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Investigation of groundwater contamination level in Guilan province arising from Edifenphos (Hinosan) fungicide using a genetic algorithm

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Abstract

Contamination of groundwater of Guilan province with ediphenfos pesicide (hinosan) was investigated and the accuracy of its prediction was the studied using artificial neural network. Collection of data was performed from the entire province and their measurement lasted two years seasonally and at a single time for each season. The analysis method was in the form of liquid phase extraction together with gas chromatography with ECD detector. The modeling was performed using GMDH neural network considering two objective functions of training error and experimental error with optimization of the factors influencing the level of the concentration of ediphenfos toxin in groundwater of Guilan province. The parameters affecting the concentration of Ediphenfos toxin included the mean diameter of the particles, distance off the farms, well depth, pH, electrical conductivity, salinity, and level of precipitation. For optimization of the parameters, multi-objective genetic algorithm was used. Eventually, the degree of significance of each parameter in the prediction of toxin's concentration was determined and the comparison of the results obtained from GMDH method with experimental data presented acceptable results. Considering the responsively of the model, it can be used for estimation of the concentration of other toxins as well.

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Introduction

Agricultural industry has claimed a major part of the water consumption of the country. Considering the wide area of agricultural lands, improper usage of water resources and inputs such as fertilizer and toxin can seriously threaten the water resources of the country both quantitatively and qualitatively. Chemical toxins and fertilizers penetrate into surface water and groundwater and develop the ground for contamination of the water resources of the country. In recent years, consumption of toxins has also significantly grown as with chemical fertilizers. However, this increase is happening while many countries especially developed countries have set strict limitations for their consumption and their usage has been experiencing a descending trend in these countries in recent years. In Guilan province also consumption of organic and chemical fertilizers has had a great variety and range to combat pests of rice plant, causing contamination of surface water and groundwater of the province and making reusability of these resources very limited. Consumption of toxins and pesticides in agricultural lands causes them to penetrate into groundwater and in turn the food cycle of living creatures including human, who use the mentioned waters for drinking purposes. The majority of pesticides are persistent organic compounds that passed through different layers of the earth considering various factors including temperature, precipitation, soil properties, and characteristics of chemicals with different rates and reach groundwater. Therefore, usage of groundwater resources in agricultural sector and rural drinking section, which often lack healthy piping system, is of importance in terms of health and environment and accordingly controlling the level of contamination of the toxins in these waters can be of significance economically, socially, and in terms of health. For management of water resources including surface and groundwater and controlling the level of their toxins using climatic conditions and the status of the region, meteorological data, and getting help from smart methods, it is possible to make decisions with a greater confidence easily in emergency situations (Noshadi *et al*, 1386). It should be noted that to present a model, valid data should be available and there should be a significant relationship between the variables influencing the developed situation and the selected dependent variable.

In recent years, application of artificial intelligence in different scientific areas such as agriculture, environment, and engineering has become prevalent. Various researchers have used artificial intelligence methods including artificial neural networks, multi-objective neural networks of Group Method of Data Handling (GMDH) type, ANFIS fuzzy- neural structures, and genetic algorithm in various areas such as environment, treatment of drinking waters, prediction of drought, prediction of the level of chlorine consumption, and the role of coagulators in water treatment process, achieving acceptable and practical results. Goloka *et al.*, (2006) applied artificial neural networks to predict pesticide concentrations in groundwater monitoring wells in USA. Pesticide concentration data are challenging to analyze because they tend to be highly censored. Input data to the neural network included the categorical indices of depth to aquifer material, pesticide leaching class, aquifer sensitivity to pesticide contamination, time (month) of sample collection, well depth, depth to water from land surface, and additional travel distance in the saturated zone. In a study Stenemo *et al* (2007) developed several simple index methods with easily accessible data in decision–support systems to estimate pesticide leaching across larger areas and A Fourier amplitude sensitivity test showed that the model output (the 80th percentile average yearly pesticide concentration at 1 m depth for a 20 year simulation period) was sensitive to all input parameters. In a study in Iran by Esfandian *et al* (2016) Artificial neural network (ANN) model was also applied for modeling of diazinon removal from aqueous solution by acid treated zeolite and modified zeolite. There was a good agreement between the experimental and predicted values with seven neurons in hidden layer. Ali Askari *et al* (1390) dealt with modeling and estimating nitrate contamination in the groundwater in the margin of Zayandehroud on the qualitative values of water using artificial neural network. For training, three-layer perceptron network with training group of back propagation and sigmoid activity function were used. Following repetitive experiments, a network with one hidden layer and 19 neurons in this layer developed the lowest error value in the network's training trend, evaluation, and validation. The results suggest that a network with a suitable estimation has been designed, with which the value of nitrate can be easily obtained without using complex mathematical relations. Daghbandan *et al* (1393) used GMDH neural network model and Bayesian self-belief network for modeling and predicting the turbidity of treated water from Guilan's grand treatment plant. For the modeling, the data obtained from the operational unit were divided into two groups of 70% for training and 30% for experiment. The results obtained from the modeling were compared with laboratory data, where the coefficient of determination of the experimental values for the two algorithms of self-belief network including EM and GD for GMDH model were 0.93, 0.91, and 0.97, respectively. Based on the results of GMDH model, when compared with BBN model, the former has a greater efficiency for predicting the turbidity of treated water. The artificial neural network model was developed by Singh *et al* (2009) to estimate the concentration of dissolved oxygen (DO) and biological oxygen demand (BOD) in Gomti River in India. The input of the presented model includes 11 qualitative water parameters which had been measured over 10 years on a monthly basis across eight different stations. They evaluated the performance of their model using correlation coefficient square (R^2), root mean square error (RMSE), and comparing it with measured values. The results of the model have a good correspondence with the measured and expected values for the river concentrations. In the investigation by Shouliang Huo *et al* (2013), artificial neural network was proposed as a data modeling approach for predicting the quality indicators of Fuxian Lake in order to determine nonlinear relationships between the qualitative factors of water and the accumulation indices. To employ the neural network model, the key factors influencing water quality such as dissolved oxygen (DO), total phosphorus (TP), Chlorophyll A (CHL-A), and disk Seshi depth in Fuxian Lake were used. The measurement data lied in the input layer and accumulation index such as DO, TN, CHL-A, and SD were presented in output layers. The results indicated that the neural network model is able to predict this index of emission of contaminants in water resources with a suitable accuracy. This study also shows that neural network is a valuable tool for lake management. In a study by Moasheri *et al* (2013), a combination of geostatistical and artificial neural networks was used to estimate the spatial distribution of the quality parameters of groundwater resources TDS in Birjand Plain. First, the analysis of geostatistical methods and interpolation using artificial neural networks were done and for optimization of the results, geostatistical methods were benefited from. By optimal design of GMDH artificial multi-objective network, a system was implemented which predicted the concentration of toxins acceptably. The parameters were chosen as they were easily measurable and available. The presented model had no limitation regarding the type and number of inputs and using this model, any system that can be modeled and its laboratory data are available can be optimized. In a study by Kheradpisheh *et al* (2015), artificial neural networks were developed by MATLAB 2013 software and qualitative parameters of Cl, EC, SO_4, and NO_3 in water resources were measured and the number of neurons in the hidden layer was obtained using trial and error method. In this research, 260 water samples were collected from 13 well rings in Bahabad Plain along 10 years. The results indicated that application of artificial neural network model was very accurate for NO_3, which can be owing to the effect of different water resources on each other or the effect of other parameters. This study confirmed that the number of neurons in the hidden layers using a special formula (two times of the number of inputs +1) cannot be correct for all parameters. Further, by setting real data as basis, this study can perform a proper comparison between smart models. Furthermore, such investigations for management of water resources seem to be logically essential. It can be stated that application of smart models can both decrease the measurement costs and compensate for the vacuum resulting from shortage of meteorological data in some regions with no stations which need estimation of - evaporation- perspiration. In order to predict the level of toxins in groundwater, first the factors influencing its incidence should be identified. In this project, the effect of environmental conditions and the level of precipitation on ediphenfos concentration in groundwater of some regions of Guilan province was estimated using neural network modeling and by genetic algorithm, the optimal conditions for having the minimum ediphenfos concentration were determined by the network and the critical season was also determined.

