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THE ARBOREA PLAIN (SARDINIA – ITALY) NITRATE POLLUTION EVALUATION

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EXTENDED ABSTRACT

La contaminazione da nitrati delle acque, sia superficiali sia sotterranee, è un problema che coinvolge ormai da diversi decenni tutti i paesi industrializzati. Il passaggio dalle pratiche agricole tradizionali a forme di coltivazione intensive e lo sviluppo dell'industria chimica di sintesi ha, infatti, determinato la diffusione dell'utilizzo di concimi azotati e fertilizzanti. Le acque sotterranee, in particolare, per natura povere di azoto, per via del sovrasfruttamento a cui sono spesso sottoposte, sono sempre più facilmente soggette a fenomeni di infiltrazione dalla superficie e di immagazzinamento nello spessore di suolo non saturo di elevatissimi quantitativi di azoto, progressivamente dilavato in falda. Il problema della contaminazione delle acque da nitrati ha interessato in maniera importante anche la Regione Sardegna (Italia) ed in particolare nelle zone nelle quali l'agricoltura intensiva e la zootecnia sono diventate le attività economiche portanti. Le pratiche agricole basate sull'utilizzo di fertilizzanti e di deiezioni animali per aumentare la produttività dei terreni, accompagnate ad un intenso utilizzo delle risorse idriche sotterranee per l'irrigazione, hanno determinato infatti un peggioramento della qualità delle risorse stesse e hanno reso queste zone particolarmente vulnerabili all'inquinamento da nitrati. La contaminazione delle acque da nitrati derivanti dalle attività agricole rappresenta un problema importante in Sardegna, dove il Piano di Tutela delle Acque (approvato dalla Regione Autonoma della Sardegna con la risoluzione n. 1/12 del 18/01/2005) ha definito diverse Zone Potenzialmente Vulnerabili da Nitrati, in tutto il territorio sardo, e una Zona Vulnerata da Nitrati (ZVN) nell'area della Bonifica di Arborea. Nel presente articolo tre differenti metodi per la valutazione della contaminazione da nitrati sono stati applicati in un'area studio situata nella ZVN della piana di Arborea. In particolare, il rischio potenziale alla contaminazione e la concentrazione dei nitrati nell'acquifero sono stati stimati attraverso l'applicazione di modelli parametrici, numerici e di Reti Neurali Artificiali (RNA).

L'articolo è organizzato come segue: nell'introduzione è riportata una riflessione sulla tematica della ricerca e l'inquadramento dell'area di studio. Nel prima sezione, dedicata alla metodologia, sono descritti tre modelli applicati. Nella seconda, dedicata ai risultati e alla discussione, sono presentati quattro paragrafi, tre dei quali riportano i risultati dei singoli modelli applicati, l'ultimo prende in considerazione il confronto tra i risultati ottenuti. Infine, la sezione delle conclusioni riassume brevemente i risultati, inquadrandoli in un'analisi più ampia aperta ad applicazioni future. I metodi parametrici hanno consistito nella combinazione dell'Indice di vulnerabilità intrinseca dell'acquifero alla contaminazione (SINTACS) con l'Indice di pericolosità da nitrati di origine agricola (IPNOA) per la definizione della mappa del Rischio potenziale da inquinamento da nitrati di origine agricola. Definita la mappa del rischio è stato possibile realizzare modelli concettuali e numerici che hanno permesso di avere una visione più approfondita dell'influenza che i diversi parametri idrogeologici e antropici esercitano sul livello di contaminazione da nitrati dell'area di studio. In particolare, è stato possibile definire il modello numerico di trasporto del contaminate sulla base del modello di flusso, ottenuto attraverso l'applicazione di un modello alle differenze finite modulare tridimensionale del flusso delle acque sotterranee (MODFLOW). Il modello di trasporto dei nitrati è stato creato attraverso l'applicazione "Modello di trasporto tridimensionale (MT3D)". Le RNA sono state usate per la stima della concentrazione puntuale dei nitrati nei 47 pozzi di monitoraggio sulla base di parametri speditivi misurati nei pozzi quali, livello della piezometrica, pH, conducibilità elettrica e temperatura. In conclusione si è evinto che i modelli parametrici possono dare un'ampia valutazione qualitativa del rischio di inquinamento da nitrati partendo da parametri quantificabili in maniera speditiva e economica. Tuttavia, i metodi parametrici non possono dare valori numerici delle concentrazioni di nitrati in punti specifici del dominio, bensì possono dare una chiara identificazione delle zone ad alto rischio di contaminazione. Al contrario, i risultati scaturiti dall'applicazione del modello numerico di flusso e trasporto e del modello basato sulle RNA possono essere messi a confronto ai fini della valutazione della performance delle due metodologie. I risultati dell'applicazione dei tre modelli consentono di monitorare puntualmente il progressivo degrado delle risorse idriche sotterranee in Zone Potenzialmente Vulnerabili e Vulnerate da Nitrati.

ABSTRACT

In this paper three different methods have been described and applied to evaluate the nitrate contamination from agricultural practices in a study area located in the Nitrate Vulnerable Zone (NVZ) of the Arborea plain (Sardinia - Italy). Potential risk of contamination and concentration of nitrate pollution in groundwater has been estimated by using respectively Parametric and both Numerical and Artificial Neural Networks methods.

Parametric methods consider the combination of intrinsic aquifer vulnerability to contamination index (SINTACS) and agricultural nitrates hazard index (IPNOA). The transport numerical model is based on flow model, obtained with Three Dimensional Finite Difference Groundwater Flow Model (MODFLOW), and it is made applying 3D Multi Species Transport Model (MT3D). Artificial Neural Networks (ANNs) are used for the estimation of the nitrate concentration in monitoring well.

Keywords: Artificial Neural Networks, IPNOA, nitrate contamination, numerical model, SINTACS, parametric methods

INTRODUCTION

Groundwater represents an important source exploited for human consumption, agricultural and industrial activities. One of the common kind of pollution, in both surface water and groundwater, that may affect agricultural areas, is represented by Nitrate contamination.

In Europe, in 1991, was established the Nitrates Directive 91/676/EEC (EC, 1991), with the objective of reducing water pollution caused or induced by nitrates from agricultural sources (fertilizer and organic slurry) and preventing further pollution by defining the Nitrate Vulnerable Zones (NVZs).

