Original Article

Investigating on the Residue of Organophosphate Pesticides in the Water of the Hablehrood River, Garmsar, Iran

Mohammad Safari[1,2]; Ali Ahmadfazeli[2]; Hassan Vatandoost[3-4]; Mostafa Karimaee[5]; Davood Panahi[1]; Mohammadali Shokri[1]; Mehdi Moradian[1]; *Zahra Soleimani[1-2]

[1]Student Research Committee, Semnan University of Medical Sciences, Semnan, Iran
[2]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran
[3]Department of Medical Entomology and Vector Control, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran
[4]Department of Environmental Chemical Pollutants and Pesticides, Institute for Environmental Research, Tehran University of Medical Silences, Tehran, Iran
[5]Department of Environmental Health Engineering, Semnan University of Medical Sciences, Semnan, Iran

(Received 27 Sep 2018; accepted 17 Aug 2020)

Abstract

Background: Organophosphate pesticides are of concern to the drinking water supply and high risks on human health.

Methods: An occurrence survey was performed in the spring and summer of 2016 for 6 months to assess the prevalence of organophosphate pesticides in the Hablehrood River that is located in Semnan Province. Besides, 10 kinds of organophosphate pesticides were sampled in 5 stations. Moreover, were measured by Gas Chromatography (GC) was supported by an electron capture detector (ECD) and Turbochrom software. In all stations, Diazinon was detected in the spring and summer, but Malathion only in the spring.

Results: The highest concentration of Diazinon was observed at the Mahmoud Abad station in spring (0.94ppb) and the Bonekooh station in the summer (0.93ppb). The highest and lowest concentrations of Malathion were detected in Mahmoud Abad (0.35ppb), and Gache station, respectively.

Conclusion: The concentration of pesticides in BoneKooh and Mahmood Abad was higher than the standard.

Keywords: Organic pollutant; Agriculture; Water; River

Introduction

In a society, healthy drinking water has the most significant impact on human health (1, 2). Pesticides are widely used to control pests in agriculture to increase their productivity (3-6). These compounds are one of the sources of water pollution with serious health risks for humans and animals. Furthermore, this makes changes in ecosystems with dangerous consequences for the environment and agriculture, as they cause the emergence and spread of new pests and diseases, thereby increasing the need for them to be used (7). As in previous decades, concerns about water pollution have increased due to the identification of a large number of pesticides (8). Despite global efforts to eliminate or reduce the release of these compounds, there is still evidence of their presence in various matrices of living and non-living organisms (4). The presence of organic pollutants in surface waters may indicate acute exposure of humans and wildlife, and consequently requires continuous monitoring of these pollutants in water resources (1). Pesticides used in agriculture enter water resources through direct washing, irrigation, and rainfall in contaminated

*Corresponding author: Dr Zahra Soleimani, e-mail: ronak_soleimani@yahoo.com

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Published Online: September 30, 2020

areas (4-7, 9-12). The resistant nature of organochlorine pesticides in the environment leads to problems like chronic toxicity in humans and animals through water, food, and air (3, 5, 10-11). These compounds are less commonly used due to their effect on the nervous system because they quickly pass through cell membranes due to their hydrophobic properties (11).

On the other hand, it is estimated that around 200,000 people die annually from pesticide poisoning. The effects of these compounds on humans and the environment depend on the concentration of input toxin, chemical quality, duration of use, exposure time, and toxicity (9). In Iran, these compounds are widely used in agriculture and horticulture (13). The first step to manage pesticide residues in water resources is measuring them and compare with existing standards (9). For drinking and environmental waters, the EU has 0.1µg/l; the maximum permitted concentration for a compound's 0.51µg/l for all pesticides (7-9). Because of the high resistance of these compounds in the environment, there is a high tendency to examine their contamination (10). Because the river is the most valuable source of drinking water, it is vital to know the presence of these compounds in water before using it (14). Studies by the US Environmental Protection Agency (EPA) show that conventional water treatment processes (coagulation, sedimentation, filtration, softening, and chlorination) cannot effectively eliminate pesticides. It was demonstrated that, throughout the chlorination process, the sulfur atom double-bonded to the central phosphorus atom in organophosphate pesticides (OPPs) is replaced by an oxygen atom, which considerably increases the toxicity of these compounds (15). Recent studies have revealed that Chlorpyrifos and Malathion derivatives are at least 100 times, and Diazinon derivatives are ten times more toxic than their original forms. This can be posed as a serious problem because the most common method for disinfecting is chlorination (15). Due to the serious problem of low water amounts in the country, it is important to manage and monitor the quality and quantity of available water resources. Awareness of the residuals of these pesticides in this river is critical for the supply of safe and healthy drinking water so that, if necessary, measures will take to control and prevent any environmental and health crisis. Therefore, this study aimed to determine the residual amounts of organophosphate pesticides in the Hablehrood River, which is the main source of drinking water in Garmsar City.

