Definition of redox and pH influence in the AMD mine system using a fuzzy qualitative tool (Iberian Pyrite Belt, SW Spain)

M. L. de la Torre,[1] **J. A. Grande**,[1] **T. Valente**,[1,2] **E. Perez-Ostalé**,[1] **M. Santisteban**,[1]
J. Aroba,[3] **I. Ramos**[4]

Abstract Poderosa Mine is an abandoned pyrite mine, located in the Iberian Pyrite Belt which pours its acid mine drainage (AMD) waters into the Odiel river (South-West Spain). This work focuses on establishing possible reasons for interdependence between the potential redox and pH, with the load of metals and sulfates, as well as a set of variables that define the physical chemistry of the water—conductivity, temperature, TDS, and dissolved oxygen—transported by a channel from Poderosa mine affected by acid mine drainage, through the use of techniques of artificial intelligence: fuzzy logic and data mining. The sampling campaign was carried out in May of 2012. There were a total of 16 sites, the first inside the tunnel and the last at the mouth of the river Odiel, with a distance of approximately 10 m between each pair of measuring stations. While the tools of classical statistics, which are widely used in this context, prove useful for defining proximity ratios between variables based on Pearson's correlations, in addition to making it easier to handle large volumes of data and producing easier-to-understand graphs, the use of fuzzy logic tools and data mining results in better definition of the variations produced by external stimuli on the set of variables. This tool is adaptable and can be extrapolated to any system polluted by acid mine drainage using simple, intuitive reasoning.

Keywords AMD · Iberian Pyrite Belt · Poderosa Mine · Heavy metals · Fuzzy logic · Water pollution

✉ M. L. de la Torre
mltorre@uhu.es

1 Centro de Investigación para la Ingeniería en Minería Sostenible (CIPIMS). Escuela Técnica Superior de Ingeniería, Universidad de Huelva, Ctra. Palos de la Frontera s/n. 21819. Palos de la Frontera, Huelva, Spain

2 ICT, Institute of Earth Sciences, Pole of the University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

3 Departamento de Tecnologías de la Información. Escuela Técnica Superior de Ingeniería, Universidad de Huelva, Ctra. Palos de la Frontera s/n. 21819. Palos de la Frontera, Huelva, Spain

4 Departamento de Lenguajes y Sistemas Informáticos, Universidad de Sevilla, Seville, Spain

Introduction

The Iberian Pyrite Belt (IPB) (Fig. 1) is located in South-West Spain and is about 230 km long and 30 km wide. It extends from Seville in southern Spain to the western coast of Portugal, crossing the province of Huelva. This province is known for its metallogenic importance, as it contains numerous giant and supergiant massive sulfide ore deposits (Sáez et al. 1999). For this reason, the IPB has long been one of the largest mining regions in the world, exploited since ancient times. The first mining works date back to the Copper Age (Nocete and Linares 1999), which is characterized by the production of copper obtained from carbonates (azurite and malachite), oxides (cuprite and tenorite), and even sulfides (calcosite and covelite) (Sáez et al. 2003). As result of this long, intense activity, the region has numerous abandoned and active mining works that provide an inexhaustible source of acid, sulfates, and heavy metals (Azcue 1994).

This pollution or AMD is produced when a sulfurous mineral finds itself in the presence of oxygen and water. A complex mechanism then occurs on the surface of the mineral, which starts with the oxidation of the sulfur, with heavy metals being released (Fe, Cu, Zn…) and generating sulfates and hydrogen ions. The latter give the water an extremely acidic

