A hybrid artificial neural network with particle swarm optimization for estimation of heavy metals of rainwater in the industrial region-a case study

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Abstract

The objective of this study was to explore the application of hybrid artificial neural network methods to predict heavy metals in rainwater based on major elements. Measurements of the heavy metals Pb, Cu, Zn, As, Ni, Hg, and Fe in soluble rain fractions were performed in rainwater collected at the Arak plain during the rainy seasons of 2012. In the soluble fractions, the concentrations of the heavy metals decreased in the order Fe, Pb, Zn, Ni, Cu, As and Hg. Enrichment factor related to the relative abundance of elements in crustal material were calculated using Fe as reference. The high enrichment factor ($EF_{crustal}$) suggested that, in general, heavy metals had an anthropogenic origin. Industrial activity and traffic are the source of heavy metals in the rainwater samples in the Arak city. Prediction of the heavy metals in the rainwater is important in developing any appropriate remediation strategy. This paper attempts to predict heavy metals of rainwater in Arak city using a new approach based on hybrid artificial neural network (ANN) with particle swarm optimization (PSO) algorithm by taking major elements (Cl, Mg, Na, SO_4) in rainwater. For this purpose, contamination sources in rainwater were recorded 50 data samples and several models were trained and tested using collected data. It determined the optimum model in each model based on four inputs and five outputs. The results obtained indicate that ANN-PSO model has strong potential to estimation of the heavy metals in the rainwater with high degree of accuracy and robustness.

Keywords: Artificial Neural Network; Particle Swarm Optimization; Heavy Metals; Enrichment Factor; Rainwater.

1- Introduction

The study of heavy metals in rainwater has increased in the last decades because of their adverse environmental and human health effects (Balogun *et al*., 2016; Castillo *et al*., 2013; Cheng and You 2010; Vuai and Tokuyama 2011; Wetang'ula and Wamalwa 2015). Anthropogenic sources have substantially increased heavy metal concentrations in atmospheric deposition (Bai and Wang 2014; Montoya-Mayor *et al*., 2013). If the concentrations are too high, many of the heavy metals can harm human health through the consumption of drinking water and/or aquatic organisms. Rainout and washout are the predominant processes of deposition by rain (Nickel *et al*., 2015; Pons-Branchu *et al*., 2015; Umeobika *et al*., 2013; Wilbers *et al*., 2013). Atmospheric transport and deposition processes are important in the global recycling of heavy metals (Lim *et al*., 2014). Since the atmosphere of Arak City is one of the most polluted cities in the Iran, it was considered important to analyze the heavy metals Pb, Cu, Zn, As, Ni, Hg, Fe and the major ions Ca, HCO_3, SO4, Na, K, Mg and Cl for the soluble fractions. Dissolved substances which have important impacts on the distribution of heavy elements near playa are scavenged by dusts and rains. More knowledge about heavy metal concentrations in rainwater can provide potential fingerprints for identifying heavy metal sources (Castillo *et al*., 2013). Hence, it is necessary to establish more baseline data regarding the chemical composition of rainwater especially for compounds related to anthropogenic activities (Cuoco *et al*., 2013; Holloway and Littlefield 2011; Lim *et al*., 2014; Niu *et al*., 2014).

Moreover, over the years, the application of artificial neural network (ANN) in different fields of engineering has been developing. ANNs have a special capacity to estimate the dynamics of nonlinear systems in many applications in a black box manner (Downs and Vogel 1993). In addition, several different efforts have been proposed by various researchers to propitiate this training problem (Sexton *et al*., 2004). Almasri and Kaluarachchi (2005) applied the modular neural networks to predict the nitrate distribution in groundwater using the on-ground nitrogen loading and recharge data. Khandelwal and Singh (2005) predicted the mine water quality by the physical parameters using back propagation neural network and multiple linear regressions. Erzin and Yukselen (2009) used the back propagation neural network for the prediction of Zeta potential of kaolinite. Singh *et al*., (2009) modeled the back propagation neural network to predict water quality in the Gomti River India. Rooki *et al*. (2011) predicted the heavy metals in acid mine drainage using ANN from the Shur River of the Sarcheshmeh porphyry copper mine, Southeast Iran.

In spite of all advantages of ANNs, these methods are associated with some limitations. To overcome these problems, the use of powerful optimization algorithms to optimize ANNs is of advantage. The PSO is an influential population-based stochastic approach for solving discrete and continuous optimization problems. Since PSO is a strong global search algorithm, it can be utilized to adjust weights and biases of ANNs in order to increase the performance of ANNs (Katherasan *et al*., 2014; Nedic *et al*., 2014). In this paper, ANN-PSO model is applied to estimation of heavy metals using real data obtained from rainwater in Arak city.

