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Occurrence of Organophosphorus and Carbamate Pesticide Residues in Surface Water Samples from the Rangpur District of Bangladesh

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Abstract We report the presence of organophosphorus and carbamate residues in 24 surface water samples and five ground water samples from Pirgacha Thana, Rangpur district, Bangladesh using high-performance liquid chromatography. A number of samples of surface water from paddy fields were found to contain chlorpyriphos, carbofuran and carbaryl at concentrations ranging from 0–1.189, 0–3.395 and 0–0.163 µg/L, respectively. Surface water from the lakes had chlorpyriphos, carbofuran and carbaryl at concentrations ranging from 0.544–0.895, 0.949–1.671 and 0–0.195 µg/L, respectively. This result indicates that the general public living in the area of Rangpur is at high risk of pesticide exposure from contaminated waters in the environment.

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Pesticides are used extensively to protect agricultural crops against the damage caused by pests. Different chemical groups of pesticides, such as organochlorine compounds, organophosphates, carbamates, pyrethroids and heterocyclic pesticides, nitro compounds and amides are routinely used for crop production (Mavrikou et al. 2008). In Bangladesh, up to 64 % of the crop-producing area is treated with carbamates and up to 35 % of the crop-producing area is treated with organophosphates. These substances can be transmitted to freshwater fish and ultimately contaminate the fish (Rahman 2000). Many pesticides used in Bangladesh contain chlorpyrifos, carbofuran and carbaryl. Even small amounts of chlorpyrifos can cause neurological disorders, such as attention deficit hyperactivity disorder (ADHD), a developmental disorder in fetuses and children (Rauh et al. 2006). Moreover, carbofuran causes serious reproductive problems, even at extremely low doses (Goad et al. 2004). According to the Environmental Protection Agency (EPA), occupational exposure to carbaryl can result in nausea, vomiting, blurred vision, coma and difficulty in breathing (EPA 1984, 1999).

Pesticides are also harmful to farmers, who are often unaware of the hazards associated with these substances and who lack proper safety protocols for working with pesticides. The use of pesticides in Bangladesh is not restricted to agriculture. Pesticides are also used for weed control in urban areas, in industrial sites, on roadsides and along railways due to their easy availability, relatively cheap cost and ease of application. Early exposure to pesticides may increase an individual's lifetime risk of cancer and harm the nervous and immune systems. Many of these compounds can cause moderate to severe respiratory and neurological damage or act as genotoxic and carcinogenic agents (Hayat et al. 2011).

It is a substantial challenge to use pesticides and simultaneously maintain water quality (Gan 2002) due to the persistence of pesticides in water. Pesticides are known to be used, both legally and illegally, in considerable quantities at Pirgacha Thana, Rangpur District, Bangladesh. This practice represents a severe threat to this heavily populated area. Pesticide contamination of ground water is an important issue because ground water is used for drinking by the majority of the population. To date, however, information about the levels of pesticide residues in various environmental water sources in this region, including paddy fields, lakes, ponds and deep tube wells, is still unavailable. Accordingly, the aim of this study is to measure the pesticide levels in samples from these sources so that the people living in the vicinity can obtain informed knowledge of the quality of the water and take necessary steps to protect their health.

Materials and Methods

Chlorpyrifos (99.0 %), carbofuran (99.5 %) and carbaryl (98.5 %) standards of reference grade were used in this study. These standards were purchased from Dr. Ehrenstorfer GmbH, D-86199 Augsburg, Germany. The acetone (BDH, England), n-hexane (Merck, Germany) and diethyl ether (BDH, England) used in the study were of analytical grade. The acetonitrile used (Scharlau, EU) was of HPLC grade.

Twenty-nine water samples from the paddy fields ($n = 12$), lakes ($n = 5$), ponds ($n = 7$) and deep tube wells ($n = 5$) of Pirgacha Thana, Rangpur District, Bangladesh were collected from May to July, 2010. The samples were kept in amber glass bottles on ice and were immediately transferred in an icebox to the laboratory at the Institute of Food and Radiation Biology. Sample collection was performed according to the recommendations of (Hunt and Wilson 1986) and (APHA 1995). The samples were stored at −20°C before analysis.

The water samples (500 mL each) were transferred to a 1,000 mL capacity separating funnel before extraction using 100 mL of solvent mixture (2 % diethyl ether in double-distilled n-hexane). The organic solvent was collected in a conical flask. Two further extractions with 25 mL solvent mixture were then performed using a similar procedure. The organic solvent layers were aspirated and combined before the addition of 20 g anhydrous sodium sulfate (Merck, Germany) to remove any residual water. The solvent was then rotary vacuum evaporated (Buchi, Switzerland) to a smaller volume (5 mL) based on the method described in the DFG Manual of Pesticide Residue Analysis (DFG 1987).

