Journal of Geochemical Exploration 124 (2013) 22–28

Contents lists available at SciVerse ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

pH, electric conductivity and sulfate as base parameters to estimate the concentration of metals in AMD using a fuzzy inference system

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ARTICLE INFO

Article history:
Received 23 March 2012
Accepted 15 July 2012
Available online 17 August 2012

Keywords:
Acid mine drainage
System modeling
Fuzzy logic
ANFIS
Cobica River
Spain

ABSTRACT

An adaptive neuro-fuzzy inference system (ANFIS) was developed to model an acid mine drainage (AMD) affected river. The inference system uses three AMD relatively expeditious indicators (pH, electric conductivity and sulfate) and gives, as response, concentration values for Fe, Mn, Cu, Zn, Cd, and As. It was based on a large database, which resulted from monitoring an AMD stream located in the Iberian Pyrite Belt (Chorrito stream, which flows into the Cobica River, SW Spain). The results indicate a high correlation between the analyzed values and the concentrations obtained by fuzzy estimation. Therefore, this modeling approach afforded a simple and cost-effective system capable of monitoring the affected river, since it avoids or simplifies the analyses of the most expensive and time consuming chemical parameters.

1. Introduction

The geochemical and mineralogical evolution of sulfide-rich wastes generates a highly contaminant effluent, generically named as acid mine drainage (AMD). An associated complex chain of biotic and abiotic reactions, which involves the oxidative dissolution of sulfides, has been the subject of extensive literature (Bhatti et al., 1993; Evangelou and Zhang, 1995; Keith and Vaughan, 2000; McKibben and Barnes, 1986; Nordstrom and Southam, 1997; Ritchie, 1994). AMD has an important environmental impact in mining regions, promoting chemical, physical, biological and ecological interactive effects on ecosystems (Gray, 1998). Very low pH values ($pH<4$) and high sulfate and metal concentrations are the main characteristics of watercourses affected by AMD worldwide (Elbaz-Poulichet et al., 2001; Sainz et al., 2004; Valente and Leal Gomes, 2007, 2009b).

An accurate AMD characterization is demanded due to the combined presence of many pollutants and their reactivity. The presence of colloidal material such as iron oxyhydroxides enhances their instability (Kimball and Stanley, 1997; Kimball et al., 1995). Such reactivity and natural variability create difficulties to obtain representative samples and to perform their analytical characterization (Valente et al., 2011a). Consequently, it is difficult to model these contaminated systems with conventional mathematical approaches. AMD environmental monitoring is also a concerning issue, which implies high efforts for analytical method adaptation and a large number of sample analysis. Therefore, the design and implementation costs for hydrochemical control networks are very steep for this kind of system.

In SW Europe this is a serious problem, which may bear influence on the environmental quality of rivers that flow into dams for public water supply. This is the case of the Iberian Pyrite Belt, where AMD affects the river network, both in Spain and Portugal. In this region, AMD is a long-lasting and typical problem that requires permanent monitoring, since the public water reservoirs are facing metallic load from polluted rivers such as the Cobica River in the province of Huelva, SW Spain, which supplies the Andévalo Dam (Fig. 1). In this scenario, the present study proposes a fuzzy logic approach to estimate metal concentrations by simply using expeditious measures, mainly obtained in the field. In comparison with classical methods, the main benefits of fuzzy logic approaches are the ability to reduce difficulties of complex system modeling and analysis, as well as the incorporation of qualitative aspects of human observation within its rules (Schurter and Roschke, 2000).

The proposed method is an adaptive-network-based fuzzy inference system (ANFIS) (Jang, 1993). Using pH, electric conductivity, and sulfate as input values, the concentration of metals and metalloids (Fe, Mn, Cu, Zn, Cd, As) was estimated for each sample. It was modeled with a large database characterizing 237 samples collected at a precise location in the Cobica River for 8 months. The developed model reveals the powerful ability of fuzzy tools to model complex natural and

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http://dx.doi.org/10.1016/j.gexplo.2012.07.013