Materials and Methods

Study area

Hablehrood Basin is located in the northwest of Semnan and northeast of Tehran Province. The region with an area of about 37570 hectares is placed between the eastern longitudes 52 º14´, 52 º35´, and the northern latitudes 35 ˚07´, 35 ˚16´. The average temperature and rainfall are 7.8 °C, 318mm, respectively, which ultimately enter Garmsar Plain. The basin includes the agricultural land of Garmsar and its suburbs that located in the western part of Semnan province. About the use of pesticides for agriculture activity, the amount of pesticides used in the southern and northern parts of the Hablehrood Basin in 2014 was 26667kg and 2251kg, respectively (16).

Sampling

In this study, sampling was done monthly in the spring and summer of 2016 (6 months). Hence, five sampling stations select according to the active water basin and agricultures activity including; Simin Dasht, BoneKooh, Mahmoud Abad, Zarrin Dasht, and Gache were identified along the river (Fig. 1). We chose these stations for two reasons: First, there was no easy access to the river from different places along the river;

second, these stations were downstream of agricultural activities. Each month, two samples were taken from each station (60 samples in the whole study). Samples collected in 1-liter dark-colored bottles, which completely covered with aluminum foil, were filled in 0.5m depth from the surface of the water. The preparation of bottles comprised washing with detergent without phosphorus compounds and distilled water. Then, by adding the preserving agent (0.5g ascorbic acid to the samples with free chlorine), samples were collected according to the standard method and transferred to the laboratory, they were stored in a refrigerator at 2 °C for analysis (17).

Extraction and analysis of samples

Chromatography techniques are perceived as the best way to detect pesticides (1, 18). The samples were filtered by fiberglass filter (0.45 microns) to separate suspended solids. All samples transport to the laboratory in Cold Box (between 1 °C and 4 °C); water samples were extracted using a solid-phase extraction (SPE) system according to the established Procedures; samples were analyzed over three days (19). The extraction EPA methods 8141B was chosen for determination pesticide (19). The gas chromatography used to measure residual pesticides was supported by Electron Capture Detector (ECD) and Turbochrom software. This detector can detect contaminants at low concentrations (ppb range). The Column Capillary Silica PE-17 was used for chromatographic separation of pesticides. Nitrogen was used as a carrier and make-up gas, and the injection method was in the division state (Table 1) (20).

Statistical analysis

SPSS 21.0 and Microsoft Excel software was used for data analysis. Data on pesticide concentration in different stations and seasons were analyzed by independent t-test and one-test was used to compare two stations or compare each season and compare with level standard concentration pesticide respectively. Besides, in various stations and seasons were analyzed by ANOVA, the Tukey test was used to compare the two seasons and station in duration sampling.

Results

The results of the analysis of water samples of the Hablehrood river during the spring and summer revealed that only the Diazinon and Malathion were present in water, and the rest were absent in any of the samples. The results of the analysis of samples are summarized in Table 2.

According to Table 2, the only pesticide detected in the spring was Diazinon, and in the summer, Diazinon and Malathion were detected. Generally, the results of this part of the research indicate that the average concentration of Diazinon in different stations is significantly higher in the summer ($P< 0.05$). Diazinon in the Hablehrood River was significantly the highest concentration of related to the Mahmoud Abad station in spring (0.94ppb) ($P< 0.05$), and the Bonekooh station in the summer (0.93ppb) Figures 2 and 3 show the concentrations of Diazinon residuals in different stations in spring and summer ($P< 0.05$).

Malathion was observed only in summer samples. The highest concentration of Malathion in the Hablehrood River was detected in Mahmoud Abad (0.35ppb) and the lowest at Gache (0ppb). The concentrations of Malathion in different stations in summer are presented in Fig. 4.