The concentrated samples were passed through a column (10 mm ID) packed with 10 g of deactivated florisil (60–100 mesh size, Sigma, USA), synthetic magnesium silicate (60–100 mesh). The top 1.5 cm of the florisil column was packed with anhydrous sodium sulfate. This extract was finally eluted with 2 % diethyl ether (double distilled using a Fractional Distillation Plant, Schott Duran, Germany) in n-hexane (double distilled) at 5 mL/min. The eluent was further concentrated in a rotary vacuum evaporator (Buchi, Switzerland) before being transferred to a glass vial. The solvent was completely dried under a gentle nitrogen flow. The dried sample was reconstituted in acetonitrile (1 mL) for subsequent analysis with high performance liquid chromatography (HPLC).

After sample cleanup, aliquots of the final volume were quantified with an HPLC (Shimadzu) LC-10 ADvp equipped with a SPD-M 10 Avp attached to a photodiode array (PDA) detector (Shimadzu SPD-M 10 Avp, Japan) (200–800 nm). The analytical column was a C18 Reverse Phase Alltech (5 μm, 250 × 4.6 mm) maintained at 30°C in a column oven. The mobile phase was a combination of 70 % ACN and 30 % water and was filtered using a cellulose filter (0.45 μm) before each use. The flow rate was 1.0 mL/min.

Prior to HPLC analysis, the samples were passed through 0.45 μm nylon (Alltech Assoc) syringe filters. The samples were manually injected (20 μL) each time. The identification of the suspected pesticide was performed relative to the retention time of the pure analytical standard. Quantification was performed based on the method described by (Bagchi et al. 2009). A typical chromatogram from the analysis is shown in Fig. 1.

The calibration curves for chlorpyrifos, carbofuran and carbaryl were prepared at three concentrations (5, 10 and 20 μg/L). The mean percentage recoveries of chlorpyrifos, carbofuran and carbaryl in the spiked positive controls of the water samples with the florisil cleanup system were 86.25 %, 90.13 % and 92.65 %, respectively (Table 1). These values were obtained from the following equation: Percentage recovery = $[C_E/C_M \times 100]$, where C_E is the experimental concentration determined from the calibration curve and C_M is the spiked concentration.

Results and Discussion

Our study is the first to report the presence of carbofuran and carbaryl in water samples from paddy fields and lakes in Bangladesh. Water samples originating from 16 of the 29 sampling locations (i.e., 11 samples from the paddy fields and five samples from the lake) were contaminated

