Forecasting Study for Nitrate Ion Removal Using Reactive Barriers

CRISTINA MODROGAN[1], ECATERINA DIACONU[2], OANAMARI DANIELA ORBULET[1], ALEXANDRA RALUCA MIRON[1]

[1] University Politehnica from Bucharest, Inorganic Substances and Environmental Protection Department, 1-7 Polizu Str., 011061, Bucharest, Romania

[2] University Politehnica from Bucharest, Machine Building Technology Department, 313 Splaiul Independentei, 060042, Bucharest, Romania

Levels of nitrates in groundwater in some instances are above the safe levels proposed by the EPA and thus pose a threat to human health. Passive groundwater remediation using permeable reactive barriers (PRBs) is a new and innovative technology for the removal of pollutants from groundwater. It acts as barrier against its contaminants, and removes them by adding an adsorption material for contaminants or a reactive material, able to interact with contaminants and diminish their bio-availability. In this paper, it was tried to find the best way to remove nitrate (NO_3^-) ion from water using elemental iron according to water pH and water temperature. The results of the experiments were processed using an Artificial Neural Network (ANN) in order to create a mathematical model capable to predict the optimum quantity of iron needed to remove nitrate ion from the polluted water with nitrates in a given concentration. The present study analyses ANN as a mean to predict the nitrate ion removal from contaminated water. The parallel and distributed structure of artificial neural networks with their capabilities of generalization, fault tolerance, adaptive and associative performance, ability to perform dynamic and real-time functions, and their limited requirement of software, ensure their appropriateness for much practical environmental application.

Keywords: artificial neural networks, nitrate, pollution prevention

Nitrogen is a major constituent of the earth's atmosphere and occurs in many different gaseous forms such as elemental nitrogen, nitrate and ammonia. Natural reactions of atmospheric forms of nitrogen with rainwater result in the formation of nitrate and ammonium ions. While nitrate is a common nitrogenous compound due to natural processes of the nitrogen cycle, artificial sources have greatly increased the nitrate concentration, particularly in groundwater. The largest anthropogenic sources are septic tanks, application of nitrogen-rich fertilizers to grass, and agricultural processes. The main source of nitrate contamination appears to be from agricultural operations, farm runoff and fertilizer usage [1]. There is also some nitrate formed in the atmosphere by oxidation of nitrogen oxides that are emitted from power plants and internal combustion engines. One other man-made source is industrial corrosion inhibitors that have leaked into the ecosystem. Naturally occurring nitrate can result from a combination of nitrogen and oxygen through electrical discharges (lightning). Also, nitrate is formed by Nitrobacteria by oxidation of nitrites. Substantial photogeneration of·OH and NO_2 by nitrate and only at a lesser extent by nitrite was observed, and the steady-state [$\cdot NO_2$] was one-two orders of magnitude higher compared to surface water samples (lake and river water) under similar irradiation conditions [2].

Nitrates in concentrations above 10 ppm expressed as N* (44.3 ppm as nitrate) are considered unsafe. Infants are particularly susceptible to nitrates because their digestive system does not operate in the same manner as adult one. Nitrates are converted by bacteria in the stomach of infants to toxic nitrites.

At levels that would not cause harm to adults, nitrates can cause methemoglobinemia in the infant case known as "blue baby" syndrome. Nitrates present in a water supply can be a symptom of other contaminants in that source of water [3, 4].

Permeable Reactive Barriers (PRB) is a subsurface construction situated across the flow paths of contaminant punctures. The contaminants are removed from the groundwater flow by geochemical processes taking place in the reactive material of the barrier filling. The main materials used as reactive components in PRBs are elemental iron, activated carbon, zeolites, iron oxides/oxyhydrates, phosphates, clay minerals. The choice of reactive materials and retention mechanisms are dependent on the type of contamination [5].