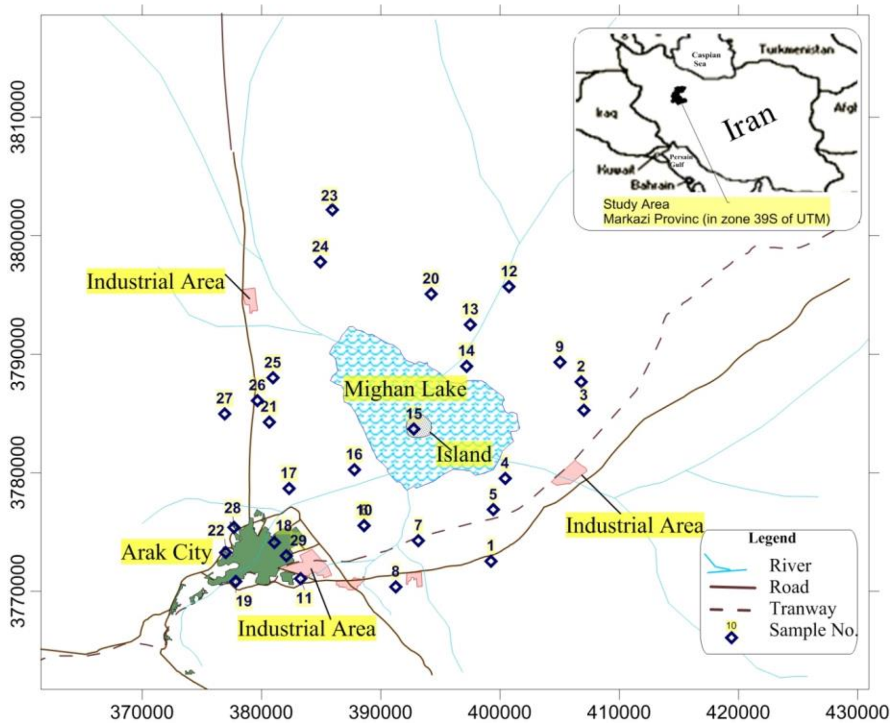

Figure 1) Location map of the collected some samples in Arak plain.

2- Materials and methods

2.1- Sampling Site

The Arak plain is bounded in south and north by high mountain's Arak and Ashtian, of Mesozoic and Cenozoic age. It also divided the region into a mountainous part and semi-arid central part (Mighan playa, Fig. 1). The Mighan playa has an annual rainfall of 300 mm and the average annual temperature 19^{o}C. The total catchment area of playa is 5500 Km^2. The playa occupies an area of about 110 Km^2 and the average depth of water is about 0.5 m. Two major ephemeral streams, namely Gharakahriz and Ashtian and many minor ephemeral streams from Farmahin, Amanabad and Haftadgholeh feed the playa. The surface of the Mighan playa presently undergoes complete desiccation every summer forming an efflorescent crust. This crust essentially consists of gypsum, glaubrite, halite and calcite minerals. It dissolves when it comes in contact with fresh run off during the next rain and this process increases the solute load of the playa brine. In terms of chemical composition, the brine is known to be practically high in SO_4 and Na. Na_2SO_4 and NaCl are the main constituents of the brine. This playa receive sediments from weathering of highly folded and metamorphosed Mesozoic rocks of the Arak mountains in south and sedimentary, volcanic rocks of the Ashtian mountains in north. The Arak Mountains included slate, phyllite, crystallized limestone. Arak plain divided to two sedimentary facies. The first facies contain terrigenous materials that are located near to mountains and include calcareous soils and were produced from weathering rocks in high lands, but the second facies are evaporate material and located near to Mighan playa and have saline soils that are rich of sodium sulfate. Arak is one of the regions affected by rainfall contamination of industrial origin. The region is one of the industrial regions in Iran where the impact of rapid population growth and industrialization on limited natural sources and agricultural lands is progressively high and as a result, the size of uncontaminated areas is getting diminished. Due to expanding industrialization and urbanization in Arak and the unrestrained disposal of factory wastes to rainfall, it is thought that heavy metal contents in this region are high. Therefore, monitoring of this change and determination of contamination in rainfall has gained importance.

2.2- Sample Collection and Analysis

50 samples of rainwater were collected on the roof of the general buildings. Rainwater samples were collected in 2012 and the rainy season in Arak City. The sampling locations were selected around and the center of city as shown in Fig. 1. The samplers used for collection contained a 20-cm diameter funnel made of high-density polyethylene, which was set at 1.2 m above the roof. The funnel was connected with a 20 L high density polyethylene container. The water volume was measured in situ and pH was measured before filtration. The filtered samples (0.45 μm) were acidified to pH less than 2 using HCl 6N. The samples were stored at 4 °C for later analysis. The samples were analyzed using Potentiometer (ION^3) for heavy elements such as Pb, Cu, Zn, As, Hg and HNO_3, SO_4, Cl, Na, K, Ca and Mg were analyzed by Multimeter. The precision and bias of the analysis for major ions and trace metals were determined from quality control check samples prepared in the laboratory. Five replicate measurements of each element were made.

3. ANN-PSO Model

3.1- Artificial Neural Networks

The ANN is an artificial intelligence technique that has been demonstrated to solve many composite engineering problems successfully. It is an information-processing system in which system information is processed by several interconnected simple elements that are known as nodes or neurons, positioned in the network layers. The best ANN has been identified as the multilayer perceptron (MLP) model, which is composed of three different layers: input, output and hidden layers (Armaghani *et al.*, 2014; Armaghani *et al.*, 2015).

ANNs provide a nonlinear mapping between outputs and inputs by its intrinsic ability (Hornik *et al.*, 1989; Kulluk *et al.*, 2012). The success in obtaining a reliable and robust network depends on the correct data preprocessing, correct architecture selection, and correct network training choice powerfully(García-Pedrajas *et al.*, 2003). Multi-layer perceptron, the most famous type of ANNs, consists of at least three layers: input, intermediate or hidden layers and output. Difficulty level of the problem determines the number of the hidden layers and neurons (Simpson, 1990).