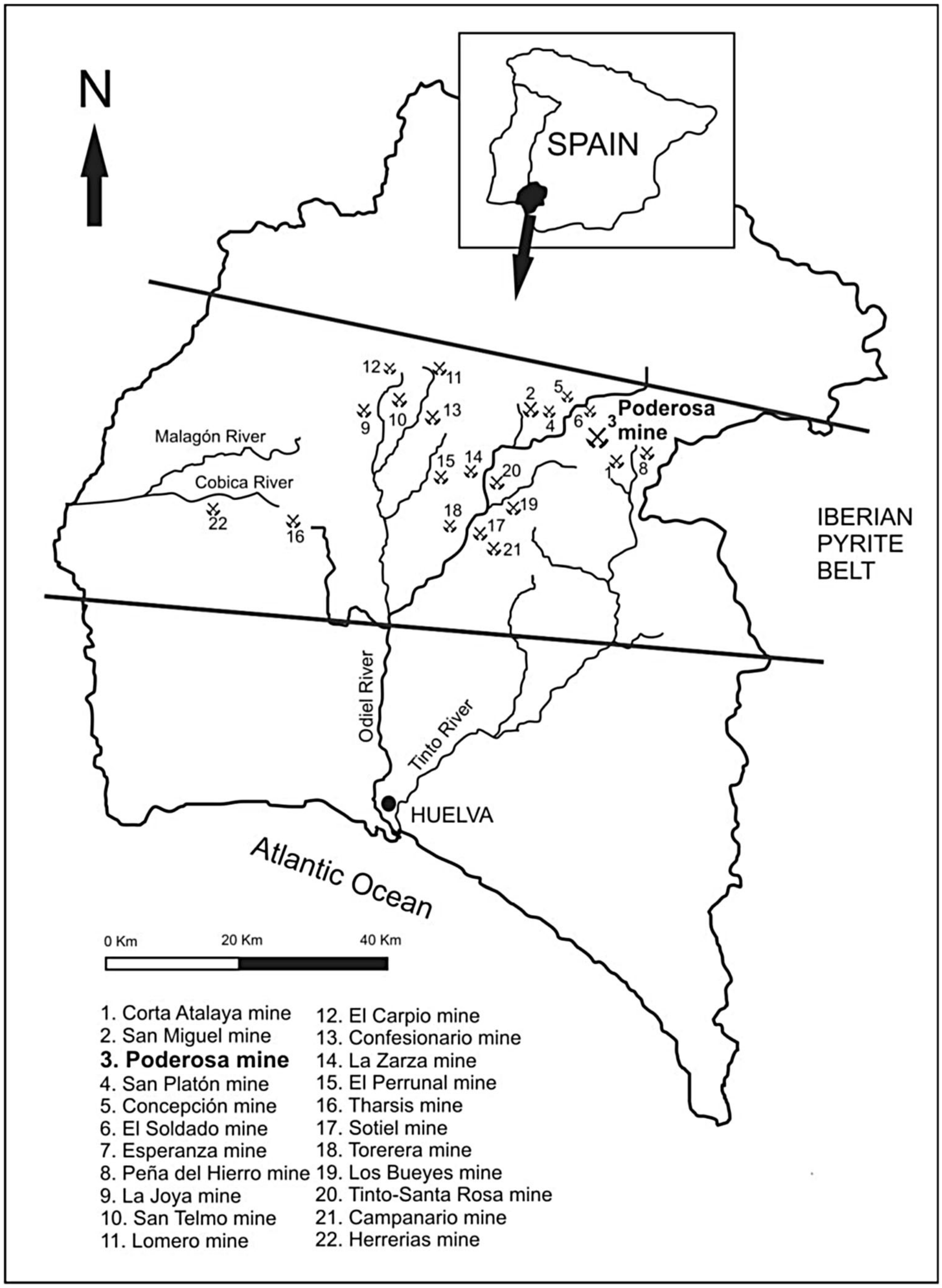

Fig. 1 Location map (modified from Grande et al. 2013)

pH (pH<3). Along with this oxidation, a series of secondary reactions is produced, which affects the constituent elements of the rock (Föstner and Wittmann 1983), with polluting particles finally being obtained that adhere to the surface of the mineral and which are subsequently dissolved by the rainwater and swept into the river beds. Although the kinetics of the reaction is very slow, this can be accelerated by the presence of the ferric ion (Dogan 1999) and by the presence of catalyzing bacteria (Nicholson 1994).

From a hydrological point of view, the Iberian Pyrite Belt is traversed from north to south by the rivers Tinto and Odiel, which are affected by processes of acid mine drainage as a consequence of waste from almost a hundred mines in their catchment areas (Sáinz et al. 2002; Olías et al. 2004; Grande et al. 2005a; Sarmiento et al. 2009). Both rivers meet in the Ría de Huelva (Fig. 1), and their waters flow into the Atlantic Ocean.

The AMD processes undergone by the drainage in the environment of the region have been described extensively by various authors: Aroba et al. (2007); Borrego (1992); Borrego et al. (2002); Borrego et al. (2012); Carro et al. (2011); Braungardt et al. (1998); Davis et al. (2000); de la Torre et al. (2011); Elbaz-Poulichet et al. (1999); Elbaz-Poulichet et al. (2000); Elbaz-Poulichet et al. (2001); Grande et al. (2005a, b); Grande et al. (2010a, b); Jiménez et al. (2009); Leblanc et al. (2000); Sainz et al. (2005).

Poderosa Mine is an abandoned pyrite mine, located in the Iberian Pyrite Belt which pours its AMD-polluted waters into the river Odiel (Grande et al. 2013). The stream under study is approximately 600 m in length. It starts at the Poderosa mine tunnel, which is located 7 km NW of the Rio Tinto mines. Initially, the tunnel provided train communication between the underground mining works and the north slope of the hill (Fig. 2). In the past, mining was performed by combining surface exploitation with underground works (using the room and pillar method) to a depth greater than 250 m. The ore paragenesis presents high levels of copper as chalcopyrite, calcosite, and covelite. The tunnels assured the exit of these minerals, transported further to the city of Huelva (Pinedo Vara 1963). More than 600,000 tons of copper ore was mined between 1864 and 1924 alone. The ore was then processed using leaching techniques. The most obvious and immediately perceptible feature of the Poderosa creek is the strong color change its waters undergo. They emerge almost transparent but rapidly acquire the typical redness of AMD streams.

