Water Resour Manage (2011) 25:201–215
DOI 10.1007/s11269-010-9695-8

Water Quality in the Future Alcolea Reservoir (Odiel River, SW Spain): A Clear Example of the Inappropriate Management of Water Resources in Spain

Manuel Olías · José Miguel Nieto · Aguasanta Miguel Sarmiento · Carlos Ruiz Cánovas · Laura Galván

Received: 29 November 2009 / Accepted: 24 June 2010 /
Published online: 17 July 2010

Abstract The Odiel River is located in southwestern Spain; the greater portion of its basin is composed of materials from the Iberian Pyrite Belt (IBP), an area with numerous massive sulfide deposits that have been highly exploited since the third millennium BC. As sulfides come into contact with the atmosphere due to mining activity, oxidation occurs, generating a highly toxic acidic leachate with large concentrations of sulfates and metals, a process which is known as acid mine drainage (AMD). As a result, the Odiel River and most of its tributaries are severely contaminated. The construction of two large dams in the Odiel River basin is planned. The most advanced project is that of the Alcolea reservoir, with a storage capacity of 274 hm^3, whose construction has already begun, with a total budget of around €164 million. There are reasonable doubts about the final quality of the reservoir water, as this dam will regulate a river with a mean pH close to 3.5 and large concentrations of toxic elements. This paper analyzes the data of water quality in the Alcolea reservoir. The results show that the reservoir water will be acidic and not useful at all, although more specific studies are necessary to obtain the exact estimation of its hydrochemical characteristics. It seems unwise to start building the dam, which requires a large economic investment and will have a vast environmental impact, without first conducting these studies. This proves that water management in Spain is still based on political motivation rather than on technical criteria and good management of natural and economic resources.

M. Olías (✉) · C. R. Cánovas · L. Galván
Department of Geodynamics and Palaeontology, University of Huelva, Campus 'El Carmen', 21071, Huelva, Spain
e-mail: manuel.olias@dgyp.uhu.es

J. M. Nieto
Department of Geology, University of Huelva, Campus 'El Carmen', 21071, Huelva, Spain

A. M. Sarmiento
University of Cádiz, 11510, Puerto Real, Cádiz, Spain

Keywords Odiel · Alcolea reservoir · Acid mine drainage · Water quality · Water management

1 Introduction

1.1 Acid Mine Drainage Process

Acid mine drainage (AMD) is one of the main causes for degradation of water resources worldwide. Kleinmann (1989) estimates that in the USA alone almost 20,000 km of river courses are affected by this problem.

Sulfides are highly insoluble minerals under reducing conditions. As long as they are not exploited (in this case the process is known as acid rock drainage or ARD), they remain in the subsoil under anoxic conditions and only a small part of these deposits outcrops at the surface. However, when they come into contact with the atmosphere, oxidation of these minerals occurs, with pyrite being the most abundant among them (FeS_2). The general reaction which controls this process is (Nordstrom and Alpers 1999):

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

In the presence of oxygen, ferrous iron undergoes the following reaction:

$$Fe^{2+} + 1/4O_{2(aq)} + H^+ \rightarrow Fe^{3+} + 1/2H_2O \tag{2}$$

The ferric iron produced can oxidize new pyrite (reaction 3) or precipitate as ferric hydroxide (reaction 4):

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{=} + 16H^+ \tag{3}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe\,(OH)_{3(s)} + 3H^+ \tag{4}$$

These reactions generate acidity and release large amounts of sulfates, iron and other accessory metals (As, Cd, Co, Cu, Pb, Zn, etc.) contained in sulfides.

The kinetic of the previous reactions is abiotically very slow, particularly that of reaction 2, which controls the speed of the entire process, but these reactions accelerate enormously when they are catalyzed by acidophilic bacteria (Blowes et al. 2004). As the acidity produced remains low due to the neutralizing capacity of the environment, these bacteria cannot develop and the production of acidic leachates is not very high. However, if acidic conditions are reached, a large increase takes place in the population of the bacteria that catalyze these processes, generating more acidity and the process is then fed back, causing acid mine waters with very low pH values and very large concentrations of toxic elements.