The aim of this study was to estimate the variation of Ediphenfos pesticide in ground water and compared them with the measured values by using of artificial neural networks. The relative importance of key input parameters was tested by the model, and it was observed that the parameters had a different impact on sampling wells. The data were collected from Guilan province located in the north of Iran. The main necessities of study in this region refer to the quality of water which has been threatened by agricultural activities and data driven from this study helps water quality problems will be solved in future.

Materials and methods

The specifications of the sampling wells

Table 1 presents the specifications of the wells of interest including the well code, name of the town, name of the village, geographical properties, and the water table level of the studied wells.

Taking the samples and the manner of measurement of Ediphenfos toxin

To conduct this research, samples were taken from 20 wells used for supplying drinking water across Guilan province in four seasons and for two years. For doing the analysis of the extent of ediphenfos fungicide, GC and GC-MS methods were used. All of the GC measurements were performed on gas chromatography device Thermo 1 Trace GC Ultra with OV-17Jenway column 30 m long and 0.25 mm in diameter together with ECD detector with beta radiation source of Ni type. The carrier gas was N_2 with a purity of 99.99%, rate of 5 ml/min, and injection value of 0.5 microL for each sample, with injection system being of splitting type. The temperature of injection was 180°C. Thermal programming ranged between 180 and 250°C with 5°/min which was kept at 180 and 250°C for 5 min. Overall, each investigation lasted 25 min.

GC-MS device was HP Agilent 6890N (G1530N) and the column was HP-5MS with dimensions of 15 µm * 30 m * 0.25 mm. the rate of helium gas was 4 ml/min and thermal programming was also the same as the method stated in GC section. Qualitative detection was performed based on interpretation of the spectra, and for greater confidence, they were compared against standard spectrum. Before each daily measurement, GC-MS device was calibrated by (C4F9)3N compound. All of the chemicals used including HCl, sodium chloride, and n-hexane solvent were purchased from Merck Co. and the utilized distilled water had a special conductivity below 10 µScm-1. For this purpose, first the water samples were acidified by HCl at pH=1 and then kept in refrigerator. For extraction, 1 L of the acidified water samples were filtered by a filter paper. Thereafter, addition of 2 g NaCl was performed to enhance the extraction efficiency across four stages, each stage with 10 ml of n-hexane (total volume of 40 ml) and the extraction was conducted. Thereafter, the extraction solution was dehydrated by sodium sulfate and its final volume was decreased to 2 ml and then transferred to sample tube. For injection to GC, first a calibration curve of hinosan toxin standard was prepared from Sigma Aldrich Co. with serial number of 17109-49-8 in a solution form the purity degree of 60% and by diluting a standard solution of 1 ml hinosan in water, and then the standard solutions required of them were prepared. Hinosan toxin was plotted through calculation of the area under peak in terms of concentration and used for quantitative measurement of the samples. The prepared samples were injected into GC device and based on the thermal conditions of the column, as mentioned above, the analysis was conducted (EPA Method 507). Next, by comparing the spectrum of the samples with standard spectra and comparing the area under the curve, the concentration of the samples was determined. For each sample, injection was replicated three times and the obtained results were reported.