The objective of this work focuses on establishing possible reasons for interdependence between the potential redox and pH, with the load of metals and sulfates, as well as a set of variables that define the physical chemistry of the water—conductivity, temperature, TDS, and dissolved oxygen—transported by a mining channel affected by acid mine drainage, through the use of techniques of artificial intelligence: fuzzy logic and data mining.

The present work aims to check and validate the results obtained in the study by Grande et al. (2013), in addition to obtaining information that might remain hidden or not be detected using the techniques of classical statistics.

Artificial intelligence (AI) is the intelligence of machines and the branch of computer science that aims to create it. Artificial intelligence has been the subject of optimism but has also suffered setbacks and, today, has become an essential part of the technology industry, providing the heavy lifting for many of the most difficult problems in computer science (Russell and Norvig 2003).

The central problems of AI include such traits as reasoning, knowledge, planning, learning, communication, perception, and the ability to move and manipulate objects (Luger and Stubblefield 2004). General intelligence (or "strong AI") is still a long-term goal of research. Several different forms of logic are used in AI research. Propositional or sentential logic (Russell and Norvig 2003) is the logic of statements which can be true or false. First-order logic (Luger and Stubblefield 2004) also allows the use of quantifiers and predicates and can express facts about objects, their properties, and their relations with each other. Fuzzy logic (Russell and Norvig 2003) is a version of first-order logic which allows the truth of a statement to be represented as a value between 0 and 1, rather than simply True (1) or False (0). Fuzzy systems can be used for uncertain reasoning and have been widely used in modern industrial and consumer product control systems.

Fuzzy logic (Zadeh 1965) operates using reasoning rules which are very close to the human approximate, intuitive way of thinking. The main characteristic of fuzzy logic is that it allows us to define values without specifying a precise value, something which is not possible with classical logic. Fuzzy logic allows us to associate each sample with a certain degree of membership of a set. This degree is called the *membership grade* of the element of the set *S*. The set *X* is called "universe of

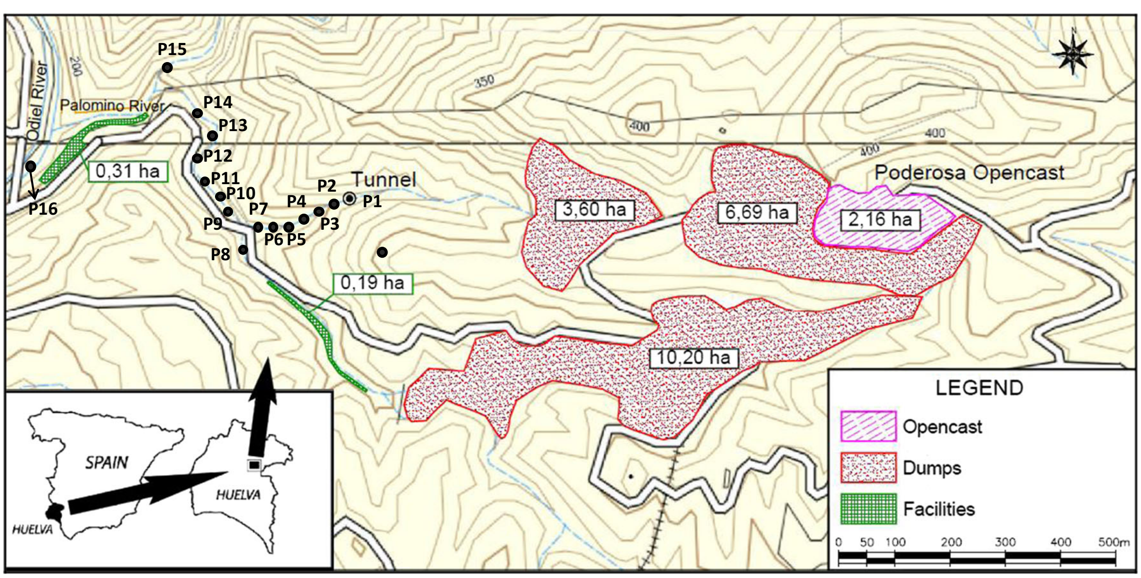

Fig. 2 Representative map of the sampling points (modified from Grande et al. 2013)

discourse" (range of values) of the variable x. The range is from 0 to 1, with each extreme value representing absolute non-membership or membership of the set, respectively. The membership grade may be represented by functions, normally trapeziums, triangles, or sigmoids. For example, let us suppose that measurements of pH in a system have been obtained and the range of values is covered by the interval [2.00–7.00]. Then, the universe of discourse for the variable pH can be covered by, for example, the following fuzzy sets (Fig. 3): very low pH, low pH, and average pH. The fuzzy sets at the extremes are right-angled triangles, and the central set is an isosceles triangle (highlighted in gray for better understanding).

Once all variables involved in a problem are coded to the qualitative domain by means of membership functions, it is possible to write a set of rules representing the relation between input and output variables. These rules are in the format *if-then* and are made up of an antecedent and a consequent; the fulfillment of the antecedent 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 inference even when the condition is satisfied only partially. That is, an *if-then* fuzzy rule can represent imprecise reasoning.