1.2 The Odiel River

The Odiel River rises at the foothills of the Aracena Mountains (Fig. 1) and flows, together with the Tinto River, into an estuary known as the Ría of Huelva. The Odiel River is 140 km long and its basin has a surface area of around 2,400 km^2. Its main tributaries are the Olivargas, Oraque and Meca rivers on its right margin, and the

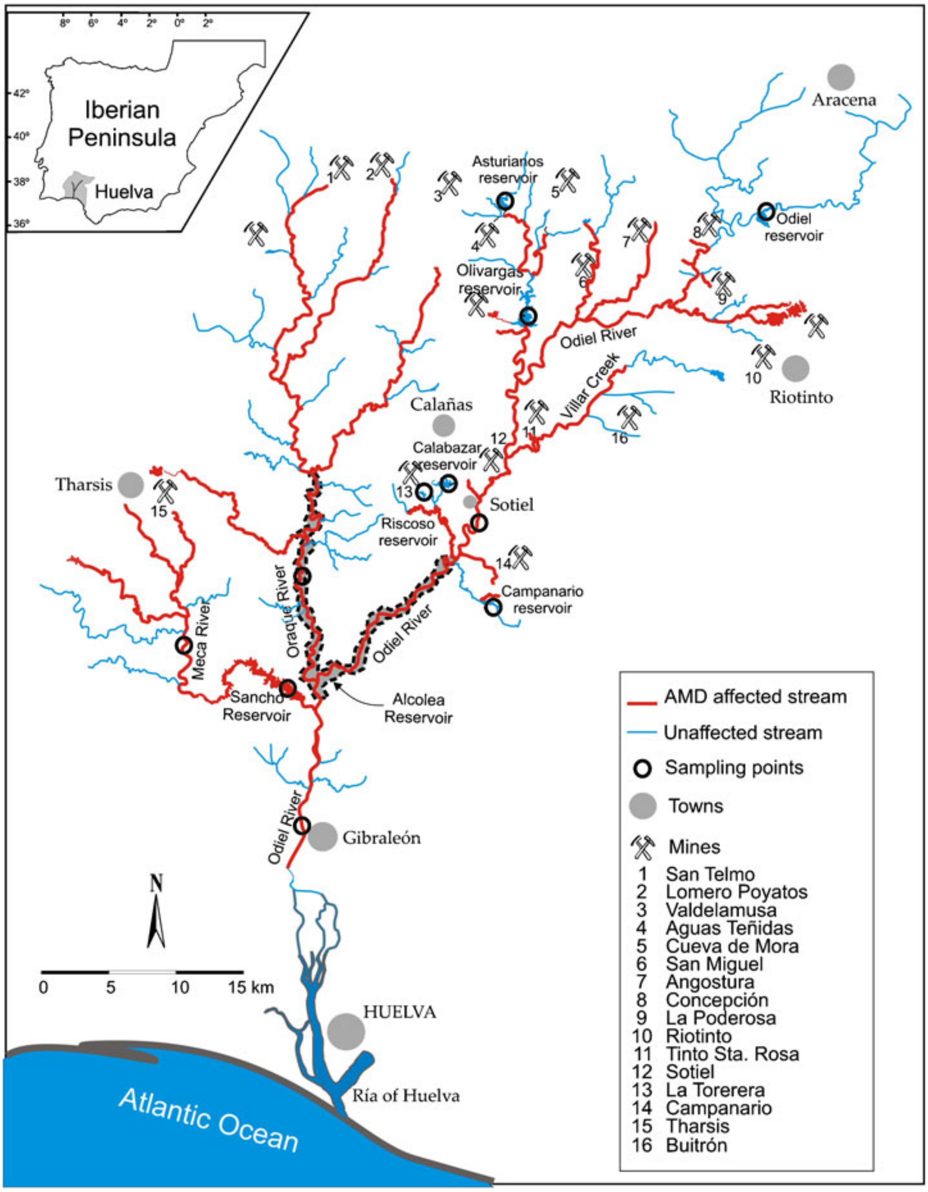

Fig. 1 Odiel River basin, with AMD-affected reservoirs and creeks and location of main mine sites (all the mines are abandoned except Aguas Teñidas)

Villar Creek on its left. The climate is of a Mediterranean type, with annual mean rainfall ranging from 600 mm in the southern zone to over 1,000 mm in the northern mountainous areas. The materials through which it flows are largely impermeable, so that the river has scarce natural regulation and responds quickly to rainfall. Its annual mean contribution is close to 500 hm^3, although it shows strong variations due to rainfall variability.

