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Presence of As in the fluvial network due to AMD processes in the Riotinto mining area (SW Spain): A fuzzy logic qualitative model

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ABSTRACT

The Tinto River crosses the mining area of Riotinto (Iberian Pyrite Belt, SW Spain), where it receives the highest contribution of contaminants (AMD). In this paper we apply a fuzzy computer tool, PreFuRGe, which allows qualitative interpretation of the data recorded in a database relating to the chemistry of water. Specifically, we aim to find information not likely to be detected by means of classical statistical techniques, and which can help in characterizing and interpreting the behavior of arsenic in a complex system. The conclusions present that the factors which most directly control the presence of total dissolved As are closely linked to the climate and are temperature and rainfall, and therefore pH. As (III) is also shown to be related to temperature and pH. In terms of temperature As (V) is found to operate in a way which is the opposite of As (III). In terms of pH the relationship is not as clear as for As (III). As for rain, the highest As (V) values are compatible with minimum or non-existent rainfall, while minimum values correspond to any value for rainfall, including very high.

1. Introduction

Geologically the Riotinto mining area is located in the Iberian Pyrite Belt in the SW of Spain (Fig. 1) and covers an area of more than 4000 ha affected by extractive and mining processing activity, which has altered the surroundings over more than 2000 years of history. This intense activity has led to the presence of large areas of slag heaps of varying granulometry and composition linked to the presence of complex sulfur compounds which [1] calculate to be more than 9 million tonnes, and which, since they have not been restored, continue to cause acid mine drainage (AMD) in response to precipitation. They have also caused large areas full of acid waters to appear, such as open pit mines, abandoned mines, and a number of dams and reservoirs, used initially for other purposes and which now store waters from a great variety of sources with the common denominator of extremely high levels of AMD pollution.

AMD processes are among the most hazardous types of water pollution due to their nature, extent and the difficulty of solving them [2] as well as the economic costs of remediation. Rivers affected by this type of contamination are characterized by their acidity, as well as the high sulfate and heavy metal content in their waters, and by the metal content of their sediments. The damage caused ranges from sub-lethal alterations for some individuals in the affected ecosystems, in the cases of very low pollution, with associated problems of bioaccumulation and biomagnification [3], to the disappearance of the river fauna, and the loss of water resources as the water becomes useless for human, agricultural or industrial use [4].

The Tinto River rises in the surroundings of Peña del Hierro Mine, where it is contaminated from the very beginning, and some hundred metres downstream it crosses the mining area of Riotinto, where it receives the highest contribution of contaminants. It flows further south, already very affected by AMD, along 80 km to its mouth in the Atlantic Ocean. This watershed has a drainage area of 700 sq. km and not only gathers leachates from mine dumps as a major AMD source, but, in the case of the Riotinto mining area, also receives water from various underground and open-air exploitations. The largest volumes of acid waters stored are to be found in the Cerro Colorado and the Atalaya open pit mines.

Both open pit mines (Fig. 1) are hydraulically connected to each other by means of a complex system of galleries, and especially by means of two large drains, Tunnel 11 or the Main tunnel, which joins the Alfredo shaft directly to the Cerro Colorado, and Tunnel 16 which used to transport the mineral from the Atalaya open pit mine to Naya to be treated in the Zarandas complex. This phenomenon also involves a process of diverting the basin of the river Odiel, which frames the Atalaya open pit as the center of production to that of the river Tinto, by means of the aforementioned tunnel 16.