Neural networks of GMDH type

In GMDH method, for optimal design, what the objective genetic algorithm is used and two objective functions, modeling error, and prediction error are optimized simultaneously (Banihabib and Jamali, 1389). The aim of performing this stage of the research following the first stage was to present a nonlinear model for prediction and analysis of the extent of consumption of ediphenfos fungicide in groundwaters of Guilan province. With optimal multi-objective design of GMDH neural networks, a system was developed that was able to predict the extent of consumption of ediphenfos in groundwater with an acceptable accuracy. The process modeling was conducted using laboratory data including 80 data series for 4 seasons of each period which was related to the concentration of ediphenfos contaminant within two ranges of 1389-90 and 1393-94 and overall 160 data series. The model included eight influential parameters as the input including the well water table level, the mean diameter of the particles, distance off the farms, well depth, pH, electrical conductivity, salinity, diffusion coefficient, and level of precipitation) along with one output which is ediphenfos concentration. For the modeling, the data were divided into two groups, with 75% and 25% of them used for training and experiment of the network, respectively. For the modeling, first multilayer perceptron neural network, which is of greater usability among other neural networks, was employed. This neural network consists of one input layer, some hidden layers, where typically one or two layers are used, and an output layer. The output and hidden layers consist of a number of neurons. The neurons of the hidden layer from sigmoid performance function and for the neurons of the output layer, linear performance function was used. The information in this type of neural networks was transferred in only one direction, i.e. from the input neurons to the output neurons. Therefore, based on this, this type of neural networks is called forward propagation networks. For training of multilayer perceptron neural networks, back propagation error algorithm was used. Generally, it can be stated that in this algorithm first a set of inputs and their corresponding outputs are taken into consideration. Next, an input pattern is introduced to a network and the corresponding outputs as well as the error value are calculated (Banihabib and Jamali, 1389). Eventually, based on the calculated error and by moving from the output layer towards the input layer, the weights of the neural network are adjusted in a way that an objective function, e.g. their some of square error becomes minimized. This process continues until the objective function of interest is minimized to the intended value. A very important characteristic of multilayer perceptron neural networks is the fact that they are able to estimate any nonlinear continuous function with a desired accuracy. In this method, once the partial systems were formed or in other words the input variables of the system were classified into dual groups along with the same outputs, for each of these formed systems, it forms the function that is the very partial system model. Note that all of the developed partial systems enjoy a structure similar to the following relation.

$$y_i = f(x_{ip}, x_{iq}) = a_0 + a_1 x_{ip} + a_2 x_{iq} + a_3 x_{ip}^2 + a_4 x_{iq}^2 + a_5 x_{ip} x_{iq}$$

Function f has six unknown coefficients. Therefore, we should adjust them in a way that per all of the bivariate samples dependent on the system, the desirable output is established.

For this reason, G function is established based on the rule of least-squares error.

$$\{(x_{ip}, x_{iq}), i = 1,2,3,\ldots,N\}$$

$$\{(y_i),\ i = 1,2,\ldots,N\}$$

$$\sum_{k=1}^{N} \left[\left(G(x_{ki}, x_{kj}) - y_k \right)^2 \right] \rightarrow Min$$

With the conditions governing the problem, an equation system consisting of six unknowns and N equations is solved:

$$\begin{cases} a_0 + a_1 x_{1p} + a_2 x_{1q} + a_3 x_{1p} x_{1q} + a_4 x_{1p}^2 + a_5 x_{1q}^2 = y_1 \\ a_0 + a_1 x_{2p} + a_2 x_{2q} + a_3 x_{2p} x_{2q} + a_4 x_{2p}^2 + a_5 x_{2q}^2 = y_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ a_0 + a_1 x_{Np} + a_2 x_{Nq} + a_3 x_{Np} x_{Nq} + a_4 x_{Np}^2 + a_5 x_{Nq}^2 = y_N \end{cases}$$

The above equation system can also be indicated in a matrix format:

$$Aa = Y$$

$$a = \{a_0, a_1, a_2, a_3, a_4, a_5\}^T$$

$$Y = \{y_1, y_2, y_3, \ldots y_N\}$$

$$A = \begin{bmatrix} 1 & x_{1p} & x_{1q} & x_{1p}^2 & x_{1q}^2 & x_{1p}^2 x_{1q}^2 \\ 1 & x_{2p} & x_{2q} & x_{2p}^2 & x_{2q}^2 & x_{2p}^2 x_{2q}^2 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 1 & x_{Np} & x_{Nq} & x_{Np}^2 & x_{Nq}^2 & x_{Np}^2 x_{Nq}^2 \end{bmatrix}$$

For solving the equation, the nonsquare matrix inverse of A should be calculated. For this purpose, to calculate the inverse of the nonsquare matrix of A, orthogonal equations (solving normal equation) was used.

In this method, the real matrix pseudo-inverse of A is unique matrix of A*, which is calculated by the following relation:

$$A^* = \left(A^T A\right)^{-1} A^T$$

therefore, the unknown coefficients vector of a was obtained by the following relation.

$$a = (A^T A)^{-1} A^T Y$$

To ensure the accuracy of the proposed method, the accuracy and validity of the presented models in relation with the behavior of laboratory data are stated by correlation coefficient and root mean square error (RMSE), suggesting the error of the presented models in relation with experimental data.

