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Comparison of Insecticides Pollution in Drinking Water Based on Ground Water Sources

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ABSTRACT

The insecticides 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 insecticides was determined by HPLC and GC/MS techniques. The results showed that the most widely used compound is Benomyl and the recorded chromatograms by HPLC and GC/MS for drinking water of each village do not show any insecticides of any kind in the sources of groundwater in this region as wells or springs.

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INTRODUCTION

The demand for water is expected to increase in the next few years while the capabilities for developing fresh water resources are declined. Water is one of the most important substances on earth. The research shows that although 70% of earth's surface is water but fresh water comprises 3% of the total water on earth only a small percentage (0.01%) of this fresh water is available for human use and about three-quarter of all fresh water is in the form of ice caps and glaciers located in polar areas far from most human habitation. Insecticides 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]. Insecticides 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 insecticides 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 insecticides requires careful selection and quantitation as well as means of application that minimize effects on non- target organisms [7]. In addition many insecticides 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, insecticides 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 insecticides 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 insecticides 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].

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

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 reference method that was followed is based on EPA Method 508 and Fatta's work [19]. Water sample of 500 ml was transferred in a separatory funnel of 1L. Five grams of NaCl were added and the funnel was shaken to completely dissolve NaCl. Then 50 milliliters of CH_2Cl_2 were added and the funnel was shaken vigorously for 3–5 min with periodic venting to release excess pressure. The separatory funnel was then kept undisturbed to separate the two layers i.e. the organic phase was allowed to separate from the water phase for a minimum of 10 min. The lower aqueous layer was redrawn into separatory funnel. The process of partitioning was repeated two more times using fresh 50 ml dichloromethane. The organic phase was then collected and transferred in a spherical flask of 250 mL. The extracts were dried by 5 g of anhydrous Na_2SO_4 were added in the extract in the flask. The flask was stirred and then was left to sit for 20 minutes. The CH_2Cl_2 was filtered into another flask. The remaining sodium sulfate was rinsed gradually with 25 mL of CH_2Cl_2 and the rinses were transferred in the flask. The sample was then evaporated to 1mL using a rotary evaporator. Ten milliliters of n-hexane (Merck) were added and then the extract was again evaporated to 1 mL.

The measurement concentration of insecticides was conducted by instrumental methods of GC (Gas chromatograph), 3800 cp, varian, USA , MS (Mass spectrometer) 2200 Saturn, Varian, USA. The carrier gas was nitrogen at a flow of 20 ml/min. The injector was set at 260 °C. Calibration was based on area given using external standards [20]. Injections of the aliquots were made by microsyringe into the GC. The identification of the suspected insecticide

was carried out in relation to the retention time of the pure analytical standard. Quantification was made with a freshly prepared standard curve of the relevant (standard) insecticide [6]. Another measurements were conducted by HPLC (high performance liquid chromatography) technique. The mobile phase was water/methanol (30/70) and water/ acetonitril (30/70),Column:C_{18}, Detector: UV-Visible, Agilent 1200, US. All standard and sample solutions were prepared with deionized triplet distilled water obtained by Aquamax Ultra 370, Young Lin Instrument Co., Korea.

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 [21]. It implies that in every consecutive week of sampling, all stations are tested in different days from the last sampling for a proper random sampling of every station. The obtained information from inhabitants showed that the applied insecticides in this region were mostly Chlordan, Dieldrin , Lindane, Aldrin, Benomyl, Heptachlorepoxide, Carbamate and particularly Benomyl. Since there are many gardens in this region, high amount of insecticides are applied and as this study has conducted on insecticides. 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[22].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. The GC/MS recording (Figure 2) shows 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. These high peaks show no relevance to the applied insecticides structures in each village when their formulation and absorption site were detected. Chromatogram and formulation of the highest peak were recorded by GC/MS for each sample. 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. The absorption site of the highest peak is not in agreement with the standard chromatogram of Benomyl and the obtained results of GC/Ms chromatograms support this finding. On this basis the highest peak of HPLC chromatograms of each water sample is not related to the applied insecticides structures such as Benomyl. The following HPLC and GC/MS chromatograms show the obtained results for every insecticide at each station separately (Figures 2-4). The HPLC report of Benomyl, the name of station, the number of station, source of water and date of sampling in selected stations are presented. (Tables 3,4). Table 5 shows the maximum allowed level (µg/l) of different insecticides according to the international standard amounts of WHO, EPA and Iran.

