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Organophosphorous Pesticides in Surface Water of Iran

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Abstract This research aims to evaluate the presence and distribution of pesticides in Babolrood River of Mazandaran Province in Iran. Mean diazinon levels in surface water ranged from 77.6 to 101.6 $\mu g\ L^{-1}$ with maximum level of 768.9 $\mu g\ L^{-1}$ and mean malathion levels ranged from 55.7 to 75.9 $\mu g\ L^{-1}$ with maximum level of 506.6 $\mu g\ L^{-1}$. The residues of malathion and diazinon pesticides in all of the stations, 2 weeks after spraying, were more than allowed limits.

Keywords Surface water · Organophosphorus · Pesticides

The main pollutions of surface and ground water are organophosphorus pesticides such as chlorpyrifos, diazinon, malathion, parathion, pirimiphos methyl, azinphos methyl and so on (Real et al. 2007). Over 13,000,000 lbs (6,000,000 kg) of diazinon is applied annually in the USA, and malathion is most widely used of them (32%–44% of total use of organophosphrous pesticides) (Zang and Pagilla 2010). Usage of organophosphorus pesticides on agricultural and urban areas has resulted in pollution of natural water resources such as surface water and ground water (Gilliom 2007). Primary pollutions may spread through runoffs from usage areas to lakes, rivers and also aquifers. Polluted surface water and ground water are eventually used as direct source or resources of raw water for community drinking water systems (Eichenberger and Litchenberg 1971). There are many reports about contamination of surface water by pesticides (Tsuda et al. 2009; Sun et al. 2006; Shayegh et al. 2001; Hela et al. 2005).

Organophosphorus chemicals do not easily volatilize from soil or water and are associated with toxicity of aquatic organisms. Organophosphorus pesticides are inhibitor of acetylcholinesterase enzyme and are also responsible for poisoning of humans (Howard 1991).

There are a few literatures about pollution of surface and ground water by organophosphorus pesticides (Wilsont and Foos 2006). Organochlorine and organophosphorus insecticide are the main causes of pollution in drinking water supplies (Pedersen et al. 2006).

Babolrood River is one of pesticide polluted rivers of Iran, especially polluted to organophosphorus one, such as malation and diazinon which are used as spray in gardens placed beside the river for control of pests on fruit trees. Malathion and diazinon, therefore, enter to the river directly or indirectly through the rain, wind and so on. Iran is an arid country according to the world nation's geographical classification. Thus, sanitation of this river is very important. Additionally, water contamination is under monitoring in Iran due to the health effects of organophosphorus pesticides and pollution of surface. The aim of this study is detection of organophosphorus pesticides in surface water of Babolrood River in Mazandaran province of Iran.

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Materials and Methods

Firstly, three stations were selected for water sampling. Fifty-four samples were collected from different parts of each station and two liters sample was prepared for each station. In order to prevent hydrolysis of pesticides in aqueous samples during carrying them to laboratory, 50 cc methylene chloride solution was added to each sample. Sample containers were sealed by parafilm, tagged and transferred to laboratory for insecticide extraction. Samples must be taken in 2 weeks after spraying maximum for each station. Sampling was done in 12 months from June 2010 to June 2011.

Water of Babolrood River was analyzed for parameters including electrical conductivity (EC), turbidity, pH, total hardness, total alkalinity, Na^{+}, Ca^{+2}, Mg^{+2}, SO_4^{-2}, HCO_3^{-} and Cl^{-} by standard methods (APHA et al. 2005). For extraction of diazinon and malathion, dispersive liquid–liquid microextraction (DLLME) technique was used (Farajzadeh et al. 2009).

A 5 mL sample (water + analyte) mixed with 500 mL extraction solution (2 mL internal standard: chlorpyrifos 1,000 mg L^{-1}, 10 mL chloroform and 100 mL of acetone). The mixture was then centrifuged for 5 min at 3,500 rpm. After this process, the upper of aqueous phase was collected by pipette; the droplets were settled at the bottom of the conical tube and 1 mL injected into GC/MS. Analyses was performed by gas chromatography mass spectroscopy (GC–MS). For identification, 1 mL of samples was injected into GC–MS (Varian CP-3800 GC with MS trap detector Varian Saturn 2200, run in EI mode). Injector temperature was 270°C and analysis was done using a capillary column (Varian DB-5 column; 30 m 250 µm id, film thickness 0.25 µm). The method started at 150°C, which was held for 2 min, then ramped to 120°C at a rate of 25°C min^{-1}, followed by an increase to 270°C (held for 2 min). Split mode was used with a split ratio of 1:10 Helium (99.999%) for carrier gas at 1 mL min^{-1}.