A well-known general-purpose fuzzy-clustering algorithm is the so-called fuzzy c-means (FCM) (Bezdek 1981; Kolen and Hutcheson 2002; Hoppner and Klawonn 2003). It is based on the minimization of distances between two data points and the prototypes of cluster centers (c-means). Basically, this algorithm tries to classify n elements $x_k \in X(1 \le k \le n)$, with p characteristics each one, that is, X(p), into c fuzzy clusters, assigning a membership function, that represents the membership grade of the kth element to the ith cluster:

$$\mu_{ik} \in [0,1], \quad 1 \le i \le c, \quad 1 \le k \le n \tag{1}$$

For this purpose, the algorithm tries to minimize the following cost function J:

$$J(U,P:\ X)\sum_{k=1}^{n}\sum_{i=1}^{c}(\mu_{ik})^m D_{ik}^2 \tag{2}$$

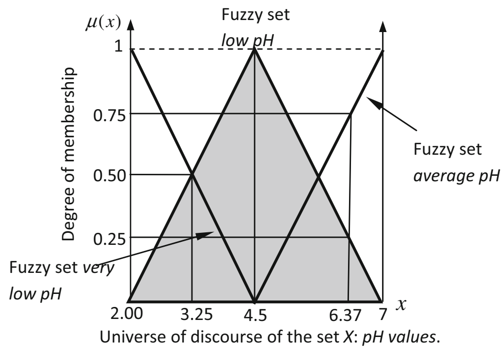

Fig. 3 Example of membership functions used to codify a set of pH values by means of fuzzy logic

Where $U=(\mu_{ik})$ is the membership matrix of X, $P=[v_1, v_2, \ldots, v_c]$ is a vector of cluster center prototypes which must be determined, and $m \in [1,\infty]$ is a weighting exponent which determines the degree of fuzziness of the resulting clusters (in this paper, $m=2$ has been considered) and

$$D^2{}_{ik} = \left|\left| x_k - v_i \right|\right|^2 = (x_k - v_i)^{\mathrm{T}}(x_k - v_i) \tag{3}$$

is the norm used for measuring distances. Finally, the cost function J is minimized to obtain the components of U and P, that is, the membership matrix and the vector of cluster center prototypes. The corresponding equations are as follows:

$$\mu_{ik} = \left[\sum\left[\frac{||x_k - v_i||_A}{||x_k - v_j||_A}\right]^{\frac{2}{m-1}}\right]^{-1} \forall i,k \tag{4}$$

$$v_i = \frac{\sum_{k=1}^{n}(\mu_{ik})^m x_k}{\sum_{k=1}^{n}(\mu_{ik})^m} \forall i \tag{5}$$

This algorithm is used by Sugeno and Yasukawa (1993) to build a fuzzy model based on rules of the form:

$$R^i:\ \text{IF } x_i \in A^i \text{ THEN } y \in B^i \tag{6}$$

where $X=[x_1, x_2, \ldots, x_n] \in \Re^{\mathrm{n}}$ are input variables, $A=[A_1, A_2, \ldots, A_n]$ are n fuzzy sets, $y \in \Re$ is the output variable, and $B=[B_1, B_2, \ldots, B_m]$ are m fuzzy sets.

Materials and methods

With the aim of achieving the objective set out, at the end of the rainy season (May 2012), and following a brief period of precipitation, when the tunnel carried a volume of water close to 10 L/s, the first step was marking the sites, measuring and sampling the waters along the river from its source to its mouth (Fig. 2). There were a total of 16 sites, the first inside the tunnel and the last at the mouth of the river Odiel, with a distance of approximately 10 m between each pair of measuring stations. Two sites were also sampled corresponding to the points where two tributaries entered the river being studied, with point 8 corresponding to the first tributary with waters from industrial installations in the mine, and point 15 located on a tributary carrying water from other lower level installations, which do not form part of the Poderosa Mine and in which the water shows characteristics that are clearly different from those of the river in the study and less affected by AMD. Point 16 corresponds to our river a few meters before the confluence with the less-affected tributary (Fig. 2) (Grande et al. 2013).

Both pH and conductivity were measured in situ during the campaign, three consecutive times to avoid reading errors. A CRISON 507 pH-meter and a CRISON 524 conductimeter were used. The rest of the physical parameters were measured using a Hydrolab Quanta portable probe. Following this, a duplicate sample was taken at each reference point; the first of them to determine the sulfate content and the second to determine the metal content, in this case acidulating with 1 % HNO_3, to preserve it correctly and avoid precipitation of the metals. Both were transported in 100-mL polyethylene containers and kept refrigerated at 4 °C in a portable icebox until they arrived at the laboratory, with the analytical work being started immediately once the samples were received at the laboratory.

All the reagents used were analytical grade or of Suprapur quality (Merck, Darmstadt, Germany). Merck AA Certificate solutions were used in all experiments as stock or standard solutions. Milli-Q water (Millipore, Bedford, MA) was used in all the experiments.