For error calculation, the following relations were used.

a) root mean square error $RMSE = \left[\frac{\sum_{i=1}^{n} (Y_{i,exp} - Y_{i,model})^2}{n}\right]^{\frac{1}{2}}$

b) correlation coefficient $R^2 = 1 - \left[\frac{\sum_{i=1}^{n} (Y_{i,exp} - Y_{i,model})^2}{\sum_{i=1}^{n} (Y_{i,exp})^2}\right]$

Results and discussion

After the modeling by GMDH neural network, by considering two objective functions of training error and experimental error, optimization of the parameters influencing the concentration of ediphenfos toxin in the groundwater of Guilan province was conducted.

Table 1. The specifications of the sampling wells

Ground water level		Latitude and longitude		Rural name	City name	Code well	Row
94-93	90-89						
4.13	4.57	370630	500639	Sadat Mahalleh	Langarud	B1	1
5.38	5.52	370713	500943	Moridan	Langarud	B2	2
5.93	6.14	370313	494715	Lish	Siahkal	V1	3
6.63	6.51	370528	494259	Radar Poshteh	Siahkal	V2	4
1.75	2.62	371201	495226	Lafamjan	Lahijan	I1	5
5.38	5.53	371217	495446	Sareshkeh	Lahijan	I4	6

8.91	8.33	370904	492910	khorum	Shaft	S	7
5.75	5.81	365260	493247	Sondos	Rudbar	R	8
5.88	5.92	371330	495242	Kaldeh	Astaneh-ye Ashrafiyeh	G1	9
7.50	7.24	371420	494727	Chahardeh	Astaneh-ye Ashrafiyeh	G2	10
4.19	4.55	371858	495552	Nazok Sara	Astaneh-ye Ashrafiyeh	G3	11
14.68	12.94	370542	501328	Narakeh	Amlash	A	12
7.13	6.92	370825	501526	Chini Jan	Rudsar	K1	13
11.88	10.71	380601	485406	Shirabad	Talesh	J2	14
7.50	7.24	374413	485613	Uleh Kari	Talesh	J3	15
0.92	1.27	372191	492330	Nargestan	Sowme'eh Sara	C1	16
1.34	1.95	371546	494452	Mojdeh	Rasht	H3	17
1.67	1.93	371522	495047	Luleman	Rasht	H4	18
6.50	6.41	373142	490908	Tarom Sara	Rezvanshahr	D	19
5.66	5.73	382554	485005	Abbasabad	Astara	A2	20

Table 2. Results of neural network model to Edifenphos data in the wells under consideration

		Model inputs								Model output
Seasons		Ground water level	precipitation	pH	EC	Salinity	Soil Penetration Rate	Distance from farms	Deep well	Hinosan concentration (ppb)
Autumn	minimum	0.92	27.4	6.87	360	0.1	0.002	1	8	0
	maximum	14.68	1094.7	8.04	2473	3	0.75	500	92	1.1386
	Average	5.91	591.58	7.46	824.5	0.435	0.238	60.25	57.45	0.1506
Winter	minimum	0.92	64.7	6.99	322	0	0.002	1	8	0
	maximum	14.68	697.9	7.95	1473	1	0.75	500	92	0.7563
	Average	5.91	416.4	7.41	748.4	0.3	0.238	60.25	57.45	0.1044
Spring	minimum	0.92	37.2	8.13	341	0.1	0.002	1	8	0
	maximum	14.68	1292.6	6.7	1348	1.1	0.75	500	92	0.4253
	Average	5.91	147	7.44	764.6	0.3475	0.238	60.25	57.45	0.1015
Summer	minimum	0.92	2.7	7.17	269	0.1	0.002	1	8	0
	maximum	14.68	414.2	8.13	1240	0.6	0.75	500	92	0.5569
	Average	5.91	268.6	7.58	732.325	0.31	0.238	60.25	57.45	0.1413

Table 3. Premier chromosomes obtained for Edifenphos concentration in autumn

Dependent variable																	
	first part of the last layer neuron	1st neuron	2nd neuron	3th neuron	4th neuron	5th neuron	6th neuron	salinity	5th neuron	7th neuron	4th neuron	8th neuron	9th neuron	10th neuron	11th neuron	8th neuron	12th neuron
		1 3	7 8	2 5	4 5	1 5	3 7	5 5	6 8	1 5	4 5	2 4	5 7	1 8	2 6	2 4	2 7
	Second part of the last layer neuron	5th neuron	13th neuron	14th neuron	15th neuron	3th neuron	11th neuron	16th neuron	Deep well	12th neuron	17th neuron	18th neuron	19th neuron	20th neuron	21th neuron	20th neuron	Soil Penetration Rate
		1 5	5 7	4 6	5 6	2 5	2 6	5 8	8 8	2 7	4 6	3 4	4 7	3 5	4 8	3 5	6 6

The influential parameters on the concentration of this toxin included the mean diameter of the particles, distance off the farms, well depth, pH, electrical conductivity, salinity, and level of precipitation.

Table 2 summarizes the output of the model along four seasons based on the input parameters. The results indicated that the highest concentration of the toxin occurred in fall.

The maximum level of hinosan toxin in other seasons was related to winter, summer, and spring, respectively.

Pareto points obtained for the multi-objective GMDH model associated with ediphenfos concentration

Figs. 3-1 until 3-4 represent the curve of the value of the prediction error in terms of training error, known as pareto curve. Evidently, all of the pare to points are not superior to each other in terms of the two objective functions. Furthermore, as shown in the figure, Point A had the lowest training error value and Point B had the lowest prediction error value. Moving from A to B, the modeling error increases and the prediction error decreases. In other words, improvement in one of the objective functions has caused aggravation of the other objective function. The compromise point of the design, among all of the pare to points, can be Point M, as the modeling error in relation with training error at this point has a greater balance in relation with other points. Furthermore, the best point at which both the training and experimental error are minimum is again point M. obtaining point M was the last stage of the modeling. In this way, the top chromosome was obtained for determining the concentration of ediphenfos across different seasons of the year. After obtaining the top chromosome, it should be noted that each number belongs to one input parameter. The order and nomenclature of the parameters were as follows: 1- the well stationary level 2- level of precipitation 3-pH, 4- electrical conductivity 5- salinity 6-soy diffusion coefficient 7- distance off farms 8-the well's depth. Tables 3, 4, 5, and 6 indicate the type of formation of chromosomes based on the number of parameters.

