Impact of AMD processes on the public water supply: hydrochemical variations and application of a classification model to a river in the Iberian Pyritic Belt S.W. Spain

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ABSTRACT

The aim of this work is to formulate a rapid method for finding out the degree of water pollution in the field, based on the toxicity produced by sulfates and metals dissolved in solution, using simple pH measurement in rivers that undergo AMD processes and which flow into public water supply dams. A classification model based on the degree of the impact is proposed, which is applied to a river affected by AMD in the Iberian Pyritic Belt, and which might serve as a reference for other dams that have to tolerate the arrival of mine water. Application of the proposed method will allow the approximate state of the water quality to be learned by simply measuring its pH. This may prove very useful during the design of hydrochemical control networks. Weighting and standardizing values allows the relative extent of the pollution to be quantified simply, still within the framework of the permitted limits for the public water supply, while the proposed graphical representation makes it significantly easier to understand the phenomenon and proves useful for comparing temporal or spatial variations over the course of a river.

Key words | acid mine drainage, drinking water, heavy metals

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INTRODUCTION

European Council directive 98/83/CE of 3 November 1998 on the quality of water intended for human consumption, defines the minimum requirements that must be met by continental surface waters intended for human consumption, for all member countries in the European Union, restricting the use of such waters based on their composition. However, according to this standard lower quality water may be used in exceptional cases if appropriate treatment is used, including mixing, which allows the quality of the water to be raised.

AMD processes

The acidity of water is a conditioning factor of its capacity to dissolve metals, with this being higher, the lower the pH. The sources responsible for an increase in acidity in natural waters are drainage from mines, industrial dumping and acid rain, with mining activity being the biggest contributor from a global point of view.

This type of pollution is produced when a sulfurous mineral comes into contact with oxygen and atmospheric humidity (USEPA 2006), a complex mechanism then starts on the surface of the mineral, beginning with oxidization of the sulfides, transforming them into sulfates with acid production. The kinetics of this oxidation by oxygen is very slow, between 1.08×10^{-15} and 1.8×10^{-14} mol/(cm^2 s), while it is possible for this rate to increase up to a hundred times in the presence of ferric ions (Dogan 1999) and the action of catalyzing bacteria (Nicholson 1994). Finally, along with the oxidation of pyrite, secondary reactions are produced between the products of the previous reactions and the remaining minerals present in the rock

(Förstner & Wittmann 1983), with the final result being a set of soluble pollutants deposited on the mineral, which are subsequently dissolved and swept away by rain or run-off water, producing a pollutant liquid torrent which carries its acidity, sulfates and heavy metals into water courses.

The costs of restoring the damage produced by mining are estimated at between two and five billion (10^9) dollars for Canada (Feasby & Reamblay 1995), with the latter sum what is estimated to remedy the state of Pennsylvania alone (Commonwealth of Pennsylvania 1994); the world-wide costs are estimated at more than ten billion dollars (Weatherell *et al.* 1997), although at present in the United States, the mining industry spends more than a million dollars every day on treating these acid effluents due to the fact that, according to data from the U.S. Bureau of Mines, past mining activity has already affected more than 20,000 km of water courses in the United States.

The seriousness of the pollution caused by heavy metals is based on three fundamental factors: (1) They are not bio-degradable, so they remain in the environment indefinitely, unless transported to other environments; (2) they can be retained by organic tissues through bioaccumulation and then transmitted to other species in a higher level of the trophic chain, thus causing biomagnification (Nebel & Wright 1999); (3) heavy metals can either be essential for life or not. Some of them such as copper, zinc and manganese are necessary micronutrients for some plants and animals, but they can become lethal above certain concentration levels (Begon *et al.* 1999). However, organisms need these metals at an optimal level, below which conditions of want appear and above which we find toxicity (Sáinz *et al.* 2002).

In Europe, the fluvial network appears intensely affected by AMD processes in the Iberian Pyritic Belt (S.W. Spain), where the proposed classification which is the object of the present work is applied. These processes have been extensively described by various authors: Amils (2006), Andújar *et al.* (2006), Aroba *et al.* (2007), Azcue (1999), Borrego (1992), Borrego *et al.* (2002), Braungardt *et al.* (1998), Cabrera *et al.* (1992), Cruzado *et al.* (1998), Davis *et al.* (2000), de la Torre *et al.* (2009), Elbaz-Poulichet *et al.* (1996, 2000, 2001), Fernández-Rubio & Lorca (1993), Grande *et al.* (2000, 2003a, b, 2005a, b), Jiménez *et al.* (2009), Leblanc *et al.* (2000), Loredo *et al.* (2008), Nelson & Lamothe (1993), Nieto *et al.* (2007), Sáinz *et al.* (2002, 2003a, b, 2004), Sarmiento *et al.* (2009) and Younger *et al.* (2002).