The contamination of water by nitrates deriving from agricultural activities represents a major problem in Sardinia Region (Italy), where Potential Nitrate Vulnerable Zones (PNVZs) have been defined in the regional Water Safety Plan (Piano di Tutela delle Acque) approved by the Autonomous Region of Sardinian resolution number 1/12 on 18/01/2005. In particular, the area studied in this work, the reclaimed area of Arborea (Western Sardinia), has been classified as NVZ. The reclaimed area of Arborea has been the subject of few studies dedicated to nitrate contamination assessment such as Mulas *et alii* (2005), Muzzu (2005), Cau *et alii* (2007) and Foddis *et alii* (2012).

In this work, three different models to evaluate the nitrate pollution of groundwater in Arborea plain are presented and compared in order to evaluate respectively the potential risk of nitrate contamination, simulation of nitrate contamination transport and punctual values of nitrate pollution estimated in selected monitoring wells.

STUDY AREA

The study area is located in the reclaimed area of Arborea (Central Western Sardinia - Italy) (Fig. 1).

Arborea plain, extends over roughly 70 km^2 and it is part of the coastal flood plain near the Gulf of Oristano, in Western Sardinia.

This area is bounded by the "s'Ena Arrubia" marsh to the N, the sea to the W, the "San Giovanni" marsh to the SW, the "Acque Medie" canal and the "Rio Mogoro" river respectively to the E and SE and the "Sassu former" marsh to the E. The "Acque Medie" canal and the "Rio Mogoro" beds have been paved, making them impermeable. There are no natural watercourses in this area supplying the aquifers, which are replenished primarily by meteoric and irrigation waters and by lateral recharge.

Up until 70 years ago, this area was a marshland in which no human activity could take place. The reclamation works in Arborea has produced radical changes in the landforms and the sedimentary environment. The actions consisted chiefly of filling in and draining the lacustrine and palustrine depressions and installing large pumping systems. Therefore, almost the entire area is characterized by sandy surface outcrop layers, caused by the wind, which has flattened the dunes, and filled the swamps depressions.

From a geological point of view, the outcropping formations are mainly variously cemented dune sands, largely Wurmian (qd). Present and recent sands of the beaches can be found along the coast (s), while silty-clayey marshy or brackish deposits (a) are located near the coastal ponds and in some other marshy internal areas (Barrocu & Soddu, 2006) (Fig. 2).

When reclamation started, the economic situation of the area completely changed and Arborea plain became one of the most productive agricultural sites in Sardinia. Whit its population of 4.048, where just over half lives in the town center and the remaining inhabitants live in houses scattered across the countryside (ISTAT data - population census 2011) the productivity of its diary system is one of the highest in Italy. The intensive agriculture and dairy farming are the mainstays of the local economy, consequently, increase the productivity of the land, the agricultural practices are based on the use of large quantities of chemical fertilizers and animal manure. These practices in conjunction with the aquifers overexploitation, the leach and the infiltration of huge quantities of nitrogen into the ground and have made this area particularly vulnerable to nitrate pollution.

The article is structured on three main sections: methodology, results and discussion and conclusions. In the first chapter the basic definitions of parametric, MT3D numerical models and ANN-based method are briefly presented. All results are explained and compared in the chapter results and discussion.

METHODOLOGY

Potential risk of contamination and concentration of nitrate pollution in groundwater of the study area has been estimated by using Parametric, Numerical and Artificial Neural Network (ANN) based methods. In the following paragraphs all methods have been reported.

Parametric models

The potential risk of groundwater contamination from nitrates of agricultural origin has been assessed on the basis of the product of two parametric indexes: Intrinsic Aquifer Vulnerability to Contamination Index, evaluated through the SINTACS method (Civita & De Maio, 2000), and Agricultural Nitrates Hazard Index, evaluated through the IPNOA method (Padovani & Trevisan, 2002). In general, the study area has to be divided into a regular grid with a square mesh in order to allow the overlapping of the thematic maps of the different factors analysed with SINTACS and IPNOA. To define the different factors needed to apply the parametric model, the maps of geology, land use, Digital Elevation Model (DEM), measurement in monitoring wells and the chemical analysis have to be taken into account.

The SINTACS method is the most commonly used in Italy and has many applications in italian case study and abroad. This method takes into consideration the seven parameters that describe the site characteristics; each of them has a score ranking from 1 to 10 depending on its influence on vulnerability taking into consideration a series of multipliers weight coefficients linked to the real impact of each specific coefficient on the vulnerability.

The parameters are: groundwater table depth from surface (*S*), infiltration through the soil (*I*), self-depuration effect unsaturated zone (*N*), soil cover and texture (*T*), hydrogeological characteristics of the aquifer (*A*), hydraulic conductivity of the

