

Kinetic Research Regarding the Nutrient Retention in the Soil Using the Neural Networks

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The sorption is one of the most important chemical processes in the soils that affect the transport of nutritive elements in soil. The quantification of the nutrient concentration in the soil and in the soil solution is an important stage in modelling the transport. The soil contamination causes a deep concern as regards the environment protection due to its hazardous effects on the human health. Both the organic and the inorganic constituents are important in the soil. In this paper, a forecasting study was prepared regarding the phosphate and nitrate retention rate on a chernozem type of soil by using the artificial neural networks. The artificial neural networks (ANN) were used for forecasting the pollutants at various moments, with very good results. The research study results show that the ANN performance surpasses, in general, the results of the traditional statistic methods, for instance, the multiple regression.

Keywords: phosphorus, nitrates, soil, sorption, artificial neural network

During the past decades, agriculture became, paradoxically, one of the water pollution sources, as a result of intensive soil fertilisation practices, ignoring their negative effects. In Romania, 62% of the surface area is occupied by plots of land used in agriculture, which points out the importance of this process [1]. Today, there is the risk of destruction, on the long term, of ecological balances related to the soil fertilisation [2]. Also, the water pollution with nitrates and phosphates has a contributory effect, an important impact of agriculture on the environment.

In order to limit the effects owed to nitrate and phosphate excess, best agriculture practices codes were proposed. By means of various human activities, increased quantities of nutrients can be introduced, which leads to the acceleration of the eutrophication and to the deterioration of the water quality. The nutrients, which determine the eutrophication, are usually soluble nitrates and phosphates. In this paper, a study was conducted regarding the retention of the nitrate and phosphate ions on the soil at different depth profiles (0-50 cm). In most cases, 50-75% of the phosphorus is in inorganic form (the rest being in organic form) [3]. The phosphate anions can be adsorbed on the soil particle surface by means of adsorption and chemo sorption processes. The phosphorus is removed from the soil by adsorption in the plants, by levigation or by other processes related to the soil dynamics. These phenomena entail the reduction of the phosphorus content under mobile form and the decrease of the soil production capacity [4].

In soil, the nitrogen is found under several forms: nitrate, nitrite, ammonium and molecular nitrogen. The nitrate anion is the main mineral compound of the nitrogen in the soil, being in the same time, the main form accessible for plant [5, 6].

Nitrate ions are very easily levigated in the ground waters, polluting them. The presence of nitrates and their abundance in different sources of vegetal and animal food was highlighted and a relationship was established between the abundance of nitrates in the environment and the morbidity and mortality due to cancer [2]. An experimental study was performed, putting in evidence the capacity of a certain type of soil (clayey levigated

chernozem) to retain these nutrients. In order to establish the degree of nutrient retention in the soil, a large number of analyses must be performed. If the main factors influencing the retention of these nutrients in the soil are known (the soil profile, the concentration of nutrients, the contact time between the applied fertiliser and the soil), the number of experiments can be reduced by applying a simulation by means of artificial neural networks.

An artificial neural network (ANN) is a system based on the simulation of the biological neural networks. It consists in a number of interconnected processing elements, which turn a set of inputs into a set of wanted outputs. The result of the transformation is determined by the features of the elements and by the weights associated to the interconnections between them [7-9, 19].

The artificial neural network is inspired by the operation of the biological neuron. A neural network gathers all the information by detecting the patterns and relations between the data, by using the experience and not the programming activity. A neural network consists of hundreds of simple units, artificial neurons or processing elements connected by coefficients representing the neural structure and being organised, disposed on layers [10].

The accuracy of the neural calculations derives from the connection of the neurons in a network. When a problem is required to be solved by means of such a network, an able pattern needs to be obtained in order to perform the transformation of a set of inputs into a set of outputs. The artificial neural network is made of three or several layers of neurons, each neuron being connected to all the other neurons on the adjacent layers. The first layer accepts inputs from the environment, processing and passing them to the next level. The signal is broadcasted through the layers until it reaches the exit layer [11-18].