AMD and public water supply dams

The occurrence of AMD phenomena in rivers which contribute their waters to dams intended for urban supply leads to waters arriving in these reservoirs with low pH and a high metal and sulfate load, as in the case of the rivers Cobica and Odiel in S.W. Spain (Figure 1).

The Odiel river is the principal river that crosses the Iberian Pyritic Belt with more than a hundred mining exploitations in its drainage area and a riverbed around 100 km in length (Figure 1). The Alcolea dam, which is currently under construction, will have a capacity of 274×10^6 cubic meters and will supply water to more than a million inhabitants, with it being installed close to the mouth of the river Odiel 5 km from the zone of tidal influence.

So, we find ourselves faced with a process of acid mine water with its corresponding metal load being contributed to a public water supply reservoir. We might suppose that when these contributions of mine water reach the reservoir a sharp increase will be produced in the pH of the acid waters in view of the large volume of the watershed, and that this rise in pH will translate into a violent reduction in the dissolving capacity of the mixing waters, which will result in precipitation in the reservoir itself of most of the metal load transported by the mine water. In any case, the metal precipitates will accumulate in the form of sediment at the bottom of the dam, still remaining subject to the variations in pH in the environment (Grande *et al.* 2005a).

MATERIALS AND METHODS

In essence the aim of this work is to formulate a rapid method for finding out the degree of water pollution in the field, based on the toxicity produced by sulfates and metals dissolved in solution, using simple pH measurement
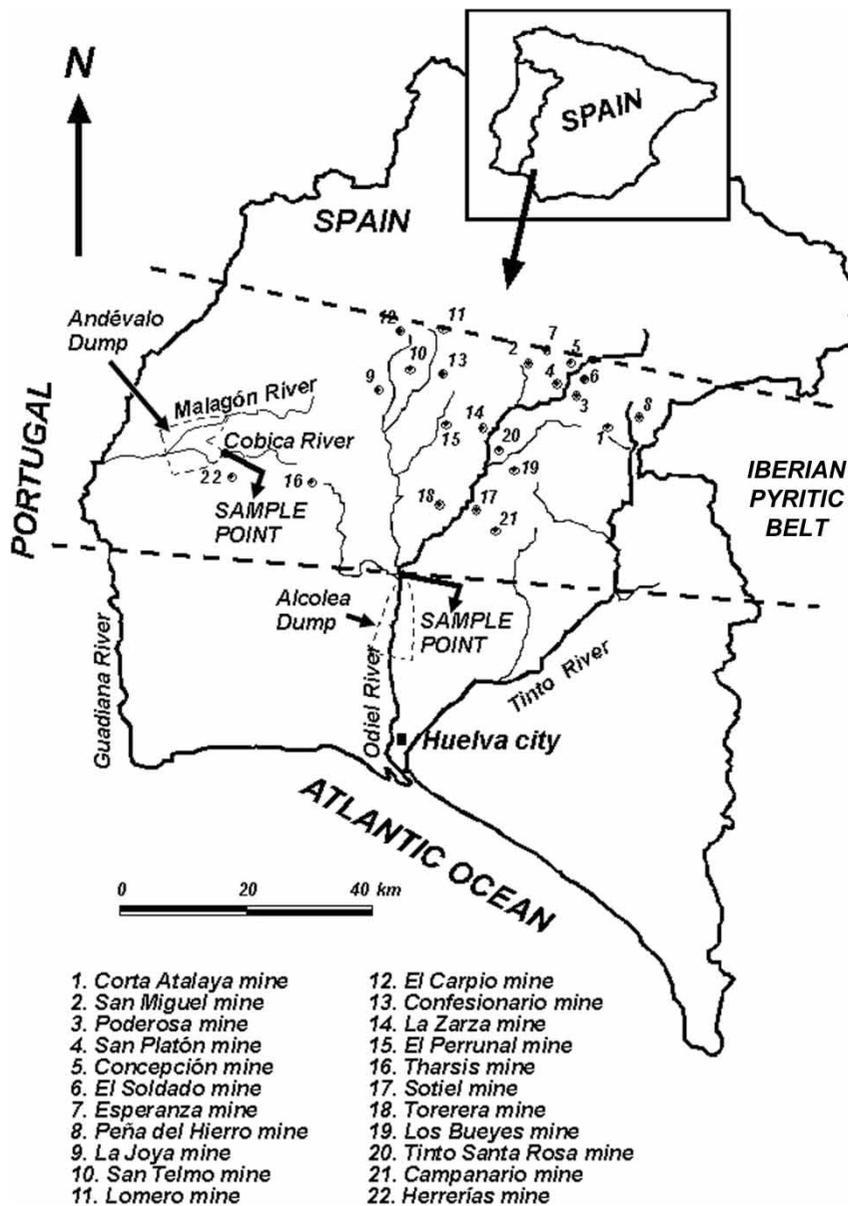
1. Corta Atalaya mine
2. San Miguel mine
3. Poderosa mine
4. San Platón mine
5. Concepción mine
6. El Soldado mine
7. Esperanza mine
8. Peña del Hierro mine
9. La Joya mine
10. San Telmo mine
11. Lomero mine
12. El Carpio mine
13. Confesionario mine
14. La Zarza mine
15. El Perrunal mine
16. Tharsis mine
17. Sotiel mine
18. Torerera mine
19. Los Bueyes mine
20. Tinto Santa Rosa mine
21. Campanario mine
22. Herrerías mine

