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Investigation of contamination of phosphorus pesticides in the groundwater of Varamin Plain

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ABSTRACT
Worldwide, insects and pests, including those that are less sustainable in the environment, are causing millions of dollars of damage to crops every year.Usually, after spraying and granulation in agricultural fields, residual pests after seasonal rainfall or irrigation will enter the water resources, including surface water and underground water.The most important pollutants of groundwater are pesticides. Therefore, the purpose of this study was to investigate the contamination of phosphorus pesticides in the groundwater of Varamin Plain. In this research, library studies have been used to collect information. The statistical population consisted of all waters in the aquifer of Varamin plain and systematic sampling from this community, thus, six wells were selected as stations in different areas of Varamin plain. SPSS 20.0 was used to analyze the statistical data and Microsoft Excel 2014 software was used to plot the graphs. Also, spatial analysis was done through ILWIS and Arc GIS software. The results showed that the residual phosphorus levels such as Dichlorvos and Dursban in the Varamin plain aquifer (WHO standard) were higher than other standard pesticides.

Keywords: Pollution, Phosphorus Pesticides, Groundwater, Varamin.

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I. INTRODUCTION

Contaminated water is blue that changes its composition and does not have its own natural state of consumption and what matters is water pollution. It is related to social health. Human activities have changed the chemical properties of water and contaminated water and even this pollution may be to a degree that is fatal and water is useless for some users. Fertilizers and pesticides from agriculture and livestock and industrial and urban wastewater, etc., pollute groundwater and surface water. The most important pollutants of groundwater are pesticides. These pollutants are chemicals that are used to kill and control pests. In the field of agriculture, these materials include herbicides, insect pests, fungi, worms and rodents Weeds are lethal toxins (Balamurugan and Dheenadayalan, 2012; Jaipieam et al., 2009).

Worldwide, insects and pests cost millions of dollars annually for agricultural products. Farmers are largely dependent on chemical technologies for pest management and profitability in their activities and investments (Abdel-Halim et al., 2006). These chemicals are commonly used to control and eliminate pests and are synthetic or natural compounds. The target organisms of the pesticides are wide-spread and include insects, rodents, nematodes, fungi, weeds, and even viruses and bacteria and organisms that are known to be pests. The use of pesticides in agriculture is called chemical control. Chemical control is the last resort in pest control. This method was expanded after the Second World War, as compared to other control methods; there were definite and immediate results on pests. Most pesticides are selected from toxic compounds, and in most cases, especially in recent years, pesticides are selected in such a way that, in a concentration that is toxic to beings, Human beings, domestic animals and useful arthropods (non-target organisms) are not toxic, therefore, the chemicals used in plant protection for chemical control of pests are considered to be pesticide (Talebi, 1998).

Organic phosphorus pesticides have been developed since the Second World War and, despite the presence of hydrocarbons containing phosphorus in their composition, instead of chlorine; they have less sustainability in the environment. In addition, there is a faster degradation in metabolic pathways in mammals, which causes the degree of damage to reach its minimum level in non-target animals. Phosphorus pesticides areDichlorvos, Diazinon, Fuzzalon, Dursban, Malathion, Azinphos-methyl, Ethionium, Phenytoin and Premium methyl (Eyer, 2003). Usually, after spraying and granulation in agricultural fields, the residual of pesticides following seasonal rainfall or irrigation is gradually washed off from crops and crops, and is easily accessed by water resources such as surface water and Underground will be. A number of residual pesticides in drinking water and thefoodare rarely high enough to cause acute effects on the health of animals and humans (Lam and Gray, 2003; Donald et al., 2007). These cases often result in chronic effects that appear through prolonged contact. In the meantime, some areas of greater potential for agriculture are more important. Varamin Plain is located 45 km south-east of Tehran and one of these areas with high crop capacity in Tehran province.

A lot of research has been done in this area, for example, Bradey et al. (2006), in a study to assess the impact of high-impact pesticides in California, showed that pesticides were reached far away from the field during the first hours of precipitation. And cause water poisoning. In another study, Bowman et al. (2002) examined the level of groundwater contamination with nitrates and agricultural pesticides in rice cultivated areas in the Philippines, which showed that pesticide levels were higher than the WHO limit.

