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Full Article

COMPARATIVE STUDIES ON DETECTION AND QUANTIFICATION OF PESTICIDE RESIDUE IN SOME VEGETABLES OF BANGLADESH

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Abstract

The prevalently used pesticide Malathion E50, Alpha-Cypermethrin, Chlorpyrifos and Lambda-Cyhalothrin residues were identified and quantified in four vegetable samples (Brinjal, Coli flower, Lady's finger and Bean) collected from three different places (Kadamtoli, Alipur and Kanarchor) of Bangladesh. The data were compared to the data of one of our previous article (Naher et al., 2016) data for another set of similar investigation for the same pesticide residues. QuEChERS method was used for extraction and Gas Chromatography-Mass Spectrometry (GC-MS) was used for detection as well as for quantification of the pesticides. From the comparison of data, it was concluded that leafy vegetables investigated in our previous work contained comparatively higher amount of pesticide residues than the four vegetables investigated in our present work. Relatively higher amount of pesticide residues were obtained in some samples. However, most of the samples were found to contain moderate to low concentration of pesticide residues. The detected pesticide concentration exceeded the Maximum Residue Limit (MRL) in some samples which is obviously harmful and alarming for sound human health of the people for whom it was marketed.

Keywords: *Leafy vegetables; Gas Chromatography-Mass Spectrometry; QuEChERS method; MRL; Chlorpyrifos; Lambda-Cyhalothrin.*

1. Introduction

Identifying and quantifying pesticides in vegetables is very important for public health and safety reasons. The determination of pesticide residues in agricultural products, plant

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and environmental samples has been major subject for many years because of their toxic potential risk for human health, persistence and tendency to bioaccumulation (Michigan USA, 2008). Plant protection products (pesticides) are widely used in agriculture to increase the yield, improve the quality, and extend the storage life of food crops (Dasika*et al.,* 2012). The applied pesticides and their degradation products may remain as residues in the agricultural products, which becomes a concern for human exposure (Hussaina*et al.,* 2010). It is very clear that pesticide residue problem is becoming serious concerning human health and environmental hazards due to indiscriminate pesticides application. An intensified use of pesticides can cause a serious public health hazard especially in the form of residues in food. In this regard it is a must to monitor the pesticide residues in our food items especially in vegetable items; the essential part of our daily dietary. Modern pesticide residue analysis in developing countries is thus focusing more and more on subtle problems, such as looking for very low concentrations of pesticides in the environment. Complicated and expensive equipment like- gas chromatography, high performance liquid chromatography, mass spectrometer etc. are being used to analyze these samples (Singh *et al.,* 2006).

There are numerous pesticides that are being used worldwide. Various methods and techniques are used to identify and quantify the pesticides' residue in various food items. For instance, multiresidue method (Dasika *et al.,* 2012; Akogbeto *et al.,* 2005; Kin *et al.,*2008; Thiam *et al.,*2009), Electron impact method (Pazou *et al.,*2006; Baig *et al.,*2009), QuEChERS (quick, easy, cheap, rugged, effective and safe) (Singh *et al.,* 2006; Lopez-Fernandez *et al.,*2012; Bouaid *et al.,*2001) etc. are the common methods employed to extract and identify the residues. The common instrumentation that is employed by different groups of researchers to quantify the residue level are GC-MS method ((Dasika *et al.,* 2012), LC-MS/MS (Chu *et al.,* 2002, Kin*et al.,*2008; Sarrio *et al.,* 2000), GC-MS/MS method (Lopez-Fernandez *et al.,*2012), GC-EI-MS (Baig *et al.,*2009), LC-ESI-MS/MS (Baig *et al.,*2009). To ensure the safe use of pesticides and to ensure sound public health; a comprehensive pesticide residue analysis program to monitor the newer as well as older pesticides' residue in the food items of Bangladesh should be conducted in a regular basis. Despite the importance, no systematic work has been carried out in Bangladesh to identify and document the vegetable species for their pesticide residue content. M.T.I. Chowdhury *et al.* worked on chlorinated pesticide residue status in tomato, potato and carrot (Chowdhury *et al.,* 2011 and Shakhaoat *et al.,* 2013) worked on health risk assessment of pesticide residues via dietary intake of market vegetables from Dhaka, Bangladesh (Hossain *et al.,* 2013) detected organophosphorus and carbamate pesticide residues in water samples collected from paddy and vegetable fields of the

Savar and DhamraiUpazilas in Bangladesh (Chowdhury *et al.*, 2012). Our group also recently carried out a work on pesticide residue investigation in leafy vegetables collected from Keraniganj near Dhaka, Bangladesh (Naher *et al.*, 2016).