The equipment used to carry out the analysis of the metals was a Perkin-Elmer AAnalyst 800-model atomic absorption spectrophotometer equipped with a hydride generator and an air/acetylene flame atomizer. The introduction of the samples was carried out using the Perkin-Elmer AS800-model automatic injector. Hollow cathode lamps were used as sources of radiation. Duplicate analyses were performed to guarantee the accuracy of the measurement.

The sulfates were determined using ionic chromatography with chemical suppression (Standard Methods, 4110). A duplicate of each of the analyses was carried out to guarantee the accuracy of the measurement.

Results

The data from the analytics were processed using the Predictive Fuzzy Rules Generator (PreFuRGe) software tool (Aroba 2003), which allows us to obtain an immediate qualitative analysis of the information contained in the resulting volume of data.

Figures 4 and 5 present, using fuzzy rule graphs, the behavior of the redox potential and pH, respectively, against the other variables corresponding to the concentrations of sulfates, Cu, Zn, Mn, Ni, Pb, As, Sb, Fe(II), Fe(III), conductivity, TDS, T, and DO. In these cases, we are discussing the pH and redox potential as "consequents." The universe of discourse of each variable, i.e., the values that the variables can take, has at its extreme values the maximum and minimum that were obtained analytically.

Figure 4 shows the values taken by the various parameters, with the redox potential as the consequent. It is worth highlighting that Cd, Ni, As, Sb, sulfates, conductivity, and TDS behave similarly in a manner which mirrors the redox, i.e., when the redox presents extreme high values, these parameters are found to have extreme low values and as the redox decreases, the parameters referred to increase in value, are always very concentrated, and are grouped tightly together, until the redox reaches an extreme low value, at which time these parameters are found to be extreme high, very concentrated values. As regards Fe(II) and Fe(III), these share similar behavior in terms of the variations in the redox potential, i.e., as the redox decreases, the values of these parameters increase, but when redox takes extreme low values, Fe(II) and Fe(III) take medium to medium-high values. As for pH and DO, these have a similar evolution to redox, except for those times when the latter presents extreme high values, at which these two parameters are only found with low values for DO and extreme lows for pH. In the case of Zn and Al, no relation is noticed with the variations in redox potential. When the latter presents extreme low values, both cations can have practically any value. However, in all other cases, both Zn and Al are found with maximum concentration values. As for Mn, it behaves similarly to the redox potential except for when the redox potential presents an extreme low value, when Mn presents low concentration values.

Figure 5 shows the values that all the parameters can take, in this case as the consequence of pH. It is observed that Cd, Ni, Sb, conductivity, and TDS present some relation with pH, with their concentrations decreasing as pH increases. This fact is clearest in the case of Ni. On the other hand, As, Fe(II), Fe(III), DO, and sulfates increase their concentrations as pH increases, although we must specify that when pH is at its extreme high, these metals do not reach their maximum value but rather the concentrations remain at medium values, and sulfates even drop to low-extreme low values, all within the range of values obtained in the analytics for each parameter, as commented previously. In terms of Cu, Zn, Mn, and Pb, these do not appear to be affected by the increase or decrease in the values of pH.

Discussion

From the previous results, we can gather that, in the case of Cd, Ni, and Sb, TDS presents similar behavior against the variations in pH and redox potential, though inverse, i.e., when the values of pH or EC increase, the concentration of these metals decreases.

On the other hand, Fe(II) and Fe(III) and sulfates have completely inverse behavior with regard to redox potential and pH, increasing in concentration when redox potential decreases and when pH increases and remaining at medium values when redox is at an extreme low and when pH is at an extreme high. This might be explained by the fact that the extreme high pH values happen to be 3.04 and 4.0, which is the pH at which Fe(II) oxidizes to Fe(III) and subsequently