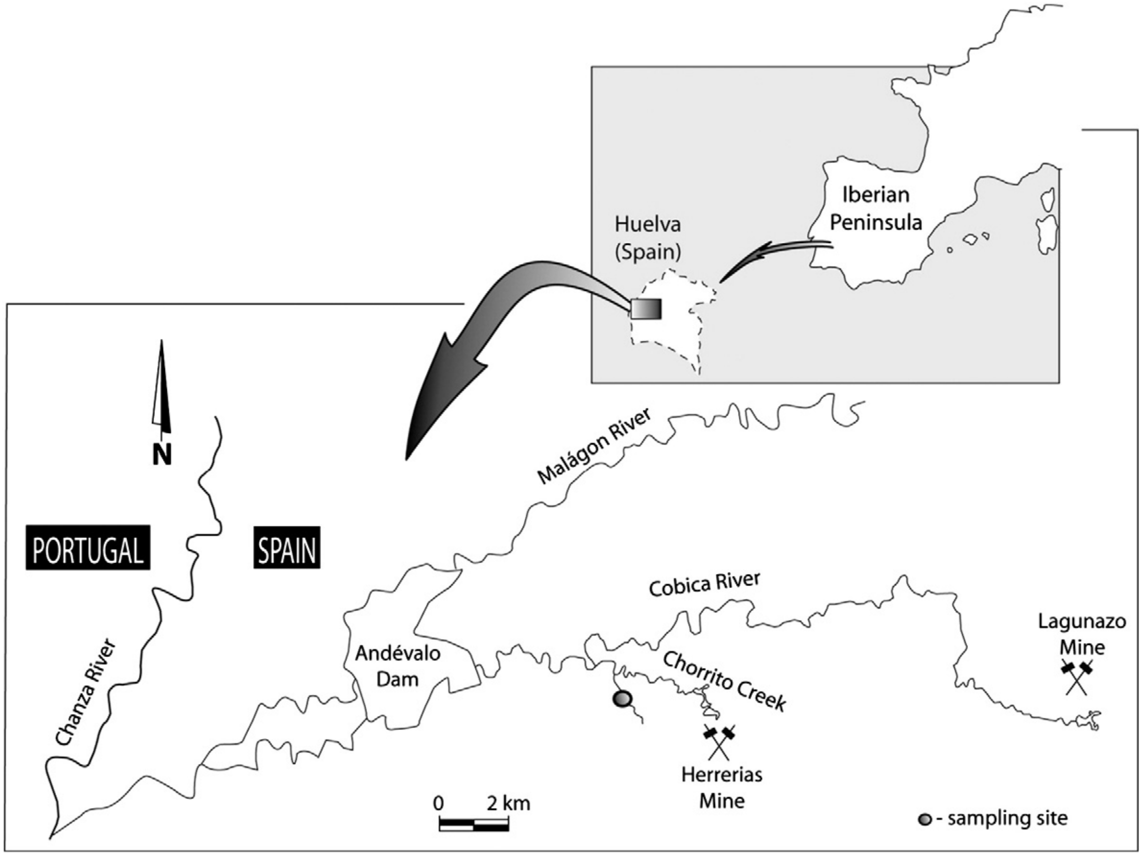

Fig. 1. Study area in SW Europe, with location of the sampling site.

heterogeneous systems (Heiss et al., 2002; Zadeh, 1965). Owing to the high correlation observed between the laboratory analysis results and the estimated fuzzy values, the present model may help to implement a long-lasting and cost-effective environmental monitoring system for this river.

2. Site description

The samples used to develop the fuzzy model are from the Chorrito stream, which flows into the Cobica River and is located in the Iberian Pyrite Belt, in SW Spain, very close to the Portuguese border (Fig. 1). This is an exemplary metallogenic region, with sizable Paleozoic massive sulfide deposits (Sáez et al., 1999) that have been exploited for more than 5000 years (Davis et al., 2000).

The Cobica stream is a typical mining channel that receives discharges from two abandoned Iberian Pyrite Belt mines: Herrerias Mine and Tharsis Mine (Fig. 1). The channel is characterized by large floods in winter and very scarce flow in low water periods (May to October). The AMD process in this river has been studied over time by different authors (Borrego et al., 2002; de la Torre et al., 2009; Grande et al., 2010a,b; Jiménez, et al., 2009).

3. Methods

This section presents the approach used to develop the fuzzy inference system and also includes the analytical procedures carried out to characterize water quality of the Cobica River. Sampling took place daily from October 2003 to May 2004 at the sampling site marked in Fig. 1. The resulting database thus covers the full range of climate and hydrological conditions observed in the affected system.

3.1. Chemical analyses

Water pH and electric conductivity (EC) were both measured in the field with a CRISON pH meter 507 and a CRISON conductivity meter 524.