The Tinto constitutes an exceptional case due to the values that the physical–chemical parameters of its waters reach as a

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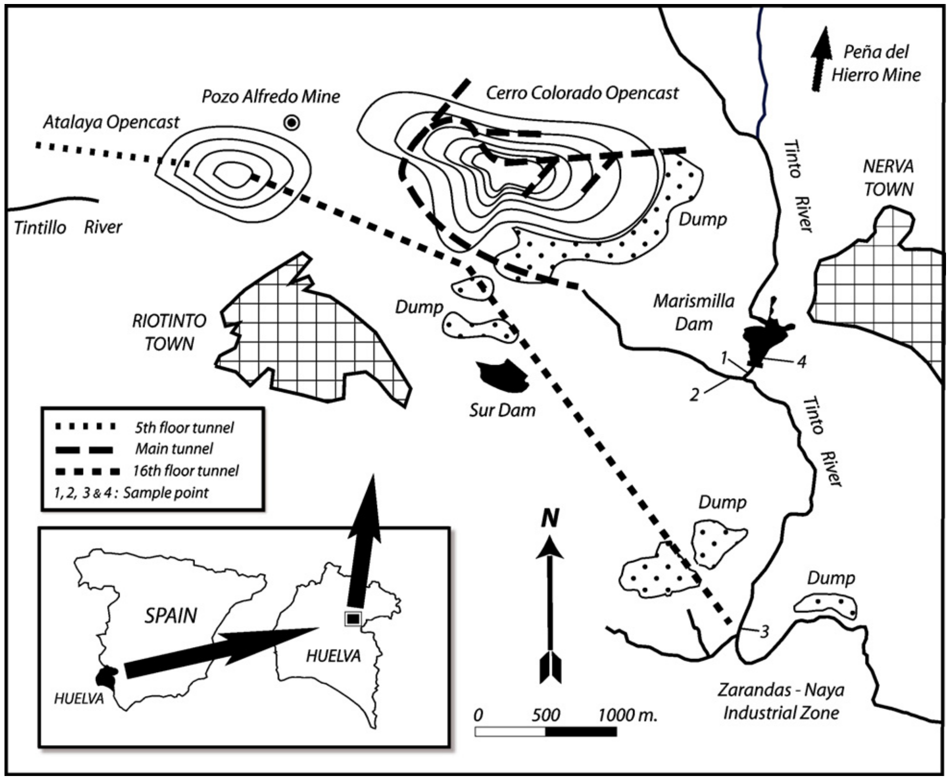

Fig. 1. Location map.

consequence of the AMD processes undergone by the drainage network in the regional surroundings, in the riverbeds affected by the Riotinto Mine complex. The phenomenon has been described extensively, by a number of authors such as [5–24] among others. In this context, the potential centers and activities involved in the contaminating process are: mine dumps, spontaneous or forced drains, crushing, washing, natural cementation, artificial cementation (heaps of ore roasted or calcined in situ and known as "teleras"), smelting, roasting which are described in detail by [12,18].

Since its birth [25] and first applications to modeling [26] and control [27] fuzzy logic (see Annex A) has achieved a great deal of success, primarily in the fields of control, modeling and industrial applications [28–31,43].

In this paper we apply a fuzzy computer tool, PreFuRGe [39] (see Annex A) which allows qualitative interpretation of the data recorded in a database relating to the chemistry of water. Specifically, we aim to find information which is apparently hidden and not likely to be detected by means of classical statistical techniques, and which can help in characterizing and interpreting the behavior of arsenic in a complex system. The authors have demonstrated that this computer tool is capable of providing interpretations of the behavior of variables in complex systems, which were not visible using classical statistical analysis of the measurements [18,19,23,29,30,32,33].

Arsenic constitutes an especially undesirable element in water from an eco-toxicological point of view. In the EU the maximum permissible concentration in drinking water is 10 μg/L. In riverbeds which undergo AMD processes the occurrence of concentrations far above these limits is commonplace. For the river Tinto [34] describe values of 550 μg/L [22], 2290 μg/L [24], 2000 μg/L [35] and 1800 μg/L. These high concentrations translate ultimately into discharges of As into the Atlantic which exceed 53 tonnes/year [16].

2. Materials and methods

The central objective of this work is essentially to establish possible reasons for interdependence between the presence of As and a group of variables in the area of the headwaters of the river Tinto, all as a result of AMD processes. These variables are: pH, conductivity, temperature, time of sampling, precipitation, redox potential, Cd, Cu, Fe, Zn, Mn, SO_4. These reasons for interdependence might serve as a basis for establishing an operating model for production of As in a fluvial system.

