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FORECASTING THE SORPTION OF PHOSPHATES IN SOIL WITH ARTIFICIAL NEURAL NETWORKS

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În cadrul acestui studiu s-a urmărit estimarea cu ajutorul modelului rețelelor neuronale cantitatea de fosfor adsobit şi viteza de sorbție a acestuia pe particulele de sol tip cernoziom prelevat din zone agricole. Modelul rețelelor neuronale a fost utilizat pentru modelarea comportării poluantului fosfat (P). Studiile efectuate au demosnstrat că modelul rețelelor neuronale are o eficiență net superioară celor statistice clasice cum ar fi regresia multiplă, modele autoregresive.

In this study, we are concerned with the prediction of adsorbed amount of phosphate and the sorption rate on soil particles in a chernozem from agricultural zone. Artificial Neural Networks (ANNs) have been used for modeling the behavior of phosphate (P) pollutant. The findings of numerous research studies also exhibit that the performance of ANNs is generally superior in comparison to traditional statistical methods, such as multiple regression, classification and regression trees and autoregressive models.

Keywords: sorption of phosphates, artificial neural networks, forecasting

1. Introduction

Soil is one of the basic and fundamental requirements for the survival of human beings. Soil contamination has been for a long time deep concern to environmentalists due to its harmful effects on human health. Both organic and inorganic contaminants are important for soil [1]. The most prominent chemical classes of organic contaminants are fuel hydrocarbons, polynuclear aromatic hydrocarbon fuels, polychlorinated biphenyls, chlorinated aromatic compounds, detergents and pesticides. Inorganic contaminants include nitrates, phosphates, and heavy metals such as cadmium, chromium and lead, inorganic acids and

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radioactive substances. Among the sources for generation of these contaminants are agricultural runoffs, acidic precipitates, industrial waste materials and radioactive fallout [2].

Sorption is one of the most important chemical processes affecting the transport of soil nutrients. Thus, quantification of adsorbed phosphorus concentration in soil and phosphorus concentration in soil solution is an important step for phosphorus transport modeling [3]. With increasing soil temperature, the process of desorption of phosphate in soil solution also increases, but at the same time, important quantities of aluminum, iron and manganese oxides dissolve slowing down the desorption by partial undissolution of water-soluble phosphates, by forming insoluble phosphates.

In common with other reactive chemicals, the degree to which phosphorus is adsorbed from solution is strongly non-linear because the energy levels vary among different centers of binding to the solid surface; high-energy centers are occupied before the low-energy ones. This nonlinearity is mathematically represented by several alternative equations (isotherms) with logarithmic transformation to make linear approximations [2]. An Artificial Neural Network (ANN) is an information processing paradigm that is inspired by the way that biological nervous systems, such as the brain, process information. The key element of this paradigm is the novel structure of the information processing system. It is composed of a large number of highly interconnected processing elements (neurons) working at unison to solve specific problems. An artificial neural network model can be used in order to predict nitrate ions behaviour in soil on groundwater pollution and phosphate retention. Neural networks, with their remarkable ability to derive meaning from complicated or imprecise data, can be used to extract patterns and detect trends that are too complex to be noticed by either humans or other computer techniques. A trained neural network can be thought of as an "expert" in the category of information it has been given to analyze. This expert can then be used to provide projections, given new situations of interest and answer to "what if" questions. Other advantages include: adaptive learning, self-organization, real-time operation and fault tolerance via redundant information coding [4].

Artificial Neural Networks can be most adequately characterized as “computational models” with particular properties such as the ability to adapt or learn, to generalize or to cluster or organize data and which operation is based on parallel processing. An artificial network consists of a pool of simple processing units which communicate by sending signals to each other over a large number of weighted connections. Each unit performs a relatively simple job: receive input from neighbours or external sources and use this to compute an output signal which is propagated to other units. Apart from this processing, a second task is the adjustment of the weights. The system is inherently parallel in the sense that many units can carry out their computations at the same time [5, 6].

Forecasting with ANN is a process that produces a set of outputs by given a set of variables. The variables are normally historical data. Basically, forecasting assumes that future occurrences are based, at least in part, on presently observable or past events. It assumes that some aspects of the past patterns will continue into the future. Past relationships can then be discovered through study and observation. The basic idea of forecasting is to find an approximation of mapping between the input and output data in order to discover the implicit rules governing the observed movements.

