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Artificial Neural Network for Modeling Nitrate Pollution of Groundwater in Marginal Area of Zayandeh-rood River, Isfahan, Iran

Kaveh Ostad-Ali-Askari*, Mohammad Shayannejad, and Hossein Ghorbanizadeh-Kharazi*****

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Abstract

Excessive use of chemical fertilizers, especially nitrogen fertilizers to increase crop and improper purification, and delivery of municipal and industrial wastewater are proposed as factors that increase the amount of nitrate in groundwater in this area. Thus, investigation of nitrate contamination as one of the most important environmental problems in groundwater is necessary. In the present study, modeling and estimation of nitrate pollution in groundwater of marginal area of Zayandeh-rood River, Isfahan, Iran, was investigated using water quality and artificial neural networks. 100 wells (77 agriculture well, 13 drinking well and 10 gardens well) in the marginal area of Zayandeh-rood River, Isfahan, Iran were selected. MATLAB software and three-layer Perceptron network were used. The back-propagation learning rule and sigmoid activation function were applied for the training process. After frequent experiments, a network with one hidden layer and 19 neurons make the least error in the process of network training, testing and validation. ANN models can be applied for the investigation of water quality parameters.

Keywords: *artificial neural network, contamination, groundwater, nitrates*

1. Introduction

Groundwater reserves are important in natural waters which are exploited by digging deep and semi deep wells, springs and quants. Approximately 97% of the Earth's fresh water is groundwater and only 3% is surface water storage (Hambright, 2006). Relative to most surface water sources, groundwater water quality is generally superior and more consistent. Groundwater in arid regions such as Iran contributed to supply a significant amount of water and agriculture water. Isfahan province, Iran, is located in an arid and semi-arid area and because of drought in recent years, the use of groundwater for irrigation and drinking water is very important (Dorsch, 1984; Acutis, 2000). Pollution of groundwater resources by harmful substances that enter into the natural environment intentionally or non-intentionally by man is important in the future exploitation of groundwater resources. One source of this pollution is related to nitrate. The maximum allowable concentration of nitrate-nitrogen (NO_3-N) is 10 mg/L for drinking water, according to the US Environmental Protection Agency and the World Health Organization, which is approximately equivalent to 45 mg of nitrate (NO_3) per liter. This cut point was determined 50 mg/L nitrate by European Union (EU) (Zhang *et al*., 2013). In Iran, 45 mg/L nitrate is considered as the maximum allowable concentration in drinking water (Sobedji, 2001; Sadek, 2002). Municipal and industrial wastewater discharge in the absorptive wells, and indiscriminate use of chemical fertilizers in agriculture, are the most important factors affecting nitrate pollution. In recent decades, the use of nitrogen fertilizers without considering their effects on soil properties, agricultural products and especially environmental pollution has increased dramatically. When Phosphorus-Nitrogen Compounds enter to lakes and rivers lead to enrich water and consequently uncontrolled growth of aquatic plants. Subsequently, a deficiency of dissolved oxygen in the water leads to aquatic organisms' death (Noh, 2006). Khossravi-Dehkordi *et al.* (2004) investigated the nitrate pollution, distribution and its change in groundwater in a marginal area of Zayandeh-rood River, Isfahan, Iran. The results showed that the average concentration of nitrate nitrogen in water of Baghbadaran, Isfahan, Iran, wells with an average depth of 9 m, Falavarjan area with an average depth of 7.5 m and Varzaneh area, Isfahan, Iran, with an average depth of 6 m was 5.28, 17.63 and 6.35 mg per liter, respectively. Consuming contaminated groundwater is harmful for plants, humans and animals. Thus identification of contaminated water sources and causes of pollution are essential. High concentrations of nitrate in soil and irrigation water cause nitrate accumulation in plants that