In our present work we have investigated for four different widely used pesticides in four different vegetables collected from three different vegetable fields of Keraniganj near Dhaka, Bangladesh and compared the data with our previous work.

2. Materials and Methods

Study area: The selected area of study was Hazratpur at Keraniganj in Dhaka. There were various vegetable fields which grown large amount of vegetables that satisfy the vegetable demand of local people as well as Dhaka city people. Four different samples from each of the three different places namely Kadamtoli, Alipur and Kanarchor of Keraniganj were collected and analyzed for widely used different pesticide residue.

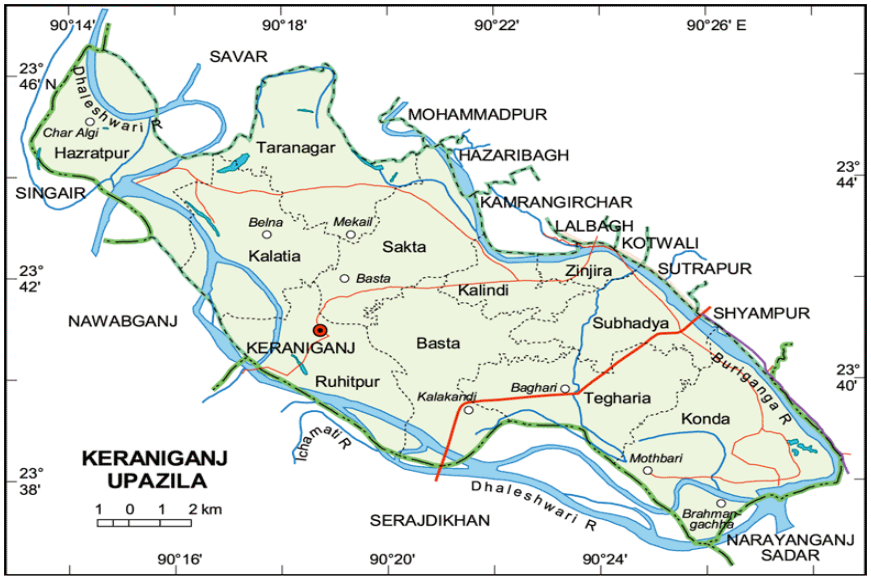

Fig. 1: Location of sampling site

Sample collection: Samples were collected from three different places in Hazratpur. Four different samples were collected from three different fields. These were Lady's Finger (Vendi), Cauliflower (Fulcopi), Bean (Shim), and Brinjal (Begun).

Chemicals: Chemical reagents and solvents that used in the study were namely Acetonitrile (MeCN), Magnesium Sulphate ($MgSO_4$), Primary and Secondary Amines (PSA), Acetic Acid (HOAc), Sodium Acetate (NaOAc), Methanol (MeOH) etc.

Analytical Instrumentals: Gas Chromatography-Mass Spectrometry (GC-MS).

Pesticides Extraction method: QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe)

Experimental:

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method of pesticides extraction was used in this experiment. In this method, at first about 200 g sample was taken and it was chopped with vertical cutter. Then the chopped sample was grinded with mortar and pestle to homogenize the sample. The homogenized sample (15 g) was transferred to Teflon tube (50 mL). Then a solution of acetic acid (1%) in acetonitrile (15 mL), anhydrous sodium acetate (1.5g) and anhydrous magnesium sulphate (6 g) was added to the sample. The mixture was then shaken vigorously, vortexed and centrifuged (~1500 rcf) for one minute each. A portion of MeCN extract (5 mL) (upper level) was collected from the mixture, and then anhydrous $MgSO_4$ (150mg) and PSA (250 mg) were added the extract. The extract with $MgSO_4$ and PSA was shaken in the vortex for 30 s and was filtered. About 1.0-1.5 mL of the extract was transferred into GC vial filtering through 0.45 µm syringe filter. Finally, the extract was analyzed by GC-MS (AOAC International, 2005). Using this procedure, pesticide residues were extracted and analyzed from all the 12 samples.