Other organophosphorus pesticides that were measured in this study comprise Dichlorvos, Trifluoralin, Methyl-parathion, Fenitrothion, Profenofos, Ethion, and TEPP. But did not detect in any of our samples. From sampling stations, Diazinon was observed in spring at all stations. The largest and lowest amount of its concentration was in Mahmoud Abad, Gache, respectively. In summer, Diazinon and Malathion have detected at all stations. Which the highest concentration of Diazinon was in Bonekooh and lowest in Gache. The highest and lowest amount of Malathion was observed in Mahmoud Abad and Ghache respectively. Total pesticides in water samples of BoneKooh and Mahmoud Abad in summer were significantly over the permitted of EC (1µg/l total allowable pesticide in surface waters) ($P< 0.05$) (21).

Table 1. Gas Chromatography condition for pesticide measurement

Modes	Amount
Injection volume	1microliter
Inlet pressure	7 psi
Injector temperature	300 °C
Detector temperature	300 °C
Gas flow ECD make up	40 ml/min
Oven programming	220–240 °C at 2 °C/min
	240–260 °C at 1 °C/min
	260–280 °C at 5 °C/min

Table 2. Results from analysis of water samples of Hablehrood River during spring and summer

Detected amount of pesticides (ppb)		Station				
Compound Name	**Season of sampling**	**Zarrin dasht**	**Ghache**	**Simin Dasht**	**Mahmoud Abad**	**Bonekooh**
Dichlorvos	**spring**	Nd	Nd	Nd	N.d	N.d
	summer	Nd	Nd	Nd	Nd	Nd
Trifluralin	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	Nd	Nd	Nd	Nd	Nd
Diazinon	**spring**	0.74	0.2	0.6	0.94	0.5
	summer	0.6	0.5	0.6	0.89	0.93
Methyl Parathion	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	Nd	Nd	Nd	Nd	Nd
Fenitrothion	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	Nd	Nd	Nd	Nd	Nd
Malathion	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	0.2	Nd	0.15	0.35	0.2
Profenophos	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	Nd	Nd	Nd	Nd	Nd
Ethion	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	Nd	Nd	Nd	Nd	Nd
Azinphos methyl	**spring**	Nd	Nd	Nd	Nd	Nd
	summer	Nd	Nd	Nd	Nd	Nd
	spring	Nd	Nd	Nd	Nd	Nd
TEPP(IS)	**summer**	Nd	Nd	Nd	Nd	Nd

Nd= Non detectable

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Published Online: September 30, 2020