In order to achieve this objective the sampling point which appears in Fig. 1 was chosen. The choice of this point is justified by the fact that a series of effluents originating from various centers converge at it and in turn, correspond to a variety of paragenesis within the complex deposit defined as "supergiant" [36]. At the same time, this point is above the possible influence that the presence of a toxic waste dump might have on the chemistry of the river Tinto. This dump was set up in 1998 immediately to the south within a watershed which connects with the Tinto downstream from our sampling point.

The reference point was sampled from 22/09/07 until 31/05/08 throughout the period the riverbed carried water in the hydrological year 2007/2008, with a total of 215 samples, corresponding to one for every day of sampling.

Both pH and conductivity were measured in situ during the operation, three times consecutively to avoid errors in reading. A CRISON n° 507 pH meter and a CRISON n° 524 conductivity meter were used. Subsequently, duplicate samples were taken at the reference point; the first to determine the sulfate content and the second to determine the metal content, in this case acidulating with 2% HNO_3 to preserve them correctly and to avoid metallic precipitation. Both were transported in 100 mL polyethylene containers and refrigerated in a portable icebox at 4 °C until they reached the laboratory.

Table 1
Statistical summary of the studied variables.

		Recount	Mean	Variance	Minimum	Maximum	Range	Bias	Curtosis
Hour		215	0.4	0.0007	0.34	0.5	0.17	1.23	2.69
pH		215	2.3	0.0149	1.7	3	1.3	−0.86	10.11
Cond	mS/cm	215	9.67	3.788	3.4	12.57	9.17	−1.10	1.15
Temperature	°C	215	12.4	7.6560	6	20	14	0.46	−0.63
Redox pot	mV	215	466.03	208.551	419	513	94	−0.097	0.54
Cd	$mg\,l^{-1}$	215	1157.61	88155	183.2	2386	2202.8	−0.303	4.12
Cu	$mg\,l^{-1}$	215	326.53	8901.09	49.99	625.1	575.11	0.070	0.77
Fe	$mg\,l^{-1}$	215	1348.42	278812	290	3042	2752	0.33	−0.606
Zn	$mg\,l^{-1}$	215	248.18	3646.83	43.76	43.76	560.4	2.067	10.03
Mn	$mg\,l^{-1}$	215	95.26	713.8	10.08	235	224.92	1.14	5.59
SO_4	$mg\,l^{-1}$	215	7800.94	1.69E7	55	15100	15045	−0.59	−0.96
Precipitation	mm	215	2.36	58.12	0	64.8	64.8	5.01	30.34
As total	$\mu g\,l^{-1}$	215	1877.03	875774	134.6	4259	4124.4	0.588	−0.154
As III	$\mu g\,l^{-1}$	215	110.62	829.49	41.18	225.31	184.13	0.614	1.9
As V	$\mu g\,l^{-1}$	215	317.37	283.02	105.4	1201.55	1096.15	2.44	6.46

2.1. Reactives and apparatus

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

Analyses of metals in the water samples were performed using an AAnalyst 800 atomic absorption spectrophotometer (PerkinElmer, Norwalk) equipped with a graphite furnace and a hydride generator. The instrumental setup employed for the As speciation analysis is based on the use of liquid chromatography (HPLC), hydride generation (HG) and inductively coupled plasma-mass spectrometry (ICP-MS). The procedure proposed by [34] for separating As species in AMD environments was followed.

2.2. Analytical procedures

a. Metal analysis: the concentrations of metals in water were determined by means of atomic absorption spectrometry, using FAAS (Fe, Cu, Mn and Zn). Each of the analyses was repeated in order to guarantee the precision of the measurement.
b. Determining sulfates, conductivity, total solids dissolved and solids in suspension: the sulfates were determined by means