Figure 2: Brinjal (Begun)

Figure 3: Cauliflower (Fulcopy)

Figure 4: Lady's Finger (Vendi)

Figure 5: Bean (Shim)

3. Results and Discussion

Pesticide residues were extracted using QuEChERS method from four different vegetables; Lady's Finger (Vendi), Cauliflower (Fulcopi), Bean (Shim), and Brinjal (Begun) (Figure 2-5) and these were identified and quantified using GC-MS. From the results shown in the Table-1, it was observed that no pesticide residue was detected in any Brinjal sample of all the four places under investigation. Also it can be seen from the table that all the four samples collected from Kadamtoli region contained none of pesticide residue. Again Chlorpyrifos is the one pesticide that was found in none of the samples. Other samples of different vegetables and different places contained moderate to high amount of pesticide residues. Malathion E50 was found in the samples B-2, C-3 and D-2 in different amounts. Alpha-Cypermethrin was found in C-2 and D-3 in moderate amount. Lambda-Cyhalothrin was detected in a very small amount in samples B-2, C-3 and D-2. This observation reveals that the presence of pesticide residues varies from place to place as well as in different samples. This may be due to the application procedure of the pesticides by the local farmers, nature of soil or decomposition rate of different pesticides, and decomposition activity of the pesticides by the individual vegetable. From these results it seems that the local people of Kadamtoli used either no pesticides or used other pesticides which were not investigated in our experiment. Chlorpyrifos was either not used in any four of the places or in the vegetables the decomposition rate of Chlorpyrifos is high. Again as in the brinjal sample no pesticide residue was observed; either no pesticides were applied in the brinjal field or brinjal could decompose all the pesticides before harvest time.

Among all the pesticides Alpha-Cypermethrin was found in the highest amount (1968.99 ppm) in Bean of Kanarchor. Also moderate amount (500.48 ppm) of Alpha-Cypermethrin was detected Lady’s Finger of Alipur . On the other hand, Malathion E-50 was detected in high amount in the Cauliflower of Alipur (858.83 ppm), in the Bean of Alipur (955.82 ppm) and in moderate amount in the Lady’s Finger of Kanarchor (302.27 ppm). Lambda-Cyhalothrin was found in very low amount in three samples namely-in the Cauliflower of Alipur (2.83 ppm), in the Lady’s Finger of Kanarchor (2.03 ppm) and in the Bean of Alipur (4.24 ppm).

The tolerance limit for the pesticides used in the samples under investigation are-Malathion E-50 is 20 ppm, Chlorpyrifos is 15 ppm, Alpha-Cypermethrin is 32 ppm and Lambda-Cyhalothrin is 25 ppm (World Health Organization 2010). Satisfyingly, Chlorpyrifos was absent in all the samples under investigation. In other cases the values indicated that the pesticide residue in the samples were quite high in some cases for instance, Alpha-Cypermethrin was found in highest amount (1968.99 ppm) in Bean of Kanarchor. Cauliflower and Bean of Alipur contained high level 858.83 ppm and 955.82 ppm respectively of Malathion E50 which is alarming for our health. However, Table-1 reveals that the level of pesticide residues is satisfactory for pesticide Lambda-

Cyhalothrin. It was present in a very low amount in all cases and the values of all were within MRL's. In many instances pesticides are absent. This indicates that either no pesticides were used for these vegetables in these areas or pesticides other than the four under our investigation were used for pest control.

Our group performed a very similar work for four leafy vegetables Red Spinach, Indian Spinach, Amaranthus Leaves, and Radish Leaves collected from the very same places (Kadamtoli, Alipur and Kanarchor). The result of our findings is summarized in the table-2. From the results it is evident that the leafy vegetables contained very high amount of pesticides in some samples for example, Alpha-Cypermethrin was found in extremely high amount (4951.33 ppm). Also it can be seen that in all cases the leafy vegetables contained relatively high amounts of the pesticides. Lambda-Cyhalothrin content in both sets of samples found to be in small amount which is not so alarming for health.