The permeable reactive barrier technology appears to be a promising approach to effective groundwater remediation even in complex cases where traditional 'pump-and-treat' methods and/or microbiological techniques have proved to be unsuccessful (e.g., heavy metals being slowly leached from a contamination source, PAH with low bio-availability, contamination of heterogeneous sediments). Although the use of PRBs is limited to certain site conditions; in places where the application is feasible they appear to be a good choice with good acceptance by end-users, especially in urban environment and built-up areas. One can add the little visibility and the lack of additional impact on the landscape by equipment such as containers, water tanks, pumps, or by noise from running machines etc. The best known reactive material is granular zero-valent iron (elemental iron, Fe^0). Some stoechiometric equations for the overall process are presented in [6]:

$$8Fe^{2+} + NO_3^- + 13H_2O \rightarrow 8FeOOH + NH_4^+ + 14H^+$$

$$8Fe^{2+} + 2NO_3^- + 11H_2O \rightarrow 8FeOOH + N_2O + 14H^+$$

$$10Fe^{2+} + 2NO_3^- + 14H_2O \rightarrow 10FeOOH + N_2 + 18H^+$$

$$2Fe^{2+} + NO_3^- + 3H_2O \rightarrow 2FeOOH + NO_2^- + 4H^+$$

$$12Fe^{2+} + NO_3^- + 13H_2O \rightarrow 4Fe_3O_4 + NH_4^+ + 22H^+$$

* email: c_modrogan@yahoo.com; Tel. 0214023824

$$12Fe^{2+} + 2NO_3^- + 11H_2O \rightarrow 4Fe_3O_4 + N_2O + 22H^+$$

$$15Fe^{2+} + NO_3^- + 13H_2O \rightarrow 4Fe_3O_4 + N_2 + 28H^+$$

$$12Fe^{2+} + 2NO_3^- + 13H_2O \rightarrow 4Fe_3O_4 + 2NH_4^+ + 22H^+$$

An extensive review on the iron technique has been given recently [7]. The widespread use of elemental iron is attributed to its ability to act as a strong reducing agent in groundwater causing abiotic reductive degradation of organic substances such as chlorinated hydrocarbons and some aromatics and reductive immobilization of some inorganic compounds such as chromium, nickel, lead, uranium, sulphate, nitrate, phosphate, arsenic, molybdenum, and others. Another reductive mechanism, particularly important for the treatment of acidic mine waters, is bacterial sulphate reduction by organic materials such as compost, wood chips, sawdust, etc. (8-10).

Today's computer architectures, operating systems, and programming have very little in common with information processing performed by the brain. Currently we are experiencing a reevaluation of the brain abilities, and models of information processing in the brain have been translated into algorithms and made widely available. The basic building-block of these brain models (neural networks) is an information processing unit that is a model of a neuron. An artificial neuron of this kind performs only rather simple mathematical operations; its effectiveness is derived from the way in which large numbers of neurons may be connected to form a network. Just as the various neural models replicate different abilities of the brain, they can be used to solve different types of problem: the classification of objects, the modelling of functional relationships, the storage and retrieval of information, and the representation of large amounts of data. This potential suggests many possibilities for the processing of chemical data, and already applications cover a wide area: spectroscopic analysis, prediction of reactions, chemical process control, and the analysis of electrostatic potentials.

An artificial neural network is a system based on the operation of biological neural networks, in other words, is an emulation of biological neural system. It consists of a collection of processing elements that are highly interconnected and transform a set of inputs to a set of desired outputs. The result of the transformation is determined by the characteristics of the elements and the weights associated with the interconnections among them. By modifying the connections between the nodes the network is able to adapt to the desired outputs [11, 12]. Artificial neural networks (ANNs) are biologically inspired computer programs designed to simulate the way in which the human brain processes information. ANNs gather their knowledge by detecting the patterns and relationships in data and learn through experience, not from programming. An ANN is formed from hundreds of single units, artificial neurons or processing elements (PE), connected with coefficients, which constitute the neural structure and are organised in layers. The power of neural computations comes from connecting neurons in a network. When a neural network approach to a problem is used, what is usually sought in some kind of a model, which represents the transformation from a set of inputs to a set of outputs. [13]. Artificial neural networks (ANNs) based on the use of principal components and the original absorbance data were proposed for the simultaneous quantitative analysis of amlodipine (AML) and atorvastatin (ATO) in tablets [14].