3.2- Particle Swarm Optimization Algorithm

The PSO was firstly suggested by Eberhart and Kennedy (1995) in order to solve problems with continuous search space. The PSO is based on the metaphor of communication and social interaction, such as bird flocking and fish schooling. The PSO uses social rules to search in the design space by controlling the trajectories of a set of independent particles. The position of each particle, x_i, representing a particular solution of the problem, is used to compute the value of the fitness function to be optimized. Each particle may change its position and consequently may explore the solution space, simply varying its associated velocity. In fact, the main the PSO operator is the velocity update, which considers the best position, in terms of fitness value reached by all the particles during their paths, P_g^t, and the best position that the agent itself has reached during its search, P_i^t, resulting in a migration of the entire swarm toward the global optimum (Hassan *et al.*, 2005).

At each iteration, the particle moves around according to its velocity and position; the cost function to be optimized is evaluated for each particle in order to rank the current location. The position of each particle is updated using its velocity vector as shown in Eq. (2) and depicted in Fig. 2.

$$V_i^{t+1} = \omega V_i^t + C_1 r_1^t (P_i^t - X_i^t) + C_2 r_2^t (P_g^t - X_i^t) \quad (1)$$

$$X_i^{t+1} = X_i^t + V_i^{t+1} \quad (2)$$

where, V_i^t is the velocity vector at iteration t, $r_1$and r_2 represents random numbers in the range [0,1]; P_g^t denotes the best ever particle position of particle i, and P_i^t corresponds to the global best position in the swarm up to iteration t (Shi and Eberhart, 1998). The remaining terms are problem-dependent parameters; for example, C_1 and C_2 represent "trust" parameters indicating how much confidence the current particle has in itself (C_1: cognitive parameter) and how much confidence it has in the swarm (C_2: social parameter), and ω is the inertia weight (Ali Ahmadi, 2012).

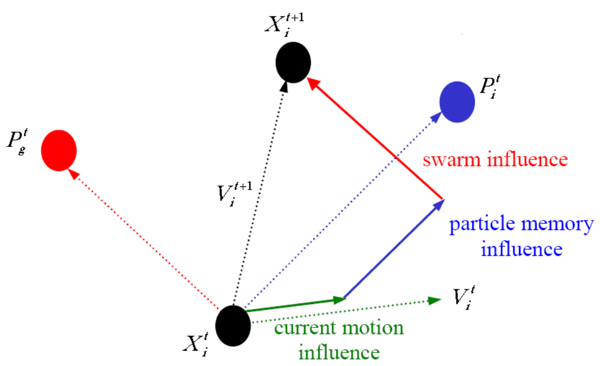

Figure 2) Depiction of the velocity and position updates in PSO

3.3- Implementation ANN-PSO Model

The main objective in ANN training is to adjust a set of weights and biases that minimized an objective function. Typically, root mean squared error (RMSE) is used as the objective function in ANNs. The PSO and ANNs employ different approaches to minimize an objective function. Usually, there is more probability for convergence at a local minimum by ANNs, whereas, PSO is capable to find a global minimum and continues searching around it. Therefore, ANN-PSO model has the search properties of both PSO and ANN; PSO looks for all the minima in the search space and ANN used them to find the best results.

With the purpose of using PSO to train an ANN, a proper representation function should be determined. Since the main target of ANNs is to obtain the minimum error between actual and predicted values, RMSE is defined as representation function. In this case, each particle represents a candidate solution to minimize RMSE. Each component of a particles position vector represents one ANN weight or bias. Lastly, the optimum weights and biases are presented to determine the minimum RMSE. Figure 3 depicts the flowchart of ANN-PSO model.