In the present paper, the authors present an ANN-based forecasting model. The elements used as network variables were time, initial nutrient concentration and the soil profile. The purpose is to determine the speed of nutrient retention in the soil. The ANN is capable of transmitting forecasts regarding the final nutrient concentration in the soil when the entry parameters are provided.

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Table 1
SOIL MACRO-ELEMENT CONTENTS

pH	Humus	N _t	P _{AL}	K _{AL}
	%	mg/kg	mg/kg	mg/kg
7.85	2.00	0.121	20	12

where: N_t - total nitrogen; P_{AL} - soluble phosphorus;
K_{AL} - soluble potassium

Table 3
SOIL MICROELEMENT CONTENTS

Zn	Cu	Fe	Mn	Pb	Co	Ni	Cr	Cd
mg/kg								
80.2	27.4	25671	740	21.7	9.7	55.8	13.2	0.01

Table 2
DATA REGARDING THE SOIL TEXTURE

Texture			
Grit, mm			
2.0-0.2	2.0-1.0	1.0-0.5	0.5-1.0
2.6 %	0.3 %	0.5 %	1.8 %
Fine sand, mm			
0.2-0.02	0.2-0.1	0.1-0.05	0.05-0.02
32.5 %	4.1 %	3.2 %	25.2 %
Dust, mm	Clay, mm		Carbonates
0.02-0.002	<0.002	<0.01	-
31 %	33.9 %	49.3 %	0 %

Experimental data

Before experiments, a soil characterization was performed. The clayey levigated chernozems, although they are rich soils, because of their less favourable physical properties, give lower productions compared to the typical levigated chernozems. The characteristics of the used soil are provided in the tables 1 to 3.

The purpose of this paper is to study the kinetics of the nutrient retention (phosphorus and nitrate) on 3 clayey chernozem soil type profiles (0 to 10 cm, 21 to 30 cm and 41 to 50 cm) at 1:5 soil: water phase mass ratio. The soil was dried in the drying chamber at 40°C for 30 min. The kinetic study consisted in putting 1g of soil in contact with 50 cm³ of solution (KNO₃ for the nitrate, KH₂PO₄ for the phosphorus) having the same concentration for different contact time intervals. The analyses were performed for the following initial concentrations: 43.4 and 100 mgN/L for nitrate and 50 and 114.5mgP/L for phosphorus, corresponding to 0.7 and, respectively, 1.61 mol/L molar concentrations. The glasses were covered with a foil, in order to prevent the evaporation, and shaken at different time intervals (0, 5, 10, 15, 20 and 30 min) at the temperature of 20°C±2°C. The shaking was performed by means of a Heidolph Unimax shaker at 300 rotations/minute. At the end of the shaking period, the samples were filtered under vacuum and brought in 50 mL measuring flask. Samples were collected from the filtrate in order to perform the analysis (the determination of the nitrate anion from the solution was performed according to (ISO 7890) and the determination of the mobile phosphorus content according to (SR 11411-2:1998). The aqueous extracts were analysed on the Cintra 5 spectrophotometer at a wavelength of 470 nm for the mobile phosphorus and at the wavelength of 410 nm for the nitrate anion [18, 19].

In the table 4 and in the figure 1 to 4, are presented the concentration variations and the speed of adsorption of nitrates and phosphates respectively in the soil.

Results and discussions

In order to determine the retention rate of the nitric nitrogen and of the phosphorus in the soil, kinetic study was performed; two initial concentrations of nitrates (43.4 and 100 mgN/L) and two for phosphorus (50 and 114.5 mgP/L) were chosen. The study was performed on a clayey type of soil collected from different depth levels.