2. Experimental

Technical means: analytical balance Shimadzu AW 220 with accuracy of 0.0001 g; UV-VIS spectrophotometer with double beam Cintra 5 (UV-VIS spectral domain (190-1100 nm); optical glass/quartz chests, 10 mm thick; microbiological incubator FOC 225E (+3°C ÷ 50°C) with a resolution of 0.1°C, the inside has two outlets controlled by external switches; magnetic stirrer thermostat model AREX (field tuning speed: 50 ... 1300 rpm); vacuum pump MZ2C-Vacuubrand diaphragm (flow rate: 1,7 m^3/h).

Reagents: the reagents were prepared according to SR 11411-2:1998. These are: nitric acid 63%, ρ = 1,41 g/cm^3; color reaction (vanadomolibdenical reagent); solutions of KH_2PO_4, concentration 10 ÷ 100 mg/L.

Soil characterization: Characterization of this soil was provided by I.C.P.A. (Agrochemical and Pedological Research Institute, Bucharest - Romania) according to table 1 and 2.

Table 1

Classification of grain size (STAS 7184/10-79)

Name of granular fractions	Particle diameter (mm)	Composition (%)
Coarse sand	1 – 0,5	1,8
	2 – 0,2	2,6
Fine sand	0,2 – 0,02	32,5
Dust	0,02 – 0,002	31
Clay	<0,002	33,9

Determinations were made on samples of leachate chernozem at three temperatures 10^{0}C, 22^{0}C, 30^{0}C and a mass ratio of soil-water phases of 1:5 wt. In the kinetic study, the samples were left in contact with solutions of KH_2PO_4 in varying concentrations (10, 20, 40, 60, 80, 100 mg/l) for variable moments (2, 5, 10, 15, 20, 30, 40, 60 minutes) under stirring at 200 rpm, and the soil suspension was vacuum filtered [7]. Similarly, aqueous extracts were analyzed with spectrophotometer at a 470 nm wavelength.

Table 2

Physical properties of chernozem soil

Property	Value	Method of analysis
pH	7,85	SR ISO 1039:1999
Humus (%)	2,00	STAS 7184/21-82
$CaCO_3$ (%)	0,00	STAS 7184/16-80
Macroelements		
N_{total} (%)	0,12	SR ISO 11261:2000
P_{AL} (mg/kg)	20,00	STAS 7184/19-82
P_{total} (%)	0,065	STAS 7184/14-79
K_{AL} (mg/kg)	12,00	STAS 7184/18-80
Microelements		
Zn (mg/kg)	80,20	SR ISO 11047:1999
Cu (mg/kg)	27,40	
Fe (mg/kg)	25 671	
Mn (mg/kg)	740,00	
Al (mg/kg)	295,00	
Pb (mg/kg)	21,70	
Co (mg/kg)	9,70	
Ni (mg/kg)	55,80	
Cr (mg/kg)	13,20	
Cd (mg/kg)	0,01	

The presented data shows that at 22^0C, the process of phosphate (P) release has a low speed constant ($k_2 = 1.39 \cdot 10^{-2}$ min^{-1}). In all cases, the coefficient of speed of physical desorption, k_2, was bigger than physical adsorption coefficient, k_1, so speed is determined by physical adsorption. With increasing temperature, the speed of evolution of desorption increases and is higher than that of adsorption. Rapid reaction is due to electrostatic interactions between P and charged functional groups on solid phases. Slower reactions are due to interparticle diffusion in meso and micro pores of particles and due to strongly kinetic nature of P sorption by the oxide and hydroxide surfaces.

3. Results and Discussion

Network database

The performance of an ANN model depends on the dataset used for its training. In this paper, the data were taken from the results of the kinetic study. These data were divided into three groups, 50% in the training set, 25% in the validation set and 25% in the test set. The temperature, time and phosphorus

initial concentration represent the input units. The output units are the sorption speed of and the quantity of adsorbed phosphate (P).
In each layer, units receive their input from preceding layer's units and send their output to units in the subsequent layer. In each unit, weighted sum of its inputs is passed through the activation function to produce the output of the neuron.In this work, the sigmoid activation function was used in the hidden layer and the hyperbolic tangent activation function for the output layer. An ANN with one hidden layer with sigmoid activation function can map any function of practical interest. In the present work, a standard feed-forward network with one hidden layer was employed. The optimal number of units in the hidden layer was determined by the trial and error procedure. Fig. 1 shows a schematic representation of the neural network architecture employed in this study.

