., Menzel, D. B., Martin, D.T. and Olcott, H.S. (1970) DDT residues in pacific sea birds, a persistence insecticide in marine food chain. Nature, London 216:589-590.

Singh, I.P. and Kalra, R.L. (1992) Determination of residues of cypermethrin in brinjal fruits, leaves and soil. Indian Journal of Entomology. 54 (2) : 207-216.

Tejada, A.W. and Calumpang, S.M.F. (1995) Insecticide Residue in Field Sprayed Eggplant. The Philippine Agriculturist. 78.(2): 119-128.