Table 4
EXPERIMENTAL DATA REGARDING THE VARIATION IN THE SPEED OF RETENTION OF THE NUTRIENTS IN THE SOIL DEPENDING ON THE TIME

C _i , nitrate mg/l	C _i , phosphorus mg/l	soil profile	time, minutes	nitrate v, mg/g(humid)	phosphorus v, mg/(kg anit)
43.4	50	0-10	0	0.481	11.806
			5	0.395	6.408
			10	0.33	4.015
			15	0.27	2.73
			20	0.24	2
			30	0.18	1.194
100	114.5	0-10	0	2.65	26.046
			5	1.22	12.073
			10	0.89	6.937
			15	0.45	4.498
			20	0.31	3.13
			30	0.17	1.791
43.4	50	21-30	0	1.29	25.1158
			5	0.58	8.85889
			10	0.33	4.48131
			15	0.21	2.69796
			20	0.14	1.80039
			30	0.08	0.96479
100	114.5	21-30	0	3.4	26.3283
			5	1.38	13.7828
			10	0.74	8.4391
			15	0.46	5.01539
			20	0.31	4.11851
			30	0.17	2.42862
43.4	50	41-50	0	2.75	16.1331
			5	0.53	7.37736
			10	0.28	4.20983
			15	0.11	2.01778
			20	0.07	1.89834
			30	0.05	1.07583
100	114.5	41-50	0	4.47	65.1675
			5	1.45	19.6545
			10	0.71	9.35783
			15	0.41	5.4351
			20	0.27	3.55157
			30	0.14	1.85611

