RESEARCH ARTICLE
• Arch Hyg Sci 2015;4(1):41-8
• Journal Homepage: http://jhygiene.muq.ac.ir

Estimation of the Concentration of Diazinon Pesticide in Drinking Water Resources in Summer Areas of Mashhad, Iran

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A-R-T-I-C-L-E I-N-F-O

Article Notes:
Received: May 4, 2014
Received in revised form: Dec 26, 2014
Accepted: Dec 28, 2014
Available Online: May 28, 2015

Keywords:
Diazinon, pesticide, HPLC, water resources, summer areas, Mashhad.

A-B-S-T-R-A-C-T

Background & Aims of the Study: Torqabeh and Shandiz are the two most well-known areas among the varied summer areas of Mashhad. The climate of these areas is appropriate for the development of agriculture and gardening and attracting tourists. Hence, maintaining the safety of drinking water is necessary in these areas. This study was carried out to investigate the diazinon concentration in drinking water resources (groundwater) in the summer areas of Mashhad city.

Materials & Methods: Sixty water samples, with the volume of 250 ml, were gathered from 10 wells and springs in the villages of Shandiz and Torqabeh in two seasons. The liquid-liquid extraction was performed using dichloromethane solvent and the concentrations were measured using High-Performance Liquid Chromatography (HPLC) system (KNAUER model) which was equipped with UV detector. The data were analyzed by SPSS software (Version 16). A probability level of $P<0.05$ was considered as statistically significant. The data were compared to the standards of WHO and EPA.

Results: A linear relationship between concentration and peak area was obtained within the range of 0.05 to 2 ppb with R^2 (Correlation coefficient) values greater than 0.99. Recoveries for spiked water samples with six diazinon standards in 0.05 to 2 ranged from 79.63 to 110.90% (with an average of 92.80±12.12). The results indicated that diazinon wasn't detectable in the springs of the studied areas while the wells of Torqabeh (with an average concentration of 0.82 µg/l) were contaminated more than the wells of Shandiz (with an average concentration of 0.48 µg/l), measured by HPLC. The maximum and minimum of contamination were observed in the villages of Veyrani1 and Nochah, respectively, measured by HPLC.

Conclusions: The concentration of diazinon in Shandiz and Torqabeh areas was higher than standard limits of WHO (0.1 µg/l) and EPA (9×10^{-6} mg/l). Also, the average concentration of diazinon in Torqabeh (0.61 µg/l) was higher than that in Shandiz (0.48 µg/l) and the contamination in wells was observed to be more (0.59 µg/l) than springs.

Please cite this article as: Moghiseh Z, Asghar Najafpoor A, Hassanzadeh Khayyat M, Esmaily H, Alidadi H. Estimation of the concentration of diazinon pesticide in drinking water resources in summer areas of Mashhad, Iran. Arch Hyg Sci 2015;4(1):41-8.

Background

Torqabeh and Shandiz are the two most well-known areas among the varied summer areas of Mashhad. The climate of these areas is appropriate for the development of agriculture and gardening and attracting tourists (1). Hence, maintaining the safety of drinking water is necessary in these areas. The overuse of pesticides causes environmental contamination (water, soil, air) which results in contaminating food and significant impacts on agriculture, groundwater, garden products and health (2-4). The contamination of groundwater needs engineering processes available for removing the contamination to acceptable limits for consumers (5). Phosphorus pesticides have been reported to be the inducer of most of the deaths (6). According to the research performed by the Ministry of Agriculture; diazinon is one of the most widely used pesticides in these areas (1). Diazinon is mobile in 80% of the soils and transfers more easily in light soils with low organic matter (such as the investigated areas in the present study) (7). Diazinon is mixable with most of the fungicides, pesticides (8). So the quality of groundwater is affected by the use of this pesticide.

Health chronic hazards of diazinon include its impacts on kidney, liver, lung, blood factors, fetus and causing breast cancer. So, the measurement of diazinon is necessary in the environment, food and body (9, 10). Monitoring the water resources has not been performed in these areas yet. So, the first step was to determine the concentration of diazinon and then compare the data to the standards of WHO and EPA. This study was carried out to investigate the diazinon concentration in drinking water resources (groundwater) in the summer areas of Mashhad city.

Materials & Methods

Materials

Diazinon (high purity) was purchased from Sigma-Aldrich (Germany). Syringe filters (PTFE) 0.45µ, Sodium thiosulfate 0.008 %, methanol (HPLC analytical grade), water (HPLC analytical grade), dichloromethane, anhydrous sodium sulfate and sodium chloride were purchased from Merck.