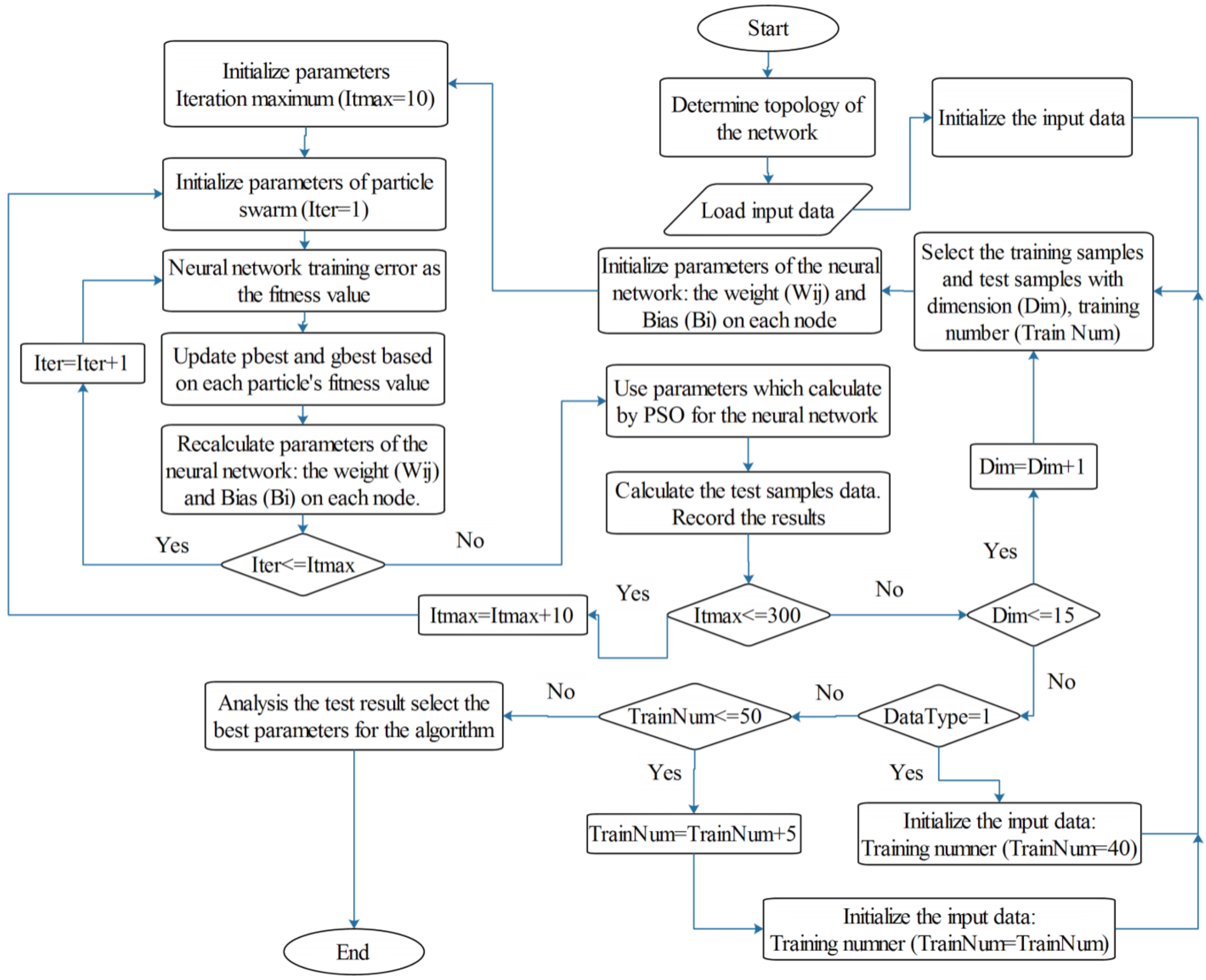

Figure 3) The flowchart of ANN-PSO model.

4- Estimation of Heavy Metals Using ANN-PSO Model

To simulate heavy metals in rainwater using ANN-PSO model, all relevant parameters should be determined, due to the fact that ANNs work based on given data and do not have previous knowledge about the subject of prediction. Following sections describe the input and output parameters and simulation of heavy metals in rainwater using ANN-PSO model.

4.1- Input and Output Data

According to the correlation matrix SO_4, Na, Mg and Cl that have most dependent on heavy metals (Pb, Cu, Zn, As and Hg) concentrations were selected as inputs of the network (Table 1) .The outputs of network were heavy metals concentrations including Cu, Fe, Mn and Zn. In ANN-PSO modeling, any type of input can be used as long as they have effects on output results.

Table 1) Correlation matrix between heavy metals concentrations and independent variables.

	Pb	Cu	Zn	As	Ni	Hg	Fe	Ca	HCO_3	SO_4	Na	K	Mg	Cl
Pb	1.00													
Cu	-0.17	1.00												
Zn	-0.25	0.02	1.00											
As	-0.16	0.07	0.52	1.00										
Ni	0.39	0.03	-0.30	0.03	1.00									
Hg	0.16	-0.15	-0.01	-0.27	-0.14	1.00								
Fe	0.48	-0.10	-0.27	-0.13	-0.08	0.03	1.00							
Ca	0.22	-0.18	0.16	-0.13	0.31	-0.40	-0.01	1.00						
HCO_3	0.23	0.21	0.22	0.05	0.33	-0.44	0.05	0.62	1.00					
SO_4	-0.72	0.74	0.72	0.76	-0.09	-0.55	-0.27	0.10	0.40	1.00				
Na	-0.60	0.63	0.67	0.65	-0.18	0.65	0.04	-0.39	0.27	0.71	1.00			
K	0.06	0.25	0.33	0.00	-0.38	-0.42	0.08	0.20	0.23	0.20	0.15	1.00		
Mg	-0.65	-0.62	0.68	0.65	-0.26	-0.51	-0.17	0.24	-0.06	0.36	-0.10	0.14	1.00	
Cl	0.65	-0.61	0.65	-0.53	-0.07	-0.57	0.46	0.25	0.48	-0.08	0.06	0.33	0.05	1.00

To train and verify the accuracy and ability of the ANN-PSO model, a total of 50 data samples records in rainwater from Arak city, Iran were used in this research. All data were randomly divided into two subsets: 80% of the total data (40 cases) was allotted to training data of ANN-PSO model construction and 20% of the total data (10 cases) was allocated for test data used to assess the reliability of the developed ANN-PSO model. In this model, four input parameters including SO_4, Na, Mg and Cl (major ions) and output including Pb, Cu, Zn, As, Hg (heavy metals) were used to estimation of heavy metals in rainwater from Arak city, Iran. A few samples of the training data sets are shown in Table 2. Also, descriptive statistics of the data sets used for modeling are shown in Table 3.

Table 2) A few samples of the training data sets, ANN-PSO model.