Considering the adverse effects of agricultural pesticides on the groundwater resources of the Varamin plain, which are the most important sources of drinking and farming in the region, as well as the proliferation of organ phosphorous pesticides use for reasons such as greater effectiveness, faster biodegradation and More safety, chemical analysis of these pesticides is essential. Considering the above-mentioned issues, the present study was conducted to investigate the contamination of phosphorus pests in underground waters of Varamin Plain.

II. METHODOLOGY

In the present study, library studies have been used to collect information and to study the subject's records both inside and outside the country. The statistical population includes all waters in the aquifer of Varamin Plain. Sampling is a systematic method for this society, meaning that sampling stations and sampling times were determined on the basis of a researcher's request. The information gathering tool in the forthcoming research is sampling groundwater as well as their chemical analysis in the laboratory. Thus, according to field observations of the area and investigation of existing wells, 6 wells have been selected as stations in different regions throughout the Varamin Plain. In terms of time, according to the data from the Agricultural Jihad in Varamin, the annual spraying time in this area for the control of agricultural pests in the two seasons is mid-March and mid-May. In order to extract and purify the samples, the mass spectrometry was performed by aQuechersmain method and chemical analysis to determine the concentration of phosphorus pestilences by gas chromatography. So, after separating the liquid phase with a separator, the samples were transferred to the balloons and the extracted materials were condensed using a rotary machine. Then, by injection of samples into the GC-MS machine, the concentration of the toxins was determined. In order to map out the Boolean logic model, the simplest and most popular models used to integrate information in GIS are used. SPSS 20.0 was used to analyze the statistical data and Microsoft Excel 2014 software was used to plot the graphs. Also, spatial analysis was done through ILWIS and Arc GIS software.

III. RESULTS

General information on the statistical indicators of the chemical evaluation of organic phosphorus pests in groundwater of Varamin plain is as follows:

Table1. Statistical indexes of pollutant measurement results in Varamin plain aquifer (in terms of ppb)

pollutant	Statistical Indices				
	Average	The standard error	Standard deviation	Maximum	Minimum
Dichlorvos	2/26	0/334	2/31	6/80	<0/10
Diazinon	0/207	0/037	0/259	0/78	0/05
Phosalone Phosalone	0/329	0/049	0/341	0/86	0/05
Dursban	1/33	0/106	0/753	3/40	1/00
Malathion	<0/10	0/00	0/00	<0/10	<0/10
Azinphos-methyl	<0/10	0/00	0/00	<0/10	<0/10
Ethion	<0/10	0/00	0/00	<0/10	<0/10
Fenitrothion	<0/10	0/00	0/00	<0/10	<0/10
Pirimiphos-methyl	0/183	0/025	0/177	0/64	<0/10
BOD_5	60/81	1/81	12/6	88/00	39/00
COD	31/10	1/14	7/9	44/00	16/00

Thus, the most important residual organic phosphorus in groundwater of Varamin plain areDiklorous with an average of 2. 26μg / l. Malathion, azinphosmethyl, Ethion, and phenothrinalthough used in agriculture in the area, remained negligible (less than 0.1 μg / l) .

The highest amount of Dolorous phosphorus residues in the underground waters of Varamin in the first and second sampling stages was recorded as 4.20 (Varamin) and 6.80 (Chemershahr), respectively. The maximum biochemical and chemical oxygen demand were 88.00 and 44.00 mg / L, respectively, at GhalehKhajeh Station and in the second phase sampling.Since the significance level of the data is more than 0.05, therefore, there is no significant difference between the observational and expected frequency of the measured data and the distribution of the normal population. Therefore, parametric tests can be used for statistical comparisons.

According to the World Health Organization (WHO) guidelines, the maximum residue limit for all organic chlorine, organic phosphorus, and carbamate in the environmental environment was 0.50 μg / L, and the statistical test showed a significant difference between World Health Guideline There are average measured values. Residues of some pesticides, including Diazinon (t-value of 7.795), Phosalone (3.464), Malathion (-1.33), azinphosmethyl (-0.336), ethion (-03.03), Fenitrothion (-0.31) and primitive methyl (12.3364) were significantly within the permitted range of the WHO standard. However, in the case of Dichlorvos and Dorstabl with t-statistic, they are equal to 759/1 and 831/0, respectively, of the residual amounts of these pesticides in the groundwater of the Varamin plain above the World Health Organization's permissible limits.

