ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

The Study of Pesticides Pollution in Drinking Water Based on Ground Water Sources

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ABSTRACT

The pesticides concentrations in drinking water were determined at different sampling stations in northern suburbs of Tehran during fall and winter 2008-2009. The level of residual concentration of pesticides was determined by HPLC and GC/MS technique. The results showed that the most widely used compound is imidocloprid and the recorded chromatograms by HPLC and GC/MS for drinking water of each village do not show any pesticides of any kind in the sources of groundwater in this region as wells or springs.

Keywords: Drinking water, pesticides, HPLC, Pollution, Sampling

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ISSN: 0975-8585

INTRODUCTION

Pesticides are employed both in agriculture and in public health, including disease vector control [1]. In 1990 the world market in pesticides amounted to about US $ 26400 million [2]. Herbicides are the most widely used pesticides constituting more than 40% of total use while insecticides account for approximately 30% and fungicides for some 20% [3]. Pesticides comprise a wide variety of chemicals with different chemical structures and consequently large differences in their mode of action uptake biotransformation and elimination[4].Chemical classes of pesticides include organochlorine compounds, carbamates, organophosphates and chlorophenoxy compounds[5].They differ widely in their capacity to persist in the environment and to exert toxic effects on human health and the environment[6].Consequently the use of pesticides requires careful selection and quantitation as well as means of application that minimize effects on non- target organisms[7].In addition many pesticides are persistent and may therefore bioaccumulate in the environment[8].The quality of drinking water is a serious public health concern world-wide. The land of Iran is covered by arid and semi-arid areas with an average annual precipitation less than one third of that of the world [9]. The water demand in Iran is supplied by surface and underground water sources. Iran is one of the countries that it almost encounters increasing water shortages every year unless some actions are taken to reduce current water consumption [10]. In most parts of the country, the scarcity of fresh water resources is noticeable. Besides, the demand for water has essentially increased by the improvement in population's living standards [11]. Groundwater supplies provide over half of the total annual water demand in Iran. The importance of groundwater as an alternative water supply is increasingly realized, due to higher costs and diminishing quality of surface waters in face of increasing water shortage problem [12]. Monitoring the quality and quantity of groundwater resources would be indispensible for improvements of population's health in some areas which are the only available source of drinking water and agricultural irrigation [13].The expansion of industries leads to the pollution of ecosystems. Most of the monitoring efforts started in the 1960s, since then the research programs have been focused on the detection of undesirable and deleterious effects of chemical pollutants [14]. Surface and underground water sources are known to contain trace elements. Toxic elements are discharged into rivers and lakes and leaches into the soil and groundwater. Chemicals of high health risk are widespread but their presence is unknown because their long term health effect is caused by chronic exposure opposed to acute exposure [15]. Besides, pesticides are not biodegradable and enter a global ecological cycle via natural water which is the main pathway. These pollutants can be concentrated easily along the food chain, cause toxicity to plants and accumulate in human tissues [16]. Therefore, the measurement of pesticides concentrations in various water supplies in Iran or other countries is important for proper evaluation of the hazards associated with their intake [17].

In this study, concentrations of pesticides have been determined at different sampling stations in the north suburbs of Tehran, during two seasons, fall and winter 2008-2009. The importance of the groundwater in the area should not be underestimated because they are the only water source for drinking, agricultural and gardening purposes for the people living in these areas. Despite the lack of alternative water sources, the groundwater geohydrology of the region remains poorly studied [18].