No.	Input				Output				
	SO_4	Na	Mg	Cl	Pb	Cu	Zn	As	Hg
1	19.5	2.75	5.21	3.0	0.013	0.220	0.132	0.162	0.006
2	19.6	2.73	5.22	2.9	0.014	0.210	0.14	0.150	0.007
3	19.7	2.74	5.21	2.9	0.013	0.220	0.135	0.150	0.0065
4	19.4	2.73	5.22	2.9	0.014	0.230	0.140	0.160	0.007
5	20.1	2.80	5.19	3.0	0.010	0.210	0.134	0.166	0.007
6	108	14.2	42	3.9	0.021	0.001	0.610	0.750	0.007
7	105	13.9	43	3.9	0.030	0.002	0.590	0.740	0.007
8	100	14.2	42	3.8	0.022	0.002	0.650	0.780	0.006
9	109	14	44	4.0	0.020	0.001	0.623	0.762	0.008
10	36	3.02	0.22	3.9	0.250	0.031	0.072	0.440	0.052

4.2- Pre-Processing of Data

In data-driven system modeling methods, some pre-processing steps are usually implemented prior to any calculations, to eliminate any outliers, missing values or bad data. This step confirms that the raw data retrieved from database is perfectly proper for modeling. In order to softening the training procedure and improving the accuracy of prediction, all data samples are normalized to adapt to the interval [0, 1] according to the following linear mapping function:

$$x_M = \frac{x - x_{\min}}{x_{\max} - x_{\min}} \quad (3)$$

Where x is the original value from the dataset, x_M is the mapped value, and x_{min} (x_{max}) denotes the minimum (maximum) raw input values, respectively. It is to be noted that model outputs will be remapped to their corresponding real values by the inverse mapping function ahead of calculating any performance criterion.

Table 3) Descriptive statistics of the data sets.

Parameter	Maximum	Minimum	Mean
Pb	0.800	0.010	0.182
Cu	0.230	0.001	0.054
Zn	0.650	0.069	0.181
As	0.850	0.032	0.263
Hg	3.400	0.001	0.297
SO_4	155	3.00	37.13
Na	100	1.08	10.077
Mg	44	0.20	9.68
Cl	14	2	4.4

4.3. Tuning Parameters for the PSO

To develop an accurate ANN model, the training, and validation processes are the important steps. In the training process, a set of input-output patterns is repeated to the ANN. From that, weights of all the interconnections between neurons are adjusted until the specified input yields the desired output. Through these activities, the ANN learns the correct input-output response behavior. The model training stage includes choosing a criterion of fit (Root mean squared error) and an iterative search algorithm to find the network parameters that minimizes the criterion. PSO is used to formalize a systematic approach to training ANN, and to insure creation of a valid model (Paoli *et al*., 2009; Rana *et al*., 2010; Wang and Wang, 2012). They are used to perform global search algorithms to update the weights and biases of ANN: Firstly, learning parameters C_1 and C_2 in PSO should be assigned in advance, and then the objective function value is calculated for each particle. Secondly, the current search point of each particle is changed using Equation 1 and Equation 2. If maximum number of generations is reached or no better parameter vector is found for a significantly long time, then stop. Lastly, all particles congregate to a position on which the coordinate represents the best solution they found in the form of minimal RMSE between patterns and outputs of ANN.

Furthermore, the selection of control PSO parameters plays an important role in the optimization. A single PSO parameter choice has a tremendous effect on the rate of convergence. For this paper, the optimal PSO parameters are determined by trial and error experimentations. The control parameters used for running the PSO shown in Table 4.

Table 4) The control parameters used for running the PSO.

Parameter	Value
Number of population (swarm size)	100
Number of generations	1000
Personal learning coefficient	1.3479
Global learning coefficient	1.3479
Inertia weights	0.64
Fitness	Root mean squared error

4.4. Network Architecture

Architecture of the ANN model includes type of network, number of input and output neurons, transfer function, number of hidden layers as well as number of hidden neurons. Generally, the input neurons and output neurons are problem specific. In this paper, multi-input multi-output structure had been utilized. The architecture of the network is given in Table 5.

Also, in this study, tansig was used as transfer function between input and hidden layer, as well as was used as transfer function between hidden and output layer, shown by the following equation:

$$\text{tansig} = \frac{2}{(1+\exp(-2x))} - 1 \qquad (4)$$

To evaluate the performances of the ANN-PSO model, RMSE and squared correlation coefficient (R^2) were chosen to be the measure of accuracy. Let y_k be the actual value and $\hat{y}_k$ be the predicted value of the k^{th} observation and n be the number of samples. The higher the R^2, the better is the model performance. For instance, a R^2 of 100% means that the measured output has been predicted exactly (perfect model). R^2=0 means that the model performs as poorly as a predictor using simply the mean value of the data.

Table 5) The architecture of the network

Parameter	Value
No. of input neurons	4
No. of output neurons	5
No. of hidden layers	2
No. of neurons in first hidden layer	20
No. of neurons in second hidden layer	24
No. of training data sets	40
No. of testing data sets	10

Also, the lower RMSE indicates the better performance of the model. RMSE and R^2could be defined, respectively, as follows:

$$RMSE = \sqrt{\frac{1}{n}\sum_{k=1}^{n}(y_k - \hat{y}_k)^2} \qquad (5)$$

$$R^2 = \frac{(\sum_{k=1}^{n} y_k \hat{y}_k - n\mu_y \mu_{\hat{y}})^2}{(\sum_{k=1}^{n} \hat{y}_k^2 - n\mu_y{}^2)^2 (\sum_{k=1}^{n} \hat{y}_k^2 - n\mu_{\hat{y}}^2)^2} \qquad (6)$$

Where μ_y ($\mu_{\hat{y}}$) denotes the mean value of the μ_k ($\mu_{\hat{k}}$), $k = 1,...,n,$ respectively.