The Odiel River, along with the Tinto River, drains materials from the so-called Iberian Pyrite Belt (IPB), which extends over the southwest of the Iberian Peninsula, between western Andalusia and the south of Portugal (Sáez et al. 1999). The Iberian Pyrite Belt is rich in massive sulfides which began to be exploited 4,500 years ago for gold, silver and copper extraction (Nocete et al. 2005). In Roman times there was a large mining activity in the area, from which numerous remains are still present. Afterwards, mining was reduced until the big resurgence which started in the mid nineteenth century and continued over the whole twentieth century. Although at present there are only two active mines (Aguas Teñidas at the Odiel basin and Las Cruces near Seville), in the large quantity of mining wastes existing in the IPB there is still sulfide oxidation and, as a result, highly polluting acidic leachates are being generated.

There are not outcrops of carbonate rocks in the IPB and rivers have a low natural alkalinity (Sarmiento et al. 2009a), so that they can not neutralize the acidic leachates received. As a result, the fluvial network of the Tinto and Odiel Rivers is intensely affected by acid mine drainage. The highest exponent of this kind of contamination is the Tinto River, which presents pH values close to 2.5 before it flows into the Ría of Huelva (Cánovas et al. 2007) and large amounts of dissolved toxic metals (Fe, Al, Cu, Zn, Mn, etc.).

The Odiel River shows less extreme conditions. However, the length of the affected reaches (Fig. 1) is higher than that of the Tinto River and, due to its more abundant discharge, it is the highest input of contaminants to the Ría of Huelva (Olías et al. 2006). Near its mouth, the Odiel River pH is close to 3.60, with high concentrations of dissolved metals (Achterberg et al. 2003; Braungardt et al. 2003; Olías et al. 2004; Cánovas et al. 2007) which have a high environmental impact on the Ría of Huelva and even on the Gulf of Cádiz (e.g. Davis et al. 2000; Leblanc et al. 2000; Elbaz-Poulichet et al. 2001; Sáinz and Ruiz 2006; Nieto et al. 2007). In the proximities of the mines the conditions are even more extreme (Sánchez España et al. 2005, 2006; Sarmiento et al. 2009a).

1.3 The Alcolea Reservoir

The Odiel River has the largest water resources in the province of Huelva. So far, its regulation is low due to the strong contamination of its basin by acid mine drainage. The largest reservoirs are Olivargas (with a storage capacity of 29 hm^3), which regulates the river of the same name, and Sancho (58 hm^3), which regulates the Meca River. To increase the water resources available in the area, basically for farming use, the construction of two large reservoirs in the Odiel River is planned: La Coronada (800 hm^3) and Alcolea (274 hm^3), with the latter being the more advanced project.

The Alcolea reservoir is located just after the Odiel River meets the Oraque. At this point the watershed area is of 1,659 km^2 and its average contribution is of 331 hm^3/year (DGOHCA 1996), with strong interannual variability depending on rainfall (minimum of 28 and maximum of 1,258 hm^3/year).

The projected dam will be a concrete arch-gravity dam, 65 m high and 520 m long at its peak and will regulate 135 hm^3/year. In 2008, the Project was awarded a total amount of €52 million and preliminary works began in 2009. Apart from the dam, it is necessary to build channels for water distribution, increasing the final budget to almost €164 million. Half of the budget will be funded by the national government and the other half by the Andalusian regional government, who will later retrieve it from the users' taxes. It is hoped that 20,000 ha in the surrounding area will be transformed into irrigated land.

There is strong opposition among ecologist groups to the construction of this dam due to doubts concerning: the final quality of the retained water; the impact on the endemic species *Erica andevalensis* and the abundant couples of eagle owls which nest in the flooding areas; the barrier effect it would produce; and the need to analyze the effect of the decrease in the amount of sediments and river water in the Marismas del Odiel Natural Park (Natura 2000 Odiel's Marshland).