ISSN: 0975-8585

MATERIALS AND METHODS

The Areas under Study

Tehran Province is one of the 31 provinces of Iran. It covers an area of 18,909 square kilometers and is located to the north of the central plateau of Iran. Tehran Province borders Provinces of Māzandarān in the north, Qom in the south, Semnān in the east, and Qazvīn in the west. The great Tehran includes 13 townships, 43 municipalities, and 1358 villages. This province has a semi-arid, steppe climate in the south and an Alpine climate in the north.The seven sampling stations were: Lavasan-e-Bozorg which is situated in the city of Tehran and its geographical coordinates are 35° 49' 30" North, 51° 46' 58" East, Barg-e-Jahān with geographical coordinates: 35° 50' 37" North, 51° 44' 2" East, Zard Band-e-Lashgarak in 35° 49' 0 North, 51° 34' 0 East, Nīknām Deh, with geographical coordinates: 35° 49' 7" North, 51° 43' 52" East, Kond-e-sofla (Kond-e-pa'in) 35° 51' 53 North and 51° 38' 49 East with approximate population for 7 km radius from this point is 1814, Rahatabad with geographical coordinates: 35° 53' 48" North, 51° 37' 1" East and Rasanan in 35° 48' 8 North, 51° 45' 21 East. The area of the sites under study was 274.78 km^2.

Fig.1 Iran map and the sampling stations

Sampling technique

First, essential information on geohydrology of the district was obtained and groundwater resources were identified. For the determination of pesticides, the samples of water were collected from seven stations. Prior to sample collection, the flasks were rinsed with tap water and then kept overnight with 1:1 HNO_3-H_2O, and finally rinsed with double-distilled water. Collected samples were stored in pure polyethylene vials for analysis. The samples were acidified with (0.2 vol%) nitric acid ultrapure (Merck, Germany) for obtaining pH less than 2. Acidification minimizes the adsorption of pesticides onto the walls of the container. The samples were stored at approximately 3-4°C in refrigerator before analysis. Sampling was performed twelve times in each station; with 84 total sampling times. The stations and the order of sampling from each station are shown in Tables 1 and 2.

ISSN: 0975-8585

Table1. Designation numbers of the stations

Number of the station	1	2	3	4	5	6	7
Name	Barg-e-Jahān	Rasanan	Lavasan-e-Bozorg	Zard Band-e Lashgarak	Nīknām Deh	Kond sofla (Kond-e-pa'in)	Rahatabad

Table 2. The order of sampling at the determined stations from the first week to the 12th week

Day	Number of the station											
Saturday	1	7	6	5	4	3	2	1	7	6	5	4
Sunday	2	1	7	6	5	4	3	2	1	7	6	5
Monday	3	2	1	7	6	5	4	3	2	1	7	6
Tuesday	4	3	2	1	7	6	5	4	3	2	1	7
Wednesday	5	4	3	2	1	7	6	5	4	3	2	1
Thursday	6	5	4	3	2	1	7	6	5	4	3	2
Friday	7	6	5	4	3	2	1	7	6	5	4	3
The number of the week	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th

Analytical methods

The measurement concentration of pesticides and Insecticides was conducted by instrumental methods of GC (Gas chromatography), 3800 cp, varian, USA and MS (Mass spectrometer), 2200 saturn, varian, USA, and HPLC (high performance liquid chromatography),by solvent: water (30%),Methanol (70%),and another solvent: water(30%),Acetonitril(70%),Column:C_{18}, Detector: uv-visible, Agilent 1200, US. [19]

All standard and sample solutions were prepared with deionized triplet distilled water obtained by Aquamax Ultra 370, Young Lin Instrument Co., Korea.

All glassware were previously soaked in 15% HNO_3 solution for at least 48 hr and afterwards rinsed with deionized water [20]. For preparing the samples, two hundred milliliters of well-mixed samples were transferred to beakers. Four milliliters of HNO_3 1:1 (v/v) were added in each sample. Watch glasses were used to cover the containers, to prevent them from contamination[21]. Then, samples were heated to 80–85°C using hotplates to obtain the final volume of about 10–20 ml before metal precipitation. The above procedure was repeated twice[22]. The beaker walls and the covers were washed carefully with ultra pure deionized water and then the rinse water was filtered. The filtrate was transferred to a 100-ml volumetric flask with the addition of about 10 ml of water. All samples were prepared in duplicate[23].The HPLC report of imidocloprid, the name of station, the number of station, source of water and date of sampling in selected stations are presented. (Table3,4)