A neural network consists of three or more layers of neurons with each neuron connected to all other neurons in the adjacent layers. The first layer accepts inputs from the environment, process them and send them to the next layer. The signal is transmitted through the layers until it reaches the output layer. Each neuron accepts inputs from previous layer, adjusts the input with positive and negative weights, sums them and sends the signal further. Using error back propagation algorithm, the network can be adjusted so that each input pattern generates a different pattern of output. This is done by training the network with known examples and adjusting the weights until the desired outputs are generated, assigning particular inputs. Compared with the production system, an ANN can modify its responses to stimulation taking into account the previous experience and the model used for the prevision of chemical compounds near emission points: Artificial Neural Networks (ANN), one of the artificial intelligence branches, used with great success for the approximation of nonlinear function due to its specificity to learn from past experiments, when inputs and outputs are feed to it. Considering these data ANN organizes itself and simulates the real influences between inputs and outputs, in order to determine future unknown outputs starting from known inputs [15-21].

The authors presented an ANN-based forecasting model and as variables of the network have been used the time of reaction, temperature, water *p*H, initial nitrate concentration of polluted water and final nitrate concentration of treated water. The objective is to determine the reduced quantity of nitrate by 1 g of iron. In this way, one can establish the structure of the PRB used to remediate polluted water of a certain nitrate concentration. The ANN is capable to send forecasting information about the final nitrate concentration of treated water knowing the input parameters.

Experimental part

In this paper nitrate ion reduction from water with zero valent iron is presented. In covered Erlennmayer jar were contactated 0.05g iron with 50 mL KNO_3 sintetic solution. The samples where stirred at 300 rot/min for 5, 10, 20, 30, 60 and 90 min using Heidolph Unimax shaker. The experiments were done at 10 and 20°C. At the end of stirring the samples were filtrated using blue ribbon filter paper and brought to a 50 mL flask. From filtrate 10 mL samples were taken and spectrofotometricaly analised. In this study, the samples were analyzed by a spectrophotometric method based on the color reaction between disulphonic phenol acid and nitrate ions in solution which leads to the formation of a yellow nitro aromatic derivative. Initially, calibration curve is achieved. From working standard solution samples of 0.25, 0.5, 1, 5, 10, 25 mL are taken which are brought to volume with distilled water in 100 mL calibrated flasks. From each flask, 10 mL, were taken and passed to evaporation vessels and then evaporated to dryness on water bath.

Over the residue left after evaporation 0.5 mL acid phenildisulphonic is added and left motionless 15 min for cooling. Then 1 mL ammonia is added, until full color development. The solution is brought to volume with distilled water in 25 mL calibrated flasks and photo-metered to the wavelength λ = 410 nm.

For analysis, samples are subjected to the same treatment, and after color development they are sufficiently diluted to fit the scale. Samples are then photo-metered to the wavelength 410 nm, determining the concentration of nitrate. The experimental results are then processed with

Table 1
EXPERIMENTAL DATA

	Time, minute	Temperature, °C	pH	C_i, mg/L	C_f, mg/L
TRN	5	10	2.5	100	64.084
TRN	5	10	8	100	69.035
TRN	5	20	2.5	100	52.1003
VLD	5	20	8	100	45.86
TRN	10	10	2.5	100	53.008
TST	10	10	8	100	66.78
TRN	10	20	2.5	100	50.1023
TST	10	20	8	100	41.5
TRN	20	10	2.5	100	53.1795
TRN	20	10	8	100	66.01
TRN	20	20	2.5	100	49.761
VLD	20	20	8	100	35.44
TRN	30	10	2.5	100	53.1315
TRN	30	10	8	100	56.9
TRN	30	20	2.5	100	28.7514
TRN	30	20	8	100	30.12
TRN	60	10	2.5	100	53.1635
TRN	60	10	8	100	58.46

an Artificial Neural Network to determine the forecasting model.