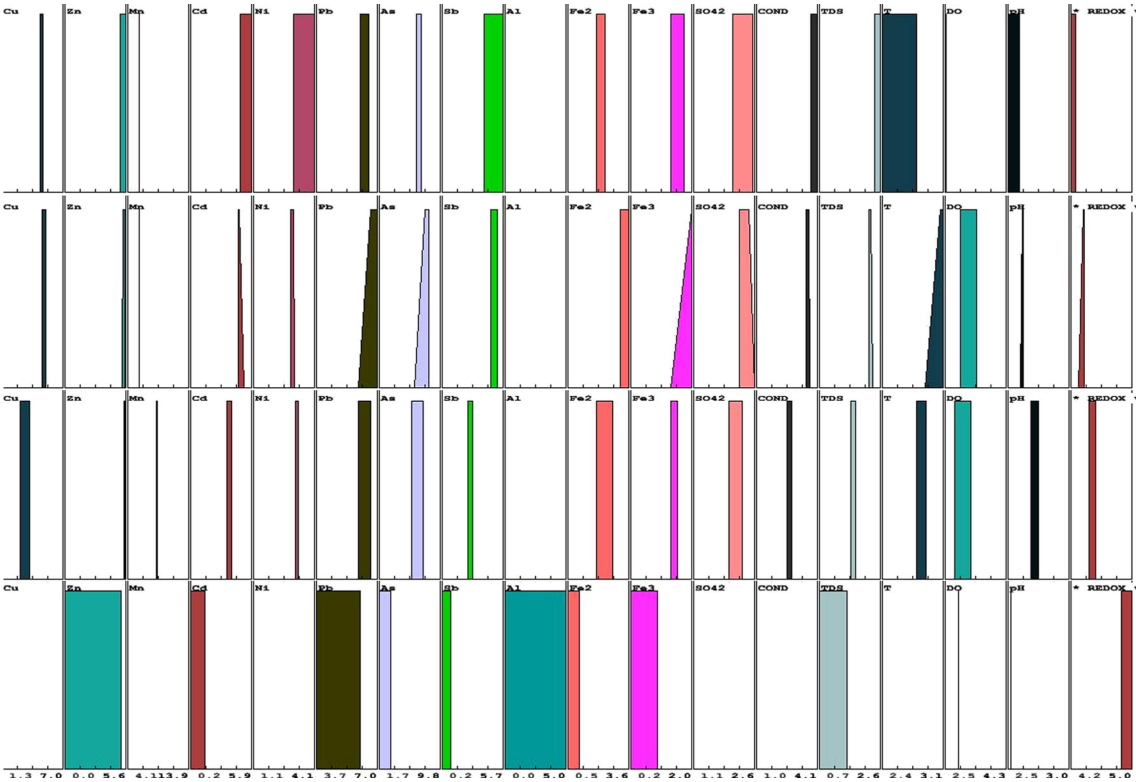

Fig. 4 Fuzzy rule graphs, the behavior of redox potential against the other variables

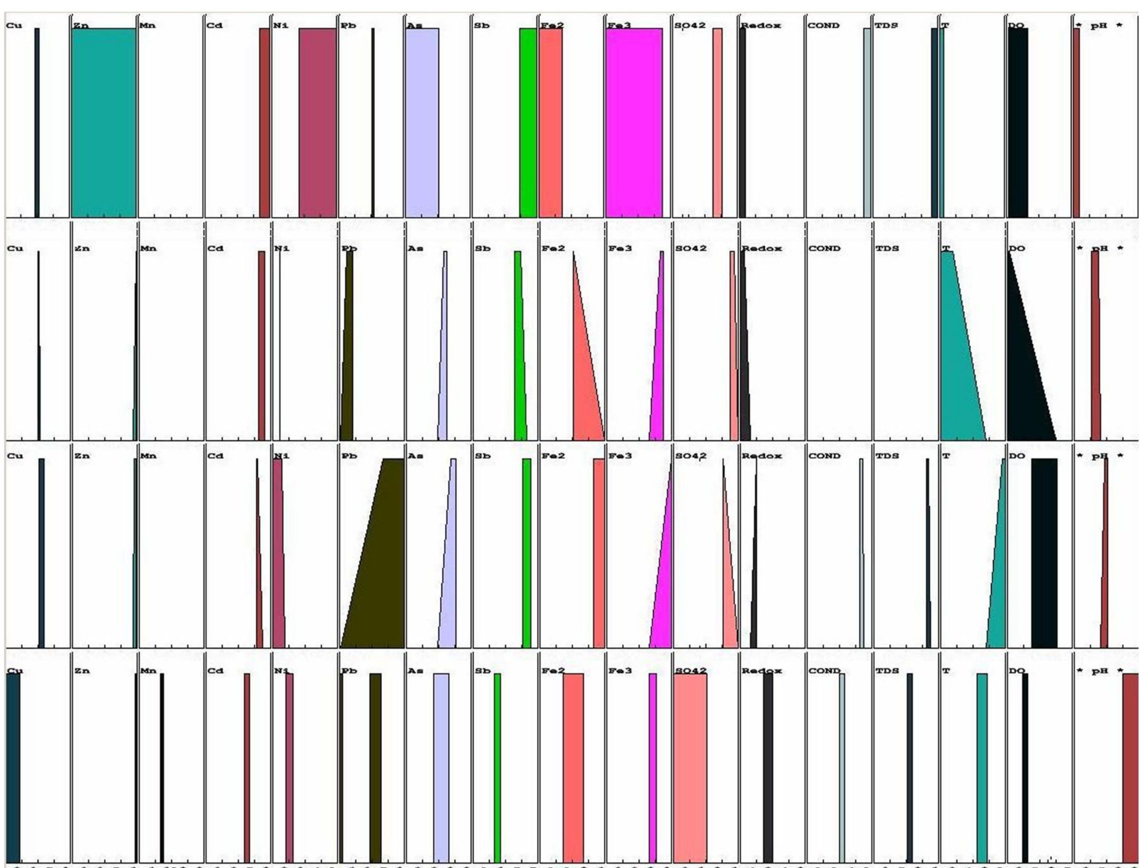

Fig. 5 Fuzzy rule graphs, the behavior of the pH against the other variables

precipitates as ferric oxy-hydroxy-sulfates (Asta et al. 2010). The values taken by As can be explained by the sorption of As to the solid phases of Fe. This process includes the oxidation of Fe(II) followed by the hydrolysis and precipitation of Fe(III) in the form of schwertmannite (Sánchez España et al. 2006). During these stages, trace elements are totally or partially sorbed and/or coprecipitated at different rates depending basically on pH, as well as on the activity of the SO_4=anion (which determines the speciation of metals) (Sánchez España et al. 2006)