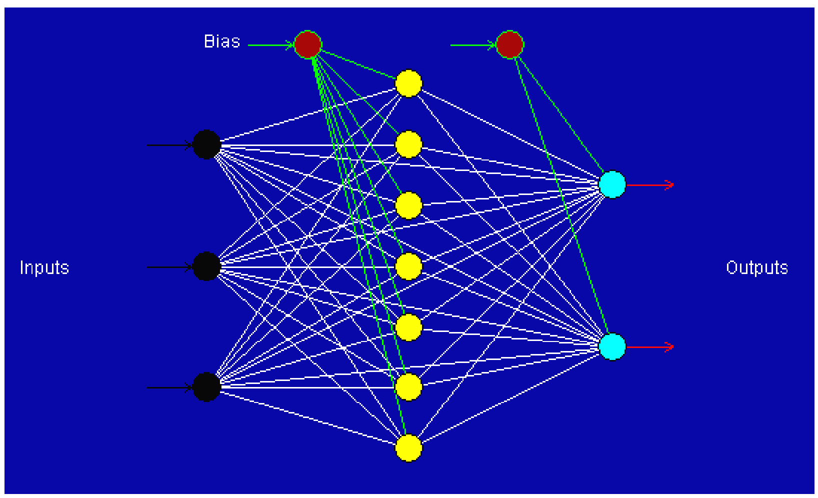

Fig. 1. ANN architecture (3-7-2)

Network training

The training set is used to determine patterns present in the data through the training process by means of a training algorithm. The objective of training is to find the set of weights between the neurons that determines the global minimum of error function. This process is equivalent to fitting the neural network model to the available training data. Training the network with an appropriate method is the key factor in order to get a well-trained network. Often the well-known back-propagation method is used to train ANNs, in which the gradient is computed for nonlinear multilayer network. An appropriate method is Quick-propagation which is much faster than standard back-propagation for many problems. Quick-propagation training algorithm was employed in this paper. The neural network can be easily over trained, causing the error rate on new unseen data to be much larger than the error rate on the training data. It is therefore important not to over train the network. A good method for choosing the number of training epochs (iterations) is the early stopping technique in which the validation data set is used to compute the error rate for it while the network is being trained. In other words, the training process must be stopped when the error measured using an independent validation set starts to increase. This stop criterion is likely to provide the best error rate in new data such as test data set. This procedure was used in the present work and the number of iterations was 3100. At this number of iterations, the root mean square error (RMSE) was 0.92947, the average correlation coefficient (R) was 0.98718 and the average determination coefficient (DC) was 0.97452.

Network testing

If the network is properly trained, it has then learned to model the function that relates the input variables to the output variables and can subsequently be used to make predictions where the output is not known. This ability is called generalization. In this paper the test set was used to evaluate the generalization ability of the trained network.

Results of the model

The generalization ability of the model and the best architecture were determined by drawing a diagram of predicted values versus measured values and analyzing the root mean square error. The diagrams are shown in Fig. 2 and 3. These diagrams show that the model prediction fits with the experimental observations. The developed network shows good performance and network results are in good agreement with experimental data.

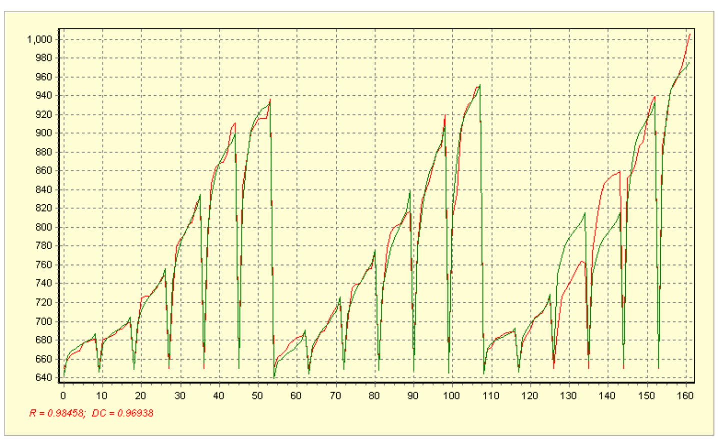

Fig. 2. Adsorbed quantity of P. Predicted values (red line) versus measured values (green line)