Table 1: Amounts (in ppm) of pesticide residues in vegetable samples.

Sample (Field)	Chlorpyrifos (ppm)	Malathion E50 (ppm)	Alpha-Cypermethrin (ppm)	Lamda-Cyhalothrin (ppm)
A-1 (Brinjal of Kadamtoli)	Nil	Nil	Nil	Nil
A-2 (Brinjal of Alipur)	Nil	Nil	Nil	Nil
A-3 (Brinjal of Kanarchor)	Nil	Nil	Nil	Nil
B-1 (Cauliflower of Kadamtoli)	Nil	Nil	Nil	Nil
B-2 (Cauliflower of Alipur)	Nil	858.83	Nil	2.83
B-3 (Cauliflower of Kanarchor)	Nil	Nil	Nil	Nil
C-1 (Lady's Finger of Kadamtoli)	Nil	Nil	Nil	Nil
C-2 (Lady's Finger of Alipur)	Nil	Nil	500.48	Nil
C-3 (Lady's Finger of Kanarchor)	Nil	302.27	Nil	2.03
D-1 (Bean of Kadamtoli)	Nil	Nil	Nil	Nil
D-2 (Bean of Alipur)	Nil	955.82	Nil	4.24
D-3 (Bean of Kanarchor)	Nil	Nil	1968.99	Nil

Table-2: Amounts (in ppm) of pesticide residues in Leafy vegetable samples (Naher *et al.*, 2016).

Sample(Field)	Chlorpyrifos (ppm)	Malathion E50 (ppm)	Alpha-Cypermethrin (ppm)	Lambda-Cyhalothrin (ppm)
Sample-1 Indian Spinach (Kadamtoli)	Nil	Nil	Nil	Nil
Sample-2 Indian Spinach (Alipur)	Nil	Nil	Nil	Nil
Sample-3 Indian Spinach (Kanarchor)	Nil	1757.16	Nil	3.27
Sample-4 Amaranthus Leaves (Kadamtoli)	Nil	Nil	Nil	Nil
Sample-5 Amaranthus Leaves (Alipur)	Nil	Nil	Nil	Nil
Sample-6 Amaranthus Leaves (Kanarchor)	Nil	951.00	Nil	2.43
Sample-7 Red Spinach (Kadamtoli)	Nil	Nil	144.21	Nil
Sample-8 Red Spinach (Alipur)	Nil	41.31	Nil	Nil
Sample-9 Red Spinach (Kanarchor)	Nil	Nil	4951.33	Nil
Sample-10 Radish Leaves (Kadamtoli)	5.93	290.06	Nil	1.59
Sample-11 Radish Leaves (Alipur)	Nil	Nil	Nil	Nil
Sample-12 Radish Leaves (Kanarchor)	Nil	1027.82	17.27	2.72

It is clear that the both sets of samples exceeded the permissible limit of the pesticide content in many cases which is obviously harmful for human health. The leafy vegetable contained relatively high amount of pesticides in comparison.

4. Conclusions

In our present study, some vegetable collected from some places contained little or no pesticide residue. Some samples however contained moderate to high amount of different pesticides. Brinjal of any of the three selected areas under investigations contained no

pesticide residue. However, the detected amount of pesticides found in this investigation which was used in vegetables such as Cauliflower, Lady's Finger and Bean were higher than that of permissible limit and hence those were harmful for the consumers. So, proper assessment, rigorous monitoring and environmental implications of synthetic chemicals should be ascertained well before allowing for large scale use. More significantly, the long-term implications on the human health and environmental need should be studied significantly for sustainable development. Government of Bangladesh should take proper action to assess the pesticide management and to regulate the use of pesticides in crops, especially in vegetables.

References

Akogbeto M, Djouaka R and Noukpo N. 2005. Utilisation des Insecticides Agricoles au Benin. *Bulletin de la Societe de PathologieExotique* 98: 400-405.