Table 4. Premier chromosomes obtained for Edifenphos concentration in winter

Dependent variable	first part of the last layer neuron	Ground water level	1st neuron	2th neuron	Distance from farms	3th neuron	4th neuron	5th neuron	2nd neuron	6th neuron	7th neuron	6th neuron	8th neuron	5th neuron	9th neuron	5th neuron	9th neuron
		1 1	2 7	5 6	7 7	1 5	4 5	3 5	5 6	1 3	2 5	1 3	6 8	3 5	3 8	3 5	3 8
	Second part of the last layer neuron	Ground water	EC	10th neuron	Distance from farms	6th neuron	EC	3th neuron	11th neuron	6th neuron	Deep well	3th neuron	12th neuron	11th neuron	9th neuron	11th neuron	9th neuron
		1 1	4 4	2 4	7 7	1 3	4 4	1 5	2 3	1 3	8 8	1 5	1 6	2 3	3 8	2 3	3 8

Table 5. Premier chromosomes obtained for Edifenphos concentration in spring

Dependent	first part of the last layer neuron	1st neuron	2nd neuron	3th neuron	3th neuron	4th neuron	5th neuron	6th neuron	7th neuron	4th neuron	3th neuron	5th neuron	8th neuron	precipitation	7th neuron	5th neuron	8th neuron
		1 3	3 7	2 3	2 3	1 4	2 5	2 4	6 8	1 4	2 3	2 5	5 8	2 2	6 8	2 5	5 8
	Second part of the last layer neuron	9th neuron	9th neuron	6th neuron	5th neuron	6th neuron	10th neuron	11th neuron	12th neuron	9th neuron	7th neuron	13th neuron	14th neuron	precipitation	10th neuron	15th neuron	16th neuron

Comparison of the real output and the modeled output associated with the concentration of ediphenfos

This program is a mathematical model presented by GMDH neural network and is of use for prediction of the concentration of ediphenfos toxin and groundwater of Guilan province four different seasons of the year.

After obtaining the proposed models are obtained by GMDH neural networks, to ensure confidence regarding the reliability of the obtained model, the results resulting from the modeling were compared against the results obtained from experiment, with the results shown in Figs. 5, 6, 7, and 8.

Note that in the mentioned figures, the horizontal diagram was laboratory data and the vertical diagram was the data of the modeling.

As can be seen in the figure, the results obtained from the modeling have a very good correspondence with laboratory data. Furthermore, the error resulting from the modeling associated with ediphenfos concentration across different seasons in Guilan province has been provided in Table 7.

Optimization of the parameters affecting the concentration of ediphenfos in Guilan province

In the previous section, modeling of determination of ediphenfos concentration was performed using GMDH neural network and considering two objective functions of training error and experimental error.

In this section, the parameters influencing ediphenfos concentration in regions of Guilan province will be optimized.

For this purpose, GMDH multi-objective neural networks which were used for modeling of the mentioned process were employed.

Table 6. Premier chromosomes obtained for Edifenphos concentration in summer

Dependent variable																	
	First part of the last layer neuron	Ground water level	1st neuron	2nd neuron	3th neuron	4th neuron	5th neuron	6th neuron	7th neuron	8th neuron	8th neuron	9th neuron	Deep well	1st neuron	10th neuron	11th neuron	pH
		1 1	2 3	2 8	3 6	1 2	6 7	5 8	6 8	1 3	1 3	1 5	8 8	2 3	7 8	2 6	3
	Second part of the last layer neuron	12th neuron	13th neuron	14th neuron	15th neuron	16th neuron	2nd neuron	17th neuron	Soil Penetration Rate	18th neuron	2nd neuron	3th neuron	3th neuron	13th neuron	salinity	3th neuron	salinity
		1 4	2 4	1 7	4 5	1 6	2 8	3 8	6 6	1 7	2 8	3 6	3 6	2 4	5 5	3 6	5

Table 7. Edifenphos concentration modeling error

MSE	R2	RMSE	Maximum Concentration (ppb)		Minimum Concentration		Hinosan Concentration
			Model	Laboratory	Model	Laboratory	
0.002	0.975	0.043	1.1431	1.1386	0	0	Autumn
0.0006	0.999	0.003	0.7560	0.7563	0	0	Winter
0.0015	0.951	0.038	0.438	0.4253	0	0	Spring
0.001	0.975	0.032	0.568	0.5569	0	0	Summer

Table 8. The effect of independent variables on the Edifenphos in groundwater in different seasons Gilan province in optimal conditions.

Seasons	Model inputs								Model output
	Ground water level	precipitation	pH	EC	Salinity	Soil Penetration Rate	Distance from farms	Deep well	Hinosan concentration (ppb)
Autumn	Decrease	Increase	Decrease	Decrease	Decrease	Increase	Decrease	Increase	Decrease
Winter	After 10 reduced	To 700 decreased and then increased	Decrease	Decrease	Decrease	Up to 0.2 increase and then decrease	Decrease	Reduced to 40, then increased to 75 and then decreases again	Decrease
Spring	To 8 reduced Then increase to 13 and re-reduced	After 1000 reduced	Less than 7 and more than 8 reduced	Decrease	Decrease	Decrease	Decrease	Decrease	Decrease
Summer	Decrease	to 200 reduced And then increased to 400	After 8 reduced	Decrease	Decrease	Increase	Decrease	Increase	Decrease

The developed models are a function of independent variables. For optimization of the parameters, multi-objective genetic algorithm was used.