Conclusions

The application of fuzzy logic techniques to characterize hydrochemical processes in the same sector and based on the same volume of data as those used in the work by Grande et al. (2013) allows the working models previously proposed using classical statistics to be expanded upon. In this way, not only can it be established if a parameter is related to another but to what extent they are related based on their development throughout the range of the variable.

While the tools of classical statistics, which are widely used in this context, prove useful for defining proximity ratios between variables based on Pearson's correlations, in addition to making it easier to handle large volumes of data and producing easier-to-understand graphs, the use of fuzzy logic tools and data mining results in better definition of the variations produced by external stimuli on the set of variables (Aroba et al. 2007).

This tool is adaptable and can be extrapolated to any system polluted by acid mine drainage using simple, intuitive reasoning.

Acknowledgements The study is a contribution to the DGCICYT-CGL2010-21268-C02-01 project, which is financed by the Spanish Ministry of Education and Science, and the Andalusian Autonomous Government Excellence Project, code P06-RNM-02167.

References

Aroba, J (2003) Avances en la toma de decisiones en proyectos de desarrollo de software. PhD Thesis, University of Sevilla, Spain

Aroba J, Grande JA, Andújar JM, de la Torre ML (2007) Application of fuzzy logic and data mining techniques as tools for qualitative interpretation of acid mine drainage processes. Environ Geol 53(1):135–145

Asta M, Ayora C, Román-Ross G, Cama J, Acero P, Gault A, Charnock J, Bardelli F (2010) Natural attenuation of arsenic in the Tinto Santa rosa acid stream (Iberian pyritic belt, SW Spain): the role of iron precipitates. Chem Geol 271:1–12

Azcue JM (1994) Introducción al tratamiento de Series Temporales. Aplicación a las Ciencias de la Salud, Diaz de Santos, Madrid

Bezdek JC (1981) Pattern recognition with fuzzy objective function algorithm. Plenum Press, New York

Borrego J (1992) Sedimentología del estuario del Río Odiel, Huelva, S.O. España. PhD Thesis. Univ. of Sevilla

Borrego J, Morales JA, de la Torre ML, Grande JA (2002) Geochemical characteristics of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). Environ Geol 41:785–796

Borrego J, Carro B, López-González N, de la Rosa J, Grande JA, Gómez T, de la Torre ML (2012) Effect of acid mine drainage on dissolved rare earth elements geochemistry along a fluvial-estuarine systems: the Tinto-Odiel estuary (SW Spain). Hydrol Res 43(3):262–274

Braungardt CB, Achterberg EP, Nimmo M (1998) Behaviour of dissolved trace metals in the Rio Tinto/Río Odiel Estuarine System. In: European Land-Ocean Interaction Studies, Second Annual Scientific Conference: Abstracts 51, eds. Morales, J.A., Borrego, J

Carro B, López-González N, Grande JA, Gómez T, Valente T (2011) Impact of acid mine drainage on the hydrochemical characteristics of the Tinto-Odiel estuary (SW Spain). J Iberian Geol 37(1):87–96

Davis RA Jr, Welty AT, Borrego J, Morales JA, Pendón JG, Ryan JG (2000) Rio Tinto estuary (Spain): 5000 years of pollution. Environ Geol 39:1107–1116

de la Torre ML, Grande JA, Graiño J, Gómez T, Cerón JC (2011) Characterization of AMD pollution in the river Tinto (SW Spain). Geochemical comparison between generating source and receiving environment. Water Air Soil Poll 216:3–19

Dogan PA (1999) Characterization of mine waste for prediction of acid mine drainage. In: Azcue JM (ed) Environmental impacts of mining activities. Springer, Berlin

Elbaz-Poulichet F, Morley NH, Cruzado A, Velasquez Z, Achterberg EP, Braungardt CB (1999) Trace metal and nutrient distribution in an extremely low pH (2.5) river-estuarine system, the Ria of Huelva (south-west Spain). Sci Total Environ 227:73–83

Elbaz-Poulichet F, Dupuy C, Cruzado A, Velasquez Z, Achterberg E, Braungardt C (2000) Influence of sorption processes by iron oxides and algae fixation on arsenic and phosphate cycle in an acidic estuary (Tinto river, Spain). Water Res 34(12-15):3222–3230

Elbaz-Poulichet F, Braungardt C, Achterberg E, Morley N, Cossa D, Beckers J, Nomérange P, Cruzado A, Leblanc M (2001) Metal biogeochemistry in the Tinto-Odiel rivers (Southern Spain) and in the Gulf of Cadiz: a synthesis of the results of TOROS project. Cont Shelf Res 21(18-19):1961–1973