After being collected, samples were filtrated with nylon filter disks 0.45 μm Millipore (Millex Ref. SLCR 013) for subsequent sulfate and metal analyses. In the sub-samples retained for metals, filtration was followed by acidification with HNO_3 65% *suprapur* Merck. The samples were immediately refrigerated, transported in polyethylene bottles, kept and stored in the dark at 4 °C until analysis.

Ion chromatography with chemical suppression was performed in order to measure the presence of sulfate (Standard Methods, 4110). Atomic absorption spectroscopy (air acetylene) with flame was used to analyze the metals Fe, Cu, Mn and Zn, whereas atomic emission spectroscopy, using inductively coupled air plasma, was employed to determine the presence of As and Cd.

3.2. Fuzzy logic fundaments

Fuzzy logic can be summarized as the generalization of the classical set theory, pioneered by Zadeh (1965). In Zadeh's own words, “one of the principal objectives of fuzzy logic is formalization/mechanization of the remarkable human ability to reason and to make decisions in an environment of imprecision, uncertainty, partiality of information and partiality of truth” (Dumitras and Moschytz, 2007). As opposed to the

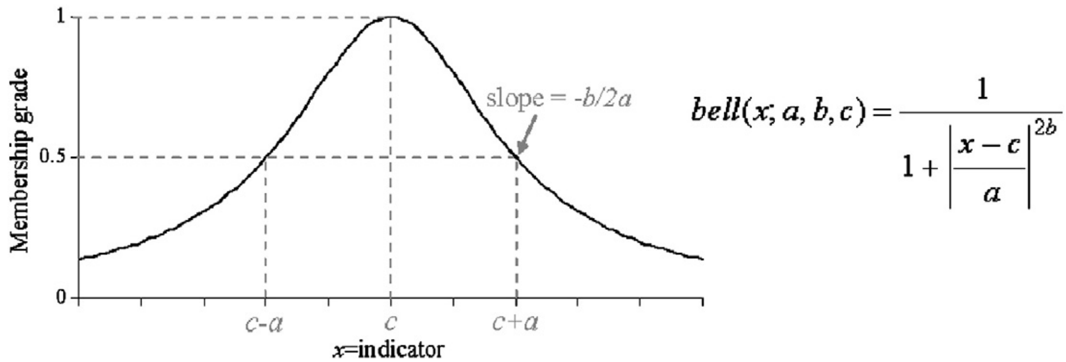

Fig. 2. Physical meaning of the parameters of a Bell function.

classical theory where sets have crisp boundaries, in fuzzy logic sets have unsharpened ones. This is an important concept, as it fits better into almost all real world sets (classes) and therefore provides a better approach to model natural phenomena.

A fuzzy set *A*, defined in the universe of discourse *X*, is a set which allows its members ($x \in X$) to have different membership grades (membership function μA) in the interval [0, 1], Eq. (1).

$$A = \{(x, \mu A(x)) | x \in X\}, \text{where } x \text{ is the fuzzy variable.} \quad (1)$$

The membership functions are generally obtained through function parameterization with simple geometric forms, such as the bell function to model the fuzzy variable *x*, exemplified in Fig. 2.

It is possible to write a set of rules representing the relation between input and output variables (Jang et al., 1997) since all variables involved in a problem are modeled to the fuzzy domain by means of membership functions. These rules are in the format *if-then* and are made up of a premise and a consequent; the fulfillment of the premise leads to the conclusion. The main characteristic of reasoning based on rules of this type is its ability to represent partial coincidence, which allows a fuzzy rule to provide an inference even when the condition is only partially satisfied (Grande et al., 2005). For example, in the following rule, there are two premises and one consequent: "IF *x* is *A* and *y* is *B* THEN *z* is *C*".

Fuzzy logic has been used recently, proving satisfactory in AMD characterization processes according to several authors (Aroba et al., 2007; Grande et al., 2010c,d; Jiménez et al., 2009; Valente and Leal Gomes, 2009a; Valente et al., 2011b).

3.3. Fuzzy inference system—ANFIS

A fuzzy inference system (FIS) formulates the mapping from a given input to an output, providing the basis from which decisions can be made or classes (patterns) discerned.