Comparison of the mean of the first and second stages of sampling showed that the significance level for all of them was less than 0.05. In fact, there was a statistically significant difference between these two times (March-March 1995 and June 1996), and in general, in the second phase of sampling (June), the level of pollutants-residual organic phosphorus pests and biochemical and chemical oxygen demand was more than the first stage (March).Analysis of variance and comparisons of pollutant emissions at different sampling stations.

Table 2. Analysis of variance test results to compare the sampling stages of the first stage at different stations

pollutant	***Source***	**the sum of squares**	df	**an average of squares**	**F statistics**	**Meaningful level**
Dichlorvos	Intergroup	68/842	5	13/768	660/90	0/000
	Ingroup	0/038	18	0/002		
	Total	68/880	23			
Diazinon	Intergroup	0/040	5	0/008	145/200	0/000
	Ingroup	0/001	18	0/000		
	Total	0/041	23			
Phosalone	Intergroup	2/581	5	0/516	144/63	0/000
	Ingroup	0/006	18	0/000		
	Total	2/588	23			
Dursban	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Malathion	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Azinphos-methyl	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Ethion	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Fenitrothion	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Pirimiphos-methyl	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			

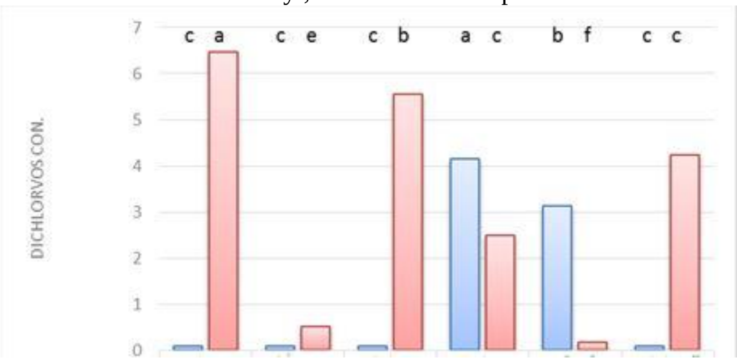
BOD5	Intergroup	1584/375	5	316/875	217/286	0/000
	Ingroup	26/250	18	1/458		
	Total	1610/625	23			
COD	Intergroup	828/875	5	165/775	107/530	0/000
	Ingroup	27/750	18	1/542		
	Total	856/625	23			

Table 3. Analysis of variance test results to compare second stage sampling pollutants at different stations

pollutant	***Source***	**the sum of squares**	df	**an average of squares**	**F statistics**	**Meaningful level**
Dichlorvos	Intergroup	136/784	5	27/357	242/303	0/000
	Ingroup	0/203	18	0/011		
	Total	136/987	23			
Diazinon	Intergroup	2/191	5	0/438	101/410	0/000
	Ingroup	0/008	18	0/000		
	Total	2/198	23			
Phosalone	Intergroup	1/587	5	0/317	190/40	0/000
	Ingroup	0/003	18	0/000		
	Total	1/590	23			
Dursban	Intergroup	21/243	5	4/249	571/654	0/000
	Ingroup	0/134	18	0/007		
	Total	21/367	23			
Malathion	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Azinphos-methyl	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Ethion	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Fenitrothion	Intergroup	0/000	5	0/000	0/000	1/000
	Ingroup	0/000	18	0/000		
	Total	0/000	23			
Perimiphos-methyl	Intergroup	1/145	5	0/229	872/714	0/000
	Ingroup	0/005	18	0/000		
	Total	1/150	23			
BOD5	Intergroup	1241/000	5	248/200	48/039	0/000
	Ingroup	93/000	18	5/167		
	Total	1334/000	23			
COD	Intergroup	332/333	5	66/467	33/701	0/000
	Ingroup	32/500	18	1/972		
	Total	367/833	23			

Analysis of variance indicated that there was a statistically significant difference between different sampling stations in the amount of Dichlorvos, diazinon, Phosalone, biochemical and chemical Oxygen Demand contaminants for both sampling steps (P<0.05). In the case of pesticides such as malathion, azinphos-methyl, Ethion, Fenitrothion in both sampling steps, since all of the stations have measured them less than 0.1, no difference was found between them Not seen (P = 1.00). However, in the case of Dursban and Perimiphos methyl, the situation is such that in the first stage there is no difference between stations, but in the second stage, there is a significant difference between them (P <0.05).