1.4 Objectives

The objective of this work is to estimate the final quality of water in the Alcolea reservoir, based on data obtained by numerous research projects that we have conducted on water contamination by AMD in the Odiel River basin from 2002 onwards. A critical assessment will be made on the study regarding the water quality carried out in the Project for the construction of the dam.

2 Methodology

Between 2002 and 2007 several samplings were performed at a control network in the Odiel River basin consisting of: four points in the main streams, two points in large reservoirs (Olivargas and Sancho) and five points in small reservoirs (Fig. 1). The sampling was made on a weekly basis at the Odiel River in Gibraleón, before it flows into the Ría of Huelva (Fig. 1). At the rest of the points, samplings were made under different hydrological conditions to make them as representative as possible. More detailed information can be found in Sarmiento (2007), Cánovas et al. (2007), Cánovas (2008) and Sarmiento et al. (2009a).

River and creek samples were taken at a point near the center of the channel to avoid stagnation problems near the margins. The reservoirs were also sampled, with the samples taken near the dams at 50-cm depth. The samples were stored in high-density polyethylene bottles first washed with 10% nitric acid and then rinsed with mili-Q (18.2 MΩ) water for cation determination, and only with mili-Q water for anions. The containers were rinsed three times with the study water, leaving the water inside the bottle for 5 min in the last rinsing in order to stabilize the components in the walls of the container. The samples were filtered 'in situ' through 0.45 μm pore size filters, and those aimed for cation determination were acidified with 2% suprapur nitric acid for conservation. They were later carried to the lab in the dark at approximately 4°C until analysis.

Electrical conductivity, pH, temperature and redox potential were measured 'in situ'. Fluorides, chlorides and sulfates were determined using a Dionex DX-120 ion chromatograph with AS 9-HC 4 × 250 mm column and ASRS-ULTRA 4 mm suppressor membrane. Bicarbonates were determined by using standardized HCl within the 48 h following the collection of the sample. Cations were analyzed using a

Jobin Yvon ICP-OES (JY ULTIMA 2). The elements analyzed were: Al, As, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Sr, Tl, and Zn (only the results of the most representative elements are shown in this work). A triplicate analysis was performed in order to evaluate the analytical precision, being below 5% in all cases. In each analysis sequence, blanks were analysed, being all elements below the detection limit of the equipment. The analytical accuracy was checked by the analysis of reference materials (NIST-1640).

3 Results and Discussion

3.1 Water Quality Data in Rivers and Reservoirs in the Area

From the data gathered at the samplings in the rivers and reservoirs across the Odiel River basin, three estimations on the water quality in the Alcolea reservoir have been made.

3.1.1 Estimation 1

Prior data on the water quality in the Odiel, Oraque and Meca rivers are available (Fig. 1) (Sarmiento 2007). Table 1 shows a summary of the results. The water quality is very bad at the three points, although the most extreme conditions are those of the Odiel River in Sotiel, with an average pH of 3.4, 12.8 mg/L of Fe, 74.5 mg/L of Al, 19.6 mg/L of Zn, etc. The contaminant levels in the Meca and Oraque rivers are similar, although they are slightly higher in the Meca.

The Meca River is regulated by the Sancho reservoir, which has pH values close to 4.2 and high toxic metal concentrations (Table 2). The waters which would reach the reservoir present worse conditions than those reaching the Sancho reservoir, which leads us to think that the Alcolea reservoir will also have acidic waters and high toxic metal concentrations.

3.1.2 Estimation 2

There are also data available from the Sancho and Olivargas reservoirs (the biggest ones in the Odiel River basin) along with other small reservoirs in the area which are not affected by acid mine drainage (Fig. 1). The reservoirs in the Odiel River basin which do not receive acidic leachates (Table 2) present bicarbonate water with a pH value close to neutrality (mean 7.2) and low mineralization (mean electrical conductivity of 157 μS/cm).