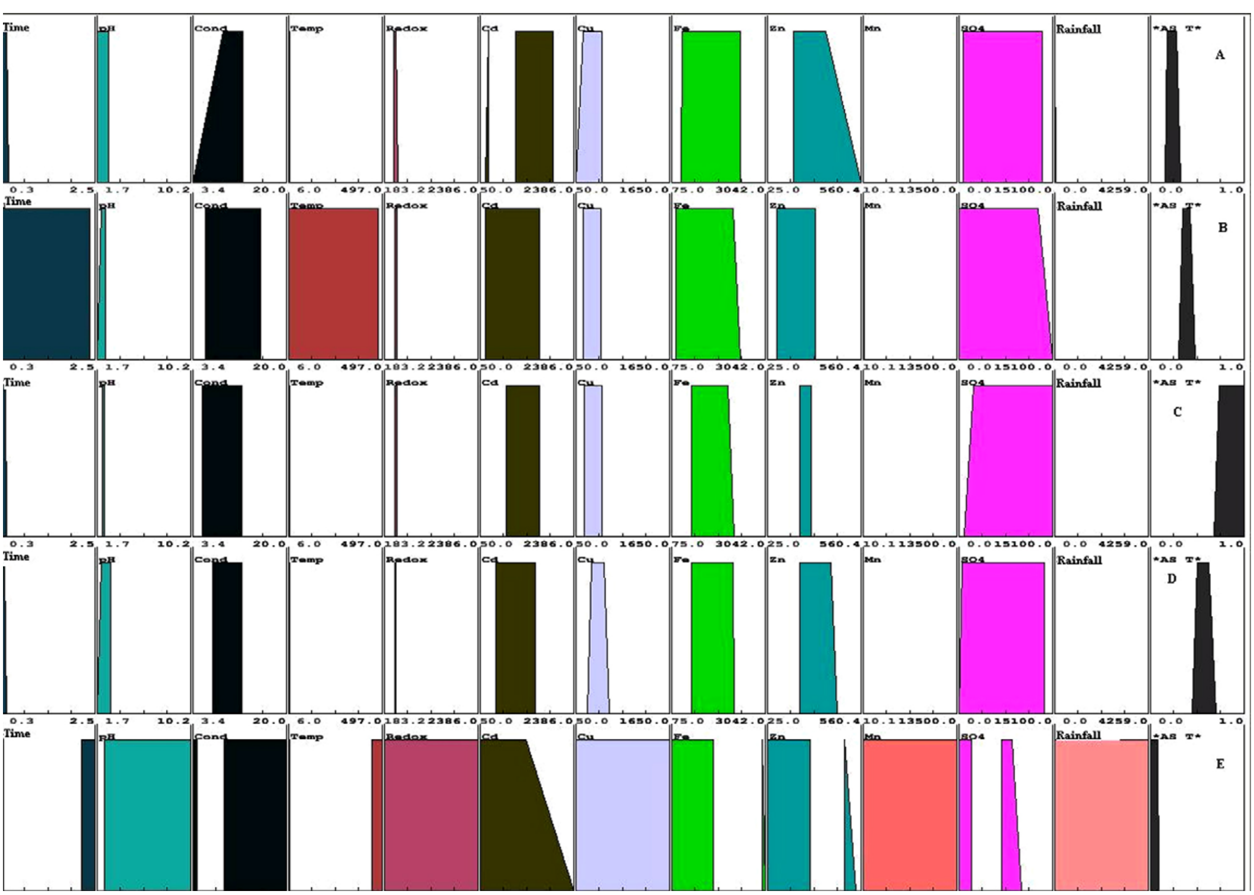

Fig. 2. Example of membership functions to codify by fuzzy logic a set of pH.

of ionic chromatography with chemical suppression (Standard Methods, 4110). Each of the analyses was repeated in order to guarantee the precision of the measurement.

2.3. Graphical-statistical processing

The next step was to obtain a statistical summary of variables by applying STATGRAPHICS Centurion Software to obtain an initial approximation of knowledge of the variables.

The high number of samples analyzed, which are indispensable for observation of cause–effect relationships in AMD processes in view of the immediacy of certain reactions following rain episodes [18] suggest the use of fuzzy logic as an advanced tool for interpreting this type of phenomenon and especially for attempting to model the process correctly (see Annex A).