ISSN: 0975-8585

Table3:The HPLC report to pesticides in selected stations(imidocloprid)

(tab-26)

Date of Sampling : Autumn-2009	Name of Village : Barg -Jahan
Source of Water : Spring	Station Number :1

Peak	Time (min)	Type	Height (MAU)	Start (min)	End (min)
1	0.998	BV	-66.5	0.000	1.088
2	1.178	VV	-44.1	1.088	1.343
3	1.507	VV	-57.4	1.343	1.595
4	1.683	VV	-56.6	1.595	2.037
5	2.391	VV	-91.2	2.037	2.532
6	2.673	VV	-85	2.532	2.817
7	2.961	VV	-84.2	2.817	3.077
8	3.192	VV	-74.3	3.077	3.417
9	3.641	VV	-86.4	3.417	4.033
10	4.425	VV	3821	4.033	4.622
11	4.818	VV	-43.3	4.622	5.115
12	5.412	VV	-39.9	5.115	5.622
13	5.832	VV	-81.1	5.622	6.232
14	6.631	VV	-79.8	6.232	6.850
15	7.068	VV	-112	6.850	7.460
16	7.851	VV	-59.4	7.460	8.055

Table4:The HPLC report to pesticides in selected stations(imidocloprid)

(tab-27)

Date of Sampling : Autumn-2009	Name of Village : Rasanan
Source of Water : Spring	Station Number :2

Peak	Time (min)	Type	Height (MAU)	Start (min)	End (min)
1	1.053	BV	-102	0.000	1.149
2	1.245	VV	-94.5	1.149	1.423
3	1.601	VV	-92.6	1.423	1.820
4	2.038	VV	-91.9	1.820	2.226
5	2.414	VV	-105	2.226	2.611
6	2.808	VV	-89.1	2.611	2.879
7	2.949	VV	-93.4	2.879	3.069
8	3.189	VV	-108	3.069	3.298
9	3.407	VV	-81.9	3.298	3.633
10	3.859	VV	3733	3.633	4.073
11	4.287	VV	-51.6	4.073	4.733
12	5.179	VV	-23.3	4.733	5.389
13	5.598	VV	-49.4	5.389	5.985
14	6.372	VV	-63.3	5.985	6.572
15	6.771	VV	-89.4	6.572	7.266
16	7.761	VV	44.6	7.266	7.993

RESULTS AND DISCUSSION

As shown in Table1, there are seven stations allocated for this study. These villages are located in the north of the city. The sampling from wells was carried out every alternate week according to Table 2 for two seasons (fall and winter); therefore the sampling was performed for twelve weeks on a rotational schedule according to which most of the stations would be sampled at least once every alternate week[24]. It implies that in every consecutive week of sampling, all stations are tested in different days from the last sampling

ISSN: 0975-8585

for a proper random sampling of every station.The obtained results from sampling and measurements shows that the applied pesticides in this region are mostly Malathion,Chlorophenoxy , Heptachlor, Toxaphene, Imidocloprid, Methoxychlor, Endrin, DDT and particularly is Imidocloprid[25].Since there are many gardens in this region, high amount of pesticides are applied and as this study has conducted on pesticides.These components in the long time was passed from the soil with raining and irrigation and these pollutants penetrate to the source of drinking water which was supplied from underground waters[26].On the other hand it is possible that these villages wastewaters were mixed with this region underground waters. The aim of this research was investigation of the villages safety and healthy due to removal probable hazards[27].GC/MS recordings show the chromatograms of drinking water samples of each village separately. The highest peak related to the highest absorption has been recorded for each sampling station [28]. These high peaks show no relevance to the applied pesticides structures in each village when their formulation and absorption site were detected.Chromatogram and formulation of the highest peak recorded by GC/MS for each sample [29]. Also recordings of HPLC show the chromatograms of each sample of groundwater for each station separately. The highest peak related to the highest absorption has been recorded for water of each village[30]. The absorption site of the highest peak is not in agreement with the standard chromatogram of imidocloprid and the obtained results of GC/Ms chromatograms support this finding [31]. On this basis the highest peak of HPLC chromatograms of each water sample is not related to the applied pesticides structures such as imidocloprid [32].The following HPLC and GC/MS chromatograms show the obtained results for every pesticide at each station separately . (Fig2-4)