The sulfate ion is a good indicator of AMD contamination because it is a non-reactive compound which is found in large concentrations in acidic leachates and in low concentrations in the AMD-unaffected rivers in the area (Sarmiento et al. 2009a). In acidic waters, the importance of natural chemical processes in removing sulfates from the water is insignificant when compared to dilution processes. Therefore, sulfates can be considered conservative ions (Nordstrom and Ball 1986; Berger et al. 2000).

Sulfate concentration in the reservoirs that do not receive acid mine leachates is significantly lower than in the Olivargas (26 mg/L) and Sancho (121 mg/L) reservoirs

Table 1 Summary of the analytical results of previous quality data of the Odiel, Oraque and Meca Rivers (*n* number of samples, *E.C.* electrical conductivity, *SD* standard deviation, *Min* minimum, *Max* maximum)

		Odiel River Odiel at Sotiel ($n = 17$)				Oraque River ($n = 11$)				Meca River ($n = 6$)			
		Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
pH		3.4	0.65	2.17	4.67	3.4	0.57	2.85	4.80	3.6	0.62	2.81	4.43
E.C.	μS/cm	1,798	1,046	512	3,544	1,291	660	394	2,540	1,434	650	706	2,440
SO_4	mg/L	1,207	773	323	2,796	635	387	120	1,465	785	464	241	1,399
Al	mg/L	74.5	52.9	9.4	179.0	27.1	21.7	5.3	81.7	45.4	28.0	14.2	86.4
Cu	mg/L	9.1	5.2	2.5	20.9	2.6	1.4	0.5	4.7	7.2	4.3	2.5	12.8
Fe	mg/L	12.8	7.9	3.2	26.5	9.3	8.3	1.8	29.0	12.3	6.6	1.9	20.2
Mn	mg/L	15.8	11.5	3.1	42.2	6.1	4.6	1.0	15.7	8.9	5.5	2.7	16.2
Zn	mg/L	19.6	13.2	5.1	52.9	10.8	7.7	1.6	28.5	13.7	9.5	4.5	28.2
As	μg/L	287	923	3	3,217	12	8	5	20	11	–	11	11
Cd	μg/L	83	50	31	195	30	15	13	62	36	28	5	79
Co	μg/L	470	330	115	1,250	257	191	27	652	563	344	185	1,044
Cr	μg/L	13	10	4	33	6	1	4	7	18	8	10	27
Ni	μg/L	241	175	61	662	149	106	9	370	252	161	62	459
Pb	μg/L	111	131	18	493	29	20	10	76	239	410	7	969

Table 2 Summary of the analytical results for the reservoirs in the Odiel River basin (*E.C.* electrical conductivity, *SD* standard deviation, *Min* minimum, *Max* maximum)

		Nonaffected reservoirs ($n = 5$)				Olivargas reservoir ($n = 8$)				Sancho reservoir ($n = 8$)			
		Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
pH		7.2	0.50	6.60	7.72	7.0	0.35	6.21	7.30	4.2	0.22	3.94	4.68
E.C.	μS/cm	157	25	120	190	209	25	168	243	362	25	328	400
SO_4	mg/L	19.5	6.5	13.9	32.1	26.3	8.3	18.9	45.3	121	31.4	78.4	185
HCO_3	mg/L	59.7	13.3	45.0	82.0	41.0	14.9	13.3	62.6	0.0	0.0	0.0	0.0
Al	mg/L	0.10	0.16	<0.08	0.38	0.20	0.33	<0.08	0.93	2.96	0.63	1.65	3.58
Cu	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.65	0.12	0.54	0.90
Fe	mg/L	0.37	0.26	0.18	0.55	0.10	0.28	0.00	0.78	0.39	0.41	0.15	0.86
Mn	mg/L	<0.05	<0.05	<0.05	<0.05	0.21	0.14	0.11	0.50	1.71	0.36	1.42	2.52
Zn	mg/L	<0.15	<0.15	<0.15	<0.15	0.78	0.43	<0.15	1.28	1.85	0.49	1.14	2.52
As	μg/L	5.1	1.9	3.0	7.9	1.3	2.3	<3.1	5.41	5.5	0.4	5.2	5.8
Cd	μg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Co	μg/L	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	<2.1	72	18	58	114
Cr	μg/L	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9	<1.9
Ni	μg/L	5.5	0.2	5.3	5.6	<1.3	<1.3	<1.3	<1.3	31	12	19	56
Pb	μg/L	13	2	11	16	11	16	4	49	17	13	8	40

(Table 2). Also, a lower sulfate concentration is observed in the reservoirs with respect to the rivers (Table 1) due to the dilution processes which take place during large floods, when the water quality in the river improves temporarily (Olías et al. 2004; De la Torre et al. 2009). Thus, for example, whereas in the Meca River mean sulfate concentration is of 785 mg/L (Table 1), in the Sancho reservoir it is of 121 mg/L (Table 2).