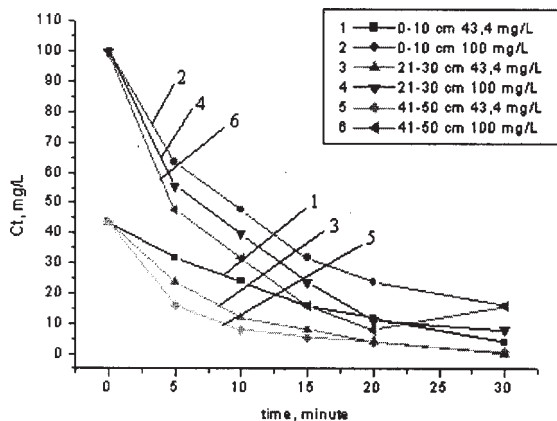


Fig. 1. Variation of the nitrate concentration in the solution

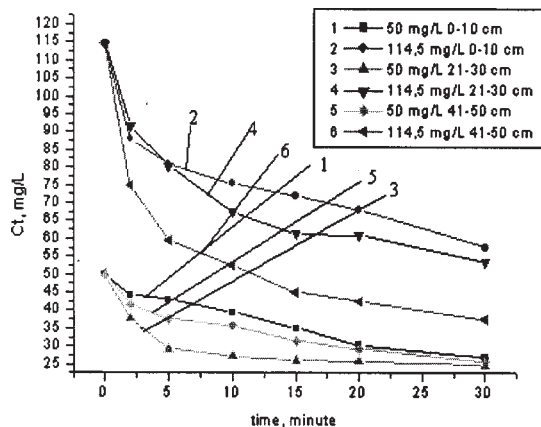


Fig. 3. Variation of the phosphorus concentration in the solution

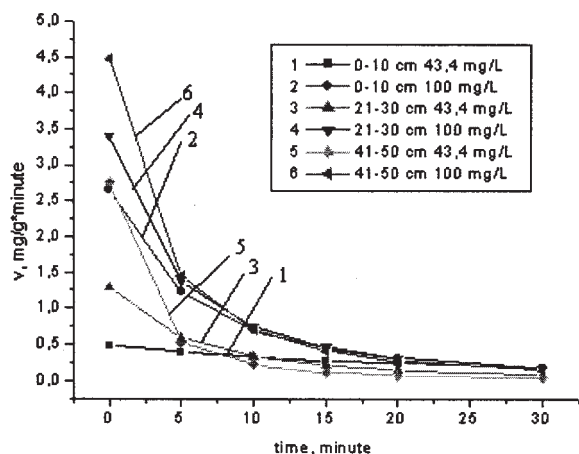


Fig. 2. Variation of the sorption rate of the nitrates in the soil

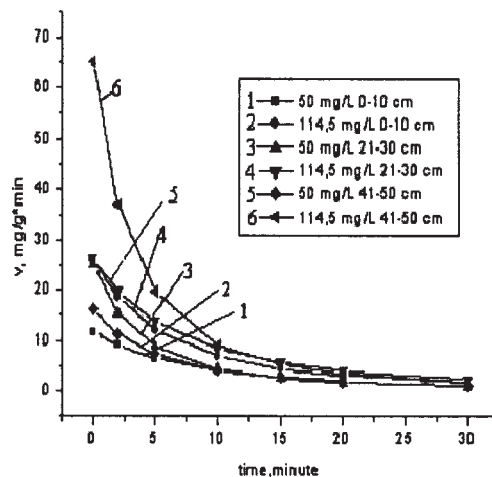


Fig. 4. Variation of the sorption rate of the phosphorus in the soil

The experimental data regarding the retention kinetics of the nitrate anion on various soil profiles are shown in figure 1. The comparative kinetic data presented in figure 1 put in evidence the fact that the retention kinetics is differentiated, depending on the studied soil profiles. Under similar conditions, the decrease in the nitrate anion concentration in the solution is higher for the soil profile 0-10 cm compared to the 41-50 cm soil profile.

For low contact times, under the mentioned conditions, the retention rate of the nitrate anion is relatively high for all the studied soil profiles. Increasing the contact time (over 10 min), the retention rate decreases. Thus, after 30 min, the retention rate reaches a value of 0.14 mg/g×min.

The kinetic curves shown in figure 3 point out a slow decrease of the concentration of phosphorus in the solution, in the time interval 0-30 min. For low contact times, under the mentioned conditions, it can be noticed that for the soil depth of 0-10 cm, for a concentration of 114.5 mg/L, during the first 10 minutes, there is a decrease of the nitrate concentration in the water of about 65%.

The kinetic curves presented in figure 4 show a high value of the retention rate of the phosphorus in the initial stage of the process. The comparative kinetic data shown in figure 4 show the fact that the ionic exchange kinetics is

differentiated for the studied soil profiles. Under similar conditions, the retention speed is higher in the case of phosphorus retention considering the depth profile of 41 to 50 cm and at an initial solution concentration of 114.5 mg/L.

In order to obtain relevant results, a large number of experiments must be performed. Their number can be reduced, simulating the process by means of the artificial neural networks.

The development of these models requires a characterisation that includes physical, chemical and biological processes taking place in the studied area. Furthermore, the full treatment of the forecasting problem is presented, explaining all the specific stages and the software features.

As input data, the following variables were chosen (table 5).

The data analysis is required as a stage preceding the pre-processing stage.

The data pre-processing represents their modification prior to be taken over by the neural network (the numeric value scaling, the transformation of the character-type data into numeric data, etc.), taking into account the fact that

Table 5
INPUT DATA OF THE ANN DESIGNED FOR THE FORECASTING PROBLEM

Variables	Minimum values	Maximum values
Contact time (t)	5 min	30 min
Soil profile (cm)	0-10 cm	41-50 cm
Initial concentration of the water polluted with nitrate anions (C _i)	43.4 mg/L	100 mg/L
Initial concentration of the water polluted with phosphate anions (C _i)	50 mg/L	114.5 mg/L

the ANN work only with numeric values within a limited interval. The post-processing is the modification of the outputs from the neural network in order to make them easily understandable and interpretable by the user. For the input data columns, the scaling interval is [-1, 1]. For the "target" (output) columns, the scaling interval depends on the output layer activation function.

