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Monitoring of Selected Pesticides Residue Levels in Water Samples of Paddy Fields and Removal of Cypermethrin and Chlorpyrifos Residues from Water Using Rice Bran

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Abstract Consumption of pesticides associated foods increased in recent decades in Bangladesh. Most of the pesticides come from paddy, as rice is the main food items here and about 70 % pesticides are used only on paddy fields. Water samples of paddy fields and Kaliganga River of Manikganj district were analyzed to provide base line data on cypermethrin, chlorpyrifos and diazinon residue by using high performance liquid chromatography. Levels of Cypermethrin, chlorpyrifos and diazinon detected in the paddy field water samples were (0.605 ± 0.011 μg/L), (0.06 ± 0.001 μg/L) and (0.039 ± 0.002 μg/L), respectively. 0.11 ± 0.003 μg/L of cypermethrin and 0.012 ± 0.0006 μg/L of chlorpyrifos were also identified in the water samples of Kaligonga River. Diazinon residue was not detected in the river water samples. The detected concentrations of pesticide residues in the river water were below the accepted maximum residue limit (MRL) value of drinking water (0.1 μg/l) adopted by the FAO/WHO Codex Alimentarius Commission. Cypermethrin and chlorpyrifos were chosen for decontamination through rice bran, as it was found in river water. Two gm rice bran could easily decontaminated 95.6 % and 96.4 % of cypermethrin and chlorpyrifos. The result of this study showed that pesticide residue was detected in water samples were below the MRLs value, which can easily be decontaminated through absorption of rice bran.

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Introduction

Agriculture is the backbone of the economy of Bangladesh. Eighty per cent of the people depend on agriculture for their livelihood (Chowdhury et al. 2011). Rice and jute are the primary crops of this country and rice is the main staple food of the people. Government emphasizes on the increase the production of the rice to combat against poverty and ensure food security (IRRI 2005). *Aush, Aman* and *Boro* are the three season for rice cultivation though most of the rice is produced in *Boro* season (Ali 1994). *Aush, Aman* and *Boro* are harvested, namely, in July–August, December–January and March–May and respectively. *Boro* as well as seasonal vegetables are widely cultivated in winter season. Eighty insects' outbreak was reported in during this period, which causes crop losses (Kalam 1998). This leads serious economical loss to the farmers. Farmers have no other choice to use various types of chemicals to combat against pest, which is known as pesticide (Arjmandi et al. 2010).

Government of Bangladesh promotes the use of pesticide to boost the rice production to ensure food securities. About 70 % of pesticides are used on rice. Currently 84 pesticides with 242 trade names are registered in this country (PAB 2000). Organophosphate and carbamate pesticides are widely applied in the paddy fields. Farmers spray excessive amount of harmful chemicals, which remain in the paddy field due to inadequate knowledge and guideline about the application of pesticide. These pesticides are drained into nearest canal and river, which is a common practice in Bangladesh. This tradition disturbs the

aquatic environment. Residues of the pesticides take by flora and fauna, which is able to pose serious environmental and health hazard (Parveen and Nakagoshi 2001). River water is used in different purposes in Bangladesh including drinking activities. Teratogenic, mutagenic and carcinogenic health hazards are reported from the consumption of pesticides in various countries all over the world (Ali and Tahir 2000). Due to less mature immune system, children are more susceptible to pesticide (Morasso et al. 2001).

There are very little amount of information available about the pesticide residue in paddy field and its residue transportation to river. Thus, the present study was an attempt to measure the levels of applied pesticide in various paddy fields and nearby river Kaligonga of Manikganj district of Bangladesh and attempt was taken to find out the probable decontamination through cheap adsorbent, like rice bran.

Materials and Methods

The present study was conducted in twenty two villages of the Ghior and Manikganj Sadar upazila of Manikganj district, Bangladesh. Numerous rivers and channels are flowed over this district as a result, there is a good irrigation facility are available. Present study was conducted in randomly selected twenty one paddy fields of the Ghior and Manikganj Sadar upazila. Kaliganga River is passed through these upazilas. Water samples of this river were taken to undertake the present study. *Boro* or winter season was selected to conduct the study due to huge amount of rice production and minimum rainfall occurs throughout the season. 1,000 ml of water samples were collected randomly from different paddy fields and river. The water samples were collected in the amber glass bottle. The samples were properly labeled and kept at −20°C to preclude the risk of hydrolysis and oxidation.