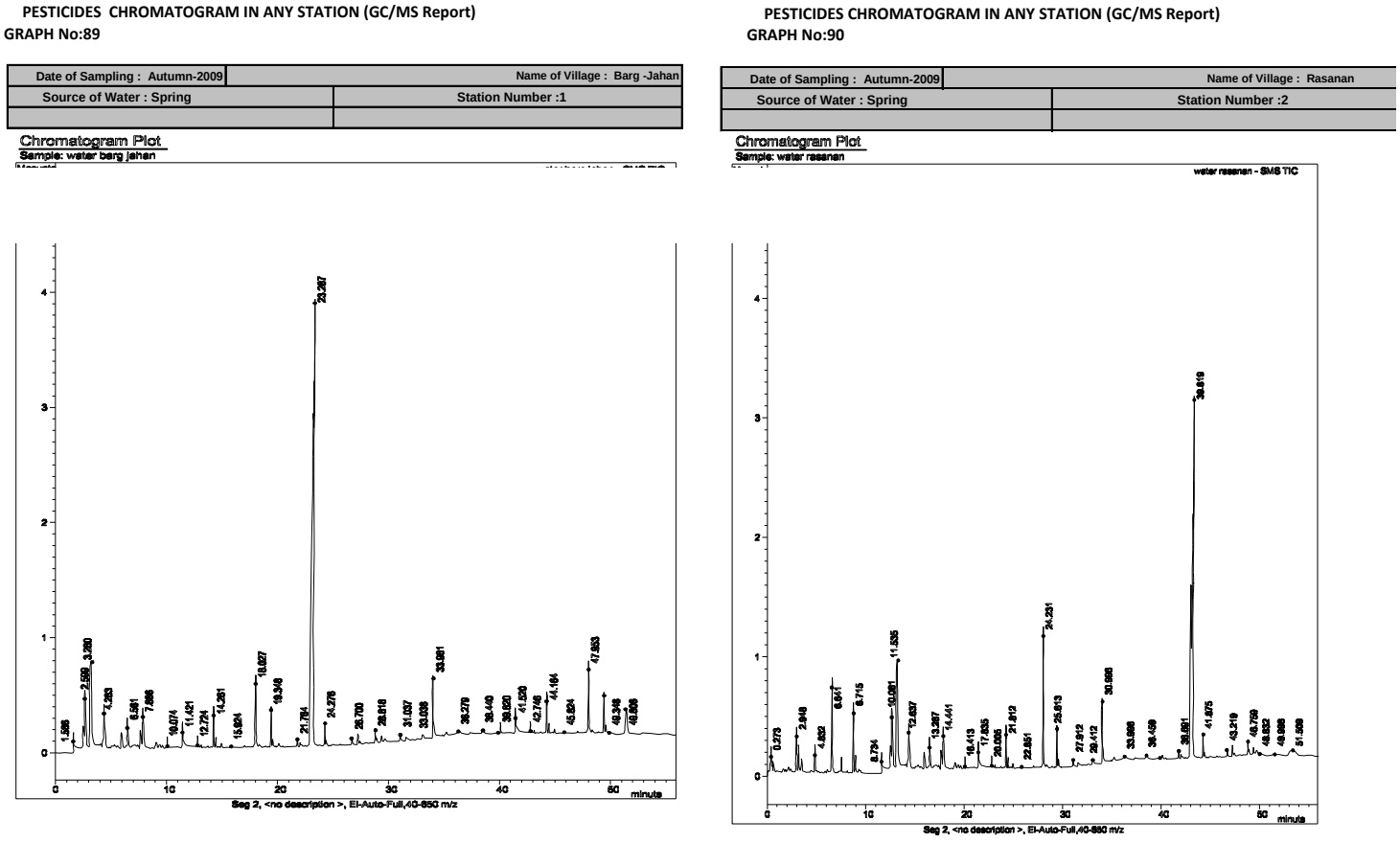

Fig2.Pesticides GC/MS Chromatograms in selected stations

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GRAPH: 96

THE HIGHEST PEAK FORMULATION OF