*Faculty Member, Dept. of Civil Engineering, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran (Corresponding Author, E-mail: Koa.askari@khuisf.ac.ir)
**Associate Professor, Water Engineering Dept., Isfahan University of Technology, Isfahan, Isfahan Province, Iran (E-mail: shayannejad@cc.iut.ac.ir)
***Assistant Professor, Water Engineering Dept., Shoushtar Branch, Islamic Azad University, Shoushtar, Khuzestan Province, Iran (E-mail: h.ghorbanizadeh@gmail.com)

can be harmful for humans and animals. Organic and inorganic nitrate reduce to nitrite, and after entering to the circulatory system, oxidizes iron in hemoglobin and converts bivalent to trivalent state which change hemoglobin to met-hemoglobin (Park, 2013). In addition, elevated nitrate levels may be associated with a prevalence of lymphatic cancer. Vitamin deficiency and conversion of dietary nitrate to nitrosamine and nitrosamid in the stomach may lead to esophageal cancer in this region (Panagopoulos, 2011). Dresch *et al*. (1984) reported the risk of congenital malformations in children whose mothers consumed water with nitrate concentration more than 5 mg per liter during pregnancy. Simulation and modeling of nitrate were assessed in various studies. Pour Farahabadi *et al*. (2007) used neural networks for simulation of nitrate concentrations in the Karaj aquifer. Nitrate concentrations in the previous season, the saturated layer thickness, the amount of exploitation wells in the target and previous season, changes in water level drop, and geographic coordinates were considered as estimators of the model. Firstly, the simulation model was developed for each season separately and then a single model was developed for all seasons. Results indicated that the estimation of changes in nitrate concentrations in summer had the highest accuracy in the validation step (efficiency index $R^2 = 74.75$) in comparison with other seasons. Autumn, winter and spring had an efficiency index of 63.35, 62.48 and 50.15, respectively. The efficiency index in the validation of the proposed model for all seasons was 61.06, which indicated efficiency of this model was appropriate to simulate nitrate concentration (Babiker, 2004).

Akuotis *et al*. (2000) used the LEACHN model (Leaching Estimation and Chemistry Model) to obtain stochastic model information on the nitrate leaching in different cultural systems. Then the results of the model were used for the evaluation of spatial variations of soil hydraulic parameters. Sobedji *et al*. (2001) studied and simulated nitrogen fate and its transport by LEACHN model under different management conditions (time and rate of nitrogen) on loamy sand and clay loam soils. This model estimates the concentration of nitrate in the soil and absorbed nitrate by the plants with high accuracy. Sadak *et al*. (2002) used the DRAINMOD model to simulate nitrate leaching in a sandy area for 30 years. Comparison between measured data and simulated data showed that nitrate concentrations in soil and nitrate leaching to drains depend on proper management, fertilization, initial conditions and the amount of rainfall and its distribution. This model was able to acceptable simulate.

In another study, a Geographic Information System (GIS) and AVSWAT (ArcView SWAT) mathematical model were used to simulate the amount of nitrate that enters the groundwater due to agricultural activities (Babiker, 2004; Panagopoulos, 2011). Since fertilizers and other chemicals used in agriculture drainage below the root zone, due to irrigation, are considered as an important non-point pollution of groundwater in irrigated lands (Tuppad, 2011). Due to the large agricultural areas in the Isfahan province and overuse of chemical fertilizers, especially nitrogen fertilizers and overuse of groundwater for public use and agriculture in this region, the investigation of nitrate contamination in groundwater in this area is extremely important and necessary. On the other hand, continuous measurement of nitrate is time-consuming and expensive and requires special equipment for measurement. Thus, in this study, the artificial neural network model with only common qualitative parameters such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (CO_3^-), sulfate (SO_4^{2-}), claire (Cl^-), pH, Electrical Conductivity (EC), hardness and Sodium Adsorption Ratio (SAR) was used to predict the amount of nitrate in groundwater.