For determination of pesticide concentration, 500 mL of water sample and 100 mL solvent (2 % diethylether in DD-hexane) was taken into a separating funnel and was shaken by mixing well for about 10 min and then kept standing for 10–15 min for settling down. Then lower water layer and upper hexane layer were collected in separate conical flasks. The aqueous layer was re-extracted be adding 50 mL solvent (2 % diethyl ether in DD-hexane) and then solvent layer was collected. The collected extract was then concentrated under reduced pressure by using a Rotary Vacuum Evaporator (R – 215, BUCHI, Switzerland). Rinsed with DD-hexane twice (first 3 and then 2 mL) and making the final volume 5 mL. the extract was clean up by florisil with 100 mL solvent (90 ml DD-hexane and 10 mL dichloromethane) again concentrate and make the final volume 5 mL by rinsing with DD-hexane twice (first 3 and then 2 mL). Then the clean extract was dry up fully by N_2 blow from a N_2 blower (PU 90003, ALFA industry, England).

Retention times (RT) of pure analytical standard of insecticides were used to identify suspected pesticide in the tomatoes. The retention featured was changed a little bit for identification and 0.05 % difference was acceptable. Quantification of the identified pesticides was performed by the calibration technique. For this purpose, injection of equal volumes of differently concentrated standard solutions into High performance liquid chromatography (CTO – 10 AC, SHIMADZU, Japan) prepared calibration curve for each pesticide (Morasso et al. 2001). Residual pesticide was calculated by following equation (Khatoon et al. 2004)

$$\text{Residual Pesticide } (\%) = X/M \times 100$$

where X is the total concentration remain (mg/kg) after treatment and M is the applied concentration for cypermethrin which is 0.45 mg/kg. To calculate the pesticide residues removal, following formula was used (Adachi and Okano 2006)

$$\text{Residual Pesticide } (\%) = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Final concentration}} \times 100$$

From the identification of water samples of river, two mostly dominated pesticides (cypermethrin and chlorpyrifos) were selected for decontamination. Four water samples were prepared for identification of the effectiveness of decontamination technique by using rice bran. Five hundred ml distilled water each was taken into 4 conical flasks. These water samples were spiked with pesticides at 0.05 ppm in the dark room to avoid photolysis. In order to assess the effects of the decontamination technique, water samples spiked with pesticides were divided into four treatment groups: (I) treatment with no rice bran (control); (II) treatment with 1 gm rice bran; (III) treatment with 2 gm rice bran, and (IV) treatment with 4 gm rice bran. The water samples were filtered by the filter paper.

The mean is the arithmetic average of a set of values, or distribution. The *arithmetic mean* is the "standard" average, often simply called the "mean". Following formula was used to calculate the mean of the concentration of pesticides:

$$\bar{x} = \frac{1}{\mathrm{n}} \cdot \sum_{i=1}^{\mathrm{n}} x_i$$

where, $\bar{x}$ = Mean of concentration of pesticides, X_i = Observed pesticide concentration in different samples. Standard deviation is the sum of the deviation of the mean of all observations. It is a square root of the

variance of a set of data. It is use to assess the variability of mean of a sample. Following formula was used to calculate the standard deviation of the concentration of pesticides:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

where, σ = Standard deviation of the data, N = Sample size. Results of the analysis were statistically analyzed by using of SPSS v.16. 95 % certainty is expressed in 95 % confidence level. Normal distribution was performed to assess 95 % confidence level due to sample size was below 30. To determine the confidence level by normal distribution, following formula was used –

$$Z = \frac{\bar{X} - \mu_0}{\sigma/\sqrt{\mathrm{n}}}$$

where, $\bar{x}$ = Sample mean, μ_0 = Mean of particular pesticide, σ = Standard deviation of corresponded pesticide, n = Sample Size.