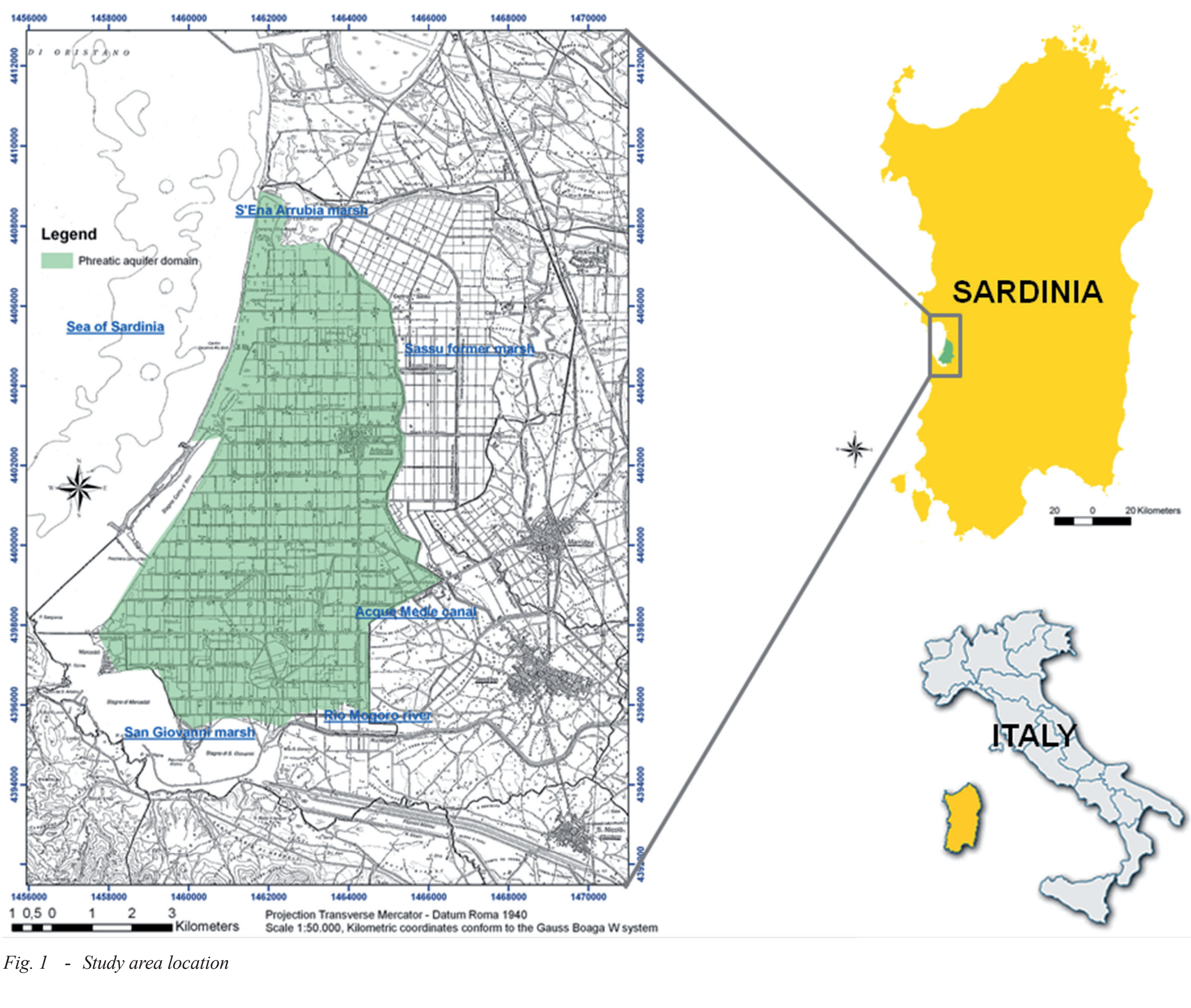

Fig. 1 - Study area location

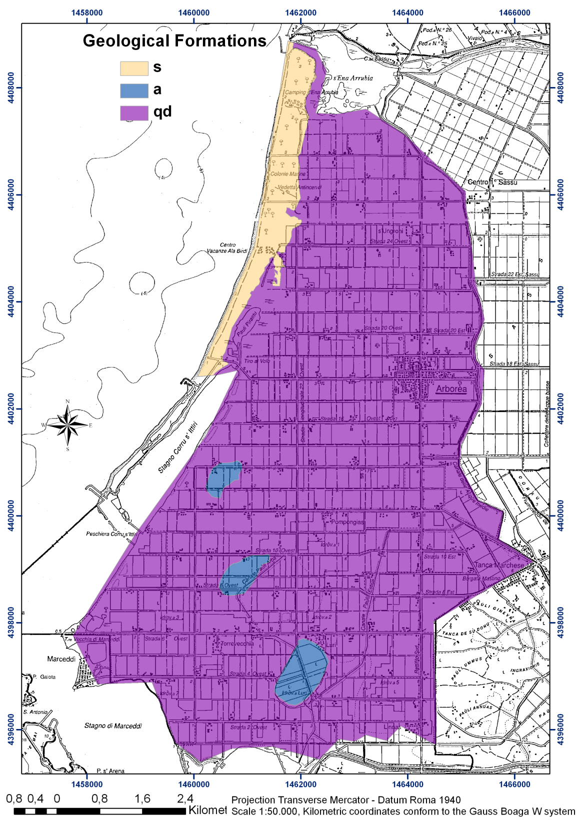

Fig. 2 - Geological map of the study area

aquifer (*C*), and topographic slope (*S*) and a series of weight coefficient multipliers for every impact situation examined. The governing equation of the model defines the Vulnerability Index V.I. as follows:

$$V.I. = \sum_{(i=1)}^{7} P_i \times W_i \quad (1)$$

where P_i is the ratings of each one of seven parameters and W_i is the relative weight of each parameter. The intrinsic vulnerability obtained with the SINTACS method is achieved by the overlay mapping of seven maps resulting from the sum of the products of scores and weights. The weight matrix plays a significant role in generation of high vulnerable zones in the contaminated areas. The results are highly influenced by the aquifer types and land use patterns (Kumar *et alii*, 2015).

The Intrinsic Aquifer Vulnerability to Contamination Index gives a value of the vulnerability degree, for each finite square element variable in a very wide range. By normalising and splitting into six vulnerability classes, the index provides as many vulnerability degrees to groundwater contamination (1 = very low, 6 = extremely high) (Capri *et alii*, 2009) (Tab. 1).

To evaluate the potential hazard of groundwater contamination by nitrates coming from agricultural sources, the italian Regulation D.Lgs 152/06 suggests a parametric system based on empirical relationships between the soil or sub soil characteristics and the N leaching risk. In this work, according to D.Lgs 152/06, the IPNOA method (Padovani & Trevisan, 2002) is applied. The method is a parametric approach that entails the selection of all of the parameters involved in the potential hazard of nitrate groundwater contamination for different agricultural activities. A progressive score is assigned to each parameter as well as synthetic indicators related to environmental factors depending on their importance and weight (Pisciotta *et alii*, 2015).