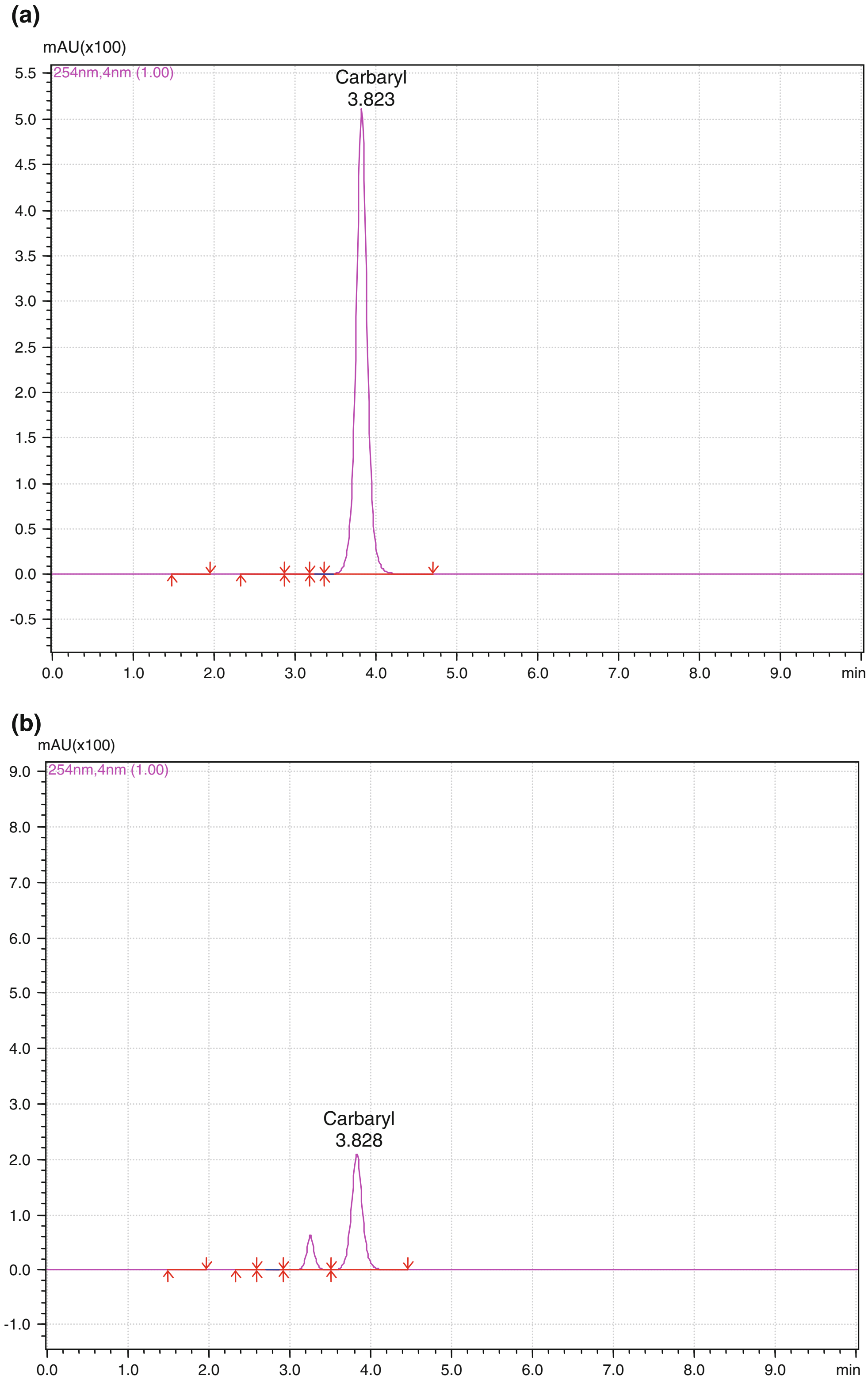

Fig. 1 **a** Typical chromatogram of a carbaryl standard injected at 2.3 µg/mL. **b** Chromatogram of water sample (WS08) indicating the presence of carbaryl

with chlorpyrifos, carbofuran and/or carbaryl (Tables 2, 3). All samples from the pond and deep tube wells were free from any contamination. All of the lake samples were contaminated with both chlorpyrifos and carbofuran. The highest concentration of chlorpyrifos pesticide detected in our study (1.189 µg/L) was found in water samples from a

Table 1 Percentage recoveries of chlorpyrifos, carbofuran and carbaryl

Analyte	Distilled water (mL)	Single spiked level (μg/L)	Mean amount (μg)*		Mean recovery (%)
			Spiked	Measured	
Chlorpyrifos	500	0.2	100	86.25	86.25
Carbofuran	500	0.2	100	90.13	90.13
Carbaryl	500	0.2	100	92.65	92.65

* Mean values of triplicates

Table 2 Concentrations of pesticide residues in water samples from the paddy fields

Sample ID	Sample source	Sample type	Mean concentration (μg/L)*		
			Chlorpyrifos	Carbofuran	Carbaryl
WS-01	Paddy field	Surface water	**0.515**	**0.975**	ND
WS-02	Paddy field	Surface water	**0.605**	**0.940**	ND
WS-03	Paddy field	Surface water	**0.530**	ND	ND
WS-04	Paddy field	Surface water	**0.523**	ND	ND
WS-05	Paddy field	Surface water	ND	**0.934**	ND
WS-06	Paddy field	Surface water	ND	**2.902**	ND
WS-07	Paddy field	Surface water	**1.189**	**3.395**	0.055
WS-08	Paddy field	Surface water	ND	ND	**0.163**
WS-09	Paddy field	Surface water	ND	**1.037**	ND
WS-10	Paddy field	Surface water	**0.640**	**1.148**	ND
WS-28	Paddy field	Surface water	**0.477**	ND	ND
WS-29	Paddy field	Surface water	ND	ND	ND
Concentration ranges			ND-1.189	ND-3.395	ND-0.163

Concentrations in bold are those that exceed levels that are safe for humans, established by the EEC at 0.1 μg/L for any pesticide (or 0.5 μg/L for total pesticides)

Limit of detection (LOD): 0.01 μg/L

WS water sample, *ND* not detected

* Mean value of triplicates

paddy field. This value was slightly higher than the highest concentration reported in Kollanpur Lake, Dhaka, Bangladesh, 0.982 μg/L (Khatun et al. 2008) and is four times higher than the highest concentration (0.29 μg/L) of chlorpyrifos pesticide residue recorded in the surface water flow associated with a tobacco crop in the USA (Bortoluzzi et al. 1987).