The present study relies on an adaptive neuro-fuzzy inference system (ANFIS), derived from one of the most well-established FIS, i.e., the Sugeno-type (Jang et al., 1997). These authors present a complete description of these systems, emphasizing their potential and the benefits of using the ANFIS. For a brief explanation, the reasoning mechanism of an ANFIS system with two inputs (*x*,*y*) and one output (*z*) (Fig. 3) will be taken as an example.

In *Layer 1*, each node is an adaptive node with the following function (Eq. (2)):

$$\begin{aligned} O_{1,i} &= \mu_{A_i}(x), \quad for\ i = 1, 2 \\ O_{1,j} &= \mu_{B_j}(x), \quad for\ j = 1, 2. \end{aligned} \quad (2)$$

$O_{1,i}$ and $O_{1,j}$ are the membership grades of fuzzy sets *A* and *B*. The membership functions can correspond to any parameterized function, such as the bell function presented in Fig. 2. The function parameters are designated as the premise part of the fuzzy rule.

In *Layer 2*, each node is fixed. The output of each node represents the firing strength of a rule and is the product of the incoming values (Eq. (3)).

$$O_{2,i} = w_i = \mu_{A_i}(x)\mu_{B_i}(y), \quad i = 1, 2. \quad (3)$$

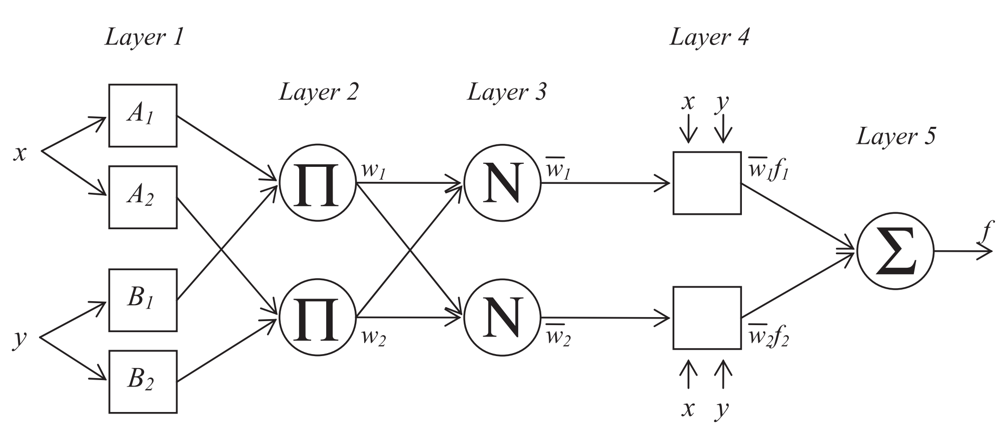

Fig. 3. ANFIS system.

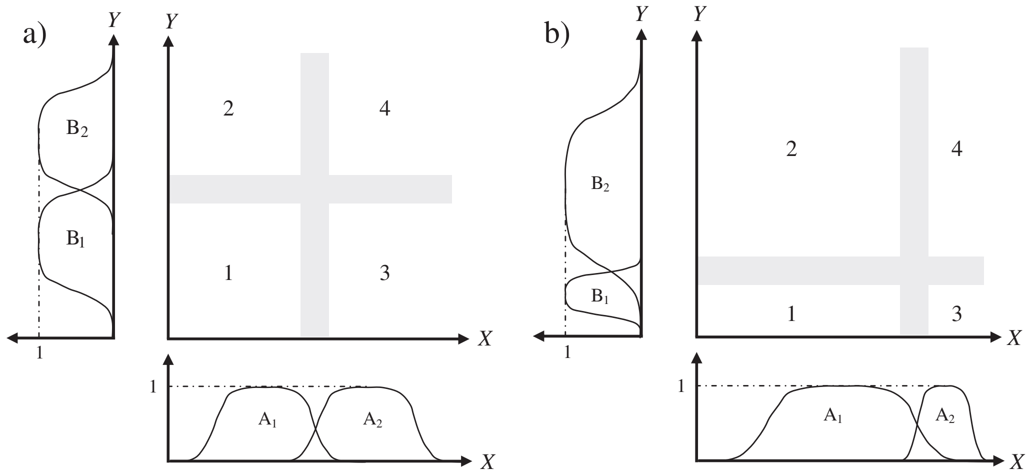

Fig. 4. Grid distribution before (a) and after (b) the training procedure.