Table3: The HPLC report to insecticides in selected stations (Benomyl)

(Tab– 35)

Date of Sampling : Autumn-2009			Name of Village : Lavasan bozorg		
Source of Water : Spring			Station Number :3		

Peak	Time (min)	Type	Height (MAU)	Start (min)	End (min)
1	0.159	BV	8.54311	0.000	0.797
2	1.175	VV	5.53267	0.797	1.552
3	1.743	VV	43.38719	1.552	1.744
4	1.882	VV	129.12111	1.744	1.897
5	1.971	VV	138.84841	1.897	1.972
6	2.365	VV	4913.97412	1.972	2.389
7	2.819	VV	112.21563	2.389	2.857
8	3.150	VV	78.88431	2.857	3.238
9	3.244	VV	47.110519	3.238	3.246

Table4: The HPLC report to insecticides in selected stations (Benomyl)

(Tab– 36)

Date of Sampling : Autumn-2009			Name of Village : Zard Band		
Source of Water : Spring			Station Number :4		

Peak	Time (min)	Type	Height (MAU)	Start (min)	End (min)
1	0.007	BV	8.69311	0.000	0.053
2	0.391	VV	4.82391	0.053	1.408
3	1.851	VV	127.74413	1.408	1.853
4	1.975	VV	5312.37115	1.853	1.988
5	2.141	VV	102.20571	1.988	2.144
6	2.344	VV	78.73381	2.144	2.356
7	2.437	VV	212.89974	2.356	2.444
8	2.908	VV	59.49332	2.444	3.047
9	3.286	VV	47.79831	3.047	3.382

PESTICIDES CHROMATOGRAM IN ANY STATION (GC/MS Report)
GRAPH No:91
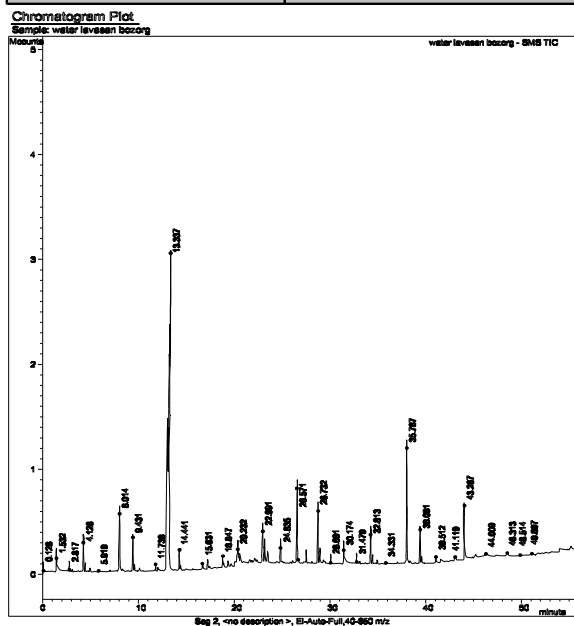
PESTICIDES CHROMATOGRAM IN ANY STATION (GC/MS Report)
GRAPH No:92

Date of Sampling : Autumn-2009	Name of Village : Lavasan bozorg
Source of Water : Spring	Station Number :3

Date of Sampling : Autumn-2009	Name of Village : Zard Band
Source of Water : Spring	Station Number :4
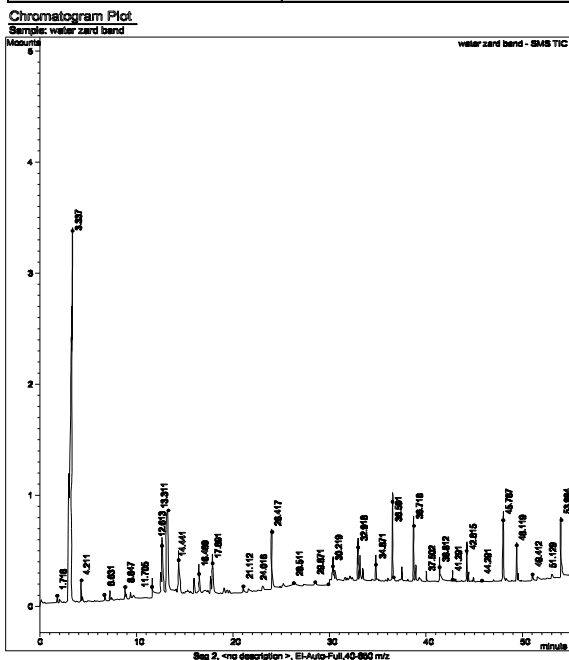
Fig2.Insecticides GC/MS Chromatograms in selected stations