3. Results

The statistical summary of the variables (Table 1) shows values which are characteristic of riverbeds that undergo AMD processes [12,13,16,17,19,21–24,34,35].

The average values of the variables for the 215 samples taken at the same point give pH values of 2.3, conductivity 9.6 mS/cm, P. redox 466 mV, concentrations of sulfates 7800 mg/L, Fe > 1300 mg/L, Cu > 326 mg/L, Zn > 248 mg/L and As > 0.110 mg/L. These average values are the result of isolated maximums which exceed 3000 mg/L for Fe, 560 mg/L for Zn, 15,000 mg/L for sulfates, and peaks above 4.2 mg/L for As.

The results of applying the PREFURGE tool [39] are shown in Figs. 2 and 3, which present the behavior of As at the sampling point by means of graphical fuzzy rules, compared with the rest of the variables corresponding to the concentrations of sulfates and metals determined analytically in the laboratory, the pH, the time of sampling, the rainfall that day and the temperature all considered together.

The universe of discourse for each variable has as extreme values the maximum and minimum which appear in Table 1 (the statistical summary). Examination of the fuzzy rules taking total As + As III + As V as consequent shows the following.

Figure 2 shows the total As as consequent and the rest of the variables as antecedents, including As III and As V. The following compatibility reasons can be observed in it.

Extremely low total As (Fig. 2e) appears when the times of sampling are later and the temperature is very high. Sulfates appear in very concentrated form in very low or average values. pH, redox, Mn, Cu and Cd can have any value. Only very low to average values for Fe. It is worth pointing out that any value measured for Mn only occurs alongside lower values for total As. Fig. 2a–d shows that Mn values are zero for the rest of the total As value bands. It is also observed that extremely low As values are compatible with the presence of rain, whatever the value. Note that although the redox potential for these very low total As values is not significant as it can have any value, for the rest of the total As values (Fig. 2a–d) redox appears extremely concentrated and the four lines have analogous, low values.

Average to very high total As (Fig. 2c and d) only occurs when there is no Mn and it does not rain, and the temperature, pH and the time of sampling have extremely low values. A specific, very low value for redox and a low value for Cu, average values for Cd, Fe, Zn, and any value for sulfates.

Low total As (Fig. 2a) occurs when rainfall is extremely low, just like the time, pH and temperature. Conductivity is average to low