Figure 1 | Location map.

in rivers which undergo AMD processes and which flow into public water supply dams.

A classification model based on the degree of the impact is proposed, which is applied to a river affected by AMD in the Iberian Pyritic Belt, and which might serve as a reference for other dams that have to tolerate the arrival of mine water.

If we accept as our starting point that the dissolved metal load is a function of pH, taking the work by Gray (1996) as a reference for a 'standard' river (Table 1), then we can discover, after measuring the pH in the field, the maximum and minimum values 'in situ' for every metal present at that precise point in the river for the pH measured, paying special attention to those metals present in the mineral parageneses of the deposits in the basin, that prove more undesirable from the point of view of eco-toxicology. Using this, after simple measurement of pH in the field we can

Table 1 | Water-quality ratings in AMD waters

pH	Sulfate (mg/L)	Iron (mg/L)	Zinc (mg/L)	Alumninum (mg/L)	Copper (mg/L)	Cadmium (µg/L)
>6.5	100–199					
5.9–6.1	300–399					
5.6–5.8	400–499					
5.2–5.5	500–599					
4.9–5.1	600–799	<0.05				
4.5–4.8	800–999	0.05–0.99				
4.1–4.4	1,000–1,499	1–4.99				
3.9–4	1,500–1,999	5–9.99	<0.05			
3.7–3.8	2,000–3,999	10–24	0.05–0.49			
3.5–3.6	4,000–5,999	25–49	0.5–0.9	<1		<10
3.3–3.4	6,000–7,999	50–99	1–4.9	1–4.9		10–24
3.1–3.2	8,000–9,999	100–149	5–9.9	5–9.9	<0.05	25–49
2.9–3	10,000–11,999	150–199	10–24	10–24	0.05–0.99	50–99
2.7–2.8	12,000–13,999	200–249	25–49	25–49	1–4.9	100–249
2.5–2.6	14,000–15,999	250–499	50–74	50–99	5–9.9	250–499
2.3–2.4	16,000–17,999	500–749	75–99	100–299	10–24	500–749
2.1–2.2	18,000–19,999	750–999	100–249	300–799	25–49	750–999
1.8–2	20,000–21,999	1,000–1,999	250–499	800–1199	50–99	1,000–1,499
1.5–1.7	22,000–24,999	2,000–2,999	500–749	1,200–1,999	100–249	1,500–1,999
<1.4	>25,000	>3,000	>750	>2,000	>250	>2,000

Modification proposed by Gray (1996).

have an idea of the level of impact on the river being studied.

The different concentration levels usually presented by pollutants in mine water can exceed 3,000 mg/L in the case of iron, and reach up to 30,000 mg/L in the case of sulfates, while other elements present in the parageneses of sulfides, such as As or Cd, which are highly soluble in these acid waters, scarcely exceed a few µg/L, with levels usually between 10 and 100 times lower than those mentioned above.

However, the greater toxicity of As, Cd or Hg suggests that some kind of weighting tool needs to be designed for the 'weight' that each metal carries in determining the degree of water pollution due to its concentration and degree of toxicity. In this regard, Directive 98/83/CE defines, for all member countries in the European Union the maximum permissible concentration values for pollutants in dams intended for the supply of drinking water (Table 2).

Based on this, a simple weighting formula is proposed which allows the level of seriousness of the impact suffered by a river to be diagnosed for each pollutant by measuring the pH in situ, reading the average values for each pollutant for the specific pH in Gray's table (1996), and then defining a weighted value for the concentration that corresponds to the number of times that this parameter exceeds the limit established by the EU for the public water supply (Table 2).

This same table also shows, in our case, the values determined analytically in the laboratory for the sample taken at the same point and time the pH was measured. It is shown that the levels of concentration are within those proposed by Gray (1996).