In order to solve the forecasting model, a software program produced by Neuro Intelligence Company has been used. Alyuda Neuro Intelligence (AN) is ANN-based application software that achieves databases pre processing and analysis, definition of the ANN with the best architecture, testing and optimizing the chosen ANN, application of ANN in solving problems. ANN interface is optimized to solve problems of forecasting, classification and function approximation. In the development of an application, both data and designed neural network pass through a sequence of stages, to achieve a maximum performance, ensuring a network error as small as possible. These stages are: data analysis, data pre processing, neural network design, ANN training, ANN testing and ANN query.

Results and discussions

As input data for prognosis study the following variables were chosen (table 2).

Data analysis is necessary as a prior step to pre processing, in order to find the aberrant values, which rejected in the construction of the neural network. At this stage, the input and output variables must be defined [22].

Data pre - processing represents those data modification before artificial neural network considering numerical values scaling character type data transformation in numerical data, etc., taking into account that ANR works only with numerical values belonging to a limited range. Post processing represents ARN output modification, making easy to be understood and interpreted by the user. For input data column scaling range is [-1, 1]. For target column scaling range depends on activation function. To design an ANN, it is necessary to specify the network architecture (number of neurons in the hidden layer, number of hidden layers) and network properties (activation function, error). Designed manually or automatically, AN creates feed-forward all connected ANN.

In order to design the ANN for our application, several features have been activated: number of output neurons (1), activation function of hidden layer (hyperbolic tangent), error function of output (the sum of least squares), activation function of output (hyperbolic tangent); number of neurons in the hidden layer (8) and number of neurons in input layer (4) (fig. 1).

The network selection is based on certain considerations relating to:

- maximum value of fitting degree between real measured results and network estimated results;
- minimum values of testing, training and validation errors;
- the closest values to 1 for correlation coefficient (CCR) and determination coefficient (R^2).

Network parameters are given by:

- type of activation function of neuron hidden layer – logistic type;
- type of output data error function – sum of square deviation;
- type of output data activation function – logistic function;
- training function – Back Propagation;
- learning rate – 0.9 and momentum – 0.95.

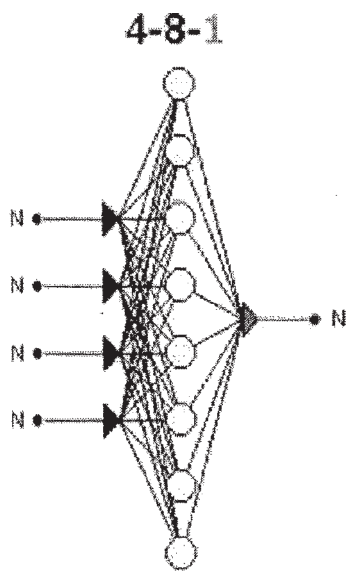

Fig. 1. ANN arhitecture, where N is the neuron

Table2
THE INPUT DATA OF ARTIFICIAL NEURONAL NETWORK DESIGNED FOR PROBLEMS PROGNOSIS

The variable	*Minimum values*	*Maximum values*
Contact time (t)	5 min	90 min
Temperature (T)	10°C	20°C
pH	2.5	8
Initial concentration of nitrate ions in waste water (C_i)	25 mg/L	100 mg/L