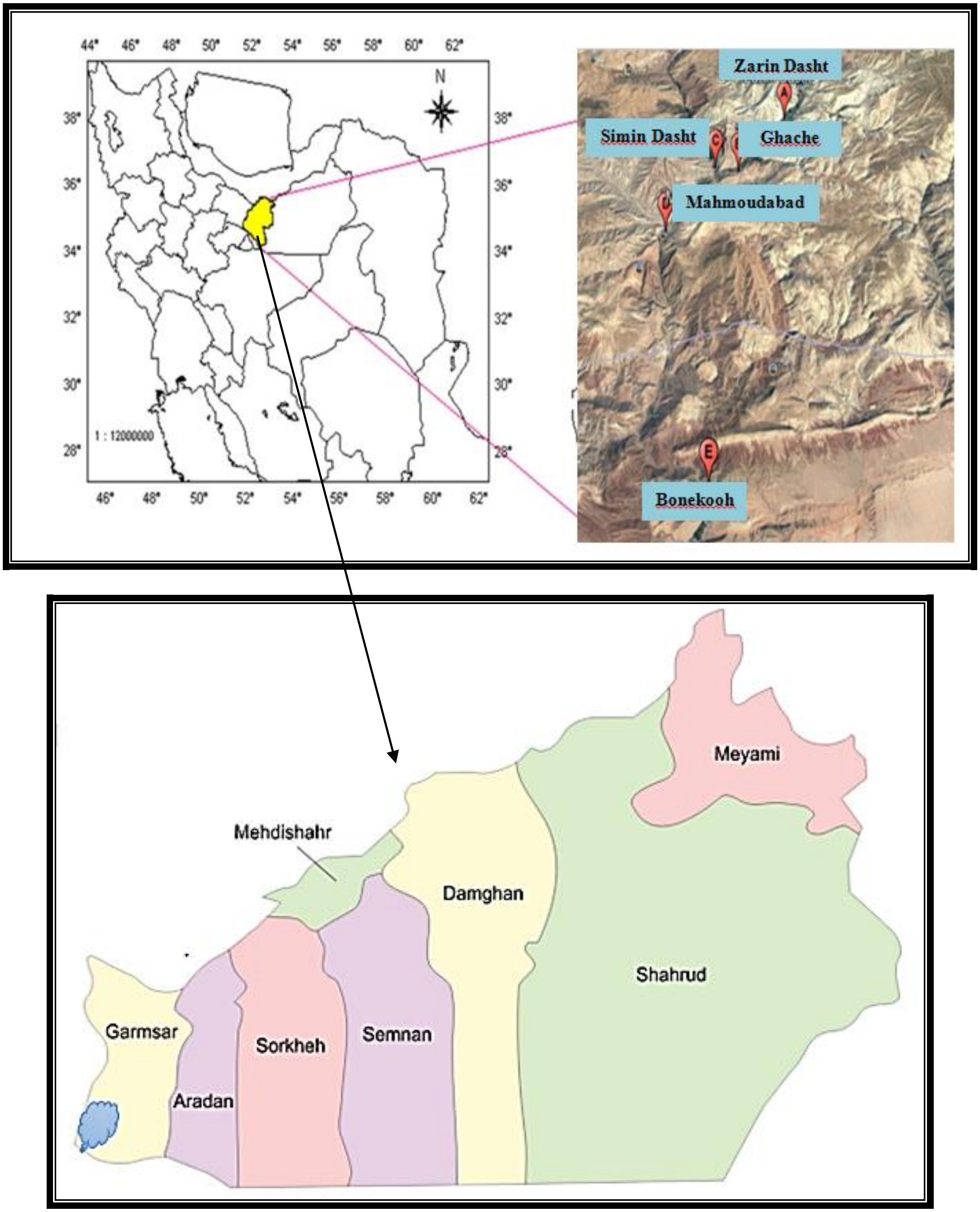

Fig. 1. Hablehrood basin and sampling stations

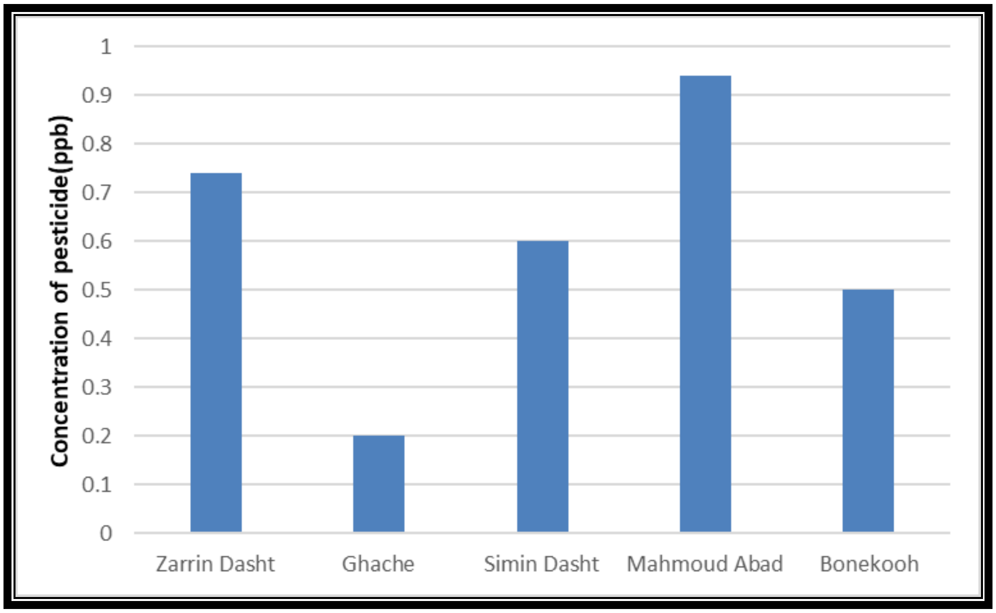

Fig. 2. Diazinon concentration (ppb) at different stations in the spring