GC/MS REPORT IN SELECTED STATIONS

GRAPH:97

THE SECOND HIGHER PEAK FORMULATION OF GC/MS REPORT IN SELECTED STATIONS

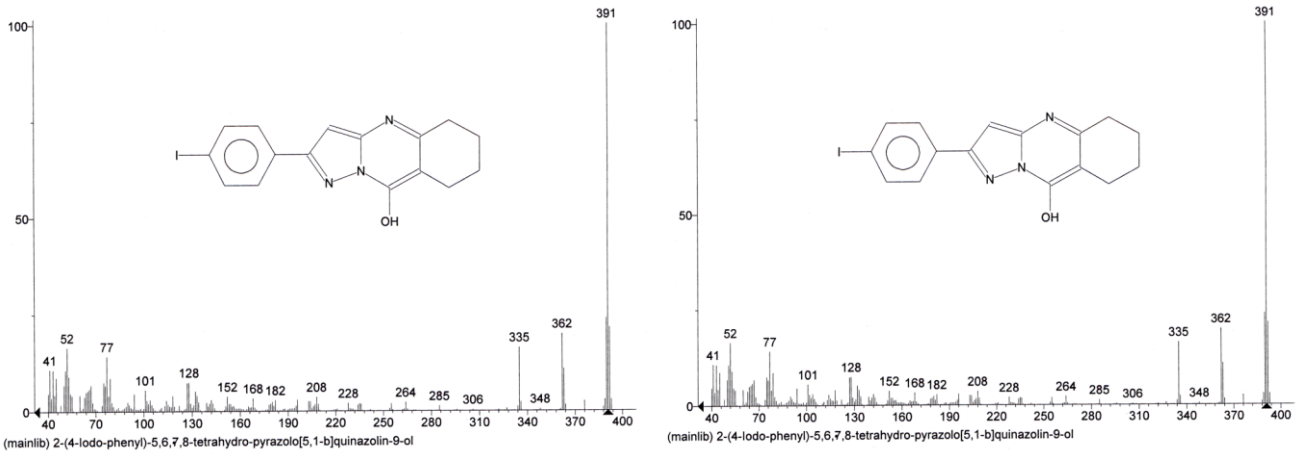
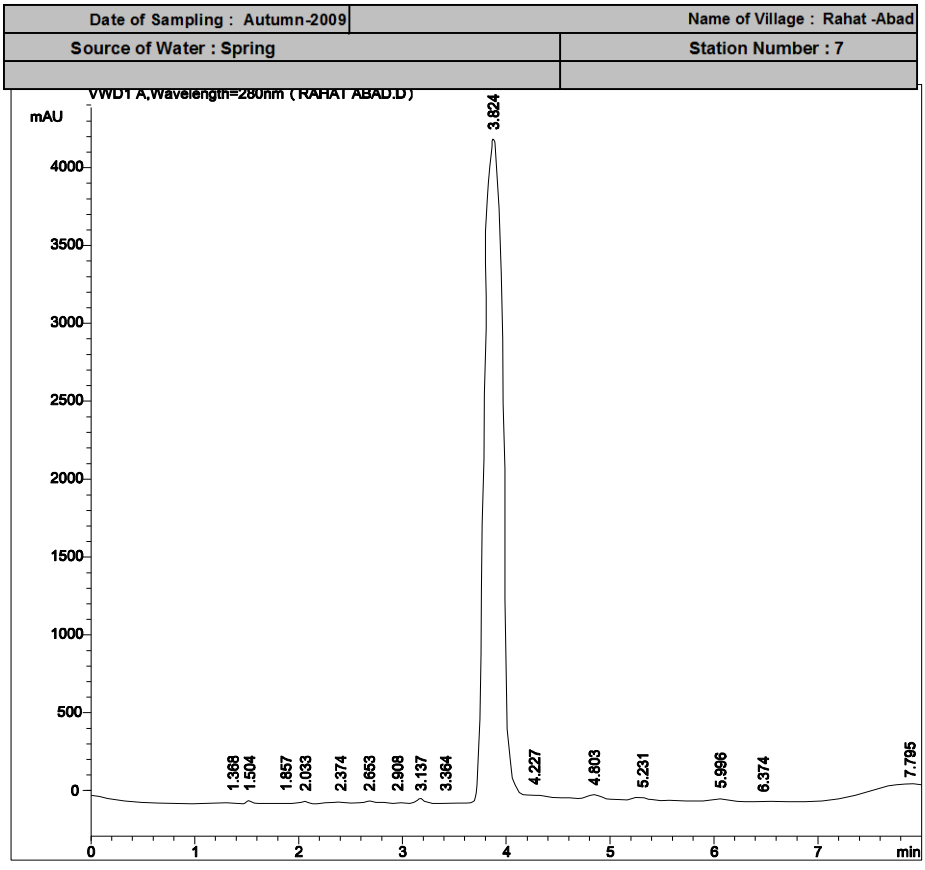