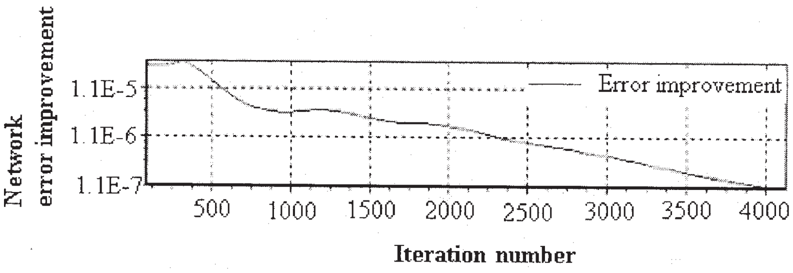

Fig. 2. ANN error during training phase

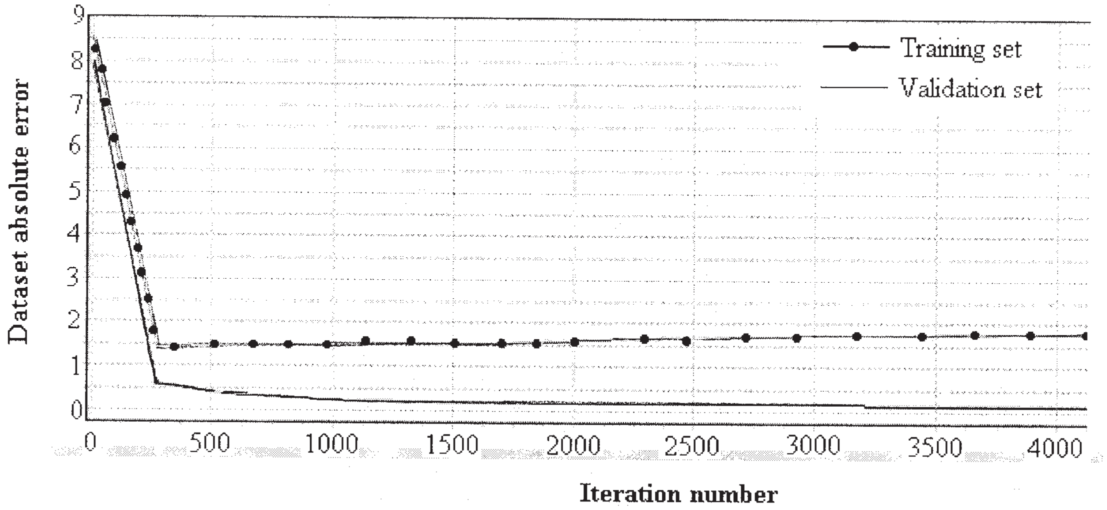

Fig. 3. Error evolution of training data

Training option allows realising the process by training graphs, histograms for error distribution and weights distribution, chart displaying the importance of input and real-time details of the training. A network can be trained several times to improve performance.

Figure 2 shows the network error reduction during the execution of 4100 iterations. Network error represents the difference between the output result and the desired result. It is observed from figure 2 that the network is capable to produce satisfactory results, without considerable errors, after 4100 iterations.

Figure 3 put in evidence the decrease of dataset errors used in training. ANN learning algorithms are based on training dataset error reduction in order to obtain network convergence and a better data generalisation. There are two different curves which describe the evolution in time of training and testing data. Training dataset records smaller errors compared with the validation ones because in the validation stage the network is processing new data that were not used in training stage. The proper network for solving our forecasting problem is the one with a significant error decrease.

AN allows the analysis of trained network performance by using the current data graphs in comparison with the outputs, time dispersion graphs, response graphs, confusion matrix. Figure 4 describes the output data fitting degree (C_f) estimated with the network versus real results experimentally measured.

After neuronal network development for C_f value estimation depending on the same entrance values(t, T, *p*H, C_i) was a final stage, in which was presented a data basis formed only with the 4 entrance data expecting as result value C_f.

Figure 5 compares the results obtained after network running with the real results. The results are satisfactory from estimation accuracy point of view, with further research possibilities in order to reduce the differences observed in figure 5.