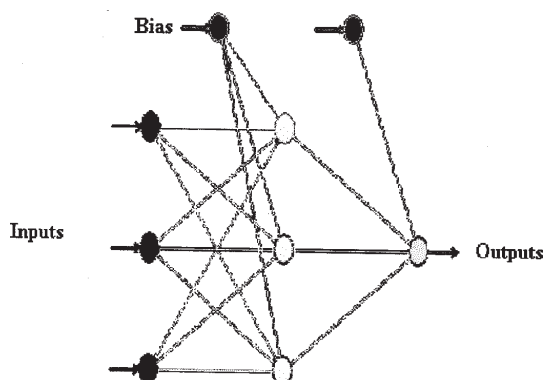


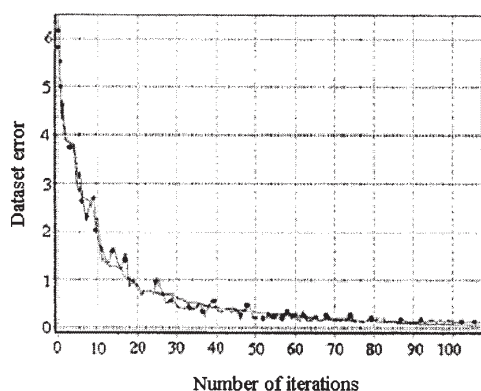
Fig. 5. ANN architecture (3-3-1)

The neural network designing begins with the specification of the network architecture (number of neurons in the hidden layer, number of hidden layers) and of the network properties (activation function, error). Whether designed manually or automatically, AN creates fully connected feed-forward ANNs. The artificial neural network considered as being optimum, following the heuristic search for the appropriate architecture, consists of 3 input neurons (initial solution concentration, soil profile, contact time), 3 hidden neurons and only one output neuron, whose value is the retention speed of the nutrients (phosphorus or nitrate) in the soil. The network was chosen based on certain considerations, such as:

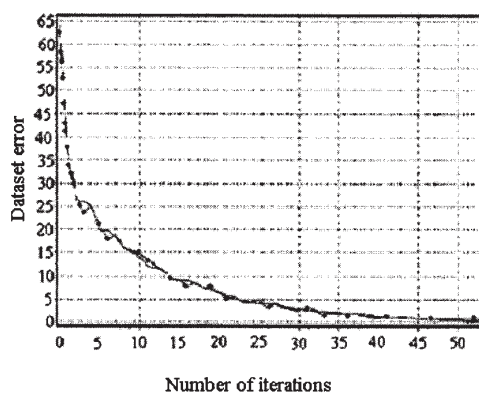
- the maximum value of the degree of matching between the real, measured results and the estimated by the network ones;
- minimum values of the testing, training and validation errors;
- the values closed to 1 of the correlation coefficient (CCR) and of the determination coefficient (R^2).

The network parameters are given by:

- type of the activation function of the hidden neuron layer – logistic type;
- type of the error function of the output data – the sum of the square deviations;
- type of the activation function of the output data – logistic type;



a. nitrate



b. phosphorus

Fig. 6. Speed of sorption. The error of the data set versus the number of iterations

- training function – Back Propagation;

The network training allows the process visualization by means of the training charts, histograms for the error distribution and for the weight distribution, the input importance chart and the exposure, in real time, of the training details. The "Continue Training" option provides the possibility of continuously training the network after having changed the training parameters and reduced the training interruption conditions. A network can be trained several times for improving the performance. This procedure was used in this paper, and the number of iterations amounted to 31,000. For this number of iteration, the root mean square error (RMSE) for the phosphates (RMSE) amounted to 9.2947, the mean correlation coefficient (R) amounted to 0.98718 and the mean determination coefficient (DC) amounted to 0.97452; as for the nitrates, the root mean square error (RMSE) amounted to 9.4947, the mean correlation coefficient (R) amounted to 0.99162 and the mean determination coefficient (DC) amounted to 0.98331.

The ANN testing allows for the trained network performance analysis to be performed by using the current data charts compared to the outputs, data dispersion charts, response charts, confusion matrix, etc. If the network is appropriately trained, it can be subsequently used for making predictions for a series of unknown date. This capacity is called generalisation. In this paper, the testing kit was used to assess the generalisation capacity of the network.

The generalisation capacity of the model and the best network architecture were determined by performing an estimated value chart compared to the measured values and the analysis of the root mean square error. The charts are presented in figure 6. These charts show that the forecast model agrees with the experimental observations. The developed network shows good performances and the results are compliant with the experimental data.