Recovery rate of malathion and diazinon was 85%–95%. The minimum detection level (MDL) for malathion and diazinon analysis by GC/MS with above methods were 0.06 and 0.08 µg L^{-1}, respectively.

Result and Discussion

General characteristics of surface water are shown in Table 1. Results of this study showed that there is a significant difference between manthion and diazinon of water samples from tree stations $p < 0.05$. Diazinon residue in water samples of stations 1, 2 and 3 were more than malation. The reason is more usage of diazinon than malathion by farmers and gardeners in that area. This pesticide is used against stem-boring caterpillar (*Chillo* spp.) and is used frequently during the farm practices. The highest amount of organophosphorus pesticide was seen in station 1, where the water was directly exposed to pesticides spraying, and the lowest amount was seen in station 3 (Table 2). Results show that amount of detectable organophosphorus pesticides in the water samples of stations decreased in cold weather. In station 1 which was close to gardens and spraying places, pesticides were detectable and more than other places. Also water pH, temperature, turbulence (dissolving more oxygen and faster regeneration of depleted oxygen), slope of river, daily and seasonal rains, time and rate of pesticide application and its concentration in first solution, have effect on amount of the pesticides in water. (Pandey and Carney 1992).

There are several reports that listed organophosphorus pesticides in surface water in different places of the world.

Table 1 Mean analytical results for water samples of Babolrood River

Parameter	Concentration/level
Temperature (°C)	25.6
pH	7.46
EC (µscm^{-1})	725
TH (mg L^{-1} CaCO3)	258.1
TA (mg L^{-1} CaCO3)	290
Turbidity (N.T. U)	12.5
SO_4^{-2} mg L^{-1}	67.98
HCO_3^{-} mg L^{-1}	353.8
Cl^{-} mg L^{-1}	80.2
Na^{+} mg L^{-1}	55.97
Ca^{+2} mg L^{-1}	82.94
Mg^{+2} mg L^{-1}	27.94

Table 2 Mean concentrations of pesticides in surface water

Station	Diazinon concentration (µg L^{-1})	Malathion concentration (µg L^{-1})
Mean 1	101.6	75.9
Max	768.91	503.58
Min	18.88	8.41
n = 18		
Mean 2	90.8	67.7
Max	650.8	421.58
Min	11.59	16.13
n = 18		
Mean 3	77.6	55.65
Max	248.83	102
Min	4.97	4.59
n = 18		
$p < 0.05$		

Hoffiman et al. (2000) have published a more detailed analysis of detection of pesticides in urban stream in the USA. Diazinon and carbaryl were most frequently detected insecticides (70% and 44% of samples, respectively).

The frequency of detection of the organophosphorus pesticides was low with the exceptions of malathion, chlopyrifos, and diazinon whose concentration ranges extended from 100 to <10 ng L^{-1}, in surface water and untreated water in the US (Blomquist et al. 2001).

In surface water resources, concentration of malathion has been reported to range from 0.005 to 6 μg L^{-1} in the US (Newhart 2006). Organophosphorus pesticides can pollute surface water and also sometimes ground water supplies (Castilho and Fenz 1999). Water polluted by pesticides can have acute effects (Abdel-Halim et al. 2006). The levels of pesticide residue in the water of Meiliangwan Bay, Taihu Lake of china were 11.6 ng L^{-1} for malathion, 2.17 ng L^{-1} for parathion and 4.12 ng L^{-1} for methyl parathion (Zhou Fang et al. 2006). European Union (EU) allows a maximum concentration of 1–3 μg L^{-1} as sum of pesticides in surface water (Ballesterros and Parrado 2004).

According to the results of this study the amounts of malation and diazion pesticides were more than allowed limits in the water of Babolrood River. One of the important reasons for this problem was the lack of knowledge of farmers about necessary dosage, methods and suitable time of pesticide application, which is a negative point for using more pesticides. Hence, education of farmers is the first step to do by directors and health authorities.

The first survey about the contamination of surface water in Iran by organophosphorous pesticides revealed that the Babolrood River has been contaminated by malathion and diazinon, so more monitoring of pesticides near to rice farms and fruit gardens is recommended there. Highest pollution of pesticides in Babolrood River of Mazandaran province is related to diazinon, since it is newly presented to rice farmers and most liked by them, also spraying over gardens of Babolrood River's sides can be the origin of contamination of the river to malathion and diazinon pesticides.

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