Layer 3 consists of fixed nodes. Here, the outputs of *Layer 2* are normalized in accordance with Eq. (4).

$$O_{3,i} = \overline{w}_i = \frac{w_i}{w_1 + w_2}, \quad i = 1, 2. \tag{4}$$

Layer 4 has adaptive nodes, which are described by the function of Eq. (5). These layer parameters, p_i, q_i and r_i, are referred to as the consequent parameters.

$$O_{4,i} = \overline{w}_i f_i = \overline{w}_i (p_i x + q_i y + r_i), \quad i = 1, 2. \tag{5}$$

Layer 5 consists of a fixed node, which computes the overall output of the ANFIS (Eq. (6)).

$$O_{5,1} = \sum_i \overline{w}_i f_i. \tag{6}$$

The advantage of the ANFIS is the possibility to iteratively adjust the premise and the consequent parameters through a hybrid learning procedure, which combines the backpropagation gradient descendent algorithm and least squares method (Jang et al., 1997). This allows for improved decision-making based on the fuzzy rules.

Fig. 4a exemplifies the initial grid distribution that results from overlapping the fuzzy regions obtained with two membership functions associated with each variable, i.e., *x*, *y*. After training, the grid was adjusted (Fig. 4b) to retain the most relevant data. The premise part of a rule defines a fuzzy region in the fuzzy universe, while the consequent part specifies the output within the region.

In the present work, the ANFIS was developed using the MATLAB fuzzy logic toolbox (Matlab, 1999).

Generally, the specification of the numbers of rules and membership functions assigned to each input variable results from the existent knowledge about the data set and, consequently, about the phenomena to be modeled. In the present case, due to the complexity of the AMD phenomena, it was only possible to arrive at these numbers through trial and error, with recourse to the fuzzy C-means clustering method (FCM) (Jang et al., 1997).

Table 1
Pearson's correlation factors between analyzed parameters.

	pH	EC	SO_4	Fe	Cu	Zn	Mn	As	Cd
pH	1.0000								
EC	−0.7869	1.0000							
SO_4	−0.7333	0.9021	1.0000						
Fe	−0.3662	0.4768	0.4670	1.0000					
Cu	−0.7636	0.7644	0.6893	0.4150	1.0000				
Zn	−0.5832	0.7132	0.6455	0.3986	0.7899	1.0000			
Mn	−0.4774	0.7601	0.6172	0.2464	0.6043	0.6860	1.0000		
As	−0.6221	0.6481	0.6682	0.4229	0.6330	0.4546	0.2878	1.0000	
Cd	−0.8252	0.8946	0.8303	0.3831	0.8543	0.7259	0.6363	0.7280	1.0000

4. Results and discussion

4.1. AMD database

The database used to develop and evaluate the fuzzy inference system results from the sampling program described in Section 2. It includes pH and EC field measurements, as well as laboratory analyses of sulfate (SO_4), Fe, Cu, Zn, Mn, Cd, and As.

Table 1 presents the correlation matrix for these physical–chemical parameters. The higher correlations (>0.80) were observed between EC and SO_4 (0.90). Cd is also highly correlated with pH (−0.825), EC (0.895), SO_4 (0.830), and Cu (0.854). In general, Fe presents the lowest correlations (<0.50 with all the parameters). The correlation between pH and EC is also below 0.80, contrarily to the results observed in other systems (Valente, 2004). De la Torre et al. (2009) have already detected and discussed this low correlation for the Cobica River.

The statistical results of Table 1 bring to light some limitations of the classical statistical estimations dealing with complex AMD samples, as stated by Valente and Leal Gomes (2009a, 2011a). Specifically, the low correlation factors observed between the metals and the sulfate and the field parameters (pH and EC) make it impossible to use that type of approach in order to perform expeditious inferences between the parameters. Such limitation is portrayed in Fig. 5, which represents estimated concentrations versus real concentrations (for Fe and Cu) with pH as base parameter. Using these simple geochemical correlations, the correlation values obtained are very low and hence unsuitable for prediction.

In view of the knowledge available on the use of fuzzy logic in AMD (Aroba et al., 2007; Grande et al., 2010c,d; Jiménez et al., 2009; Valente and Leal Gomes, 2009a; Valente et al., 2011b), fuzzy approaches were expected to be more powerful and hence capable to overcome the classical limitations.

4.2. Application of the ANFIS

To model the behavior of each metal, an ANFIS was developed using pH, electric conductivity and sulfate as inputs. Therefore, the application consisted of 6 ANFIS with 3 input variables and one output.