Figure 6 put in evidence the agreement between the output data, estimated by means of the network, reported upon the real, experimentally measured results. The purpose of training the network with the available database is that of minimising the difference between the two values.

Figure 7 shows the surface area correlating the 3 variables: retention rate, initial concentration and soil profile. Thus: the retention rate increases with increasing of C_i and decreasing of soil profile. In the case of nitrates, the maximum retention rate reaches maximum values of the soil profile and of the C_i .

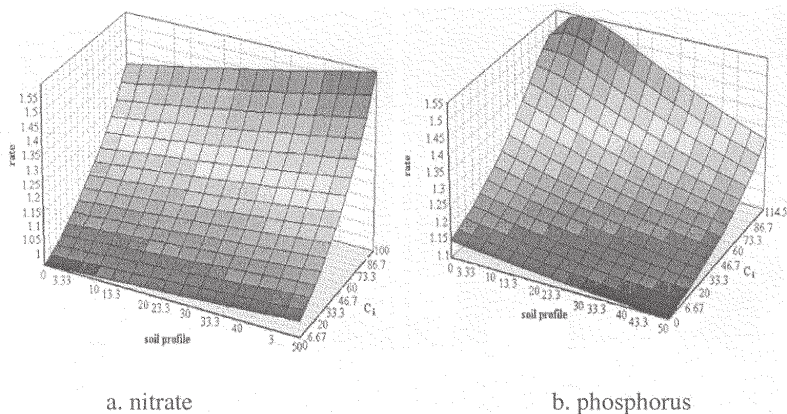


Fig. 7. The dependence of retention rate on concentration and soil profile

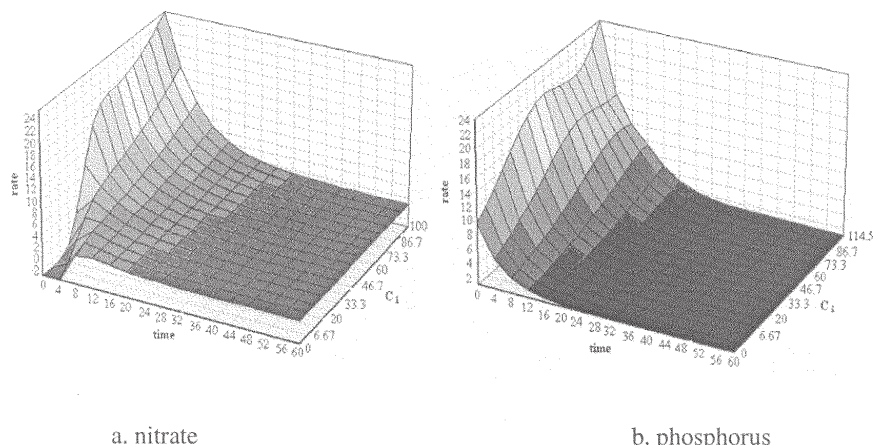


Fig. 8. The dependence of retention rate on contact time and initial concentration