SINTACS	Classification
1	Very low
2	Low
3	Moderate
4	High
5	Very high
6	Extremely high

Tab. 1 - SINTACS classification

The IPNOA requires the calculation of three Hazard Factors (HF) that contribute to the nitrate infiltration of the soil and four Control Factors (CF) that amplify or decrease the effect of the nitrate load (Ghiglieri *et alii*, 2009). The three HF are mineral fertilization (*HFmf*), organic fertilization (*HFof*) and depuration sludge (*HFds*). The four CF are total N content in the soil (*CFn*), type of climate (*CFc*), agronomic practices (*CFap*) and irrigation type (*Cfi*). A score is assigned for each HF and CF. This score value is allocated to the measured factors using appropriate conversion tables; a score of zero was given to non agricultural land use units (urban and natural areas) (Pisciotta *et alii*, 2015).

The IPNOA index, for each finite square element, is obtained from the sum of the three HF multiplied by the product of the four CF. The final value is classified by six degrees of nitrate contamination hazard from agricultural sources. The raw IPNOA indices are then ranked, based on the 135.125 possible combinations, into classes on a percentile basis using a scale ranging from 1 to 6, according to their hazard level, 1 is assigned to the areas with the least hazard and 6 to those with the highest hazard. Once the hazard and control factors were defined, the index values were determined for each cell and then converted into raw IPNOA scores using the following equation (Pisciotta *et alii*, 2015):

IPNOA Index = (HFmf + HFof + HFds) x (CFn x CFc x CFap x CFi) (2)

The hazard rating was then assigned to each class as shown in Tab. 2.

Potential hazard class	IPNOA value	Potential hazard
1	2.54 – 3.18	Improbable
2	3.19 – 5.88	Very low
3	5.89 – 7.42	Low
4	7.43 – 9.31	Moderate
5	9.32 – 11.10	High
6	11.11 – 17.66	Very high
Urban area	0	

Tab. 2 - Potential hazard rating

The IPNOA gives an evaluation of how the propensity of agricultural and livestock activities influences the presence of nitrates at the soil level, while SINTACS evaluates physical characteristics of both aquifer and soil that influence the vulnerability to nitrate pollution.

The potential risk Rpot, given by the Potential hazard index and Intrinsic Aquifer Vulnerability to Contamination Index, has been calculated using the following Equation (3):

$$Rpot = Ip \ x \ Iv \quad (3)$$

where Ip is the IPNOA index and Iv is the vulnerability index. SINTACS and IPNOA results have been combined to obtain the Potential agricultural nitrates pollution risk map of the reclaimed area of Arborea.

MT3D numerical model

In order to understand and define the groundwater flow and transport mechanism it is needed the schematization and simplification of the real hydrogeological units and groundwater flow system thought a conceptual model. In a first phase, the aquifer has to be studied from a geological, pedological, morphological, hydrological, hydrogeological point of view. Land use and economic activity have to be evaluated, as well, in order to define the hotspots linked to agricultural and livestock activities. The simplification of the system mainly concerns its geological and hydrogeological characteristics, such as the definition of the boundaries geometry of the domain, the reconstruction of the stratigraphy, the flow, the properties of the fluid phase, the identification of all the elements that constitute aquifer recharges, the aquifer losses and the potential sources of pollution. Once the conceptual model is created, the flux and transport numerical model can be built and simulated by means of a specific numerical model. In this work the commercial software Groundwater Modeling System 6.0 (GMS6.0 http://www.aquaveo.com/software/gms-groundwater-modeling-system-introduction) has been used. This software provides tools for site characterization, model development, post-processing, calibration and visualization of the results. The flow equations have been calculated exploiting the Three-Dimensional Finite-Difference Groundwater Flow Model (MODFLOW). The numerical code, MODFLOW, simulates steady and non steady flow in which aquifer layers can be confined, unconfined, or a combination of confined and unconfined.

A general form of the governing equation, which describes the three dimensional movement of groundwater flow of constant density through the porous media is (Freeze & Cherry, 1979):

$$\frac{\partial}{\partial x}\left(Kx\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(Ky\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(Kz\frac{\partial h}{\partial z}\right)-w=Ss\frac{\partial h}{\partial t} \quad (4)$$

where: *Kx*, *Ky*, *Kz* are values of hydraulic conductivity along the *x*, *y* and *z* coordinate axes (Lt^{-1}), h is the potentiometric head (*L*), *w* is the volumetric flux per unit volume and represents sources and/or sinks of water per unit time (t^{-1}), *Ss* is the specific storage of the porous material (L^{-1}), *t* is time.

The first part of this problem was run to get a steady state solution that takes the form:

$$\frac{\partial}{\partial x}\left(Kx\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(Ky\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(Kz\frac{\partial h}{\partial z}\right)-w=0.0 \quad (5)$$

Starting from the steady state solution, the hydraulic conductivity for model aquifers can be found. Then the equation is solved for transient case in order to solve for storage coefficient (Abu-El-Sha'r & Hatamleh, 2007).

The transport equations for the nitrate contamination have been solved by exploiting the modular 3D Multi-Species Transport Model (MT3D). In particular, MT3D is a finite difference numerical code that allows one to simulate advection, dispersion and chemical reactions of contaminants in groundwater systems. In (6) the partial differential equation for three-dimensional transport of contaminants in groundwater is reported (Freeze & Cherry, 1979):

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_i}\right]-\frac{\partial}{\partial x_i}(v_iC)+\frac{q_s}{\theta}C_s+\sum_{k=1}^{N}R_k \quad (6)$$

where: *C* is the concentration of contaminant dissolved in groundwater, *t* is the time, x_i is the distance along the respective Cartesian co-ordinate axis, D_{ij} is the hydrodynamic dispersion coefficient, v_i is the seepage or linear pore water velocity, q_s is the volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative), C_s is the concentration of the sources or the sinks, θ is the porosity of the porous medium and R_k the chemical reaction term.

The results of flow model obtained with MODFLOW have been used as input to apply MT3D. In fact, to solve the transport equation of the contaminant it is necessary to know the groundwater flow equation of the aquifer.

The numerical model of the flux and transport of nitrate pollution can be simulate for various years on the basis of the data available case by case.