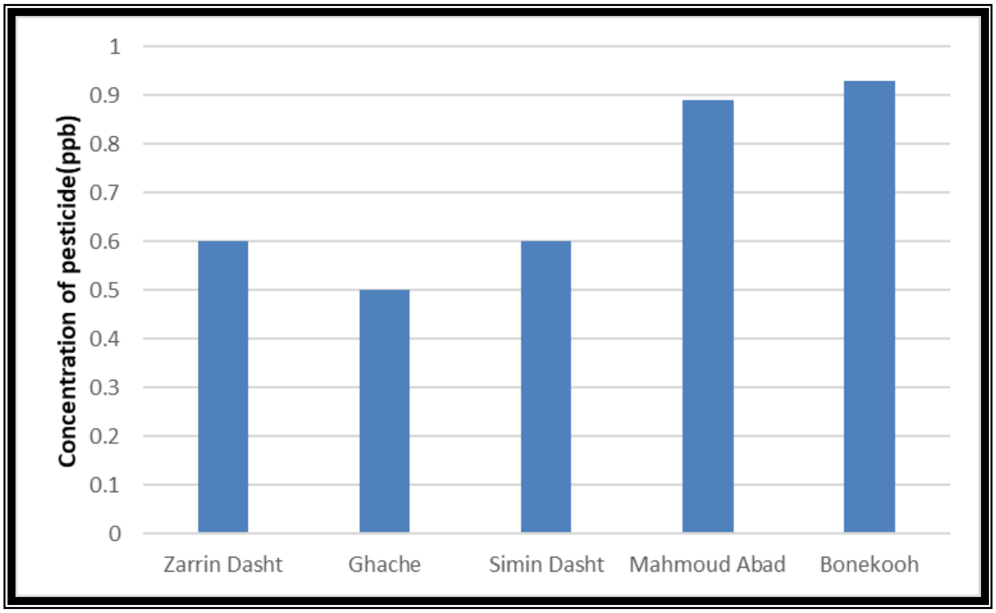

Fig. 3. Diazinon concentration (ppb) at different stations in the summer

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Published Online: September 30, 2020