Using this algorithm, the influential parameters were optimized and provided in Table 8.

Optimization of the network according to different seasons of the year and determination of critical conditions

The aim of designing GMDH neural network is to prevent network divergence and associate the form and structure of the network to one or several numerical parameters, such that by changing these parameters, the structure of the networks would also change.

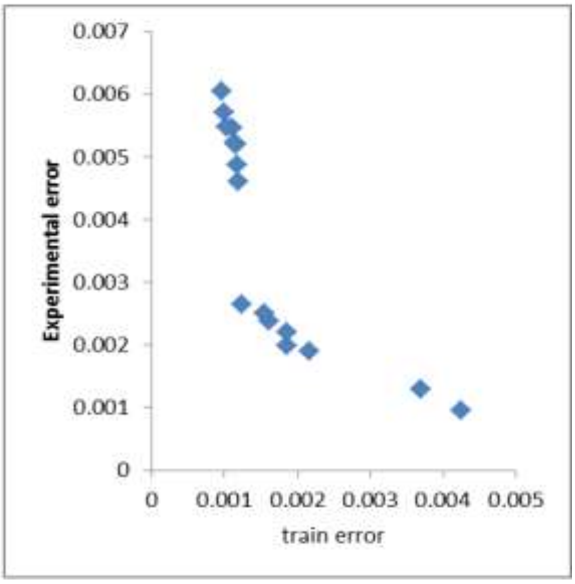

Fig. 1. Pareto points for the multi-purpose GMDH model on Edifenphos concentration in autumn

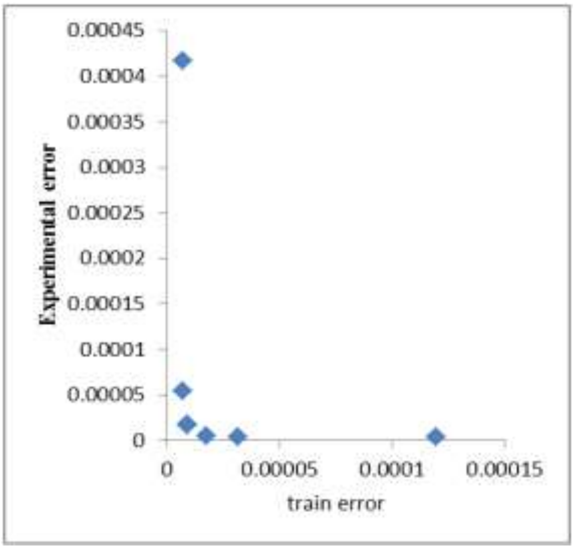

Fig. 2. Pareto points for the multi-purpose GMDH model on Edifenphos concentration in winter

It should also have had none of the mentioned limitations and be able to adapt itself with any complex system. Based on the mentioned points, the genetic algorithm used in this research had an acceptable power in prediction of the studied parameters. Overall, regarding prediction, one can develop different situations and scenarios and by giving the value of variables into the model, it is possible to obtain the output which is the level of ediphenfos toxin.

To employ the model, it is also possible to benefit from suitable software in which this program has been written.

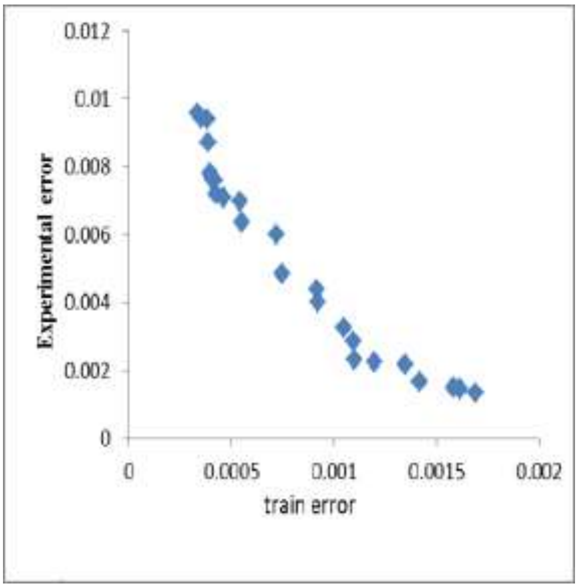

Fig. 3. Pareto points for the multi-purpose GMDH model on Edifenphos concentration in spring

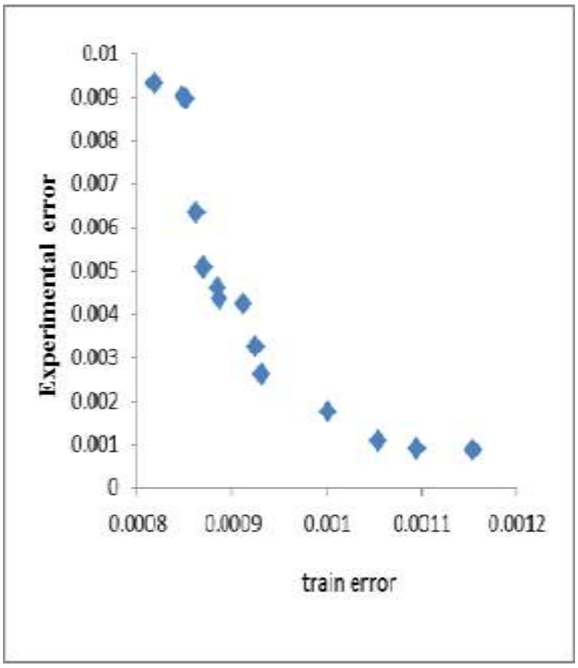

Fig. 4. Pareto points for the multi-purpose GMDH model on Edifenphos concentration in summer

The results of optimization considering the genetic algorithm indicated that fall season is the most critical season in terms of the concentration of hinosan and has the highest value.