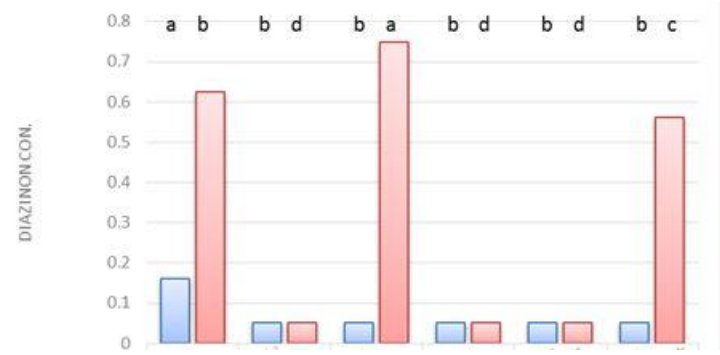
Figures (1) to (7) show the results of the Duncan post hoc test for Dichloro, Diazinon, Phosalone, Dursban, Premium methyl, BOD5 and COD pollutants:



	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First stage	**0.1**	**0.1**	**0.1**	**4.15**	**3.125**	**0.1**
second stage	**6.475**	**0.5125**	**5.555**	**2.5**	**0.1725**	**4.2275**

Fi**gure 1.** Comparison of Dichlorvos average at different stations

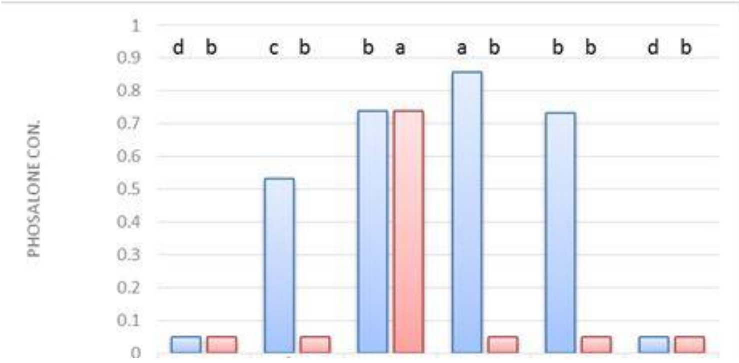
Figure 1 show that in the first stage of sampling,Dichlorvosconcentrations were significantly different at the stations of Charmshahr, Mohammad Abad, Pishva and Khajeh castles. However, there is a significant difference between the residual and the impurities in Varamin and Qarchak.In the second sampling period, the highest amount of this pesticide was observed in the leather (6.47 µg / l), and all stations have statistical differences with each other.



	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First stage	**0.16**	**0.05**	**0.05**	**0.05**	**0.05**	**0.05**
second stage	**0.625**	**0.05**	**0.7475**	**0.05**	**0.05**	**0.56**

Figure 2 Diazinon average at different stations

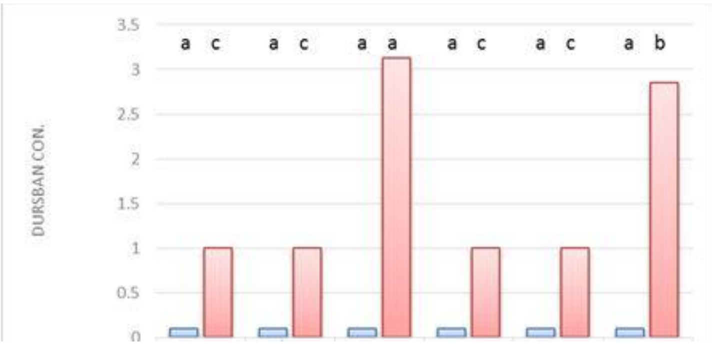
Figure 2 shows that in the first stage, the sampling of the remaining Diazinon at the Charmshahr station is significantly higher than the other stations(0.16 µg /l). However, in the second stage of sampling, Pishva station (747/0 micrograms per liter) was significantly higher than the others with the remainder of this poison.