Sampling

Sixty water samples were collected from 10 wells and springs in the villages of Shandiz and Torqabeh, namely Veyrani1, Nochah, Mayan olia, Islam rod, Sarborj, Sagheshk and etc in two seasons of winter and spring. Sodium thiosulfate 0.008 % was used for the neutralization of resituated chlorine. Then, 10 ml dichloromethane was added to the samples for preventing diazinon to be dissolved. Collected samples were preserved for chemical analysis at 0-4ºC (11).

Sample Extraction

Diazinon was extracted using liquid-liquid extraction (12, 13). In this method, 250 ml water, 2 ml saturated sodium chloride ($20^{°C}$) and 40 ml dichloromethane solution was used for diazinon extraction in the separatory funnel. Dichloromethane was added in three separate stages with the volumes of 12.5, 15, 12.5^{cc}, respectively, with the aim of more efficient extraction. Each layer (the water and dichloromethane) could be easily separated using this method, after shaking. In each stage, the bottom layer was drained into a clean Erlenmeyer and 7 gr of anhydrous sodium sulfate was added to that and then left in the laboratory temperature to be evaporated. The residue was redissolved in 1000 µl of methanol (14, 15).

Pesticide Analysis

The samples were analyzed by a High-Performance Liquid Chromatography (KNAUER Model) with an UV detector (220 nm). The separation was performed on a Column C18 Reverse phase (150×4.6 mm) using methanol/water (70:30v/v) as mobile phase at a flow rate of 0.8 ml/min.

Preparation of Standard Solutions and drawing the calibration curve for diazinon

A stock solution was prepared at a concentration of 10µg/10ml with methanol. Using this stock solution, a standard solution of 10 ppb was prepared from which 0.05, 0.1, 0.5, 1, 1.5 and 2 ppb solutions were made using methanol.

Data Analysis

The data were analyzed by SPSS software (Version 16). A probability level of $P<0.05$ was considered statistically significant (tests of Kruskalvalis and Manvitni were used).

Results

Injecting the standard to the device, the retention time of diazinon was 15.417 minutes. The standard Chromatograph of 0.5 ppb and sample's Chromatograph are presented in figures 1-2.