The database, consisting of 237 samples, was randomly divided into a training set and a testing set, representing 75% and 25% of the samples.

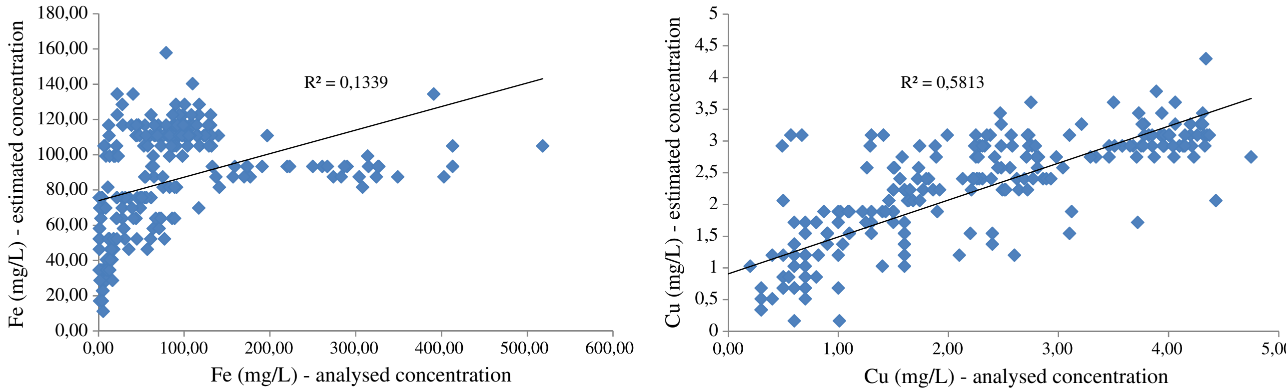

Fig. 5. Estimated concentrations versus real (analyzed) concentrations for Fe and Cu, using simple geochemical correlation, with pH as base parameter.

The training set was used to adjust the network parameters, while the testing set allowed for the efficiency of model training to be assessed upon entering of new data.

Using the training dataset, the FCM provided 13 clusters for each input variable of each ANFIS, which correspond to 13 membership functions. At the beginning of training, the initial premise parameter values were set in such a way that the membership function centers are equally spaced along the range of each input variable. The learning procedure was monitored through an objective function based on mean square error. When the total squared error sum reached a value lower than 0.0002, the training stopped. This took place during ten training epochs, as shown in Fig. 6.

The testing dataset was presented to the system in order to test the performance of the ANFIS after training. This performance was