Baig SA, Akhtera NA, Ashfaq M and Asi MR. 2009. Determination of theOrganophosphorus Pesticide in Vegetables by High Performance Liquid Chromatography.*American- Eurasian Journal of Agricultural and Environmental Sciences* 6(5): 513-519.

Bouaid A, Ramos L, Gonzalez MJ, Ferna´ ndez P and Ca´ mara C. 2001. Solid-Phase Microextraction Method for the Determination of Atrazine and Four Organophosphorus Pesticides in Soil Samples by Gas Chromatography. *J. Chromatogr*939: 13-21.

Chowdhury MAZ, Banik S, Uddin B, Moniruzzaman M, Karim N andGan SH. 2012. Organophosphorus and Carbamate Pesticide Residues Detected in Water Samples Collected from Paddy and Vegetable Fields of the Savar and DhamraiUpazilas in Bangladesh. *Int. J. Environ. Res. Public Health* 9(9): 3318-3329.

Chowdhury MTI, Razzaque M A and Khan M S I. 2011. Chlorinated Pesticide Residue Status in Tomato. Potato and Carrot. *Journal of Experimental Sciences* 2(1): 01-05.

Chu YF, Sun J, Wu X and Liu RH. 2002. Antioxidant and ant proliferative activities of common vegetables. *Journal of Agricultural and Food Chemistry* 50: 6910-6916.

Dasika R, Tangirala S and Naishadham P. 2012. Pesticide Residue Analysis of Fruits and Vegetables. *Journal of Environmental Chemistry and Ecotoxicology* 4(2):19-28.

Hossain MS, Hossain MA, Rahman MA, Islam MM, Rahman MA and Adyel TM. 2013. Health Risk Assessment of Pesticide Residues via Dietary Intake of Market Vegetables from Dhaka, Bangladesh. *Foods* 2(1): 64-75.

Hussaina Z and Siddiqueb S. 2010. Multi-Residue Method for Determination of 85 Pesticides in Vegetables, Fruits and Green Tea by Stir Bar Sportive Extraction and Thermal Desorption GC-MS. *Scientific Research* 02: 0555-7674.

Kin CM, Huat TG and Kumari A. 2008. Application of Solid-phase Micro Extraction for the Determination of Pesticides in Vegetable Samples by Gas Chromatography with an Electron Capture Detector. *Journal of Analytical Sciences* 12(1): 1-9.

Lopez-Fernandez O, Rial-Otero R, Gonzalez-Barreiro C and Simal-Gandara J. 2012. Surveillance of Fungicidal Dithiocarbamate Residue in Fruits and Vegetables. *Journal of Food Chemistry* 134(1): 366-374.

Naher S, Haque MA, Al Hamide MA, Khan M and Afroze M. 2016. Studies on Detection and Quantification of Pesticides Residue in Some Leafy Vegetables of Bangladesh.*Jagannath University Journal of Science* 5(1): 1-5.

Official methods of analysis of AOAC International. 2005. Chapter-10, page-21, 18th edition, Toxicological Profile for Malathion. 2008. U.S., Department of Health and Human Services, Agency for Toxic Substances and Disease Registry: Atlanta.

Pazou EYA, Boko M, CAM GV, Ahissou H, Laleye P andAkpona S. 2006. Organochlorine and Organophosphorous Pesticide Residues in the Oueme River Catchment in the Republic of Benin. *Environment International* 32(5): 616-623.

Singh J, Upadhyay AK, Prasad K, Bahadur A and Rai M. 2007. Variability of Carotenes,

Vitamin C, E and Phenolics in Brassica Vegetables. *Journal of Food Composition and Analysis* 20(2): 106-112.

Sarrio´ MN, Santos FJ andGalceran MT. 2000. Gas Chromatography/Ion Trap Tandem Mass Spectrometry for the Analysis of Halobenzenes in Soils by Solid-Phase Micro Extraction. *Rapid Commun Mass Spectrom*14: 2271–2281.

Thiam M and Touni E. 2009. Pesticide poisoning in West Africa. *Pesticides News* 85:3-4.

World Health Organization (WHO). 2010. Recommended Classification of Pesticides by Hazard and Guidelines to Classification.