2. Artificial Neural Network

The general structure of artificial neural networks is according to the biological system of human brain. Artificial neural networks are able to perform functions similar to natural neural systems. In other words, they can exhibit some characteristics similar to the human brain. In situation that there is precise definition of the problem, apply the well-known rules is useful. However, in situations where understanding the phenomenon is difficult, the use of known rules and methods may not be very appropriate. The scientists try to design an artificial intelligence system with the capability of learning, creativity and flexibility (such as biological systems) similar to man and present neural computing techniques. This method does not require the setting of specific rules for problem solving but basically relies on a progressive education system.

Artificial neural networks process the experimental data and transfer them to the network structure. So this network is called the intelligent system and learns the general rules with computations on numerical data or examples. There are some configured parameters in the structure of these systems. Configuration of these parameters is for desired action of system to external stimuli and data that is called training of system. In fact, these systems are able to learn and collect appropriate information to deal with the phenomenon. The learning process of these systems can be done in various ways that organize the main topic in artificial neural networks. Artificial neural network models are constantly developing and improving basic theoretical models and their applications increase along with the promotion of basic theoretical models.

Artificial networks have similar structures despite the diversity. An artificial neural network is usually made three layers including input layer, hidden layer and output layer. The input layer receives information only and acts like an independent variable. Thus, the number of neurons in the input layer is determined based on the nature of the problem and depend on the number of independent variables. The output layer acts as the dependent variable and the number of its neurons depend on the number of dependent variables. However, unlike the input and output layer, the hidden layer does not represent any concept and is only an intermediate result in the process of calculating the value of the output. Fig. 1 shows the outline of an artificial neural network.

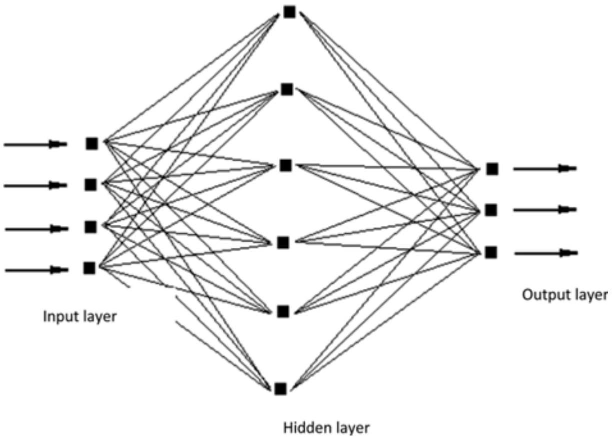

Fig. 1. Overview of an Artificial Neural Network

3. Methodology

3.1 Data Preparation

To achieve the objectives of the study, 100 wells (77 agriculture well, 13 drinking well and 10 gardens well) in the marginal area of Zayandeh-rood River, Isfahan, Iran were selected with north latitude of 32º 25' 28" to 32º 32' 8" and east longitude of 51º 11' 39" to 52º 38' 31". The following items were measured in the spring of 2013, sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{+2}), magnesium (Mg^{+2}), bicarbonate (CO^{3-}), sulfides (SO_4^{-2}), chlorine (Cl^{-}), hardness, Electronic Conductivity (EC), (pH), is the absorption ratio (SAR) and sodium nitrate (NO_3). The area for study began from Baghbadran and continued along 200 km of the river, including Madise, Golden City, Mynadsht, Jafar Abad, Garyakhan, Kelishadi, Dorcheh, Isfahan, Eshkavand, Dashti, Rashenan, Hyderabad, Zeyar, Aichi Hermedan, Sharif Abad, Barsian, Golestane, Izhe, Nikabad triode, Varzaneh and Segzi (these are the names of some areas across to the marginal area of Zayandeh-rood River, Isfahan) (Fig. 2). The mean of the wells depth was between 2.5 and 15 m. The average depth of wells in the Baghbadran area was 9 m, in the Falavarjan area it was 7.5 m and in Varzane it was 6 m.