ANN-based method

An Artificial Neural Networks (ANN) (Principe *et alii*, 2000) consists of a number of interconnected processing elements (Perceptrons) called Artificial Neurons (AN). The ANN is symbolized like a graph where patterns are represented in terms of numerical values attached to the AN, the nodes of the graph. The ANs are partitioned into layers and those can be numbered in such a way that the nodes in each layer are connected only to nodes in the next layer and interact with each other through the weighted connection. The partition of layers consists in three or more layers: an input layer, an output layer and one or more hidden layers with non linear Perceptrons. The hidden layers are not directly connected to the outside world. A Multi Layer Perceptron (MLP) ANN is used in this work to

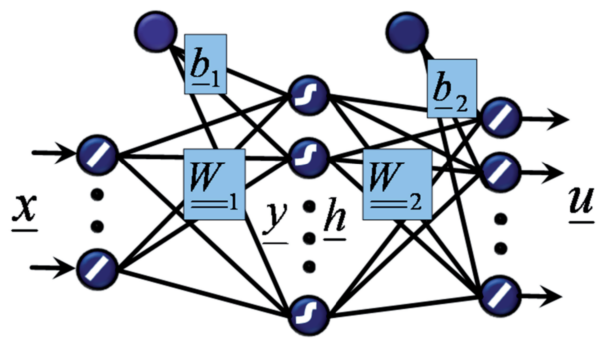

Fig. 3 - General MLP's structure

model the system under study (Fig. 3).

The MLP ANNs, can approximate any continuous function with an arbitrary precision, provided that the number of hidden neurons is sufficiently large. The model of a system can be create only on the basis of a suitable set of input/output pairs of example patterns. Commonly MLPs may be trained so that a particular input leads to a specific target output. In particular, the training of the MLP ANN consists in a learning rule where weights of the connections are adjusted, based on a comparison of the output (output calculated by the network) and the target (desired output that corresponds to the output pattern) until the network output matches the target. The MLP ANN is trained, using the standard Levenberg-Marquard algorithm that provides a numerical solution to the problem of minimizing a function, generally nonlinear, over a space of parameters of the function. These minimization problems arise especially in least squares curve fitting and nonlinear programming, therefore a sufficient low number of iterations is required (Ingrassia, 2002).

Levenberg-Marquardt realizes the relationship between input and output patterns by the following algebraic equations system:

$$\begin{array}{ll} \text{Input layer} & \\ \text{Hidden layer} & \\ \text{Output layer} & \end{array} \begin{cases} \underline{\underline{W}}_1 \cdot \underline{x} + \underline{b}_1 = \underline{y} \\ \underline{h} = \sigma(\underline{y}) \\ \underline{\underline{W}}_2 \cdot \underline{h} + \underline{b}_2 = \underline{u} \end{cases} \qquad (7)$$

where: $\underline{x}$ is the input of the network, $\underline{\underline{W}}_1$ is the weights matrix of the input layer, $\underline{b}_1$ is the bias vector of the input layer, $\underline{y}$ and $\underline{h}$ are the input and the output of the hidden layer respectively, $\sigma(\underline{\cdot})$ is the hidden neurons logistic activation function, $\underline{u}$ is the output of the network, $\underline{\underline{W}}_2$ is the weights matrix of the output layer, $\underline{b}_2$ is the bias vector of the output layer.

The critical issue in developing an ANN is generalization. In fact, the loss of the generalization capability makes an ANN unusable. Such situation may be generated by an exasperate training. To avoid such risks, it is useful to find rules that permit the evaluation of the best duration of the training phase. Learning rules that allow to establish a limit of the training phase assume a key role in order to safeguard the generalization capacity. Typically, a threshold value of the error that determines once reached the training stop is established. Depending on the choice of the threshold, the overfitting event may arise. The overfitting determines an excessive specialization of the network on training examples creating a disadvantage in the generalization ability. Different methods can be used to for the training interruption; in this work, the cross validation method is used. In the cross validation method, the patterns are divided in two different sets, the first set is used to train and build the artificial neural network (training set), while the second set is used to verify the performance of the network and for error evaluation (test set). When the error on the second set begins to increase, the training process is interrupted. If neither the cross-validation condition nor the mean squared error are met, the training ends when the fixed number of epochs is reached.

In this work Levenberg-Marquardt algorithm and the cross validation method been used to train the network for the estimation of agricultural derived nitrate concentrations, on the basis of economical quantifiable parameters such as pH, electrical conductivity, temperature, groundwater level. The goal of the training process was to make the ANN able to generalize the acquired information and to reconstruct the input-output relationship. On the basis of the four input parameters above mentioned, the nitrate concentration in the monitoring well has been determined, even for examples not included in the patterns of the training set.

RESULTS AND DISCUSSION

The performance of the proposed methodologies has been evaluated for the estimation of the potential risk of contamination and concentration of nitrate pollution from agricultural practices in groundwater in a study area located in the Nitrate Vulnerable Zone (NVZ) of the Arborea plain (Sardinia - Italy). To elaborate all reported methodologies different data set has been take into account. In particular, agronomic and irrigation data, used in this work, has been provided by the Reclamation Consortium of Oristano province (Consorzio di Bonifica dell'Oristanese). The geological stratigraphy, the measurement performed during the years from 2007 to 2010 in the 47 monitoring wells, reported in Fig. 3, and the chemical analysis have been provided by the Regional Agency for Environmental Protection of Sardinia (ARPAS) of the Autonomous Region of Sardinia.

Following a detailed explanation of the results is reported and discussed method by method. A comparison of the results obtained with the three methods applied has been discussed in the last paragraph.

Parametric models for the calculation of potential agricultural nitrates risk

To define the different factors needed to apply the parametric model the maps of geology, land use and Digital Elevation Model (DEM) respectevely has been created. The study area was divided into a regular grid with a square mesh of 10 m, and the thematic maps of the different factors, analyzed on the SINTACS and IPNOA methods, were overlapped. The SINTACS Index and IPNOA Index results have been combined in order to obtain the Potential agricultural nitrates pollution risk map showed in Fig. 4. As one can see in the map, the zones with a high potential risk of nitrate groundwater pollution are located where there are greater development of agricultural and livestock activity. The map have been validated by comparing the values of Potential agricultural nitrates pollution risk with the chemical analysis on water samples collected in 47 wells coming from various monitoring campaigns made from 2007 to 2010. The areas where Potential agricultural nitrates pollution risk is high are characterized by high level of nitrate contamination measured in monitoring wells.