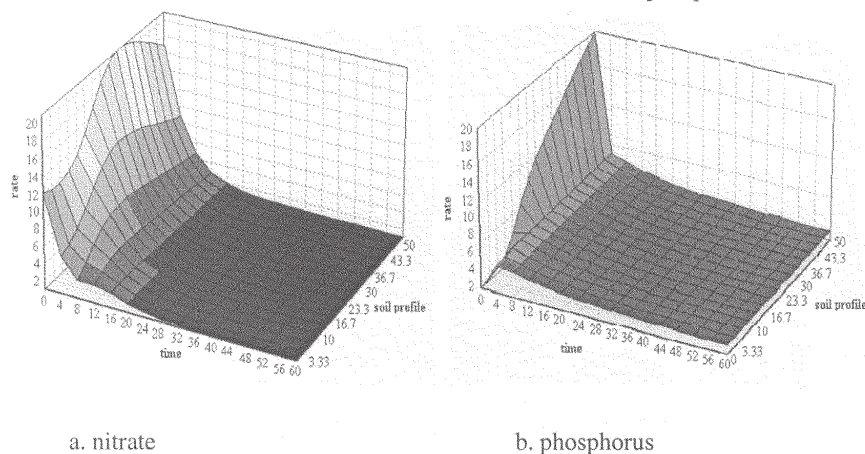


Fig. 9. The dependence of retention rate on contact time and soil profile

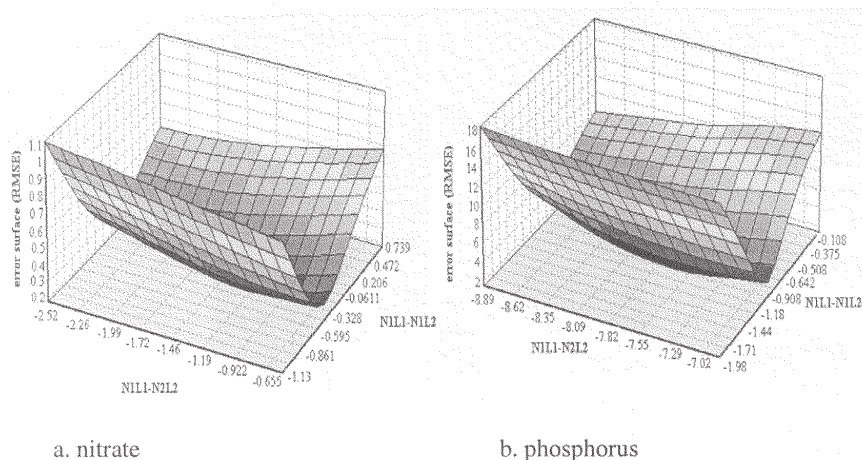


Fig. 10. RMSE vs. connection weights NIL1-NIL2 and N2L1-NIL2

Figure 8, shows the influence of the nutrient retention speed on time and initial solution concentration. The sorption speed increases at the same time as the initial concentration in solution and at low contact times (both for phosphorus, and nitrates). The sorption speed decreases in time.

Figure 9 shows the influence of the nutrient retention speed on the time and soil profile. The sorption speed is lower and similar as in the case of the phosphorus retention, and in the case of nitrate retention, it takes place at higher speed on the soil profile of 41 to 50 cm. The sorption speed decreases in time.

Figure 10 shows the error surface correlation between the mentioned network and the standard root mean error (RMSE). N1L1 means the first neuron in the input layer in the first line, N1L2 means the first neuron in the second state, which is the hidden layer.

During the training stage, the RMSE value must decrease. Figure 10 shows the point where the error is minimum, the optimum number of iterations being at the parameters indicated as such. Moreover, an increase in the error will be noticed, therefore a network over-training, inducing deviations in the results.

Conclusions

From kinetic study of nitrogen and phosphorus retention, it has been concluded that for both nutrients, retention rate is increasing while ion concentrations in aqueous solution are greater. Based on experimental data, variation in time of nitrate and phosphate concentration in aqueous solution has been presented. Based on the above mentioned data, retention rates of nitrate and phosphate ions have been calculated. Nutrients retention rates are similar in the first 30 min, due to the fact that soils profiles textures are similar. In the first 10 min, sorption rate achieves high values, then retention rate decreases continuously in time. Regarding phosphorus retention, one can observe that sorption rate in surface and medium profiles have small values, as long as in the deepest profile, phosphorus retention occurs at a higher rate. This trend is due to precipitation processes, which lead to mobile phosphorus transition into low soluble forms.

While comparing retention of both phosphates and nitrates, a similarity has been observed. Thus, for the surface profile, a lower retention rate and a higher concentration in aqueous phase have been observed, while, for the deeper profile samples, retention occurs faster. In consequence, it has been concluded that retention rate for both nitrates and phosphates increases while soil depth increases. By analyzing sorption rates, it has been observed that phosphates sorption occurs faster than in the case of nitrates.