Fig3.The highest and second higher peak formulation of GC/MS Chromatograms in selected stations

HPLC Report)



THE STANDARD DIAGRAM OF IMIDOCLOPRID IN HPLC REPORT

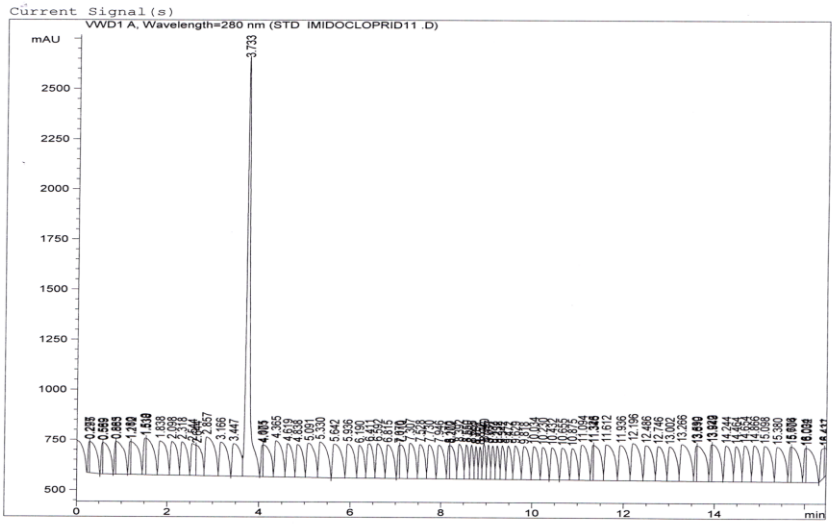


Fig4.Pesticides HPLC and standard chromatogram in selected stations (Imidocloprid)

Table5.Drinking water of the villages in this region compared to the international standard amounts of WHO, EPA and Iran

Type of pesticide	Malathion	Chlorophenoxy	Heptachlor	Toxaphene	Imidocloprid	Methoxychlor	Endrin	D.D.T
Maximum allowed Level (µg/l)	0.1	100	0.001	5	0.01	0.03	0.004	0.001

CONCLUSION

The study conducted on the applied pesticides in the gardens of this region shows that the most widely used compound is imidocloprid and the recorded chromatograms by HPLC and GC/MS for drinking water of each village do not show any pesticides of any kind in the sources of groundwater in this region as wells or springs. It means that high peaks having the highest amount of absorption when their formulations are detected are not related to the pesticides components and the molecules of this compounds are disintegrated after they absorbed by the trees and soil surface and before they can reach the sources of groundwater. On this basis, drinking water of the villages in this region compared to the international standard amounts of WHO, EPA and Iran has no this compound residues and is suitable for drinking and many other purposes (Table5).

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