Table 1 Concentrations of different pesticide residues in the water samples of the paddy field

Sl no.	Sample name	Cypermethrin (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/l)
1	MNJ – 1	0.18	BDL[a]	BDL[a]
2	MNJ – 2	0.011	BDL[a]	BDL[a]
3	MNJ – 3	BDL[a]	0.03	BDL[a]
4	MNJ – 4	0.12	BDL[a]	BDL[a]
5	MNJ – 5	0.25	BDL[a]	BDL[a]
6	MNJ – 6	0.31	BDL[a]	BDL[a]
7	MNJ – 7	0.01	BDL[a]	BDL[a]
8	MNJ – 8	0.098	BDL[a]	BDL[a]
9	MNJ – 9	BDL[a]	0.34	BDL[a]
10	MNJ – 10	0.039	BDL[a]	BDL[a]
11	MNJ – 11	BDL[a]	BDL[a]	0.027
12	MNJ – 12	0.15	BDL[a]	BDL[a]
13	MNJ – 13	0.031	BDL[a]	BDL[a]
14	MNJ – 14	0.09	BDL[a]	BDL[a]
15	MNJ – 15	BDL[a]	BDL[a]	BDL[a]
16	MNJ – 16	BDL[a]	0.029	BDL[a]
17	MNJ – 17	BDL[a]	0.03	BDL[a]
18	MNJ – 18	0.004	BDL[a]	BDL[a]
19	MNJ – 19	0.0053	BDL[a]	BDL[a]
20	MNJ – 20	0.0027	BDL[a]	BDL[a]
21	MNJ – 21	0.16	BDL[a]	BDL[a]
Mean		0.069571	0.020429	0.001286
Std. Deviation		0.090584	0.072202	0.00575
95 % Confidence Interval		0.038743	0.030881	0.002459

[a] Below the detection limits which stand 0 for mean calculation. Detection limit – 0.01 µg/L

Results and Discussion

Residues of cypermethrin and chlorpyrifos are detected among water samples of paddy field in selected upazilas. However, diazinon residue was detected in only one sample. Table 1 shows the concentration of pesticide residues in different paddy fields of the study area. The recommended total pesticide level for drinking water is 0.5 µg/L and individual pesticide is 0.1 µg/L (Dahal 1995). Seven samples out of 21 samples were found contaminated with pesticide residues above the MRL value 0.1 µg/L of drinking water. Except one sample of Manikganj Sadar upazila, all water samples of the study area were found contaminated with the pesticide residues. The quantity of cypermethrin (0.0696 ± 0.02 µg/L), chlorpyrifos (0.0204 ± 0.01 µg/L) and diazinon (0.0013 ± 0.001 µg/L) were detected.

Out of eleven samples of river water, six were contaminated by pesticide residues. Cypermethrin and chlorpyrifos were detected whereas no diazinon identified in the water samples. Table 2 is illustrated the detected concentration of pesticide residue in water. The water samples of the Kaliganga River were found contaminated with the pesticides but their concentrations did not exceed the MRL value 0.1 µg/L of individual pesticide in drinking water. The quantity of cypermethrin and chlorpyrifos detected were 0.11 ± 0.003 and 0.012 ± 0.0006 µg/L, respectively. Total pesticide residues of study area are shown in Fig. 1.

Farmers of Manikganj district used huge amount of pesticide to protect the *boro* crops from brown plant hoppers and green plant hoppers (Akther et al. 1998).

Table 2 Concentrations of different pesticide residues in Kaliganga River water

Sl no	Sample name	Cypermethrin (µg/L)	Chlorpyrifos (µg/L)	Diazinon (µg/L)
1	MNJ – 1	0.2	BDL[a]	BDL[a]
2	MNJ – 2	BDL[a]	0.01	BDL[a]
3	MNJ – 3	BDL[a]	BDL[a]	BDL[a]
4	MNJ – 4	0.51	BDL[a]	BDL[a]
5	MNJ – 5	0.28	BDL[a]	BDL[a]
6	MNJ – 6	BDL[a]	BDL[a]	BDL[a]
7	MNJ – 7	BDL[a]	0.12	BDL[a]
8	MNJ – 8	BDL[a]	0.01	BDL[a]
9	MNJ – 9	BDL[a]	BDL[a]	BDL[a]
10	MNJ – 10	BDL[a]	BDL[a]	BDL[a]
11	MNJ – 11	0.23	BDL[a]	BDL[a]
Mean		0.11	0.012	0.0
Std. Deviation		0.164	0.034	0.0
95 % Confidence Interval		0.003	0.0006	0.0