3.2 Modeling using Artificial Neural Networks

Providing an artificial neural network model requires the design of each of its components. The three-layer perceptron neural network with the back-propagation learning method was used to achieve the desired goals. We try to select the best and most efficient networks with minimum error rate. In order to select the best model, the statistical correlation coefficient (R) and Mean Square Error (MSE) were used. In addition, sensitivity analysis was used for determination of the main factors related to nitrate contamination.

3.3 Data Standardization

In most cases, inputting raw data leads to reduced speed and accuracy of network. Input data should be standardized in order to equalize the value of the data and increase the speed and accuracy of model. This will prevent excessive decrease of the weights. Also, all data are between 0 and 1 by standardizing. This is advantageous because the output of most of the functions have a threshold between zero and one. In the present study, the following equation was used to standardize the data (1):

$$X_{standard} = \frac{X - X_{min}}{X_{man} - X_{min}} \tag{1}$$

In this equation, x, $x_{standard}$, x_{min}, x_{max} indicate an input variable values, the standardized value, the possible minimum and maximum

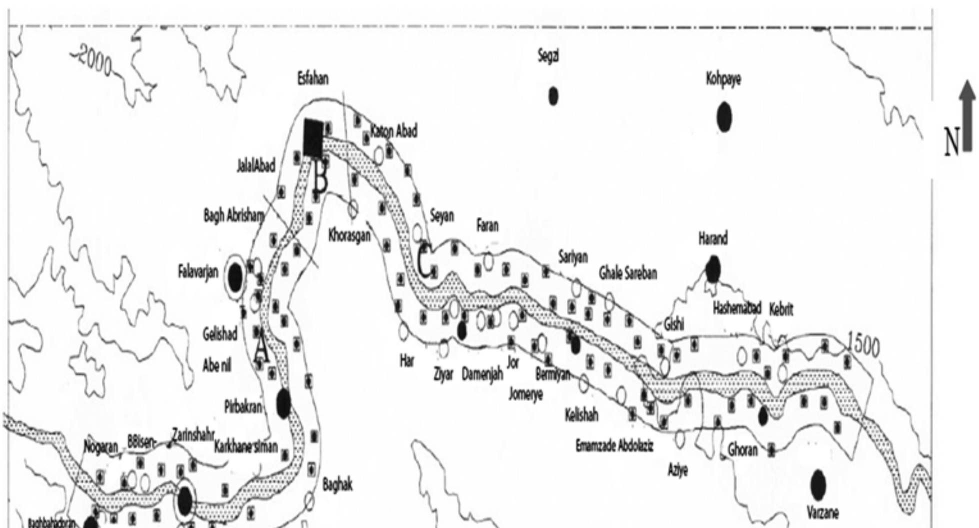

Fig. 2. 100 Selected Wells Across to Marginal Area of Zayandeh-rood River, Isfahan, Province, Iran (▣ represent the position of selected wills)

values, respectively.

3.4 Data Classification

Artificial neural network models need three categories of data including training data, validation and testing for design. Training data is used to find the relationship between inputs and outputs, the validation of learning is used to control and monitor the network properly and the test data is used for evaluation of designed network performance. In this study, we used 50% of the available data for training, 30% of the data for validation and the remaining 20% data for testing of the model.

4. Results

Nitrate concentration in the Baghbaderan wells was 5.28 mg/L, in the Falavarjan area it was 17.63 mg/L, in Varzane it was 6.35 mg/L, in the Jalalabad area (in 1 km of marginal area of Zayandeh-rood River) was 70.8 mg/L and in the Baghmalek area (the first area of the study) it was 0.23 mg/L.

The maximum, minimum and average nitrate nitrogen concentrations and other parameters in Zayandeh-rood River, Isfahan, Iran margin is shown in Table 1.