Therefore, the extent of sensitivity of hinosan with all of the input parameters has been shown across Figs. 9, 10, 11, 12, 13, 14, 15, and 16.

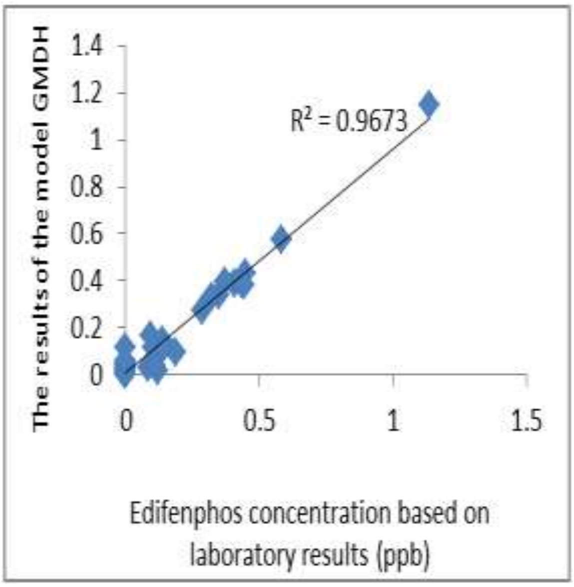

Fig. 5. Compare the actual output and output related to the concentration of Edifenphos in autumn

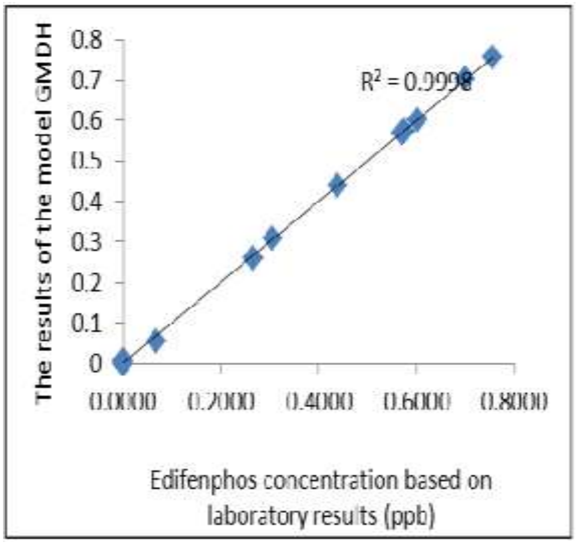

Fig. 6. Compare the actual output and output related to the concentration of Edifenphos in winter

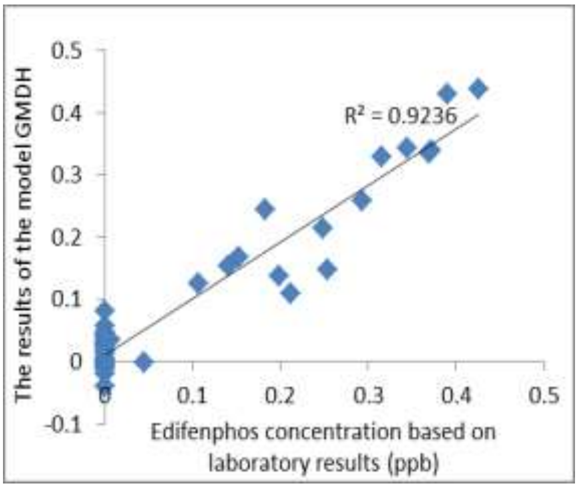

Fig . 7. Compare the actual output and output related to the concentration of Edifenphos in spring

Based on these figures, in the critical season of fall, the greatest and slightest impact belong to salinity and mean diameter of the particles, respectively on the concentration of the toxin. Furthermore, the general order was as follows: salinity, the well stationary level, and distance off the farms, electrical conductivity, pH, precipitation, the well's depth, and the mean diameter of the particles.

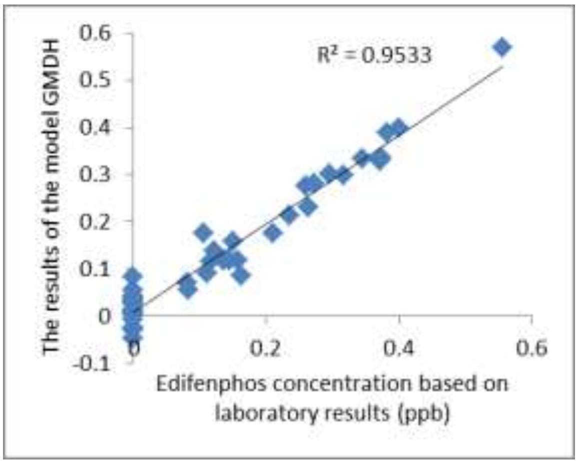

Fig. 8. Compare the actual output and output related to the concentration of Edifenphos in summer