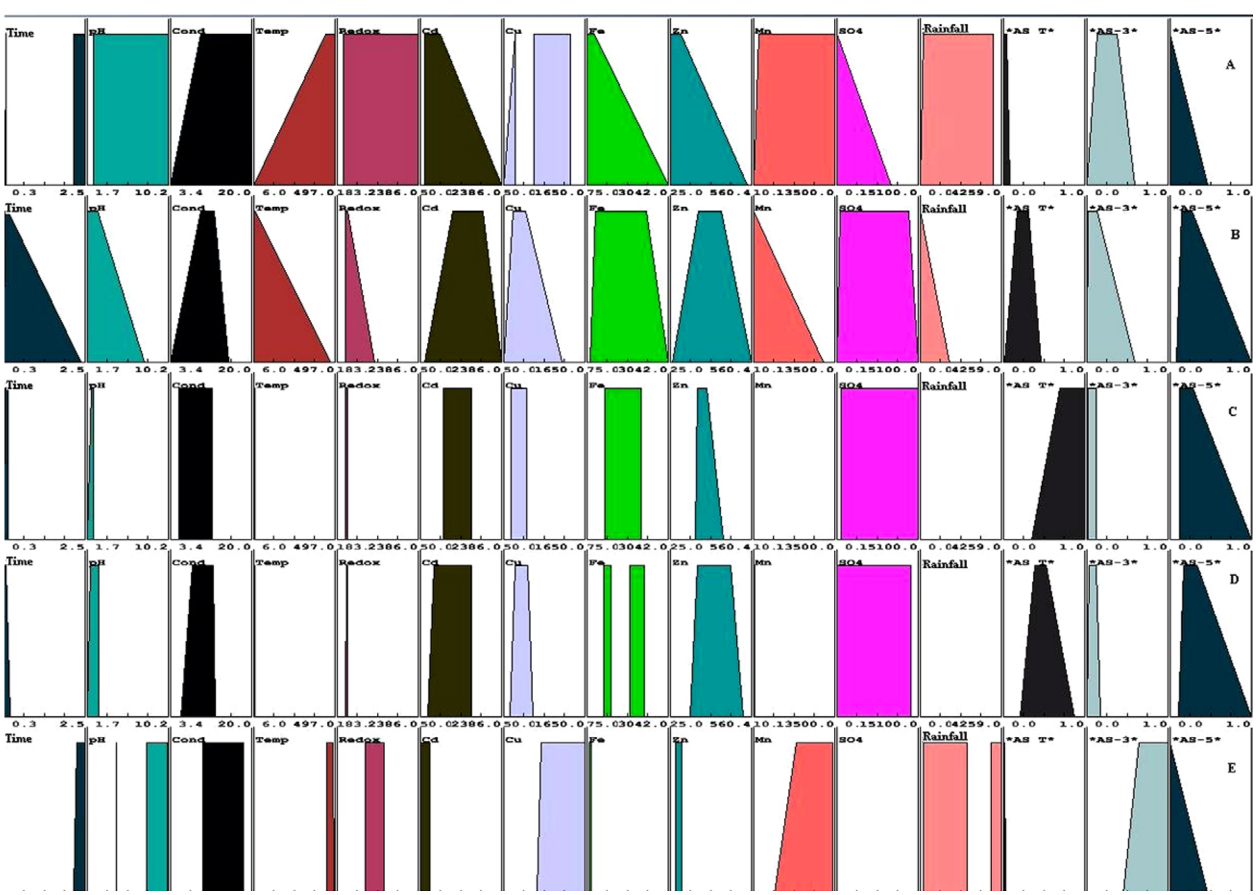

Fig. 3. Example of graphical fuzzy rules.

and Cu is low, and at the same time redox is very concentrated at low values. There are average values for Fe and Zn and sulfates can have any value.

Average-low total As (Fig. 2b) occurs for similar values to the above, but in this case it can happen at any time. In terms of the functioning of the temperature–total As pairing, it is observed that we can have average values for total As at any temperature, while for extremely high temperatures the total As has very low values (Fig. 2e). On the other hand, when the total As is extremely high, the temperature is very low. The temperature in turn presents behavior identical to that for the time of sampling.

Figure 3 shows the total As, As III and As V together as consequents, and the rest of the variables as antecedents. The following observations prove clear from it.

Very low total As values, low As III and low to very low As V (Fig. 3a) are compatible with any value for rainfall, pH, Mn and redox. They prove equally compatible with average to very low values for sulfates, Fe, Zn and Cd. Conductivity and temperature have any value except extremely low.

Low total As values, low to very low As III and any value for As V except very low (Fig. 3b) are compatible with low to very low rainfall and redox values and essentially low to very low values for time and temperature.

Average to very high total As values, very low As III and low to very high As V (Fig. 3c and d) are compatible with: complete absence of rainfall, complete absence of Mn, average values for Fe, Zn, Cd and conductivity, extremely low temperatures and early sampling times, with extremely low pH, as well as low redox at a very specific value. Conversely, sulfates can have any value.

Extremely low total As values, high As III and low to average As V (Fig. 3e) can occur with almost any rainfall value, but only with extremely low values for Zn, Fe, and Cd, at the same time as extremely high values for pH, sampling time and temperature, while Cu, Mn and conductivity have average to high values and there can be no sulfates.

Observing all the lines together reveals that As III follows behavior similar to Cu, with both of them varying evenly (Fig. 3a–e). At each value for As III in each line there can be different values for As V and total As. As V behaves just like Fe and Zn.

As III is heavily influenced by pH, in such a way that only at very low pH can we find little As III, or in other words, this species will on average be more abundant for high pH values within the range of both variables. Let us remember that the maximum pH for the 251 samples is 3.0.