GRAPH: 96

GRAPH:97

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

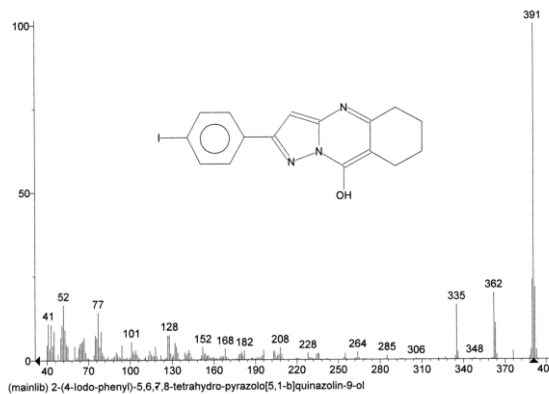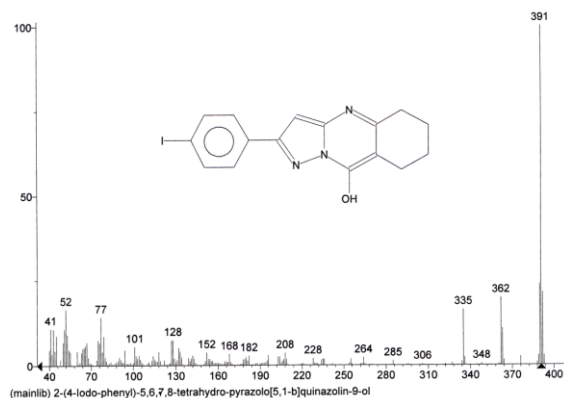THE SECOND HIGHER PEAK FORMULATION OF GC/MS REPORT IN SELECTED STATIONS

(mainlib) 2-(4-Iodo-phenyl)-5,6,7,8-tetrahydro-pyrazolo[5,1-b]quinazolin-9-ol

(mainlib) 2-(4-Iodo-phenyl)-5,6,7,8-tetrahydro-pyrazolo[5,1-b]quinazolin-9-ol

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

PESTICIDES CHROMATOGRAM IN ANY STATION (BENOMYL HPLC Report)
GRAPH No:87

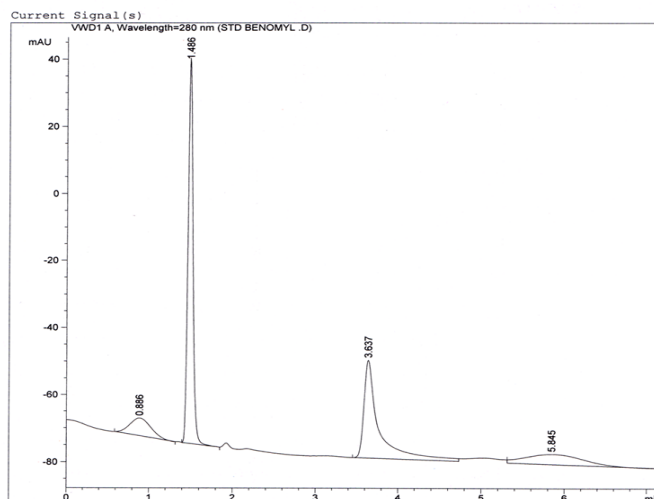| Date of Sampling : Autumn-2009	Name of Village : Rahat -Abad
Source of Water : Spring	Station Number : 7
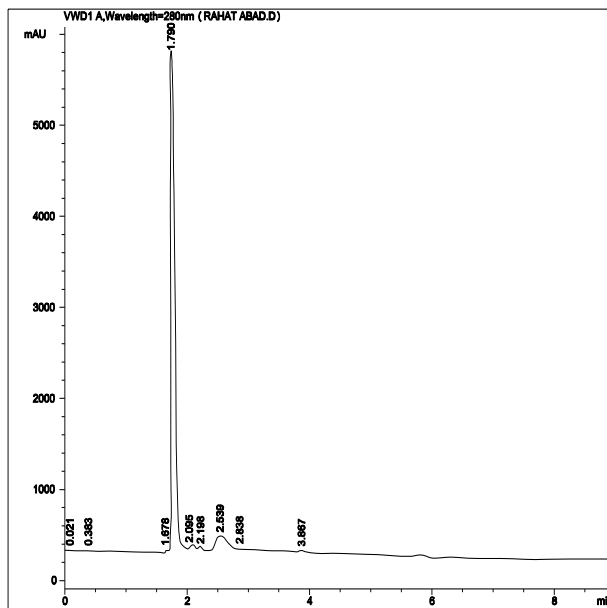
THE STANDARD CHROMATOGRAM OF BENOMYL IN HPLC REPORT