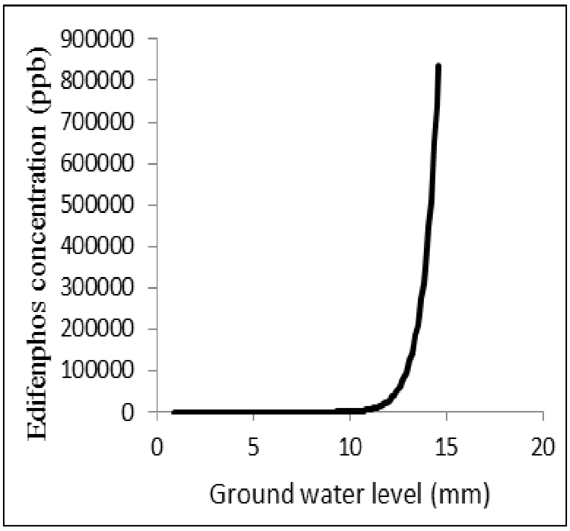

Fig. 9. The effect of gro on the concentration of toxin in optimal conditions

The optimized forms in fall indicated that with the increase in the well stationary level up to the maximum level of 11 m, the concentration of toxin diminished. However, after that the toxin level increases significantly and as a rule this should not exceed 11 m. for precipitation values lower than 200 mm of this parameter, the level of the toxin increases, but values above 200 have no effect on the level of the toxin. The mean diameter of the particles is suitable for 0-41-0.65 mm, and with its reduction, the level of toxin increases.

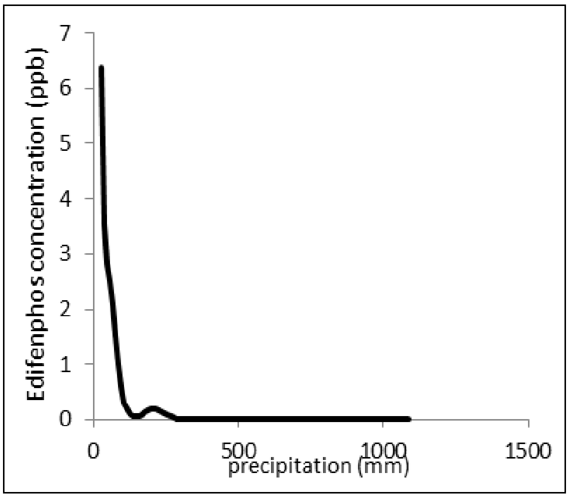

Fig. 10. The effect of precipitation on the concentration of toxin in optimal conditions

The parameter of distance off the farms is suitable for values below 420 m, while for further distances, the level of the toxin increases. With the increase in the depth of the well, the level of toxin diminishes. For pH values above 7.8, it has a developing trend and is suitable if it is lower. Electrical conductivity of over 2400 mho/cm has an intensifying effect on the toxin and is suitable to be lower. For salinity, values above 2.7 mg/L bring about significantly developing effects on the toxin, and should be lower.

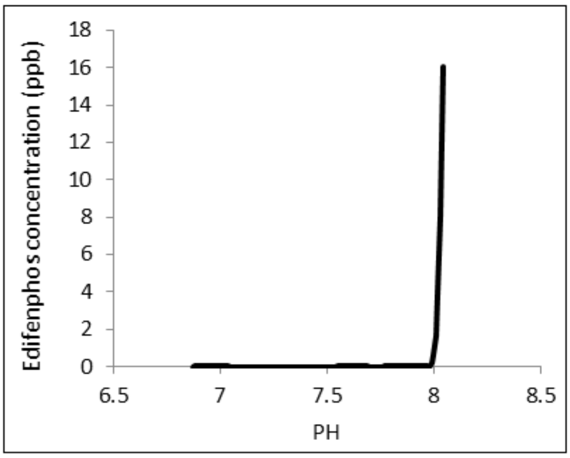

Fig. 11. The effect of PH on the concentration of toxin in optimal conditions

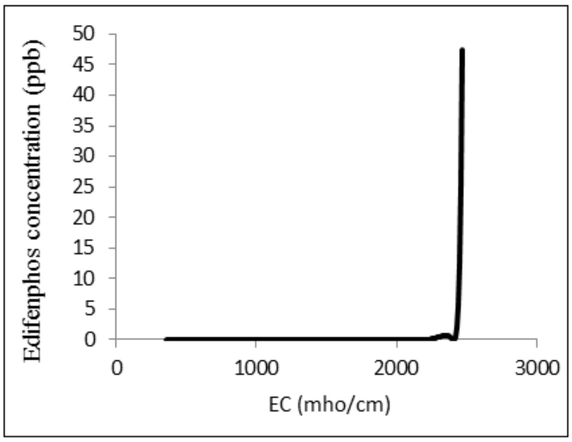

Fig. 12. The effect of electrical conductivity on the concentration of toxin in optimal conditions

Conclusion

in this research atoms have been made to take steps for modeling the concentration of toxins considering the available input variables using neural networks. The major aim of this research was to present a model that had a high accuracy per experimental values and was able to diminish the user interference.

To evaluate them model, error and determination coefficient values were used. Overall, it can be stated that in the course of the year, with the decrease in the independent variables including the well stationary level, electrical conductivity, salinity, and distance off the farms, the concentration of ediphenfos toxin will diminish. PH is better to lie within the range of 7.1 and 8. In a wide range of the extent of precipitation, the concentration of ediphenfos toxin did not show any significant change and in fall and winter within a certain range below 200, with the increase in precipitation the toxin concentration diminishes, while in spring the precipitation level of over 1000 has a descending effect. The increase in the diffusion coefficient within a certain range increases the ediphenfos concentration and with the growth of the well depth the level of ediphenfos will decrease. Further, the effect of the parameters of precipitation, salinity, and distance off the farms was greater than that of others. Eventually, based on the obtained results and comparing them with experimental data, it was found that GMDH network presented acceptable results and can be a more suitable substitute for expert experience. Considering the responsibility of the model, it can also be used for estimation of the concentration of other toxins.

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