To describe the correlation between sorption rate and other parameters (as components concentrations in aqueous and solid phases, temperature, pH), heuristic mathematical models or artificial neural networks can be used. Artificial neural networks pose the advantage of a high flexibility, thus they allow ones to pass over heterogeneities in experimental data. In this work, usage of artificial neural networks allowed authors a fast and effective modeling of experimental data regarding kinetics of nutrients retention in soil. Model generalization capacity is confirmed by the statistical parameters of this technique. Thus, the proposed modeling technique based on artificial neural networks is validated by statistic descriptors;

average error square root (RMSE) between experimental and simulated data is 9.4947 in the case of nitrate retention and 9.2947 for phosphorus retention, the linear Pearson's correlation coefficient (R) has values of 0.99162 for nitrates retention, and 0.98718 for phosphates retention, results which validate the proposed simulation method, based on artificial neural networks.

References

1. TEODORESCU, L., *Mediul și Agricultură*, p. 5, 2006
2. LĂCĂTUȘU, R., LUNGU MIHAEL, A., KOVACSOVICS, 2003, *Diversitatea sortimentului de îngrășăminte și îmbunătățirea calității acestora în raport cu cerințele agriculturii durabile*, Bacău, p. 151
3. SHARPLEY, A. N. (2006), USDA (United States Department of Agriculture), Agricultural Research Service;
4. LĂCĂTUȘU, R., 2006, *Agrochimie*, Ed. Terra Nostra, Iași
5. KOROM, S.F., 1992. **28**, p.1657
6. VINTILĂ, I., BORLAN Z., RĂUȚĂ C., DANILIU D., ȚIGĂNAȘ LETRITIA, 1984, Editura Cerers, București
7. MCGECHAN, M.B., LEWIS, D.R., *Biosystems Engineering*, vol. 82, no. 1, 2002, p. 1
8. NOLAN, B.T., K. J. HITT AND B.C. RUDDY, *Environmental Science and Technology*, 2002, Vol. 36 (10), p. 2138
9. DAVIDESCU, D. VELICICA DAVIDESCU, I. CALANCEA, O. PETRESCU, 1976, Editura Academiei Republicii Socialiste România, p. 20
10. KOROM, S.F., SCHLAG, A.J., SCHUH, W.M. AND SCHLAG, A.K., 2005. *Groundwater Monitoring and Remediation* 25 (1), p. 79
11. FORD, M. AND TELLAM, J.H., 1994, UK. *Journal of Hydrology* **156**, p. 101
12. FUKADA, T., HISCOCK, K.M., DENNIS, P.F., 2004. *Applied Geochemistry* **19**, p. 709
13. LERNER, D.N., YANG, Y., BARRETT, M.H. AND TELLAM, J.H., 1999. *Proceedings of IUGG 99 Symposium HS5, Birmingham, July 1999 IAHS Publication No. 259*, p. 117
14. PARKIN, T.B., 1987. *Soil Science Society of America Journal* **51**, 1194
15. GOULDING, K.W.T., WEBSTER, C.P., POWLSON, D.S, POULTON, P.R. AND BAKAR, R.A., 1993, **44**, p. 63
16. BAKAR, R.A., GOULDING, K.W.T., WEBSTER, C.P., POULTON, P.R. AND POWLSON, D.S, 1994. *Journal of the Science of Food and Agriculture* **66**, p. 509
17. *** Artificial Neural Network Model for Grain Refining in Stainless Steels, Mirzadeh H., Najafzadeh A., Department of Materials Engineering, Isfahan University of Technology, Isfahan, Iran
18. BARBES L., NEAGU C., MELNIC L., ILIE C., VELICU M. *Rev. Chim.(Bucharest)*, **60**, no. 3, 2009, p. 301
19. MODROGAN C., DIACONU E., ORBULET O.D., MIRON A. R., *REV. Chim.(Bucharest)*, **61**, no. 6, 2010, p. 580
20. *** Stas (ISO 7890), *Determinarea nitraților din ape*
21. *** SR 11411-2-98, (1998). *Îngrășăminte chimice complexe. Determinarea fosforului. Metoda spectrofotometrică*

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