4. Discussion and conclusions

In the case of this work the values measured correspond to a point clearly located in an AMD-producing environment due to its proximity to slag heaps and abandoned mines. In this context the average, maximum and minimum values for the variables analyzed match those determined for riverbeds of this type by a variety of authors [16,17,19,21–24,34].

The proposals for procedures put forward by [34] based on data-processing using classical statistics were tested for this river, while at the same time the applicability of the PREFURGE tool was again validated, and with it fuzzy logic techniques for qualitative modeling of water-contaminating processes (easily interpretable from visual analysis of the graphs shown in Figs. 2 and 3).

The obvious relationship between water temperature and sampling time is easily interpretable as a result of the relationship of dependence between both, indeed samplings carried out early in the morning will give a clearly lower temperature reading than those performed in the afternoon after many hours of sunshine. In turn, rainfall and pH reveal parallel and almost identical levels of variation as already reported by [18], for AMD environments based on large quantities of data.

4.1. Total As behavior

Figs. 2 and 3 reveal that the factors which most directly control the presence of total dissolved As are closely linked to the climate and are temperature and rainfall, and therefore pH. It is obvious that this hypothesis is conditioned by the mineral paragenesis of the deposit and in this case by the layout and mineralogy of the slag heaps and centers of AMD production. If there is no As available in the environment, it cannot be dissolved.

Indeed, the total As is at its highest (Fig. 2c) when the temperature is very low, there is no rainfall and the pH stays very low, concentrated and at a very specific value. The total As is at its lowest when the temperature is at its highest and the rainfall and pH can have any value (Fig. 2e).

The presence of total As is very closely linked to pH, as might be expected in environments of this type affected by AMD processes [4]. Thus, very high total As values are only compatible with extremely low pH levels (Fig. 2c).

4.2. As III behavior

As III is also shown to be related to temperature and pH: the higher the temperature, the greater the presence of As III, with extremely high pH (Fig. 3e). Rainfall also conditions the process; the minimum As III values seen in Fig. 3c–d are only possible when there is no rainfall, just as suggested by [34] and also [24]. The pH for these values also remains restricted to minimum values of extreme acidity.

As III follows behavior which is almost identical to Cu and very similar to Mn, with both controlled by pH, which in turn depends on rainfall.

4.3. As V behavior

As V is found to operate in a way which is the opposite of As III in terms of temperature. For this species, once again confirming the hypothesis put forward by [34] the highest temperatures (Fig. 3e) only make the existence of very low As V values possible. In terms of pH the relationship is not as clear as for As III. As for rain, the highest As V values are compatible with minimum or non-existent rainfall, while minimum values correspond to any value for rainfall, including very high.

As V follows very similar behavior to Cd, Fe and Zn, with certain similarity to sulfates.

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Appendix A. Annex A

A.1. Fuzzy logic

Fuzzy logic [25] 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. In classical logic, membership of one class or set is binary, i.e., one is either a member or not, so that only two precise values are used (1 and 0, yes or no). This way, for example

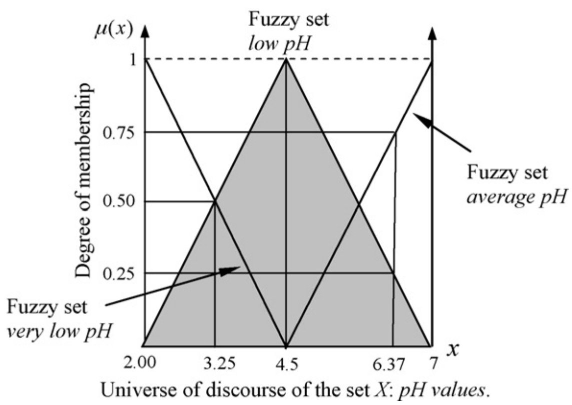

Fig. A.1. Graphic fuzzy rules for qualitative behavior of As total as opposed the rest of variables.

if it is defined for specific samples the set "pH very low", is evident that a sample with pH = 2 belongs to the set, and another sample with pH = 6 does not belongs, but ¿how can we classify a sample with pH = 4.2? In the answer to this kind of questions is where the classical logic shows its limitations, and is where the fuzzy logic shows its better qualities.