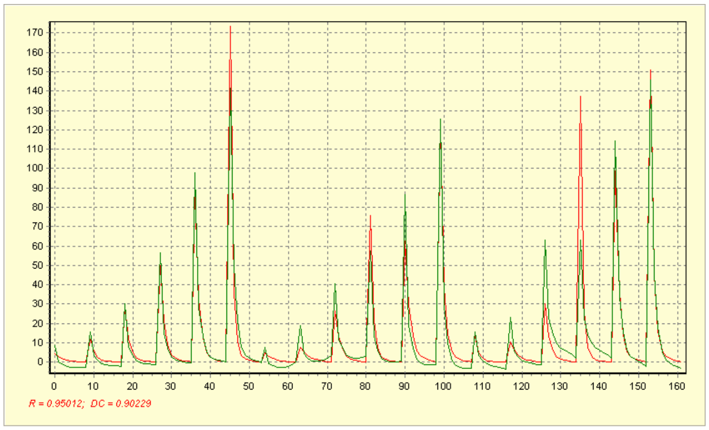

Fig. 3. Speed of sorption. Predicted values (red line) versus measured values (green line).

Regarding the importance level of input data, time is the variable with the greatest impact on the outputs, then initial concentration and temperature (Fig. 4).

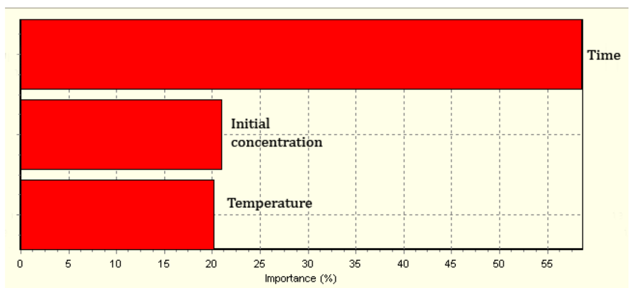

Fig.4. The analysis of input data importance

Data interdependence analysis is designed to show the relationship between output items and one (2-D) or two (3-D) input items.

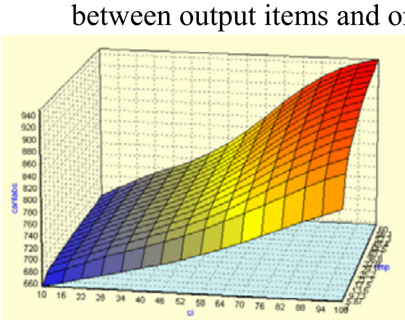

Fig. 5. Absorbed quantity vs. time and initial concentration

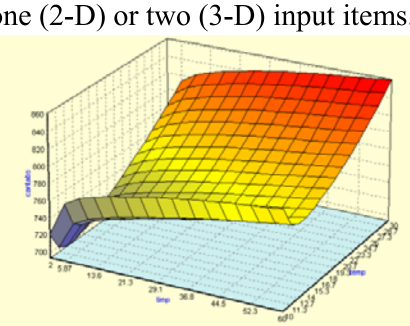

Fig. 6. Absorbed quantity vs. time and temperature

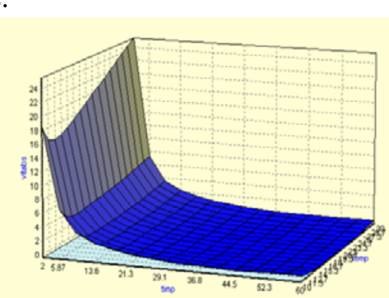

Fig. 7. Speed of absorption vs. time and temperature

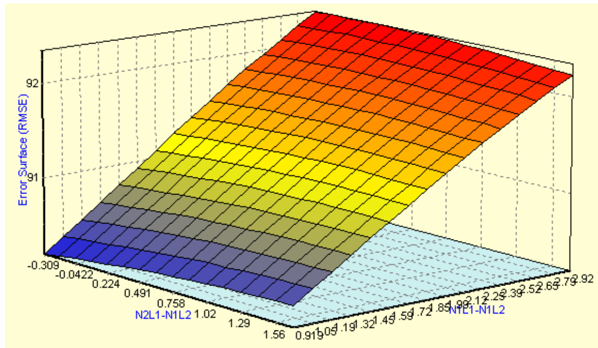

Fig. 8. RMSE vs. connection weights N1L1-N1L2 and N2L1-N1L2

The error surface consists in graphic illustration of the relationship between specified and root mean standard error, RMSE. N1L1 means the first neuron from the first input layer, N1L2 means the first neuron from the second layer which is the hidden layer (Fig. 8).

4. Conclusions

In this study, Artificial Neural Networks (ANNs) are employed to predict the adsorbed amount of phosphate in soil. The generalization ability of the model is confirmed by root mean square error (RMSE) and correlation coefficient (R) between observed and predicted data. The evaluation of model results shows that the forecasting of adsorbed amount of phosphate and the sorption rate had a promising success.

R E F E R E N C E S

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