	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First stage	0.05	0.05325	0.74	0.8575	0.7325	0.05
second stage	0.05	0.05	0.74	0.05	0.05	0.5

Figure 3 Comparison of the mean of Phosalone in different stations

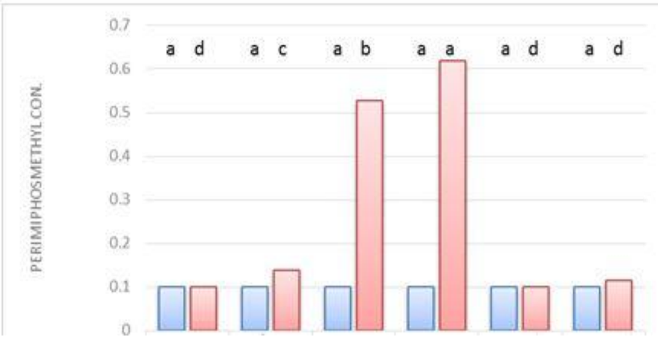
Figure 3 shows that the highest residue was recorded at the sampling station at Varamin Station (0.85 µg / L). However, in the second stage, the amount of this pesticide at the station was not significantly different with other stations, except for the station, which showed a constant amount (0.44 µg / l) at both times.



	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First stage	0.1	0.1	0.1	0.1	0.1	0.01
second stage	1	1	3.125	1	1	2.8525

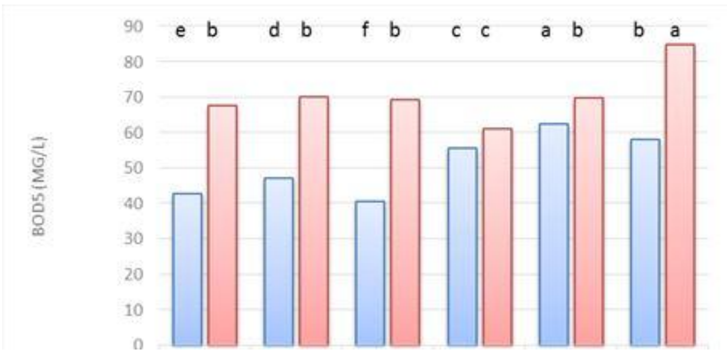
Figure 4 Comparison of Durban average at different stations

Figure 4 indicates that the remainder of the Dursban has a steady sampling rate at all stations (less than 0.1 µg / L). In the second step, the maximum residual samples were detected in Pishva (3 125.3 µg / L) and then Khajeh castle (2.85 µg / L), which showed significant difference with each other and with other stations 1 µg / l).



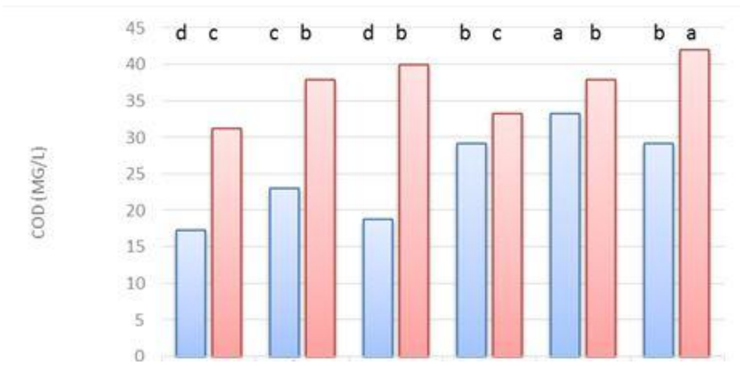
	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First stage	0.1	0.1	0.1	0.1	0.1	0.01
second stage	1	0.1375	0.5275	0.6175	0.1	0.115

F**igure5.** Comparison of Perimiphos-methyl Methane at Different Stations



	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First stage	42.75	47.25	40.5	55.75	62.5	58
second stage	67.75	70.25	69.25	61	69.75	85

Figure6. Comparison of BOD5 Indicators at Different Stations



	Charmshahr	Mohamad Abad	Pishva	Varamin	Qarchak	Khajeh castle
First	17.25	23	18.75	29.25	33.25	29.25

stage						
second stage	31.25	38	40	33.25	38	42

Figure7. Comparison of COD Indicator Mean at Different Stations

Based on Figures 6 and 7, the BOD5 index in the first stage of sampling was significantly different at all stations, and its maximum was recorded in Qarchak (62.5 mg / L). In the second stage sampling, the highest rate of this index was observed in Khajeh castle (85 mg / L), which was significantly higher than others.Regarding the COD index, respectively in the first and second stages respectively, the maximum values were measured in Qarchak (33.25 mg / L) and Khajeh castle (42 mg / L).Considering that pollutant index including residual pesticides in this study were measured at scattered stations in Varamin plain, their mapping could help to better understanding of the distribution and emission of contamination in this aquifer. The maps showed that the points of the aquifer with the highest accumulation of Dichlorvos remained as the most commonly used pest in the Varamin plain for the first stage of sampling in Varamin area and for the second stage of CharmShahr and then Mohammad Abad. In the case of Diazinon in the first stage, the sampling was made of leather, and in the second phase of Mohammad Abad and then Charmshahr; in the first phase, Phosalone was used to sample Varamin, then Mohammad Abad and the second phase of Mohammad Abad.