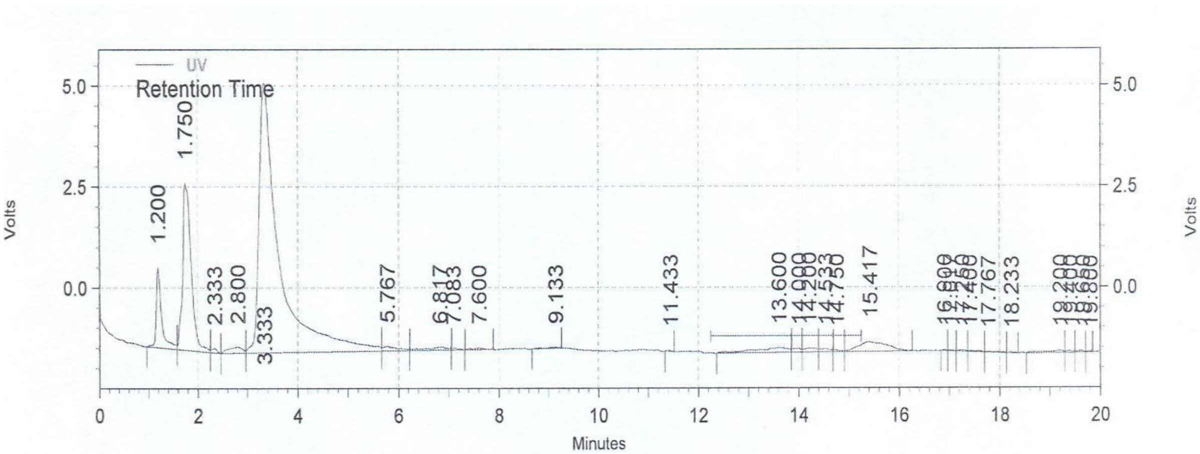

Figure 1) The standard Chromatograph of 0.5 ppb

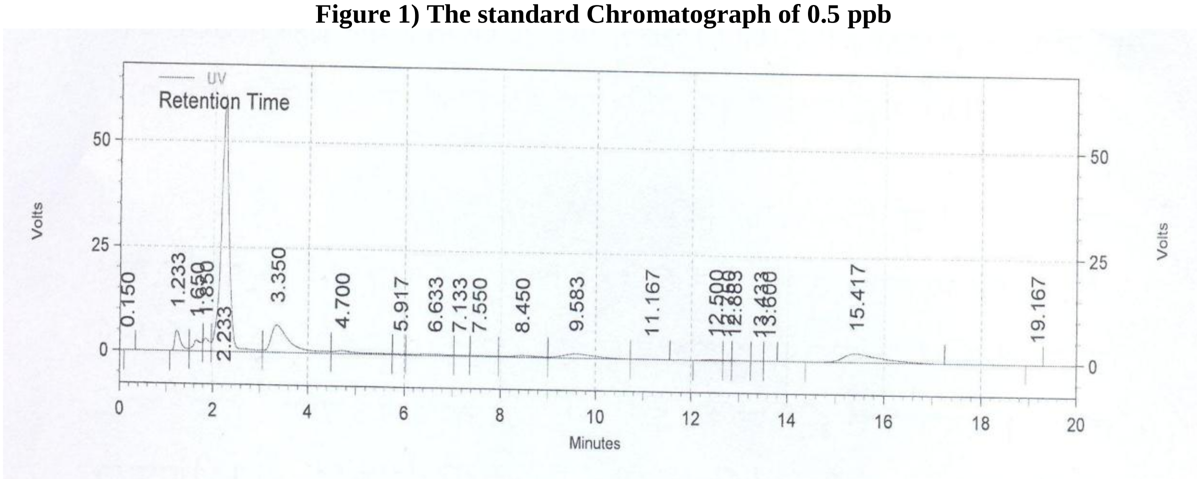

Figure 2) The sample's Chromatograph in spring season

The results indicated thata 0.025 ppb Limit Of Detection (LOD) (S/N≥3) demonstrates the high sensitivity for the analysis of diazinon. Limit Of Quantification (LOQ) was 0.05 ppb.

The contamination in Torqabeh (4.84 ppb) was higher than that in Shandiz (3.64 ppb). Furthermore, the maximum of diazinon concentration was observed in the villages of Sarborj and Veyrani1 in Shandiz and Torqabeh areas, respectively.

According to the table 1, in Torqabeh the water samples were more contaminated in the spring season (with an average concentration of 0.84 µg/l) in compare with winter.

The graph is designed to compare diazinon concentration during the seasons of sampling. considering the average and the maximum diazinon concentration in different seasons, samples collected in winter (with an average and maximum diazinon concentration of 0.58 µg/l and 3.66 µg/l, respectively) were observed to be more contaminated than the ones collected in Spring (With an average and maximum concentration of 0.48 µg/l and 4.84 µg/l, respectively).

According to the table 3, diazinon wasn't detectable in the springs of Torqabeh while its concentration was considered statistically significant in its wells ($P<0.05$).

The maximum concentration of diazinon in these areas was considered for comparison with standards.

Table1) The mean and Standard Deviation of diazinon concentration in the studied villages and areas (ppb)

Area	village	Mean	Standard Deviation	Minimum	Maximum
Shandiz	**Veyrani1**	1.59	1.76	nd	3.64*
	Veyrani2	nd	nd	nd	nd**
	Chaheshk1	nd	nd	nd	nd
	Chaheshk2	0.69	0.84	nd	2.01
	Chah khase	0.19	0.48	nd	1.17
	Sagheshk	0.41	0.85	nd	2.12
	Total	**0.48**	**0.99**	**nd**	**3.64**
Torqabeh	**Mayan olia**	nd	nd	nd	nd
	Islam rod	0.97	1.36	nd	3.66
	Sarborj	1.4	1.9	nd	4.84
	Nochah	0.1	0.24	nd	0.61
	Total	**0.61**	**1.25**	**nd**	**4.84**

*Samples are diluted and final concentration is determined by equation of standard.
** Not Detectable

Table 2) The mean and Standard Deviation of diazinon concentration in the studied Seasons and areas (ppb)

Area	Season	Mean	Standard Deviation	Minimum	Maximum	*P*-value
Shandiz	Winter	0.71	1.27	nd	3.64	***P*=0.47**
	Spring	0.25	0.56	nd	2.01	
	Total	**0.48**	**0.99**	nd	**3.64**	
Torqabeh	Winter	0.39	1.07	nd	3.66	***P*=0.07**
	Spring	0.84	1.42	nd	4.84	
	Total	**0.61**	**1.25**	**nd**	**4.84**	

Table 3) The mean and Standard Deviation of diazinon concentration in the studied resources and areas (ppb)