Based on these values we can propose impact indices such as 'none, moderate, average, high, and extremely high' and assign them standardized values between 0 and 5 based on the number of times the water sample exceeds the limit imposed by the legal standard (Table 3), finally representing each standardized value corresponding to our

Table 2 | Integrated data for the preparation of Figure 2

Variable	Legal limit D. 98/83/CE	AMD water quality ratings Gray (1996)	Average value for Odiel	Weighting factor (average Gray/limit)	Standardized value Odiel
pH		3.5–3.6	3.6		
Sulfate (mg/L)	250	4,000–5,999	4,250	18	4
Iron (mg/L)	0.2	25–49	26.7	187	5
Zinc (mg/L)	5	0.5–0.9	0.3	0.15	1
Aluminum (mg/L)	0.2	<1	0.65	5	3
Copper (mg/L)	2	<0.05	0.009	0.025	1
Cadmium (µg/L)	5	<10	0.12	2	2

Table 3 | Parametric and weighted values for pollution

Pollution	Parametric value	Weighted value
None	Not detected	0
Slight	Below legal limit	1
Moderate	Between 1 and 2 times the limit	2
Average	Between 2 and 10 times the limit	3
High	Between 10 and 50 times the limit	4
Extremely high	Over 50 times the limit	5

Figure 2 | Radial diagram.

water sample in a radial diagram made up of six concurrent half-lines as a modification of the Tickle diagram.

RESULTS: APPLICATION OF THE MODEL

The proposed model is applied to the River Odiel (Figure 1), a highly affected water course in the Iberian Pyritic Belt, and the object of damming for urban and agricultural water supplies. The physicochemical characteristics are compiled in Table 2. The polluting contributions to the dam under construction should match those determined for the Huelva estuary by Sáinz *et al*. (2004). These authors calculate the orders of magnitude at values close to 160 kg/h of Cu, 374 kg/h of Zn, 1.4 kg/h of Cd, etc., since the Alcolea dam will collect water from the Odiel only a few kilometers from its mouth and below any mining exploitation.
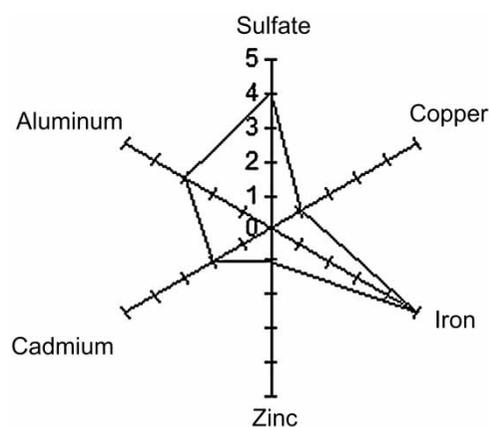
The data used to draw up the model appear in Table 2, where the values considered for each variable, pH, sulfate, iron, zinc, aluminum, copper and cadmium, are shown in successive columns with the following meaning:

- Legal limit for each of the variables in this type of water as laid out in Directive 98/83/CE.
- AMD water-quality ratings proposed by Gray (1996).
- Value determined in the laboratory for the water sample from the river Odiel to be classified. These values serve as a check for the levels proposed by Gray for the pH measured at the point where the sample is taken.
- Weighting factor which is the result of dividing the average value for each of Gray's water-quality ratings by the value imposed by the legal limit for each variable.
- Standardized value for the Odiel between 0 and 5.

The representation of these values in a radial diagram appears in Figure 2.

DISCUSSION

The usefulness of employing a weighting factor becomes clear when the variables sulfates and iron are taken as a reference (Table 2). Indeed, although the concentration of sulfates is 160 times higher than that of iron, and, bearing in mind that the maximum legal concentration limit for iron is 1,250 times lower, following application of the proposed weighting formula. The result is a weighting factor 10 times greater for iron, which reveals the greater toxicity of the water sample in terms of this variable.

We can say something similar for cadmium in relation to zinc, since although the zinc concentration is 2,500 times lower in the same water sample, the weighting factor produces a figure 13 times higher for cadmium, again the result of much more restrictive limits for cadmium.

Once these weighted values, which are compiled in Table 2, have been obtained, standardization of these values becomes necessary. This necessity is imposed by the various magnitudes they can reach. The choice of a standardization framework between 0 and 5 was considered in this case as it can be adapted better to the radial diagrams in which these results are ultimately represented.

The radial diagram as a means of expressing the standardized values graphically makes it easier to understand the phenomenon.

CONCLUSIONS

The present work involves a modification of the Gray proposal (1996) and also places its 'water-quality ratings' within the limits of European guidelines.

Application of the proposed method will allow the approximate state of the water quality to be learned by simply measuring its pH. This may prove very useful during the design of hydrochemical control networks.

Weighting and standardizing values allows the relative extent of the pollution to be quantified simply, still within the framework of the permitted limits for the public water supply, while the proposed graphical representation makes it significantly easier to understand the phenomenon and proves useful for comparing temporal or spatial variations over the course of a river.

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