[a] Below the detection limit which stand 0 for mean calculation. Detection limit – 0.01 µg/L

Excessive amount of pesticide is drained into contaminated the river water by the drainage of the paddy field water. The result of the present study found that the concentration of the pesticide residue in Kaliganga River was below the MRL value of drinking water, which is consistent with the result of pesticide residue in fresh water in spring season in USA (Gallagher et al. 1996; Pfeuffer 1991). Similarly, pesticide residues were detected in the river water during low rainfall season in south East Asia including Pakistan, India and Bangladesh (Perveen and Maud 1988; Begum et al. 2009). Organochlorine pesticide residues were detected by several investigators in Bangladesh in winter season (Rahman and Alam 1997; Hassan et al. 2010).

Cypermethrin was found in groundwater in France and river water and sediment in United Kingdom (Bedos et al. 2002). 0.05 µg/L of cypermethrin and 0.02 µg/L of diazinon were detected in the summer season of Don River of Toronto, Canada. Thirty one per cent sample of the Humber River of Canada was contaminated by the diazinon. The concentration of diazinon was below the MRL value of drinking water (Bailey et al. 2005). Pesticide residue was detected in surface water of various rivers of different districts of Bangladesh in recent years, the level of various harmful pesticides was exceeded the standard limit (Rahman and Alam 1997).

Fifty µg/l concentrations of the cypermethrin and chlorpyrifos was treated separately with rice bran in water. One, 2 and 4 gm of rice bran were used to treat the spiked water sample. Table 3 illustrates the gradual reduction of the pesticide by rice bran treatment. Treatment of rice bran showed good response to remove the pesticide in water. The chromatogram of the study revealed that the gradual decrease of the cypermethrin in first trail. The gradual reduction of pesticide is shown in Fig. 2. It was found that 90 % and 95.6 % cypermethrin removal were made by 1 and 2 gm of rice bran, respectively. Table 4 illustrates the gradual reduction of the pesticide by rice bran treatment. The chromatogram of the study revealed the decline in concentration of chlorpyrifos spiked water samples and the gradual reduction of pesticide is shown in Fig. 3. Ninety five point seven per cent and 96.8 % chlorpyrifos removal were made by 1 and 2 gm of rice bran, respectively.

Residue of some pesticides is able to persist for extended periods before completely degrade by natural processes. These long-lived compounds migrate far afield by cycling into plants and animals, and into air, water and soil systems (Arjmandi et al. 2010). The extensive production

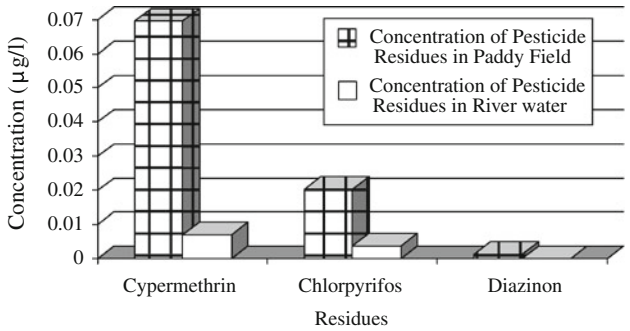

Fig. 1 Total pesticide residues detected in the water samples in the study area

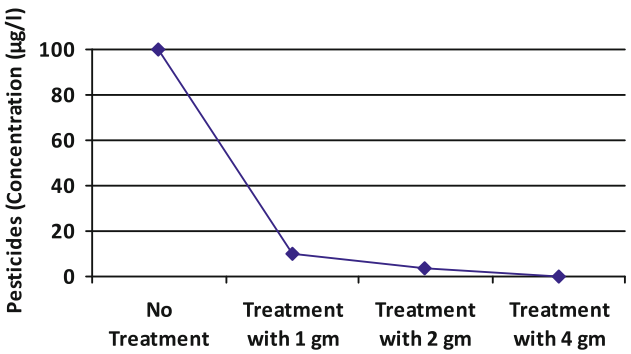

Fig. 2 Removal of cypermethrin residues through rice bran treatment

Table 3 Reduction of cypermethrin as treated with various concentrations of rice bran