Nitrate pollution estimation with modflow and mt3d models

The behavior of the Arborea Plain phreatic aquifer has been estimated by means of the numerical model MODLOW and MT3D respectively for groundwater flow and transport of the nitrate contamination. The simulation of the flux and transport of nitrate pollution has been applied for three years: from 2007 to 2010. The model domain and grids used in this study are the same for both the flow and transport model. The model covered 72 km^2 and the whole area is divided into 438 columns and 494 rows for a total number of 216.372 cells.

Transient simulation as well as flow calibration begin with the steady-state initial conditions with the same boundaries. Parameters and methods of advection ends before or when a new steady state is reached. Both the time and the stress period were divided into several steps. The first step started from the beginning of the 2007s till the end of 2009 of a total number fifteen time steps. This represents the steady state period where there was no significant change in nitrate concentrations. After that, the simulation of transient conditions started in 2010 when a significant drawdown in water level occurred and caused an increase in the values of nitrate concentration. Calibration was achieved by adjusting the Hydraulic Conductivity parameter. The amounts of recharge were as well adjusted during the process of calibration.

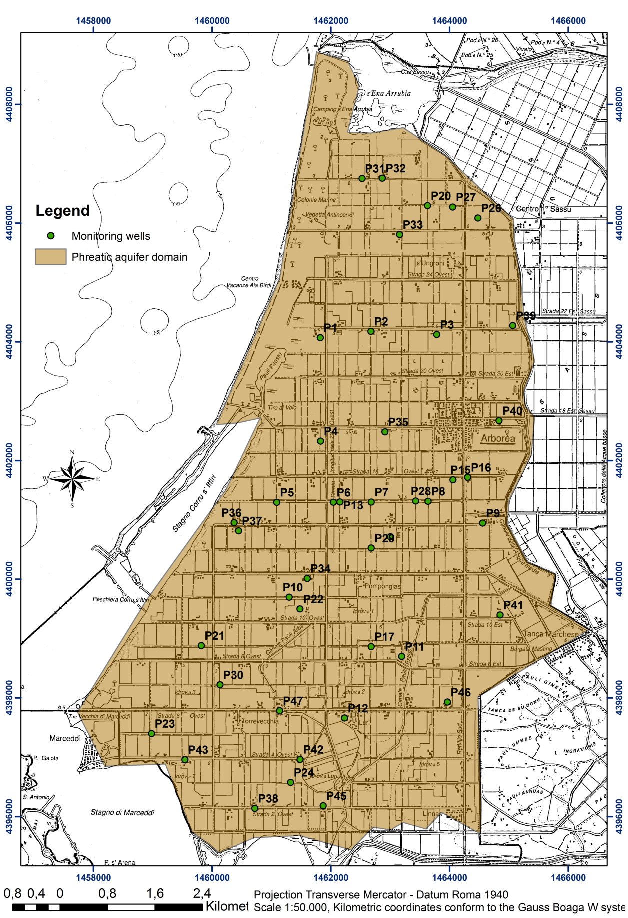

Fig. 4 - Location of the 47 monitoring wells in the phreatic aquifer domain

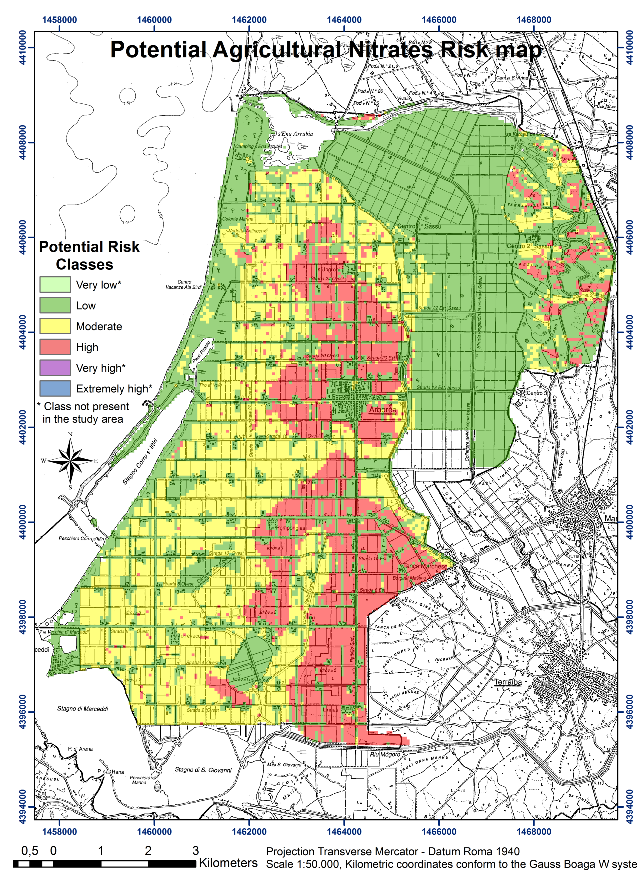

Fig. 5 - Potential agricultural nitrates risk map

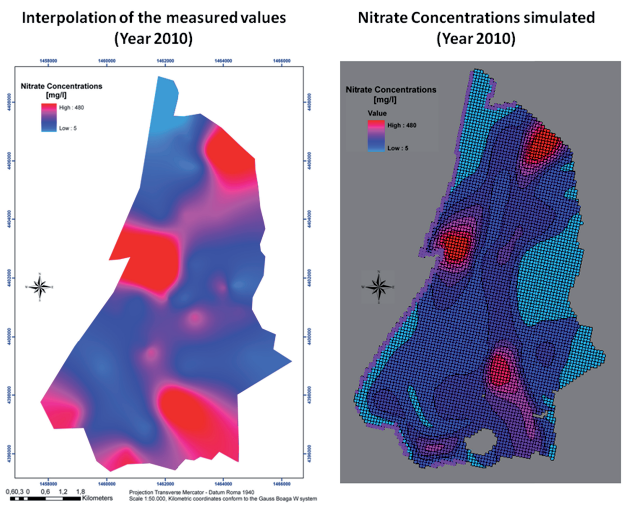

Fig. 6 - Comparison between the measured and the estimated nitrates with MT3D

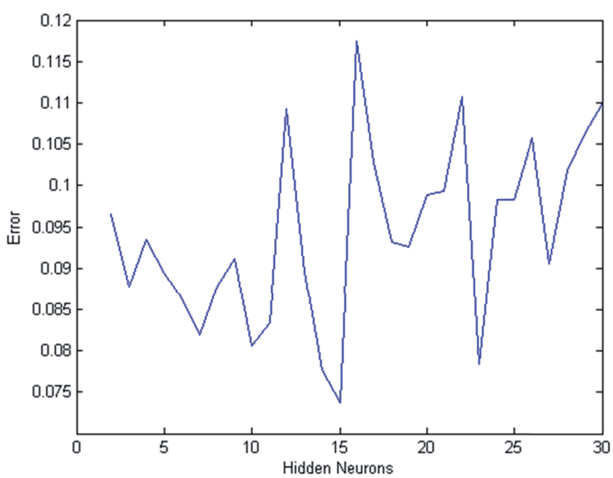

Fig. 7 - Test set error on the basis of the number of each hidden neurons

The validity of this methodological approach has been assessed by comparing the transport of nitrate pollution obtained through the MT3D method with the measurements of nitrate contamination and chemical analysis performed in the monitoring wells from 2007 to 2010 on water samples collected in 47 wells by the ARPAS. Figure 6 shows the interpolation of the measured values of nitrate concentration performed with ArcGIS and the nitrate concentration simulated with MT3D Model. With regard to the contaminant transport model, the results shows that the simulated values of contaminant transport in the aquifer are very close to those actually measured in 2010 by ARPAS on monitoring network. As one can see, in Figure 6, in 2010 the transport simulations show peaks of nitrate concentrations of as much as 100-400 mg/L, well above the water quality standard of 50 mg/L set by the Nitrates Directive 91/676/EEC. In most of the reclaimed area of Arborea simulated concentrations average around 50-100 mg/L except for the area of Arborea's town and the beach where the values are lowest (15-50 mg/L), as clearly no crops are cultivated in these areas. In the South of the studied area, where is located the Pumping station of Luri, the numerical simulation confirms that it was not possible to calculate the nitrate transport on the pumping system due to the continuous pumping and recirculation of the groundwater.

ANN models for nitrate pollution estimation