Area	Resource	Mean	Standard Deviation	Minimum	Maximum	*P*-value
Shandiz	Well	0.48	0.99	nd	3.64	-
	Total	**0.48**	**0.99**	nd	**3.64**	
Torqabeh	Well	0.82	1.07	nd	4.84	***P*=0. 039**
	Spring	nd	1.42	nd	nd	
	Total	**0.61**	**1.25**	**nd**	**4.84**	

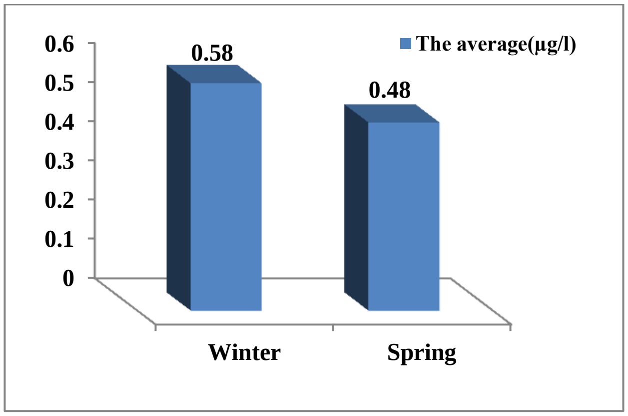

Figure 3) The average diazinon concentration of the studied seasons

The concentration of diazinon in both areas was higher than standards (WHO (0.1 µg/l) and EPA (9×10^{-6} mg/l).

The maximum concentration of diazinon in Shandiz and Torqabeh areas were 3.64 µg/l and 4.84 µg/l.

The graph shows the comparison between the maximum concentration of diazinon and standards.

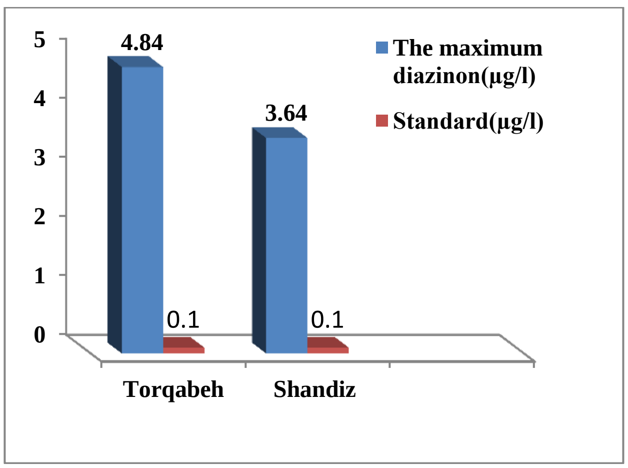

Figure 4) The comparison between the maximum diazinon concentration in the studied areas to standard

Discussion

Diazinon can contaminate water, soil and plants by human activities because diazinon is one of the most widely used pesticides (8).

Also, water is one of the most important resources for human needs. Diazinon or its metabolites in water can be absorbed by human daily. So, this study was carried out to investigate the diazinon concentration in drinking water resources (groundwater) by HPLC.

The average of diazinon concentration of the studied villages is shown in table 1. The range of concentration was 0.1- 1.59 µg/l according to the figure 4, the maximum concentration of diazinon in Torqabeh (4.84 µg/l) and Shandiz (3.64 µg/l) areas were higher than standard limits of WHO (0.1 µg/l) and EPA (9×10^{-6} mg/l). The solubility of diazinon in water and low organic matter content of soil can be the reason of such higher concentrations. Khazaii et al. who studied the groundwater's of Mazanderan reported the diazinon concentration to be in the range of 0.02 to 2.533 µg/l which, similar to our study, exceeded the standards of WHO (0.1 µg/l) and EPA (9×10^{-6} mg/l) (5); but in the study carried out by Khazaii, the measured diazinon was higher than our studied areas which might be because of higher level of groundwater in Mazanderan in compare with our studied areas. In addition, Taghavi et al. have documented that the concentration was more than the standards in samples of drinking water of Rasht during summer and believed that the contamination was caused by the agricultural effluents, especially rice lands effluents (16). Therefore in the present study, the orchards and agricultural effluents in the studied areas can be considered as the reason of the high concentration of diazinon. However, the concentration of diazinon in well samples was detected to be 32.1 mg/l by Abedi et al. which was lower than the standards (17).

According to the table 1, the maximum and minimum of diazinon concentration were measured in the villages of Veyrani1 (with an average concentration of 1.59 µg/l) and Nochah (with an average concentration of 0.1 µg/l). The sorption of diazinon on sediments, water temperature and neutral pH were the factors increasing its persistence in water which is confirmed by the research conducted by Williams et al. and Villarosa (18, 19).