Sl no	Sample code	Description	Concentration (µg/L)		Mean concentration (µg/L)	Reduction (%)
			1st trail	2nd trail		
1	CYP-1	50 µg/L cypermethrin	50	50	50	–
2	CYP-2	Treated with 1 gm of rice bran	5.4	4.7	5.05	89.9
3	CYP-3	Treated with 2 gm of rice bran	2.1	2.3	2.2	95.6
4	CYP-4	Treated with 4 gm of rice bran	BDL[a]	BDL[a]	BDL[a]	–

[a] Below the detection limit. Detection limit – 0.01 µg/L

Table 4 Reduction of chlorpyrifo as treated with various concentrations of rice bran

Sl no	Sample code	Description	Concentration (μg/L)		Mean concentration (μg/L)	Removal (%)
			1st trail	2nd trail		
1	CP-1	0.05 μg/L chlorpyrifos	50	50	50	–
2	CP-2	Treated with 1 gm of rice bran	2.1	2.2	2.15	95.7
3.	CP-3	Treated with 2 gm of rice bran	1.7	1.5	1.6	96.8
4.	CP-4	Treated with 4 gm of rice bran	BDL[a]	BDL[a]	BDL[a]	–

[a] Below the detection limit. Detection limit – 0.01 μg/L

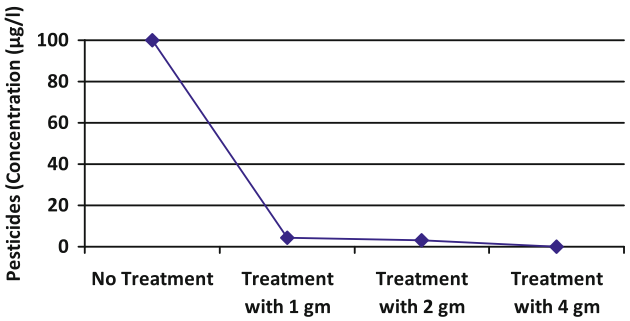

Fig. 3 Removal of chlorpyrifos residues through rice bran treatment

and use of such pesticides cause the economic problems and health hazards of persistent residues on the other (Kalam 1998). Pesticide residue was detected in water samples of wet land and paddy field around the world (Parveen and Nakagoshi 2001; Rahman and Alam 1997; Street 1969). There were several investigations performed to degrade the pesticide residue as well as decontaminate the water in developed countries (Honeycutt et al. 2001; Romeh et al. 2009). The result of the present study is good agreement with the findings of previous investigation. Romeh et al. (2009) were used rice husk and charcoal to decontaminate cypermethrin and organophosphate pesticides. 55.73 % and 87.14 % were dislodged of the initial amounts in 144 h of treatment by rice husks. Activated carbon in water is able to cause lower availability of the pesticide residues. The technique was successfully used to eliminate phytotoxic effects of residual herbicides (Kalam 1998). Adachi et al. (2000) observed almost 88 % removal of cypermethrin residue possible by rice bran paste. Adachi et al. (2002) were performed similar type of investigation to address rice bran efficiency to remove harmful chemicals from tap water.

The study result revealed that, 0.695, 0.06 and 0.039 μg/L of concentration of cypermethrin, chlorpyrifos and diazinon residues were found in paddy field water respectively. The pesticide residues were mixed with nearest river and contaminated surface water as low levels of pesticide residues were also detected in river water. Treatment by rice bran showed good response to removal of pesticides in the samples. The result of the current study revealed that a successful absorption of cypermethrin and chlorpyrifos from water by small quantity of rice bran.