5- Results and Discussion

5.1- Heavy Elements Concentrations

Metal concentration ranges are presented in Table3. The most abundant heavy metal in rain was Fe (180 µg/kg) followed by Ni (9.39 µg/kg), Hg (0.43 µg/kg), As (0.26 µg/kg), Pb (18.90 µg/kg), Zn (18µg/kg) and Cu (9.11 µg/kg). Such a large amount of all above metals in rainwater has been found in many polluted sites worldwide (Chudaeva *et al*., 2008; Farahmandkia *et al*., 2011; Koulousaris *et al*., 2009; Melaku *et al*., 2008; Özsoy and Örnektekin, 2009; Viklander, 1999). Information for Hg and As is limited. The metal concentrations in rainwater, cited from literature, were compared with our data (Table 6). The concentration of Ni in Arak was comparable to the values cited in Turkey (Özsoy and Örnektekin, 2009) and Cu was also in agreement with Paris district (Garnaud *et al*., 1999). However, our data for Zn and Pb were near the Dutch delta area (Nguyen *et al*., 1990) whereas those for Fe were near the minimum. Among the rare metals, As was almost lower than in concentration to the cited values by (Andreae, 1980), but Hg was considerably higher than those in the Central Coast of California (Flegal *et al*., 2011).

Table 6) Concentration of heavy metals in rain water (µg/kg) in different studies.

Reference Site	*	Ni	Cu	Pb	Zn	Fe	As	Hg
Nguyen *et al*,. 1990	IA	-	6.2-90.4	31.6-284	32-1318	-	-	-
Nguyen *et al*., 1990	UA	-	3.71-27.8	14.3-47	16.3-26.4	-	-	-
Garnaud *et al*., 1999	UA	-	7.2	10.5	29.8	-	-	-
Viklander *et al*., 1999	UA	-	255	237	646	-	-	-
Melaku *et al*., 2008	UA	-	-	2.9-137	-	-	-	-
Chudaeva *et al*., 2008	RA	-	1.3-31.6	0.17-0.69	21.6-113	-	-	-
Koulousarais *et al*., 2009	RA	-	2.9	3.3	39 1.2	-	-	-
Ozsoy and Ornektekin, 2009	UA	7.23	3.94	11.4	50.2	743	-	-
Andreae 1980	UA	-	-	-	-	-	0.59	-
Flegal *et al*., 2011	UA	-	-	-	-	-	-	0.002-0.018
Farahmandkia *et al*., 2011	UA	-	-	5.8-22.2	29.26-70	-	-	-
This study	UA	9.39	9.11	18.9	18	180	0.26	0.05

5.2- Enrichment Factor

EF_{crust} is source estimators of heavy metal and have been used to estimate anthropogenic or crust origins in rainwater (Chabas and Lefevre, 2000). Fe is selected as a reference element for calculation of EF_{crust} Eq. 7.:

$EF_{crust}X = [(X/Fe)_{rain}]/(X/Fe)_{crust}$ (7)

The $(X/Fe)_{crust}$ is taken from (Taylor and McLennan, 1985). EF_{crust} fall in a range of 1–10 which suggests crust sources, 10– 500, moderate enrichment, and >500, extreme enrichment, respectively (Poissant *et al*., 1994). A severe contamination caused by human activities can be indicated by extreme EF enrichment. Using the UCC (Taylor and McLennan 1985) concentrations of each trace metal in Arak, the EF_{crust} factors were calculated using the Fe concentration determined in the rainwater samples. Figure 4 shows the box-whisker graph of the EF_{crust} of the heavy elements. The high values of EF_{crust} found for all of the metals (except Hg) show that these metals in rainwater are non-crustal and indicated anthropogenic sources. However, these values may be different due to the chemical composition of local industrial activity. Fig. 4 shows the EF obtained, which were calculated from the upper continental crust (UCC) averages of metal concentrations (Pb=20; Cu=25; Zn=71; As=1.5; Ni=20; Hg=0.05 and Fe=35000mg/kg) (Taylor and McLennan, 1985). EF_{crust} for Pb, Cu, Zn, As and Ni were between 10 and 500, which was regarded as moderately enriched. The remaining metal, namely Hg had EF_{crust} lower than 10, and were classified as low enriched.

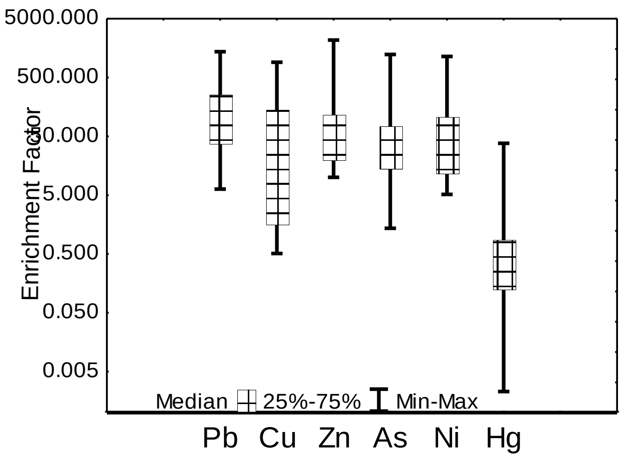

Figure 4) The Box-Whisker graph corresponding to EF_{crust} values calculated for heavy metals.

Therefore, Hg enrichment might have occurred mainly by leaching of Hg from crustal materials (soil dust) during atmospheric washout processes, rather than by contamination. Other metals in rainwater, is, Pb, Cu, Zn, As and Ni (EF_{crust}: 10–500) are likely to be of anthropogenic origin. Zinc is known to be a marker element for burning fossil fuels and smelting non-ferrous metals and Zn released from such processes can be easily dissolved in rainwater (Halstead *et al*., 2000). Although the EF_{crust} in Arak was comparable to values from Canada (Poissant *et al*., 1994). Lead was the most highly enriched metal, and there is no doubt that this resulted from anthropogenic emissions such as burning of fossil fuels (including vehicle exhausts). Copper, Ni and As emanate from smelters and from oil-fired furnaces and ferroalloys smelters (Szefer and Szefer, 1986) and Hg has natural source (EF_{crust}< 0.05).