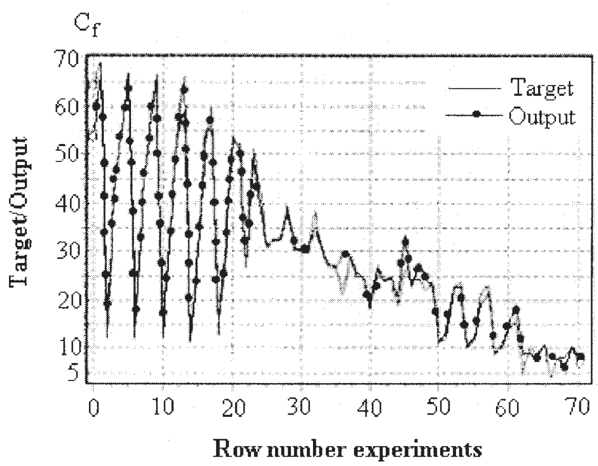

Fig. . 4. The representation of estimated C_f values with ANN versus real values

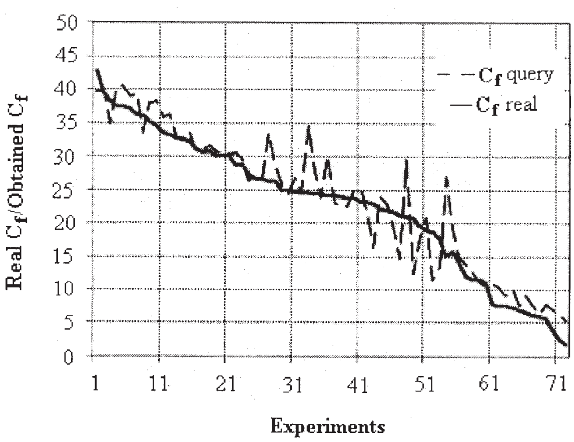

Fig. 5. Results of ANN interrogation phase

Conclusions

In aerobic conditions and at constant *p*H 2.5, adjusted with HCl, nitrate ions are reduced to ammonium and molecular nitrogen rapidly and completely in the presence of zero valent iron. The *p*H effect on nitrate reduction kinetic in acid conditions can by modelled and explained in two ways: (a) H^+ ions are involved directly in reduction reaction of nitrate ions after a first order kinetic and (b) H^+ ion influences adsorption. The best reduction in presence of zero valent iron occured at *p*H 2.5. The experiments realised in order to determine the temperature influence on nitrate reduction with zero valent iron at constant *p*H (2,5) show that at 20°C the nitrate removal efficiency was almost 55% while at 10°C was 45%.

The most interesting phenomenon observed during the experiments was that besides nitrate reduction, a black material was formed in few minutes on the iron grains in acidic conditions at low *p*H (2.5) while hydrogen bubbles were generated continuously.

From experimental data obtained at 20°C results that at *p*H = 8, nitrate ions removal efficiency is lower at *p*H = 2.5. From the analysis of data obtained at 10°C can be concluded that nitrate ion removal efficiency in first 20 min is higher at *p*H = 8 (30%) then at *p*H = 2.5 (20%). After 20 min contact time, nitrate ions removal efficiency rises at *p*H = 2.5, reaching in 90 min 45%, compared with *p*H = 8 when the value was 35%. In the first minutes of contact, nitrate ions are quickly removed, solution concentration decreasing from 100 mg/L to 70 mg/L. In time, nitrate ions concentration decreases from la 70 mg/L to 66 mg/L. The temperature has a low influence on nitrate ion removal; at 20°C after 90 min of contact the ion concentration decreases until 64.3 mg/L compared with 10°C when nitrate ion concentration attains 66.3 mg/L.

An artificial neuronal (ANR) explores simoultaneously many competitive hypothesis using a massivelly parallel network consisting of non-linear computional elements interconnected by links with variable weights. The set of weights contains knowledge generated by ANR. ANR are formed by a big number of simple processing units interacting with each other through inhibitory or excitatory connections.

The representation distributed on a big number of units togheter with interconectivity between processing units, determines an error tolerance. The learning is realised by a rule to adjust the weights of connections as answer to entrance models. Changes in the weights associated to connections allow adaptibillity to new situations.

Neuronal networks are suitable for time series estimation, mainly because their ability of learning only from examples, without the need to add supplementary information which may bring more confusion than a predictive effect. Neuronal networks are capable to generalize and are noise resistant.

On the other hand, it is not possible to determine exactly what a neuronal network has learned to do and is difficult to estimate the possible prediction error. Nevertheless, ANR have been often used to successfully estimate time series being ideal especially when there is no other description of the series.

Based on the above mentioned reasons an ANR was used for the problem of estimating the scarceness of nitrate in water, due to non-linear character of the process.

The network can be further interrogated with values that were not presented to the network before, in order to estimate the output desired variable, saving the time conferred for laboratory experiments.