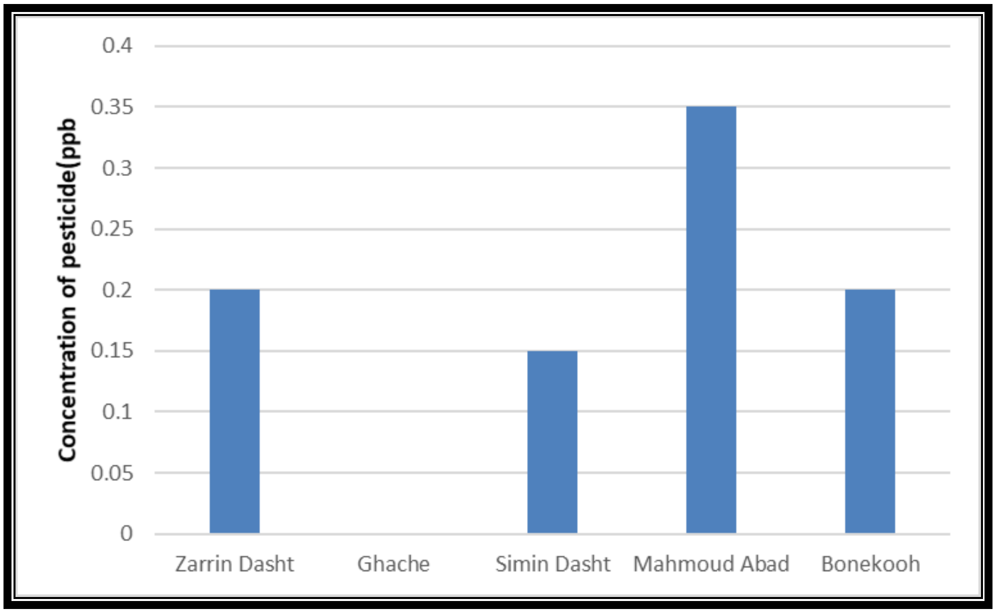

Fig. 4. Malathion concentration (ppb) at different stations in the summer

Discussion

Most farmers use more organophosphate pesticides than others because of their low cost and a wide range of uses. Malathion and Diazinon have been used in all over Iran (22). As it is discussed, these organophosphate pesticides were detected in all stations of Hablehrood River consequently, it is suggested to survey these pesticides in other water supplies. Furthermore, due to the lack of education and awareness, farmers do not take caution when using pesticides, which increases pesticide-related diseases in agricultural areas. Organophosphate pesticides have adverse effects on the body by inhibiting the activity of Acetylcholinesterase enzyme. The effects of carcinogenesis, mutagenesis, and teratogenicity of this group of pesticides have been proven. Moreover, these disrupt sexual hormones, reproductive problems, and stop human growth (23). It is well-known that many of pesticides that are used do not remain in their target area and are transferred through penetration into the soil and runoff, and also become new compounds, and many of them enter surface and underground waters, and their metabolites may remain for many years (24-25). The amount of pesticide residues in the water resources depends on different factors, such as the application of each pesticide, proximity of agricultural land to the river, metabolism of pesticides to other compounds, absorption of pesticides into organic matter in water and soil, water temperature and pH (26). For this reason, the residual concentrations of diverse types of organophosphate pesticides are various in different sources. In the present study, Dichlorvos, Trifluoralin, Methyl-parathion, Fenitrothion, Profenofos, Ethion, and TEPP were not detected in any of the analyzed samples due to their low application and high hydrolysis rates. The study of Dehghani et al. (2012) on Kashan water resources, which is consistent with the results of the present study, showed that the rate of removal of Chlorpyrifos is higher than Diazinon and its amount was much lower than of it (27). In the study by Kent et al. (2005), who studied the pesticide residues

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Published Online: September 30, 2020

in California's surface waters, it has been observed that 92% of the samples contained at least one pesticide. Moreover, the concentration of Diazinon in some samples was higher than the standard values (28). The results of this study were also consistent with Kent's study, and in summer, the total pesticide concentrations at Mahmoud Abad station was higher than standard values, which could be due to low knowledge of farmers about the application of pesticides. Farmers to prevent the occurrence of diseases for their products and higher productivity, use various fertilizers and pesticides. Due to many problems of pesticides on the environment and human health, increasing farmers' awareness about the correct way of cultivation, amount of pesticides, and the natural combating means for agricultural pests can be effective in decreasing the concentration of pesticides in aquatic resources and environment. The consumption of Diazinon for agricultural products is high in spring and summer. Additionally, the high residue of Diazinon in water samples can be due to the high solubility of Diazinon in water and also atmospheric falls in the early spring and the entry of this to surface waters (29). Besides, Diazinon is used more often than other pesticides. Among the studies that are consistent with the results of the present study and the level of pesticides exceeds the maximum permissible standard concentration can be found in the study by Chowdhury Maz et al. (30), Lari et al. (31), and Székács et al. (32). Because of its high solubility rate relative to other pesticides, huge levels of its application, and frequency of use during the crop year, its residual amount was also higher than other pesticides studied in water samples, which is consistent with the results of Khazaei et al. (33). Malathion has a lower consumption than of Diazinon. Malathion was not observed in any of the spring samples but was observed in summer samples at different stations except Gache station. Another reason for the high level of Diazinon and Malathion at Mahmoud Abad and BoneKooh stations could be due to extensive agricultural and horticultural activities in this area. Therefore, as much as we move alongside the river from upstream to downstream, the concentration of pesticides used increases. This can be due to increased agricultural activity and the accumulation of pesticides used in the study area. In other words, a part of a pesticide is degraded and converted to its derivatives, but another part of it goes downstream. The pesticides used in each area are added to it. The residual pesticides in BoneKooh station were lower than other stations, because this station had a large distance from the other station, and there is a considerable distance from the agricultural activity area to this station; so part of the pesticides will be decomposed into their derivatives before reaching to this station.

Conclusion

Diazinon and Malathion were observed in Hablehrood River samples. Because there is no comprehensive national standard for the maximum residual concentration of pesticides in water resources, the European Union (EC) standard was used (34). The concentration of pesticides in BoneKooh and Mahmood Abad in summer was higher than the standard. The mobility of chemicals and their traits, as well as the proximity of agricultural land to Hableh Rood, affects the possibility of contamination of the river by pesticides. The presence of pesticides in water resources can be due to reasons such as uncontrolled manual spray, poor management in the process of pesticides using, and unnecessary and inappropriate application of pesticides. However, the proper use of pesticides at the right time and preventing the entrance of pesticides into the water can reduce their concentration in water resources. Furthermore, continuous monitoring and measuring of pesticides should be a priority for drinking water resources to protect the health of the community and the environment.

Acknowledgements

This article is a result of the A-334, A-1031 project sponsored by the Student Research Committee of Semnan University of Medical Sciences. Semnan, Iran.

The authors declare that they have no conflict of interest.

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