In another study, Josef et al. suggested that the higher recharge rate of irrigation water in areas of coarse-grained, low clay, the organic matter content, high porosity and low soil moisture holding capacity is an important factor affecting pesticide transport to ground water (20). Furthermore, the soil of investigated areas has such properties that might have helped in high leaching of diazinon from the soil. The organic matter content of soil of these areas is lower than the standard (1.5-2%) so diazinon cannot adsorb to soil.

The mean of diazinon concentration in the drinking water resources (well and spring) of Torqabeh and Shandiz areas is shown in table 3. Diazinon wasn't detectable in the spring's of Torqabeh. This result is similar to that carried out by Karyab et al. who showed the springs water samples not had diazinon but deep wells were the polluted water samples (21) .But Rahmanikhah et al. found that diazinon concentration in the springs was higher than wells. Rahmanikhah analyzed the residues of diazinon of the groundwater by gas chromatography (GC). Furthermore, the concentration of diazinon was 0.041 µg/l in the surface water samples while it was 0.019 µg/l in the ground waters (22). Also, Mean diazinon levels in Babolrood River of Mazanderan ranged from 77.6 to 101.6 µg/l (23).

In addition, the total concentration of diazinon was between 0.01 and 46.99 µg/l in the Tajan river. A study has shown that the diazinon residue in the Tajan river was affected by three processes (microbial, hydrolysis, photolysis) and sedimentation. However, the river discharge played the important role in the transport of diazinon from Tajan river. So, the concentration of diazinon in the resources (well and spring) of the studied areas was less affected by the changes than the surface waters (e.g. river) and this is why the concentration of diazinon in the studied areas was lower than 0.01-46.99 µg/l (24).

According to the table 3, not observing diazinon in spring water may be because of its degradation by the sunlight. A study reported photo degradation as the major method of diazinon degradation (25).

According to the graph, the samples in the winter (with an average and the maximum concentration of 0.58 µg/l and 3.66 µg/l, respectively) were more contaminated than Spring (With an average and maximum concentration of 0.48 µg/l and 4.84 µg/l, respectively) but this result is different from that carried out by Albanis et al. They found that the highest concentrations in groundwater were observed during spring following seasonal application and decreased significantly during the autumn and winter. Albanis observed that the diazinon concentration in the months of June, September, January and March were 0.023, 0.022, 0.005 µg/l and not detectable, respectively. Diazinon in June was higher than other months (26) while seasonal variation of the diazinon concentration in this study is in accordance with that investigated by Ezemonye et al. It is reported that higher concentrations of diazinon (3.61 µg/l) occurred in dry season (February) in Warri river and may be attributed to the planting season while the concentration was 0.01 µg/l in the raining season (27) but it was not similar to the study of Khodadi et al. that showed that the highest concentration of diazinon was in autumn season on Okbatan dam and its minimum concentration was in winter (2).

Therefore, water can be contaminated by using diazinon in late winter and also runoff of the rain and snow in this season (most of the raining in these areas is happening in May). Besides, diazinon is soluble in water and Bradyet al. concluded that mass transport of esfenvalerate (one of pyrethroid insecticides) in the runoff was less than the mass transport of diazinon under similar situations (28). Moreover, Vryzas et al. showed that an increase in pesticide concentrations was observed at the beginning of the irrigation season or after high rainfalls. It is suggested that the increased loading seems to be a result of the application of insecticide and high rainfall during the application period (29). Hence, the result of study of Vryzas was similar to this study.

Conclusion

Since these areas are appropriate for the development of agriculture and gardens, diazinon is one of the most widely used pesticides in these areas. The concentration of pesticides (such as diazinon) in environment depends on the applied amount, time, method and environmental chemical, biological and physical processes. The concentration of diazinon in Shandiz and Torqabeh areas was higher than standard limits of WHO (0.1µg/l) and EPA (9×10^{-6}mg/l). Also, the average concentration in Torqabeh was higher than that in Shandiz and the contamination in wells was more than springs.

This paper suggests more attempt to quantify the levels and distribution pattern of diazinon in soil and river. Also, the water treatment processes perform before contamination.

Footnotes

Acknowledgments:

The results were part of a master's degree thesis. The authors are appreciative of the Vice Chancellor of Research, Mashhad University of Medical Sciences, for financial support.

Conflict of Interest:

The authors declare no conflict of interest.

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