5.3. Estimation of Heavy Metals

A comparison between predicted values of heavy metals in the rainwater by the ANN-PSO model and measured values for 50 data sets at training and testing phases is shown in Figs. 5 and 6. As shown in Figs. 5 and 6, the results of the ANN-PSO model in comparison with actual data show a good precision of the ANN-PSO model (see Table 7).

Table 7) Performance of the model for estimation of heavy metals in the rainwater.

	Description	R2	RMSE
Pb	Training datasets	0.77	0.125
	Testing datasets	0.72	0.119
Cu	Training datasets	0.88	0.027
	Testing datasets	0.91	0.032
Zn	Training datasets	0.93	0.047
	Testing datasets	0.95	0.044
As	Training datasets	0.75	0.143
	Testing datasets	0.83	0.157
Hg	Training datasets	0.87	0.371
	Testing datasets	0.66	0.432

The performance indices obtained in Table 5 indicate the high performance of the ANN-PSO model that can be used successfully for the estimation of heavy metals in the rainwater.

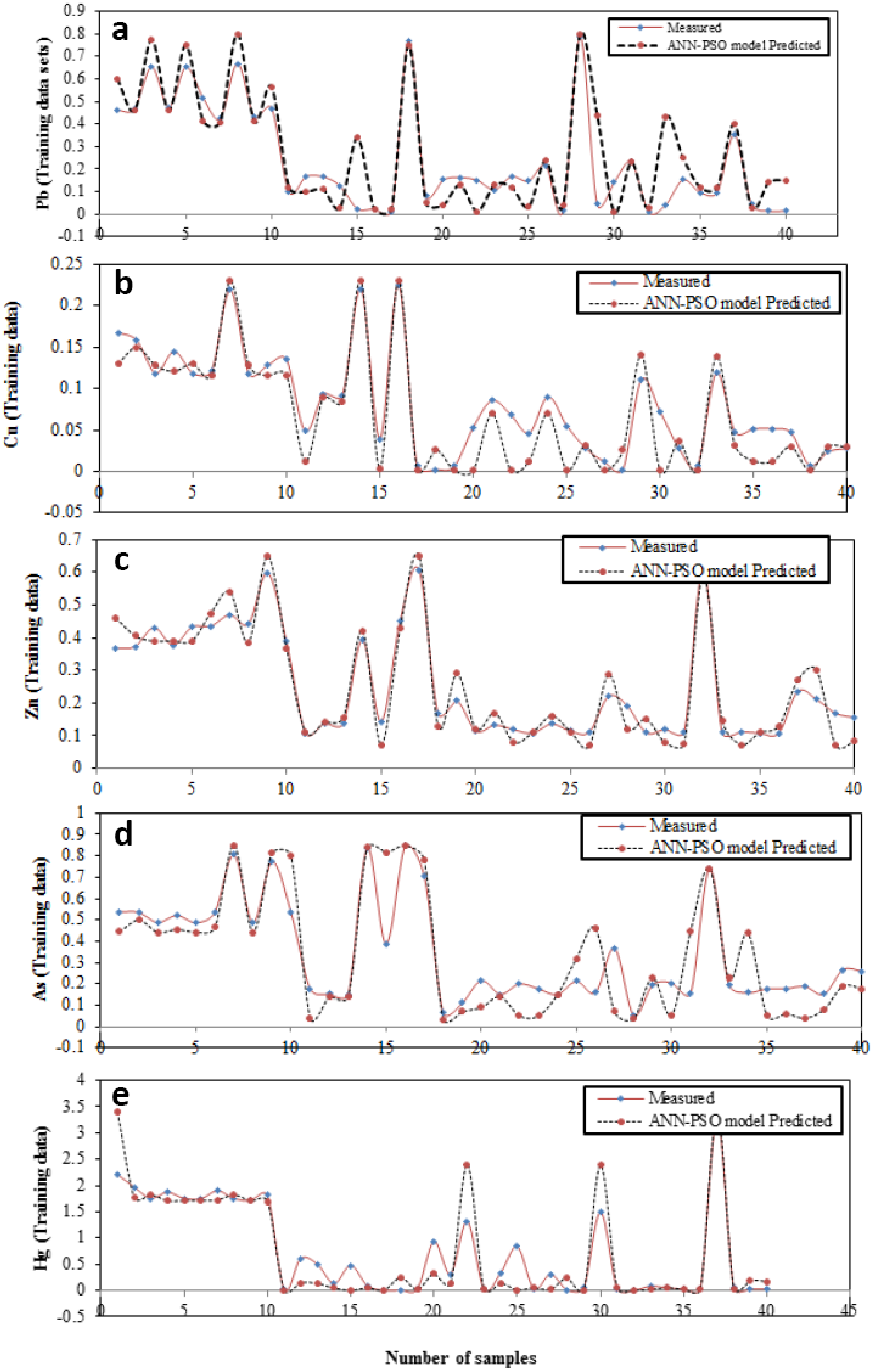

Figure 5) Comparison between measured and predicted heavy metals in the rainwater for training data sets, a) Pb, b)Cu, c) Zn, d) As, f) Hg.