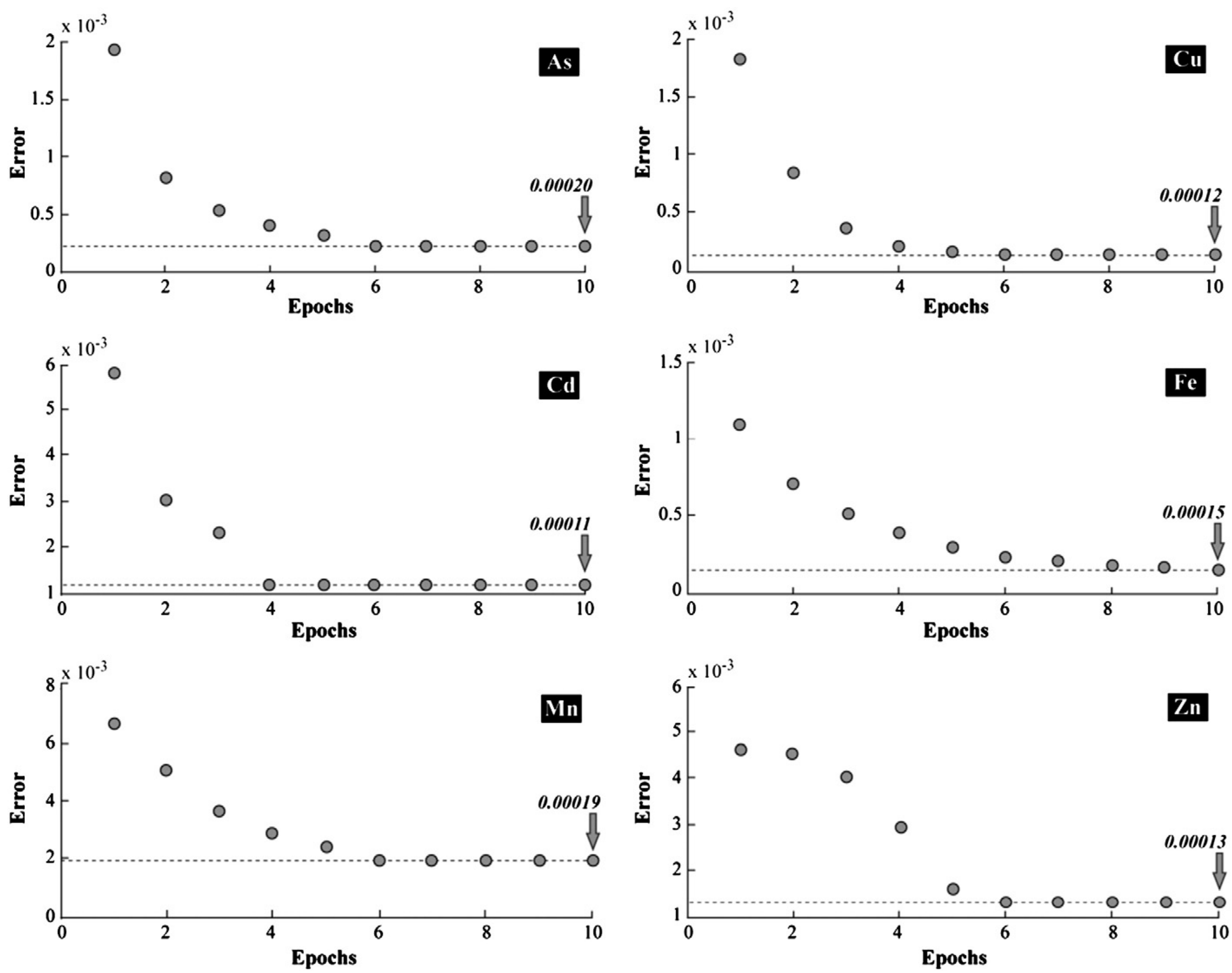

Fig. 6. Number of training epochs versus total sum of squared error.