As reported in the 3rd paragraph of the section dedicated to the Methodology, ANNs allow to analyse a physical system where mathematical models are complex or not existent. The ANN dissociates itself from the system physical model and based on external data is able to build simple algebraic equations that can reproduce the phenomena cause-effect relationship. Exploiting this ability of the ANNs, the agricultural derived nitrate concentrations have been estimated by using easily and economical quantifiable parameters such as pH, electrical conductivity, temperature, groundwater level. Data used for training and validating the ANNs derive from a set of 483 measurements coming from 47 monitoring wells distributed in the study area. In order to define the best topology of the ANN and the best dimension of respectively the training and the test sets a growing procedure and a trial and error procedure has been applied. To determine the best structure of the MLP, namely the number of hidden neurons, an iterative trial and error procedure has been set up. The procedure consisted in to perform several trainings assuming a growing number hidden neurons. In Figure 7 has been reported the evolution of the error in the test set on the basis of the number of the hidden neurons.

Once the best dimension of the training set, test set and the best number of hidden neuron is fixed a new training session has been performed. The Levenberg-Marquardt (Ingrassia *et alii*, 2002) algorithm has been used to train the network a 4-15-1 MLP ANN (Fig. 8). The 4 neurons in the input layer corresponds to pH, electrical conductivity, temperature, groundwater level and the only neuron in the output corresponds to the nitrate concentrations.

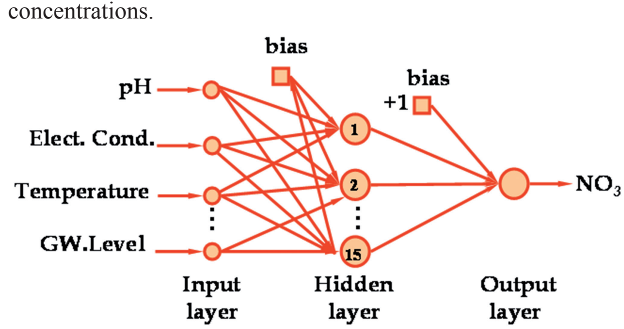

Fig. 8 - MLP ANN trained for the nitrate estimation

The training set and the test set were composed respectively by 427 and 55 patterns. The goal of the training process was to reconstruct the input-output relationship. After the training the network algebraic equations system realizes the relationship between input and output patterns. Feeding the network with an input that does not belong to the training set the corresponding output may be calculated. On the basis of the four input parameters above mentioned the nitrate concentration in the monitoring well has been determined.

Discussion of the comparison of the results obtained with the three methods applied

Parametric models can give an extensive qualitative estimation of the nitrate pollution risk on the basis of easily and economical quantifiable parameters. Therefore, parametric methods cannot give numerical values of nitrate concentrations in specific points in the domain. However, the Potential agricultural nitrates pollution risk map showed in Figure 5 confirms that the zones with a high risk of nitrate groundwater pollution are located where there are greater developments of agricultural and livestock activity.

On the contrary, in MT3D model the extended hydrogeological database of the aquifer has been used for solving the equations governing contaminant transport phenomenon. The numerical model of nitrate groundwater contamination estimated with MT3D can be easily exploit to be compared with the results obtained with the ANN models. Punctual nitrates concentration values may has been predicted with ANN models based on simply and economically measurable parameters. The results obtained with the MT3D and ANN models have been compared in Figure 9, where the ANN estimated nitrates (red stars), the MT3D estimated nitrates (green stars) with the measured nitrates (blue stars) for the 55 examples of the validation set. The Nitrate Directive threshold is as well shows in the graphic (black dashed). The results obtained with these two methods are very close each other. However, in general the estimations performed with MT3D gives values of nitrate contamination higher than real nitrate concentrations measurements. In Table 3 the maximum, minimum and medium error of nitrates estimation has been reported for the two methods.

As one cans see, tor both the two methods, the maximum error was less than 30 mg/L. In particular, the estimation error was less than 10 mg/L in the 65% of the MT3D estimations and in the 45% of the ones of ANNs. Only 5 MT3D estimations and 4 ANN estimations had error in the range between 20 and 30 mg/L.