Regarding the toxic properties of Dorstab and Primyfus methyl, only the sampling time in the stations was variable, only at the same time the map was prepared. Mohammad Abad The maximum region of the remaining Dorseban, as well as Varamin and then Mohammed Abad, were the largest region of the remainder of the primitive Methylium.

It is therefore quite clear that, in general, the areas of Mohammad Abad, Varamin and Charmshahr are the most important areas of the use of pesticides and, consequently, their accumulation, and areas such as Qarchak, Pishva, and Khajeh Castle are of lesser importance in this regard.

Also in Fig. 8, three-dimensional maps of Dichlorvos, Diazinon and Phosalone distribution, which were obtained from the integration of the first and second stages of sampling, were presented respectively.

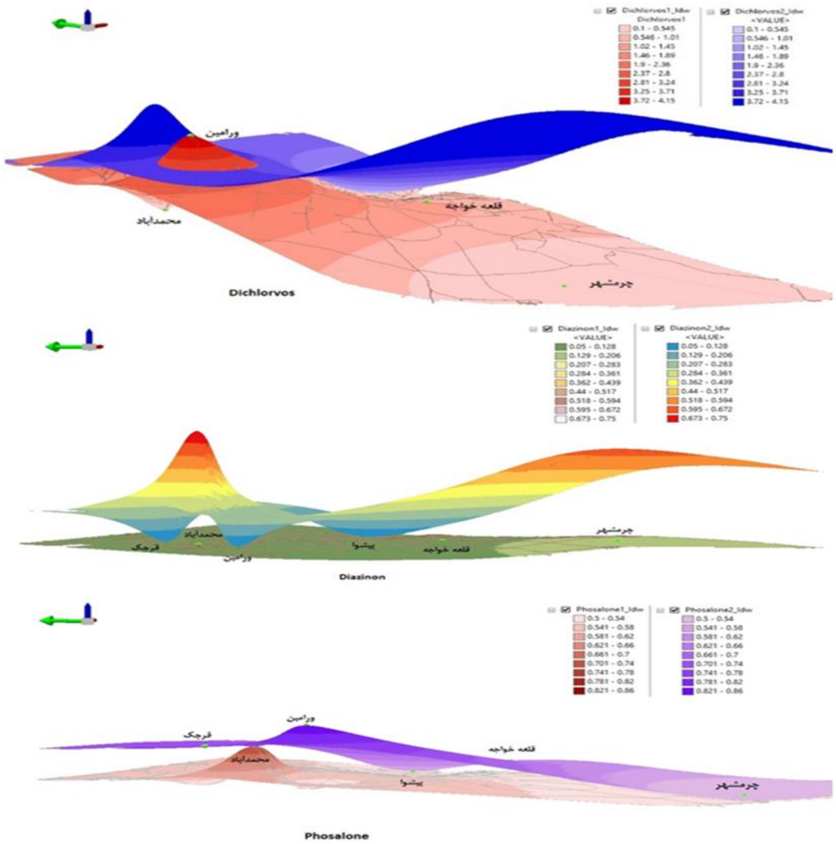


Figure 8 Three-dimensional maps of Dichlorvos (high), Diazinon (middle) and Phosalone (low)

IV. CONCLUSION

The analysis of the data collected in the research indicated that a number of phosphorus residues such as Dichlorvos and Dursban in the Varamin plain aquifer are higher than the standard (WHO standard), but other pesticides within the range Standardized. The existence of large quantities of agricultural pesticides remaining in the groundwater of the Varamin and Mohammad Abad regions indicates the accumulation of agricultural land and crops. However, in the case of leather, which is considered an industrial area, the most important reason for this problem can be the slope of the Varamin Plain the south and southwest, leading to groundwater contaminated with pesticides.

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