References

Adachi A, Okano T (2006) Pesticide residues reduction in selected vegetables using rice bran. J Health Sci 52(3):320–323

Adachi A, Takagi S, Okano T (2000) Studies on removal efficiency of rice bran for pesticides. J Health Sci 47(2):94–98

Adachi A, Takagi S, Okano T (2002) Adsorption and adsorption mechanism of rice bran for chloroform from tap water. Chemosphere 46:87–92

Akther N, Rahman A, Chowdhury M (1998) Environmental investigation and evaluation of sericulture programme and ayesha abed foundation. Available via www.bracresearch.org/reports/sericulture.pdf. Accessed 3 Jan 2010

Ali MY (1994) Fisheries and environment: environment and development in Bangladesh 2. University Press, Dhaka, pp 71–72

Ali RB, Tahir A (2000) Preliminary survey for pesticide poisoning in Pakistan. Pak J Biol Sci 3(11):1976–1977

Arjmandi R, Tavakol M, Shayeghi M (2010) Determination of organophosphorus insecticide residues in the rice paddies. Int J Environ Sci Technol 7(1):175–182

Bailey P, Waite D, Quinnett-Abbott L, Ripley BD (2005) Residues of DDT and other selected organochlorine pesticides in soils from Saskatchewan, Canada (1999). Can J Soil Sci 85:265–271

Bedos C, Cellier P, Calvelet R, Barruiso E (2002) Occurrence of pesticides in the atmosphere in France. Agronomie 22:35–49

Begum A, Krishna H, Khan I (2009) A Survey of persistent organochlorine pesticides residues in some Streams of the Cauvery River, Karnataka, India. Int J Chem Technol Res 1(2):237–244

Chowdhury MTI, Razzaque MA, Khan MSI (2011) Chlorinated pesticide residue status in tomato, potato and carrot. J Exp Sci 2(1):1–5

Dahal L (1995) A study on pesticide pollution in Nepal. National conservation strategy implementation project, National Planning Commission, HMG Nepal and IUCN-The World Conservation Union, Kathmandu, pp 51–57

Gallagher DL, Dietrich AM, Reay WG, Hayes MC, Simmons, GM Jr (1996) Ground water discharge of agricultural pesticide and nutrients to estuarine surface water. Ground Water Monit R 1996 Winter:118–129

Hassan S, Rabbinic KA, Raman ML, Husain MA (2010) Persistent organic pollutants and pesticide residues in seasonal waters of rural Bangladesh. Available via www.binbd.com/benjp/iceab10/43.pdf. Accessed on 21 July 2010

Honeycutt R, Paulson D, LeBaron H, Rolofson G (2001) Chemical treatment option for pesticide wastes disposal. Available via www.p2pays.org/ref/13/12389.pdf. Accessed on 10 Jan 2011

IRRI (International Rice Research Institute) (2005) Medium Term Plan 2006-2008, Achieving the UN Millenium Development Goals begins with Rice Research. IRRI, Manila (Philippines), pp 5–8

Kalam KMHA (1998) Bangladesh country paper. Environmental assessment for agricultural development in Asia and the Pacific. Asian Productivity Organization (APO), Tokyo, pp 141–152

Khatoon JA, Islam MS, Talukdar MN, Hossain MA (2004) Monitoring of the residue level of three selected pesticide in red amaranth. Pak J Bio Sci 4(4):474–479

Morasso G, Bolognesi C, Duglio E, Musso M (2001) Pesticides as food contaminants: a pilot project for correct public information. Trends Food Sci Technol 11:379–382

PAB (2000) Pesticides consumption report for the year 1999/2000. PAB, Dhaka, pp 18–19

Parveen S, Nakagoshi N (2001) An analysis of pesticide use for rice pest management in Bangladesh. J Int Dev Cooper 8(1):107–111

Perveen Z, Maud SZ (1988) Organochlorine pesticide residues in cattle drinking water. Pak J Sci Ind Res 31:53–56

Pfeuffer RJ (1991) Pesticide monitoring in sediment and surface water within the south Florida. Water Manage Fla 2:8–17

Rahman MH, Alam MJB (1997) Risk assessment of pesticide used in Bangladesh. J Civil Eng CE 25:97–106

Romeh AA, Ashour M, Hendawi MY, Ramadan AR (2009) Decontamination of Cyanophos residues from water containing Catfish (*Clarias Lazera*) using activated charcoal and rice husk ash. J Appl Sci Res 5(7):820–826

Street JC (1969) Methods of removal of pesticide residues. Can Med Assoc J 100:154–160