MATLAB software and network-layer perceptron (MLP) were used for network training. Back-propagation (BP) and sigmoid activation function was used for training. The values for the number of hidden layer neurons 1 to 2n + 1 (n is the number of input neurons) were applied, and in the end the best network structure with the minimum Mean Square Error (MSE) and the highest correlation coefficient (R) was selected. The mean square error is calculated by the following Eq. (2):

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(X_i - Y_i)^2 \quad (2)$$

where x_i is value of the simulated data, y_i is value of the measured data, i is counter and n is the number of measured data. The MSE indicates the amount of estimation. When the predicted values are equal to measured values, the amount of the MSE is zero.

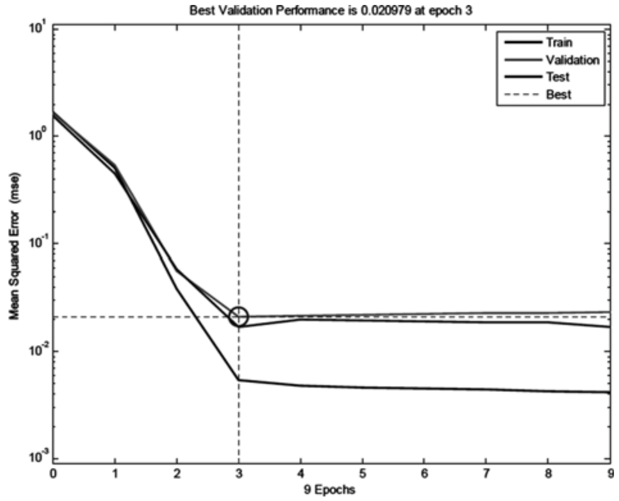

Fig. 3. The Changes Mean Square Error Over the Three Step of Train, Validation And Test

We can provide the least error in the training, assessment and validation of network, after repeating of the network with one hidden layer and 19 neurons. Fig. 3 shows the correlation between observed and calculated values by the artificial neural network. Nine epochs in the training cycle has been presented to the network that the best validate performance was obtained in epoch 3.

As shown in Fig. 3, the best line represents the best amount of MSE for the designed network.

Network training process is correct when the amount of validation and test are close to each other,

Table 1. Maximum, Minimum and Average Nitrate Nitrogen Concentration and Other Parameters in Zayandeh-rood River, Isfahan, Iran Margin

	Amount	Year				
		2010	2011	2012	2013	2014
NO_3^- N (ppm)	Maximum	24.5	37.5	38.1	70.8	46.9
	Minimum	0.23	0.32	0.44	0.98	1.01
	Mean	5.64	6.6	9.6	11	13.9
HCO_3^- (ppm)	Maximum	18	11	8.5	12.8	1
	Minimum	3	1.5	1.5	1.5	0.45
	Mean	6.6	3.71	3.16	3.53	2.93
Cl^- (ppm)	Maximum	99	50	49	40.5	31
	Minimum	0.5	0.82	0.6	0.5	0.5
	Mean	14.6	13. 01	8.19	5.72	4.58
SO_4^{2-} (ppm)	Maximum	110	80	115.6	80	48
	Minimum	0.2	0.4	1.5	0.8	0.65
	Mean	15.92	14.32	21.05	8.12	4.9
K^+ (ppm)	Maximum	84	85.4	25	21	25.5
	Minimum	1	0.73	0.6	1.2	1.1
	Mean	6.78	4.9	4. 57	4.47	3.88