Föstner U, Wittmann GTW (1983) Metal pollution in the aquatic environment. Springer-Verlag. Berlin

Grande JA, Beltrán R, Sáinz A, Santos JC, de la Torre ML, Borrego J (2005a) Acid mine drainage and acid rock drainage processes in the environment of Herrerías Mine (Iberian Pyrite Belt, Huelva-Spain) and impact on the Andevalo dam. Environ Geol 47:185–196

Grande JA, Andújar JM, Aroba J, de la Torre ML, Beltrán R (2005b) Precipitation, pH and metal load in AMD river basins: an application of fuzzy clustering algorithms to the process characterization. J Environ Monit 7:325–334

Grande JA, Andújar JM, Aroba J, Beltrán R, de la Torre ML, Cerón JC, Gómez T (2010a) Fuzzy modelling of the spatial evolution of the chemistry in the Tinto river (SW Spain). Water Res Manag 24:3219–3235

Grande JA, Andújar JM, Aroba J, de la Torre ML (2010b) Presence of As in the fluvial network due to AMD processes in the Rio Tinto mining area (SW Spain): a fuzzy logic qualitative model. J Hazard Mat 176(1-3):395–401

Grande JA, de la Torre ML, Santisteban M, Valente T, Fernández JP, Perez E (2013) Spatial evolution of an AMD stream in the Iberian Pyrite Belt: control factors on the hydrochemistry. Hydrol Sci J. doi: 10.1080/02626667.2014.983515

Hoppner F, Klawonn F (2003) A contribution to convergence theory of fuzzyc-means and derivatives, IEEE Trans. Fuzzy Syst 11(5):682–694

Jiménez A, Aroba J, de la Torre ML, Andújar JM, Grande JA (2009) Model of behaviour of conductivity versus pH in A.M.D. water bases on fuzzy logic and data mining techniques. J Hydroinform 11(2):147–153

Kolen JT, Hutcheson T (2002) Reducing the time complexity of the fuzzy c-means algorithm, IEEE Trans. Fuzzy Syst 10(2):263–267

Leblanc M, Morales JM, Borrego J, Elbaz-Poulichet F (2000) 4.500 year-old mining pollution in Southwestern Spain: long-term implications for modern mining pollution. Econ Geol 95:655–662

Luger, G.; Stubblefield, W. (2004). Artificial intelligence: structures and strategies for complex problem solving (5th ed.). The Benjamin/Cummings Publishing Company, Inc.. ISBN 0-8053-4780-1

Nicholson RV (1994) Iron-sulfide oxidation mechanism en White AF, Brantley RJ (eds Chemical weathering rates of silicate minerals Mineralogical Society of America, Env In Mineralogy 31, 173-225)

Nocete F, Linares JA (1999) Las primeras sociedades mineras en Huelva Alosno. En: Historia de la provincia de Huelva. Cap 4:50–64

Olías M, Nieto JM, Sarmiento AM, Cerón JC, Cánovas CR (2004) Seasonal water quality variations in a river affected by acid mine drainage: the Odiel river (south west Spain). Sci Total Environ 333: 267–281

Pinedo Vara I (1963) Piritas de Huelva. Summa, Madrid, 1003p

Russell SJ, Norvig P (2003) Artificial intelligence: a modern approach (2nd ed.). Upper Saddle River, NJ: Prentice Hall, ISBN 0-13-790395-2

Sáez R, Pascual E, Toscano M, Almodóvar GR (1999) The Iberian type of volcano-sedimentary massive sulphide deposits. Miner Deposita 34:549–570

Sáez R, Nocete F, Nieto JM, Capitán MA, Rovira S (2003) The extractive metallurgy of copper from Cabezo Juré, Huelva, Spain: chemical and mineralogical study of slags dates to the third millenium BC. Can Mineral 41:627–638

Sáinz A, Grande JA, de la Torre ML, Sánchez-Rodas D (2002) Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers. J Environ Manage 64(4): 345–353

Sainz A, Grande JA, de la Torre ML (2005) Application of a systemic approach to the study of pollution of the Tinto and Odiel rivers (Spain). Environ Monit Assess 102:435–445

Sánchez España J, Lopez Pamo E, Santofimia E, Reyes J, Martín JA (2006) The removal of dissolved metals by hydroxysulphate precipitates during oxidation and neutralization of acid mine waters, Iberian Pyrite Belt. Aquat Geochem 12(3):269–298

Sarmiento AM, Nieto JM, Casiot C, Elbaz-Poulichet F, Egal M (2009) Inorganic arsenic speciation at river basin scales: the Tinto and Odiel rivers in the Iberian Pyrite Belt, SW Spain. Environ Pollut 157: 1202–1209

Sugeno M, Yasukawa A (1993). A fuzzy-logic based approach to qualitative modeling. IEE trans. Fuzzy Syst 1:7–31

Zadeh LA (1965) Fuzzy sets. Inf Control 8:338–353