Fig4.Insecticides HPLC and standard chromatogram in selected stations (Benomyl)

Table5. The maximum allowed level(µg/l) of different insecticides according to the international standard amounts of WHO, EPA and Iran

Type of insecticide	Chlordan	Benomyl	Dieldrin	Lindane	Aldrin	Carbamate	Heptachlorepoxide
Maximum allowed Level(µg/l)	0.01	0.3	0.03	0.01	0.03	100	0.1

CONCLUSION

The study conducted on the applied insecticides in the gardens of these region shows that the most widely used compound is Benomyl and the recorded chromatograms by HPLC and GC/MS for drinking water of each village do not show any insecticides 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 insecticides 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.

REFERENCES

[1]   Zanta D. Michael C. J hazard material 2007; 145: 169- 179.
[2]   Younes M and GALAL Gorchev H. Food and chemical toxicology 2000; 38: 88-90.
[3]   Turgut C. Environmental International 2003; 29 (1): 29-32.
[4]   Sackmauerova M, Palusova A. Szokolay. Water Research 2003; 11 (7): 551- 556.
[5]   Rachwal A. 1991 New treatment processes for insecticides in drinking water, Water and environment journal 1991; 5 (4): 466- 476.
[6]   Matin M, Malek A, Amin MR, Rahman S, Khatoon J, Rahman M. Agriculture ecosystems and environment 1998; 69: 11- 15.
[7]   Ioannis K Konstantinou, Dimitra G Hela, Traintafyllos A Albanis. Env pllut 2006; 141(3): 555- 570.
[8]   Foster SSD, Chilton PJ, Marianne E Stuart. Water and Environment Jour 1991; 5(2): 186- 193.
[9]   Baghvand A, Nasrabadi T, Nabi Bidhendi GR, Vosoogh A, Karbassi A, Mehrdadi N. Desalination 2010; 260: 264–275.
[10]   Brian w. Biological conservation 1980; 19 (1): 51- 80.
[11]   Georgopoulou E, Kotronarou A, Koussis A, Restrepo PJ, Gomez-Gotor A, Rodriguez Jimenez JJ. Desalination 2001; 136: 307-315.
[12]   Arlosoroff S, Roche R, Wright F. Developments in water science 1989; 39; 519-530.
[13]   Gül A, Rida F, Aw-Hassan A, Büyükalaca O. Applied Energy 2001; 82 (4): 285-299.
[14]   Oertel N and Salanki J. 2003 Chapter 10, Biomonitoring and bioindicators in aquatic ecosystems in Ambasht RS, Ambasht NK, Kluwer (Ed.) Modern Trends in Applied Aquatic Ecology, Academic Plenum publishers, USA.
[15]   Barkacs K, Ovari M, Oertel N, Szabo E, Szurdoki E, Zaray Gy. Microchemical Journal 2002; 73: 99–111.
[16]   Fatta D, Canna-Michaelidou St, Michael C, Demetriou Georgiou E, Christodoulidou M, Achilleos A, Vasquez M. Journal of Hazardous Material 2007; 145: 169–179.
[17]   Guidelines for drinking-water quality standard of Iran, Iran water resources management Co., Deputy of research, office of standard and technical criteria 2009.

[18]   Farahmand F. Information technologies & management 2009; 7: 169-185.
[19]   Fatta D, Michael C, Canna-Michaelidou St, Christodoulidou M, Kythreotou N, Vasquez M. Desalination 2007; 215: 223–236.
[20]   Turgut C. Environment International 2003; 29: 29– 32.
[21]   Guidelines for drinking-water quality, 2nd Edition, Volume 1, Recommendations, By World Health Organization, Geneva, 1993.
[22]   Kolpin WD, Barbash EJ, Gillion R. Ground water 2000; 38 (6): 858- 863.