Fuzzy logic allows us to associate each sample with a certain degree of membership of a set. This degree is called the *membership grade* μ_s (x) of the element $x \in X$ of the set S. The set X is called "universe of discourse" (range of values) of the variable x. The range of μ_s it 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. A.1): *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). Then, as an example, the expression: *the pH of the sample is average*, is true with a grade of 0.75 for a sample with pH = 6.37. However, for the same sample, the expression *the pH of the sample is low* is true with a grade of 0.25. Note that, an element can belong to more than a one fuzzy set simultaneously and, also, with a different membership grade in each case. This is a very important characteristic when it is necessary to group and/or classify elements (samples for example).

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. For example: *IF x is A THEN y is C* or *IF x is A and z is B THEN y is C*, where *A*, *B* and *C* are fuzzy sets; and *x*, *y* and *z* are variables defined in their respective universes of discourse. The first rule has a single antecedent, and the second has a compound antecedent.

A.2. Fuzzy c-means algorithm

Classical clustering algorithms generate a partition of the population in such a way that each case is assigned to a cluster [42]. These algorithms use the so-called *rigid partition* derived from classical set theory: the elements of the partition matrix obtained from the data matrix can only contain values 0 or 1; with zero indicating null membership and one indicating whole membership. Fuzzy partition is a generalization of the above, holding the same conditions and constraints for its elements, except that in this case real values between zero and one are allowed (partial membership grade). Therefore, samples may belong to more than one cluster, so that the selecting and clustering capacity of the samples increases.

A well-known general-purpose fuzzy-clustering algorithm is the so-called fuzzy c-means (FCM) [37,40,41]. 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, $X \subset \Re^p$, into c fuzzy clusters, assigning a membership function μ_{ik}, that represent the membership grade of the kth element to the ith cluster:

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

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

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

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

$$D_{ik}^2 = ||x_k - v_i||^2 = (x_k - v_i)^T (x_k - v_i) \tag{E.3}$$

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:

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

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

This algorithm is used by Sugeno and Yasukawa in [38] to build a fuzzy model based on rules of the form:

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

where $X = [x_1, x_2, \ldots, x_n] \in \Re^n$ 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.

A.3. The computer tool PreFuRGe

PreFuRGe (predictive fuzzy rules generator) [39], it is a data mining computer tool based on the previously described methodology [38], and represented by (E.6). This initial methodology has been adapted and improved in the following aspects:

1. It allows working with quantitative databases with n input and m output variables.
2. The different target variables can be weighted for the calculation of distances between points in the space being partitioned.

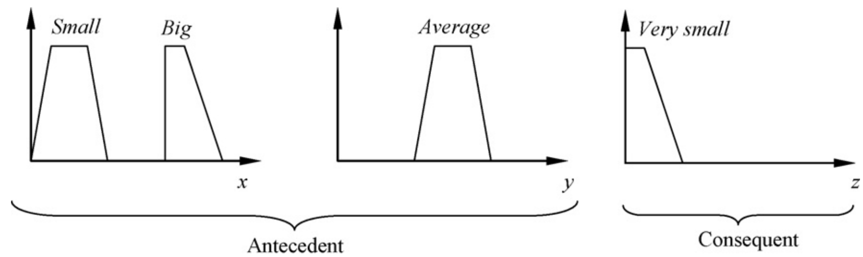

Fig. A.2. Graphic fuzzy rules for qualitative behavior of As total, As III and As V as opposed the rest of variables.

3. The achieved fuzzy clusters are processed to obtain the usual approximations by trapeziums (Fig. A.2).
4. An algorithm processes and solves cases of multiple projections in the input space (mounds) (Fig. A.2: antecedent *x*).
5. An algorithm automatically provides the interpretation of the graphic fuzzy rules in natural language. For example, the fuzzy rule of the Fig. A.1 can be interpreted as follows:

   IF *x* is small or big and *y* is average THEN *z* is very small.

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