Table 3 Concentration of pesticide residues in water samples from the lakes

Sample ID	Sample source	Sample type	Mean concentration (μg/L)*		
			Chlorpyrifos	Carbofuran	Carbaryl
WS-11	Lake	Surface water	**0.895**	**1.278**	**0.195**
WS-12	Lake	Surface water	**0.699**	**1.671**	ND
WS-13	Lake	Surface water	**0.629**	**1.523**	ND
WS-14	Lake	Surface water	**0.740**	**1.198**	ND
WS-15	Lake	Surface water	**0.544**	**0.949**	ND
Concentration range			0.544–0.895	0.949–1.671	ND-0.195

Concentrations in bold are those that exceed levels that are safe for humans, established by the EEC at 0.1 μg/L for any pesticide (or 0.5 μg/L for total pesticides)

LOD: 0.01 μg/L

WS water sample, *ND* not detected

* Mean value of triplicates

It can be postulated that these pesticides are widely used by the farmers to kill both insects and nematodes to ensure the proper growth of their paddy in the Rangpur District of Bangladesh because both chlorpyrifos and carbofuran were detected in high concentrations in the paddy fields. It is therefore advisable that the people living in this area not consume fish or other aquatic animals caught in the paddy field because the high pesticide levels in their environment may contaminate the aquatic animals. The farmers may also be directly exposed to the harmful effects of these pesticides. It is also possible that harmful residues may remain in the edible portion of the plants and may reach humans because humans are the highest animal on the food chain and are therefore most susceptible (Bakore et al. 2004).

All of the lake samples were contaminated with both chlorpyrifos and carbofuran. One sample from the lake contained all three pesticides at levels above the levels recommended by the EEC as safe for consumption. This situation is dangerous because the consumers of aquatic products from the lake will experience substantial exposure to high pesticide levels. Moreover, it is possible that these levels are influenced by water containing pesticides heavily used in agriculture in the paddy fields in Rangpur District. This water originates in the paddy fields and is transported by the rivers to the lake.

The highest concentrations of carbaryl (0.195 μg/L) detected in the lake by our study may be compared with the higher carbaryl concentrations (0.33–0.9 μg/L) detected by (Wilson and Foos 2006) in surface water samples in the USA. However, no carbofuran was detected in the samples collected by that study. This difference could be due to the difference between the pattern of pesticide use in the USA and in Bangladesh. Due to the toxic properties of organochlorine pesticides and the potential consumer risk that they pose, their residues in food commodities represent an issue of public concern and are controlled by legislation (Kin et al. 2006). Currently, organophosphate insecticides are used in Bangladesh because most of the organochlorine insecticides have been banned due to their toxicity, persistence and bioaccumulation in the environment (Molto et al. 1991). These insecticides are transported into the ground water through leaching, channelling (downward percolation), direct spillage and wind drift. Drinking water is generally obtained from surface water sources (such as rivers, canals or lakes) or from underground aquifers. The quality of surface water is deteriorating as a result of the disposal of untreated municipal and industrial wastewaters and saline drainage effluent from agricultural areas (Aziz 2005; Iram et al. 2009).

We found that all of the samples from the pond and deep tube well sources were free from contamination with the residues of identified pesticides. Bagchi et al. (2009) reported similar results. This outcome is desirable because ground water from the deep tube well is also consumed as drinking water by the general public. It is also possible that in Rangpur District, the bunds around the ponds and the soil mass above the ground water may protect these two types of water sources from contamination by the movement of pesticides.

The present study indicates that chlorpyrifos and carbofuran pesticides are widely used, perhaps indiscriminately, by the local farmers in Rangpur District. These results are in contrast to the findings of the study regarding the use of carbaryl in the district. This study indicates that pesticides are used indiscriminately by farmers on their paddy fields. These pesticides may be transported to the lakes and may contaminate the aquatic environment. It is advisable that the people living in the vicinity of Rangpur District not consume aquatic products from the paddy fields or from the lakes because these products may be heavily contaminated by pesticides. Samples taken from the ponds and deep tube wells indicate that the water from these two sources is free from contamination and is therefore safe for consumption.

It is recommended that future studies collect more numerous water samples at different time intervals because the nationwide patterns of pesticide use may vary over a year. Water samples need to be assessed on a routine basis because a number of samples were found to be contaminated with pesticides at levels that exceeded the safe levels required for good health.

We conclude that the water quality of two of the sources studied, the paddy fields and the lake, has been compromised by the presence of dangerous pesticides that may also affect the aquatic environment. The farmers living in the part of Bangladesh investigated by our study should be more cautious about applying pesticides not only to prevent their own direct exposure but also to avoid possible environmental contamination and ensure a higher quality of life. The results of this study may be used by researchers in the future to help adopt better measures to control the threat of water pollution.

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