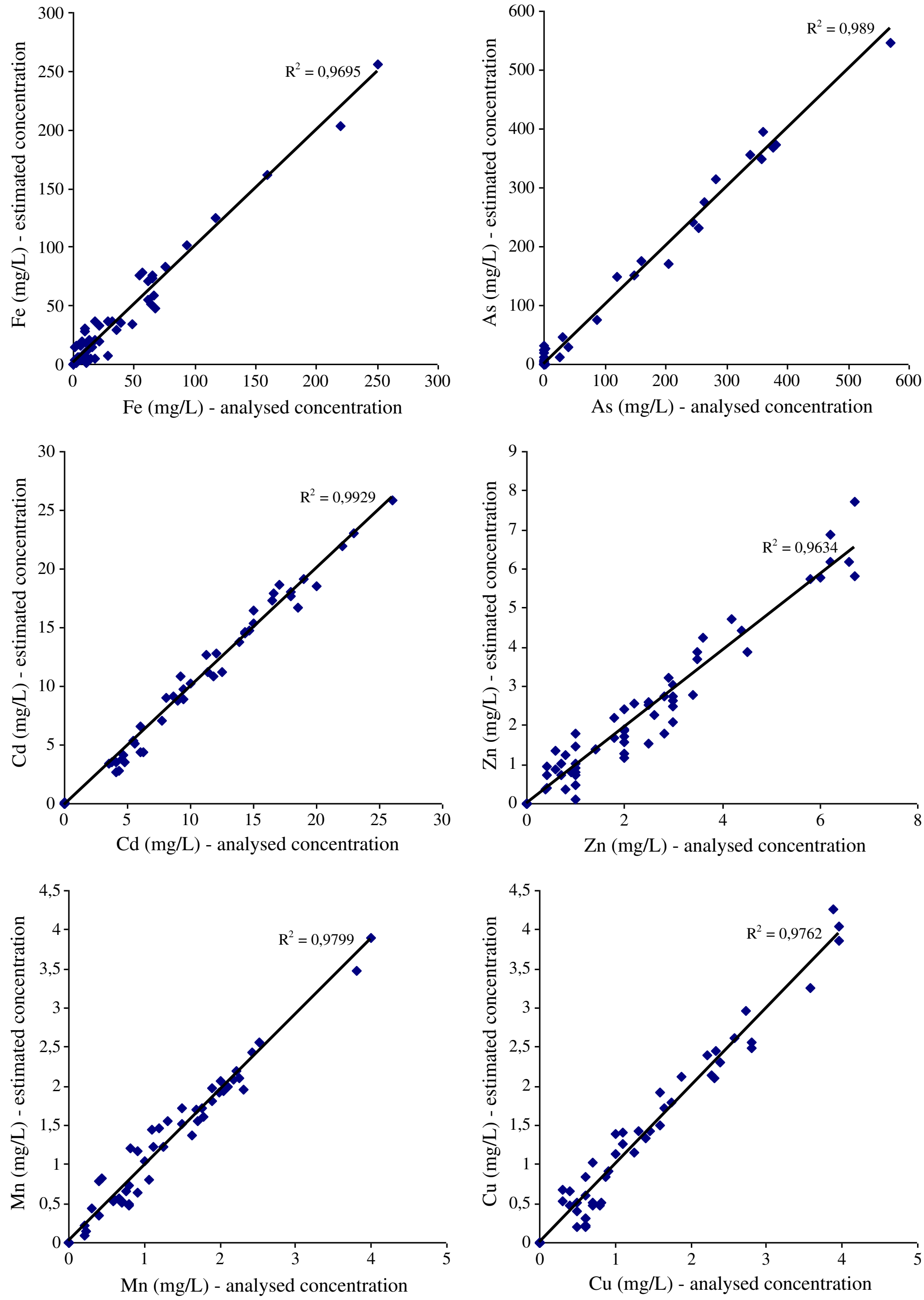

Fig. 7. Estimated concentrations versus real (analyzed) concentrations for testing dataset.

evaluated by comparing the predicted values with the real (analyzed) values for each metal. Fig. 7 represents the estimated concentration against the real concentration for the tested metals.

The analysis of Fig. 7 demonstrates, in general, high Pearson's correlation factors, in the order of 0.99. The lowest values were obtained for Mn and Fe, but even for these the correlations are higher than 0.96.

The results show good ANFIS performance with these types of AMD samples, presenting an expeditious means to deduce metal concentrations from the input parameters (pH, EC, and SO_4).

Generic application of this system to other streams depends on the nature and size of the database, as changes in source and AMD properties must be considered. This is a critical issue to be taken into account when specifying this kind of approach. For instance, in an active mine, AMD hydrochemistry is more variable due to paragenetic changes in ore deposit. This variability should prove more difficult to model. To minimize this difficulty, the training dataset should cover, as much as possible, all situations, namely those regarding climate, geological and paragenetic variations. Nevertheless, the developed model was especially designed for abandoned mines, to which low cost and expeditious monitoring programs are particularly suited. In such cases, AMD is typically controlled by seasonal climate variations, which should be covered by means of daily sampling during a hydrological year.

5. Conclusions

AMD samples are very difficult to analyze due to their complex matrix. Additionally, the presence of iron colloids contributes to their reactivity and often creates chemically heterogeneous systems. These properties impose difficulties in designing appropriate and cost-effective monitoring strategies for the affected rivers.

The developed system offers a simple way to estimate metal concentrations in AMD samples collected in a highly polluted river. This possibility may be used to plan and to implement cost-effective monitoring procedures for this kind of river systems.

Although it was developed for this particular AMD-affected river (Cobica River), the approach may be applied to monitor other aquatic systems provided ANFIS is submitted to the new training data set. This generic application depends on the source and hydrochemical properties of AMD. Therefore, the training dataset should cover, as much as possible, all situations, namely those regarding climate, geological, paragenetic, and hydrological variations.

Depending on the purposes established for monitoring and on the quality control demands, the ANFIS may serve mainly as: i) an expeditious procedure to deduce metal concentrations, avoiding the laboratory analysis of metals; ii) an effective tool to optimize laboratory routines, as it gives a quite reasonable idea of the concentration, which saves time and the use of reagents with these more complex samples.

Acknowledgments

The present study is financially supported by the Spanish Science and Technology Ministry project CICYT REN2002 – 01897/HID. The Portuguese Republic provides funding to the Center of Geological Research, Management and Valorization of Resources through the project PEst-OE/CTE/UI0697/2011, funded by the Foundation for Science and Technology. The authors acknowledge and appreciate the comments and suggestions made by Drs. Dave Craw and Ron Watkins, which have helped to improve the manuscript.

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