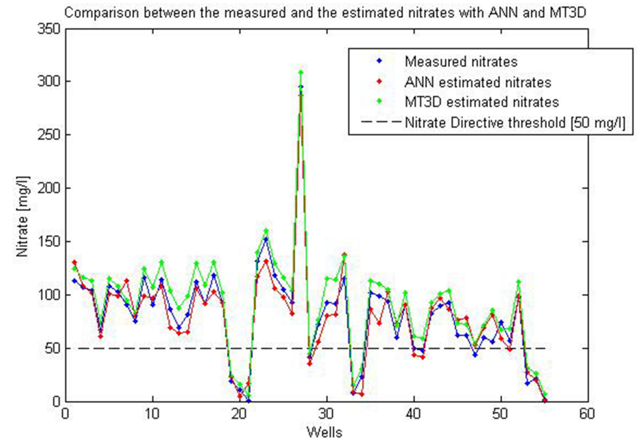

Fig. 9 - Comparison between the measured and the estimated nitrates with ANN and MT3D

Error	ANN estimated nitrates [mg/L]	MT3D estimated nitrates [mg/L]
Maximum	25.8	29.0
Minimum	0.3	4.0
Medium	9.9	11.2

Tab. 3 - ANN and MT3D estimated nitrates [mg/L] errors

CONCLUSION

In this paper three different methods to evaluate nitrate contamination from agricultural practices have been presented.

Parametric methods, based on the analysis of anthropic activities, soil and aquifer properties, have been used to evaluate the Potential agricultural nitrates pollution risk. This kind of methods can give an extensive qualitative estimation of the nitrate pollution risk on the basis of easily and economical quantifiable parameters. Therefore, parametric methods cannot give numerical values of nitrate concentrations in specific points in the domain.

On the contrary, in MT3D model the extended hydrogeological database of the aquifer are taken into account for solving the equations governing contaminant transport phenomenon.

Punctual nitrates concentration values may be predicted with ANN models based on simply and economically measurable parameters. Furthermore, the ANN approach has proved to be time and cost efficient.

The results obtained with the three methods presented in this work may offer a valuable contribution to the pool of existing solutions in the field of nitrate groundwater pollution by allowing to punctually monitor the progressive degradation of groundwater resources in NVZs and then to identify action plans aimed at informing and training farmers in much better fertilization management and agricultural practices. In addition this study provides the political authorities with a planning tool for water resources and soil protection aimed at a sustainable land use and at environmental protection.

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REFERENCES

Abu-El-Sha'r W.Y. & Hatamleh R.I. (2007) - *Using Modflow and MT3D groundwater flow and transport models as a management tool for the Azraq* Groundwater System. Jordan Journal of Civil Engineering, **1** (2).

Barrocu G. & Soddu S. (2006) - *Saltwater intrusion in the Arborea area (central-western Sardinia).* Proceedings 1st SWIM-SWICA Joint Saltwater Intrusion Conference 175-181, Cagliari-Chia Laguna, Italy - September 24-29, 2006.

Capri E., Civita M., Corniello A., Cusimano G., De Maio M., Ducci D., Fait G., Fiorucci A.,Hauser S., Pisciotta A., Pranzini G., Trevisan M., Delgado Huertas A., Ferrari F., Frullini R., Nisi B., Offi M., Vaselli O. & Vassallo M. (2009) - *Assessment of nitrate contamination risk: the Italian experience.* Journal of Geochemical Exploration, **102**: 71–86.

Cau P. & Paniconi C. (2007) - *Assessment of alternative land management practices using hydrological simulation and a decision support tool: Arborea agricultural region, Sardinia*. Hydrol. Earth Syst. Sci., **11**: 1811-1823.

Civita M. & De Maio M. (2000) - *Valutazione e cartografia automatica della vulnerabilità degli acquiferi all'inquinamento con il sistema parametrico SINTACS R5.* Pitagora Editrice, 248 pp.

Foddis M.L., Montisci A., Uras G., Matzeu A., Seddaiu G. & Carletti A. (2012) - *Prediction of nitrate concentration in groundwater using an Artificial Neural Network (ANN) approach.* CIGR Ageng Conference 2012, 8-12 July 2012, Valencia.

Ghiglieri G., Barbieri G., Vernier A., Carletti A., Demurtas N., Pinna R. & Pittalis D. (2009) - *Potential risks of nitrate pollution in aquifers from agricultural practices in the Nurra region, northwestern Sardinia, Italy.* Journal of Hydrology, **379**: 339-350.

Ingrassia S. & Davino C. (2002) - *Reti neuronali e metodi statistici.* Franco Angeli, Milano.

Kumar P., Bansod B.K.S., Debnath S.K., Thakur P.K. & Ghanshyam C. (2015) - *Index-based groundwater vulnerability mapping models using hydrogeological settings: a critical evaluation.* Environmental Impact Assessment Review, **51**: 38–49

Mulas M.G., Testa M. & Uras G. (2005) - *Vulnerability to nitrates of agricultural origin in Sardinia.* The Arborea area - 4° Conv. Naz. sulla Protezione e Gestione delle Acque Sotterranee – Reggia di Colorno (PR), settembre 2005. ISBN 8890134224.

Muzzu M. (2005). -*Applicazione del metodo Galdit per la valutazione della vulnerabilità dell'acquifero costiero di Arborea.* University of Cagliari, Italy. Tesi di laurea (unpublished).

Padovani L. & Trevisan M. (2002) - *I nitrati di origine agricola nelle acque sotterranee - Un indice parametrico per l'individuazione di aree vulnerabili.* Pitagora Editrice, Bologna. 103 pp.

Pisciotta A., Cusimano G. & Favara R. (2015) - *Groundwater nitrate risk assessment using intrinsic vulnerability methods: a comparative study of environmental impact by intensive farming in the Mediterranean region of Sicily, Italy.* Journal of Geochemical Exploration, **156**: 89-100.

Principe J., Euliano N. & Lefebvre C. (2000) - *Innovating adaptive and neural systems instruction with interactive electronic books.* Proceedings of the IEEE, special issue on engineering education, January 2000.

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