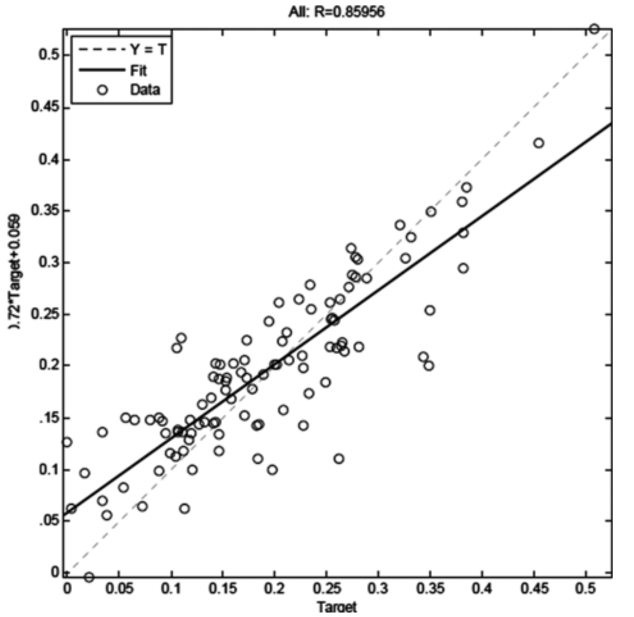

Fig. 4. Comparison of Actual and Calculated Values by Neural Network

As shown in Fig. 3, the best validation is in the third step of training which is equal to 0.020979.

In Fig. 4, calculated values by the network are plotted against the actual values. The correlation coefficient (R) was obtained (0.859) and was acceptable.

4.1 Sensitivity Analysis

The sensitivity analysis process shows the sensitivity rate of the model based on the input variables. Sensitivity analysis evaluates the contribution of each input variable to the neural network. It is a method to assess the behavior of a model and the importance of each input variable on the values of the output variable of the model (Park, 2003). Sensitivity analysis was performed to delete those inputs that did not have a significant effect on model performance. This analysis was used to decide which inputs must be retained and which must be deleted by applying some degree of judgement (Zealand, 1999). There are many ways to carry out the sensitivity analysis. In this study, the Stat-soft method was performed for sensitivity analysis. The sensitivity coefficients of input variables were obtained by dividing the error of the network in the absence of a variable on the network error with all input parameters. Results are shown in Table 2 and Fig. 4. If the sensitivity coefficient of a variable is greater than one, it has a great contribution in the variability of the functional variables. Parameters sensitivity coefficient in Statsoft method were shown in Fig. 5.

Table 2. Sensitivity Coefficient of Parameters in Statsoft Method

Deleted factor	MSE	Deleted factor sensitivity index
Without deleted factor	0.021	1
Cl	0.024	1.129
HCO_3	0.023	1.092
K	0.019	0.899
Na	0.016	0.764
Ca	0.024	1.126
Mg	0.022	1.035
SO_4	0.017	0.834
EC	0.025	1.203
Hardness	0.018	0.869
Sodium absorbance ratio	0.020	0.964
pH	0.025	1.899