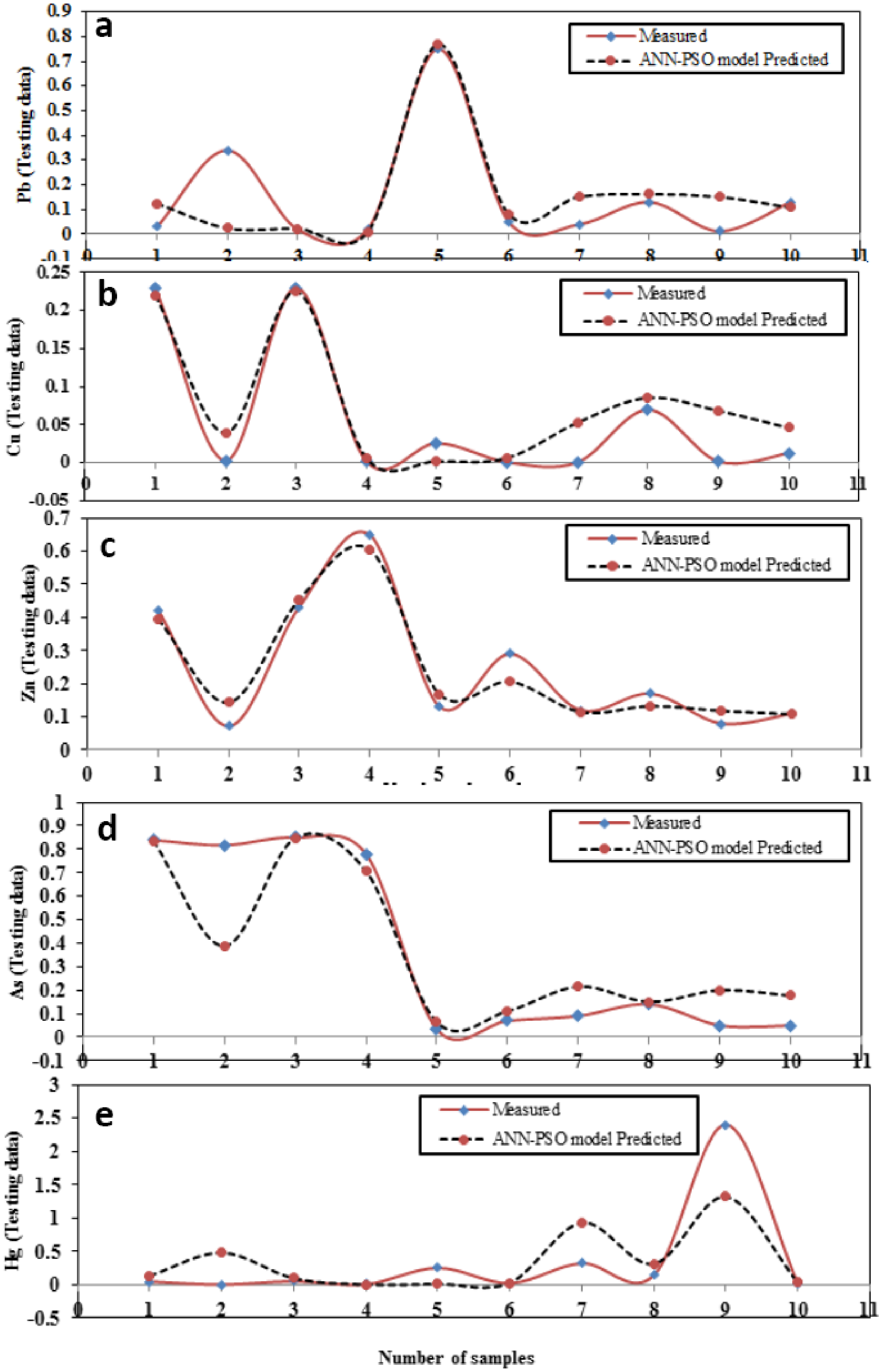

Figure 6) Comparison between measured and predicted heavy metals in the rainwater for testing data sets, a) Pb, b) Cu, c) Zn, d) As, f) Hg.

In order to increase the accuracy and applicability of ANN for estimation of heavy metals in rainwater, PSO algorithm was used to weighting ANN. Several ANN-PSO models were trained and tested using obtained data from Arak city, to determine the optimum network. Performances of the selected ANN-PSO model using training and testing datasets are shown in Figs. 5 to 6 and Table 7.

The predicted heavy metals fit the measured heavy metals almost perfectly for training datasets. Nevertheless, the predicted heavy metals denote fit perfectly to the measured heavy metals for testing datasets. In general, it can be said that the proposed ANN-PSO model is able to predict heavy metals with high degree of accuracy.

6- Conclusion

High concentrations of Pb, Cu, Zn, As and Hg were found in rainwater of Arak City. The high enrichment factors ($EF_{crustal}$) suggested that heavy metals were emitted mainly by anthropogenic sources. Industrial activity and traffic are the source of heavy metals in the rainwater samples in Arak city. Prediction of the heavy metals in the rainwater is important in developing any appropriate remediation strategy. In this paper, a new approach was developed based on the ANN-PSO model to estimation of heavy metals in rainwater from Arak city. To generate the proposed ANN-PSO model, a dataset consists of 50 samples was used. Four variables including SO_4, Na, Mg and Cl (major ions) were used as input variables and Pb, Cu, Zn, As, Hg (heavy metals) were used as output variables. Consequently, it may conclude that ANN-PSO is a reliable system modeling technique for estimation of heavy metals in rainwater from Arak city, with highly acceptable degree of accuracy and robustness.

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