ANR usage starting from anlaysis stage and finishing with cheking and processing data, can be considered a success for the proposed objectives.

Working with some data and variables that can not be simulated on the basis of classical algorithms provides the opportunities and benefits derived from using artificial neural networks for further research much more laborious.

In order to prevent problems arising from the heterogeneity of nitrate ions neural network model can be easily changed in order to obtain the best results.

The using of artificial neural networks in this work, facilitates the rapid and efficient assessment of data from the study of nitrate removal from water.

It is preferable to have continuous communication between local monitoring agencies in order to have easy and fast access to environmental data which enables and ensures an efficient data processing and developing appropriate environmental decisions.

References

1. ALMEIDA, M.C., BUTLER D, FRIEDLER E**.,** 1999 Urban Water ,1, p. 49
2. VIONE D., RINALDI E., MINERO C., MAURINO V., OLARIU R. I., ARSENE C., Rev. Chim. (Bucharest) , **60**, no. 6 2009, p.551
3.. SHRIMALI, M., SINGH, K.P., 2001, Elsevier, Enviromental Pollution 112, p. 351
4. REDDY, K. J., JIANPING LIN 2000, Water Research 34(3) p. 995
5. ROEHL, K.E.; CZURDA, K., MEGGYES, T., SIMON, F., STEWART, D.I. 2005 Elsevier, New York, p. 1
6. OTTLEY, C.J., DAVISON, W., EDMUNDS, W.M., 1997, Geochimica Cosmochimca Acta 61, p. 1819
7. TRATNYEK, P.G., SCHERER, M.M., JOHNSON, T.L. & MATHESON, L.J. (2003), Marcel Dekker, New York, p. 371
8. BENNER, S.G., BLOWES, D.W., GOULD, W.D., HERBERT JR., R.B. & PTACEK, C.J. (1999), Environ. Sci. Technol., 33, p. 2793
9. BLOWES, D.W., PTACEK, C.J., BENNER, S.G., MCRAE, C.W.T., BENNETT, T.A. & PULS, R.W. (2000): Cont. Hydrol., 45: p. 123
10. WAYBRANT, K.R., PTACEK, C.J. & BLOWES, D.W. (2002, Environ. Sci. Technol., 36: p. 1349.
11. FOX, KEVIN L., HENNING, RHONDA R., REED, JONATHAN H. (1990). In Proceedings of the 13th National Computer Security Conference.
12. HAMMERSTROM, D. (1993). Neural Networks At Work. IEEE Spectrum. p. 26
13. CURTEANU S, ONISCU C, DUMITRESCU A, , Rev. Chim. (Bucharest), **58** ,no 11, 2007, p 1085
14. DINÇ E, KÖKTAS N. Ş., BALEANU D. Rev. Chim. (Bucharest), **60,** no. 7, 009, p 662
15. BARBES L., NEAGU C., MELNIC L., ILIE C., VELICU M**.** Rev. Chim. (Bucharest), **60**, no. 3, 2009, p. 301
16. DEBAR, H., BECKE, M., & SIBONI, D. (1992). In Proceedings of the IEEE Computer Society Symposium on Research in Security and Privacy
17. DEBAR, H. & DORIZZI, B. (1992). In Proceedings of the International Joint Conference on Neural Networks. p. (II) 478
18. FRANK, JEREMY. (1994). In Proceedings of the 17th National Computer Security Conference.
19. RYAN, J., LIN, M., MIIKKULAINEN, R. (1997). AI Approaches to Fraud Detection and Risk Management: Papers from the 1997 AAAI Workshop (Providence, Rhode Island), p. 72
20. TAN, K. (1995), In Proceedings of the IEEE International Conference on Neural Networks, **1**, p. 476
21.TODEREAN, G., COSTEIU, M., GIURGIU, M. Editura Micro-informatica, Cluj-Napoca, 1999
22. BODEA, C., IVAN, I., CREŢU, A., Editura Inforec, Bucureşti, 1997.
23. ENĂCHESCU, C., Editura Casa Cărţii de Ştiinţă, Cluj-Napoca, 1998

Manuscript received: 6.01.2010