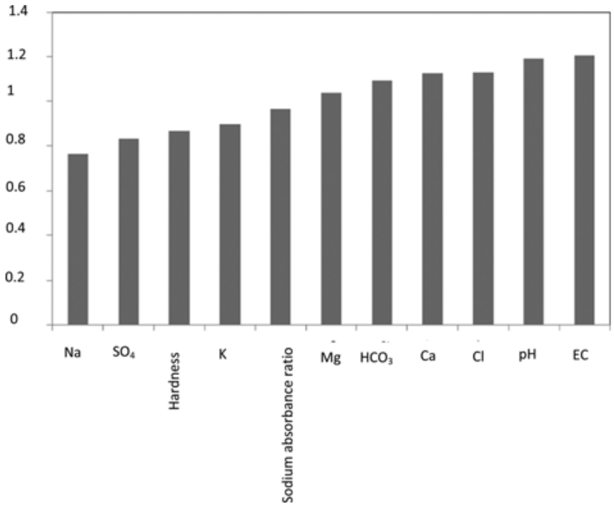

Fig. 5. Parameters Sensitivity Coefficient in Statsoft Method

5. Discussion

In the present study, artificial neural networks were used as a tool for estimating groundwater nitrate based on other parameters of water quality analysis including sodium, potassium, calcium, magnesium, bicarbonate, sulfate, chloride, pH, conductivity, hardness, sodium adsorption ratio. MATLAB software and three layer perceptrons were used for the training network. The rule of Back-Propagation (BP) and sigmoid activation function were used for training processes. After repeated network experiments with one hidden layer and 19 neurons, the lowest error in training process error, assessment and validation was established in this layer. The best validation was obtained in the third step of training and MSE was equal to 0.020979. The value of the correlation coefficient (R) was 0.859 which was in an acceptable range and confirmed that the model is able to well serve the purpose. Sensitivity analysis was performed by Statsoft method that according to the timetable analysis, sensitivity coefficient ranges were between 0.76 and 1.2. This shows that the maximum effect on the model was applied by electronic conductivity and pH parameters and the minimum effect by sodium.

ANNs have been carried out to model groundwater, investigate water quality, forecast precipitation and stream flow. Researchers applied ANNs to predict the concentration of nitrogen in streams from watershed features, for optimization of water pollution control and river pollution planning and for optimization of groundwater remediation (Rogers, 1994; Wen, 1998; Lek, 1999).

The ANN approach has several advantages. It sets input data without any assumptions, and develops a mapping of the input and output variables that can predict desired output. Any smooth, measurable function between input and output can be approximated by multi-layer neural networks through selecting a suitable set of connecting weights and transfer functions. ANN models have been widely applied to water quality problems (Singh, 2009).

The artificial neural networks use in various branches of engineering including water engineering. Some of them have been mentioned below:

Prediction of rainfall in space and time (French, 1992), optimization of groundwater (Rogers, 1994), drainage design in unsteady conditions (Shukla, 1996), land drainage engineering (Yang, 1996, 1997), prediction of water levels in rivers (Thirumalaian, 1998) flow forecasting to reservoirs (Jain, 1999). These researchers used artificial neural networks to achieve their goals. Bruton *et al.* (2000), estimated daily pan evaporation using artificial neural networks. Sample size was 2044 from various cities of the world as Rome from 1992 to 1996. Input data included: rainfall, temperature, relative humidity, solar radiation, wind speed. The pan evaporation that was estimated by artificial neural networks had less error than other methods. The amount of error was 1.11 mm/day.

Odhiambo *et al.* (2001) estimated grass evaporation by artificial neural networks. Input data were solar radiation, relative humidity, wind speed and temperature. Error was 0.48 by artificial neural networks and was 0.56 by FAO Penman-Monteith method.

Kumar *et al.* (2002) estimated grass evaporation by artificial neural networks. Data including minimum and maximum air temperature, minimum and maximum relative humidity, wind speed and solar radiation were calculated. Data were normalized. Finally, the best results were obtained by network with one input layer, one hidden layer and one output layer. The amount of error was 0.6 mm/day by artificial neural networks. While, the amount of error was 0.97 mm/day by Penman-Monteith method.

Nor *et al.* (2015) used a three-layer multilayer perceptron. Their results showed that the model detect the presence of nitrate added in distilled water and was capable of distinguishing the concentration level in the presence of other types of contamination with a RMSE of 0.0132.

Keskin *et al.* (2015) predicted water pollution sources by ANNs in Sivas, Karabük and Bartın areas of Turkey, which have different types of rocks, agricultural activity. They showed ANN could be used for assessment of groundwater pollution sources.

Trajkovic *et al.* (2003), used artificial neural networks for evapotranspiration prediction. In this case, they used the amount of evapotranspiration of 11 and 23 days ago for prediction of evapotranspiration in the coming day. Ratio of predicted evapotranspiration to measured evapotranspiration was 0.994 that these results showed good performance of this method.

6. Conclusions

After repeated network experiments with one hidden layer and 19 neurons, the lowest error in training process error, assessment and validation was established in this layer. The best validation was obtained in the third step of training and MSE was equal to 0.020979. These findings showed ANN models can be applied for the investigation of water quality parameters.

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