Following sulfate concentration, it can be deduced that the Sancho reservoir receives a larger contaminant and acidity load than the Olivargas reservoir. In the latter the dilution produced by run-off waters during floods and natural self-depuration is enough to compensate the acidity input. As pH increases, iron precipitates first and is almost completely removed when water reaches pH 3.5 (Nordstrom and Alpers 1999; Blowes et al. 2004). Aluminum is the next element to precipitate with pH values between 4 and 5 (Nordstrom and Ball 1986). Subsequently, with pH values close to neutral, other metals such as Cu, Co, etc, precipitate. The most mobile toxic metals (as Mn and Zn) need pH values over 8 to precipitate (Nordstrom and Alpers 1999).

In the Olivargas reservoir, where dilution with clean water is enough to balance acidity, the mean pH is 7.0 (Table 2) and most toxic elements precipitate, accumulating on the bottom sediments (Sarmiento et al. 2009b). Nevertheless, Zn and Mn concentration is significantly higher than in the reservoirs unaffected by acid mine waters (Table 2), since the pH they need to precipitate is not reached. Manganese is typically the most difficult metal to remove from solution due to the high pH required to form insoluble precipitates (Clayton et al. 1999). According to thermodynamic calculations with the code PHREEQC (Parkhurst and Appelo 1999) in the Olivargas reservoir the pH necessary to precipitate $Zn(OH)_2$ is 8.6 while Mn will not precipitate as $Mn(OH)_2$ even at pH 10.

The Sancho reservoir receives an acidity load four times higher than that of the Olivargas, according to sulfate concentration. In this case, the dilution produced by floods and self-depuration processes is not enough to balance acidity, and the pH remains close to 4.2. Under these conditions, only Fe precipitates and most toxic elements remain dissolved (Table 2).

It can be deduced that those reservoirs with sulfate content similar to or higher than that of the Sancho reservoir will receive an acidity load too high to be neutralized and will have acidic waters, with high concentrations of toxic elements.

3.1.3 Estimation 3

From the annual contaminant load of the Odiel River in Gibraleón, calculated by Olías et al. (2006), we can obtain the mean composition that a potential reservoir built at that point would have by dividing the contaminant load for each element (147,200 tonnes of sulfates, 2,850 tonnes of Fe, 4,560 tonnes of Al, etc.) by the annual river water contribution. Results are shown in Table 3. The dilution of contaminants produced by floods has already been factored into these calculations.

The results of this estimation show that sulfate concentration in a potential reservoir located in Gibraleón would be larger than in the Sancho reservoir. The water composition in the Alcolea reservoir would be worse than that obtained at Gibraleón, since between these two points the Odiel River receives runoff water from AMD-unaffected areas, producing an additional dilution which would not occur in the case of the Alcolea reservoir.

Table 3 (1) Mean water concentration of selected parameters in a potential reservoir located in Gibraleón from data by Olías et al. (2006), (2) water quality in the Alcolea reservoir according to the Project of the Alcolea Dam (DGOHCA 1996), (3) maximum levels, before being treated, for water to be used for urban supply according to the Spanish Water Law (between brackets recommended values) and (4) recommended maximum concentrations in irrigation water from Ayers and Westcot (1985)

		(1)	(2)	(3)	(4)
SO_4	mg/L	157	292	250	–
Al	mg/L	4.90	–	–	5
Cu	mg/L	1.34	2.8	(1)	0.2
Fe	mg/L	3.05	2.5	(1)	5
Mn	mg/L	1.55	2.3	(1)	0.2
Zn	mg/L	2.79	5.3	5.0	2.0
As	μg/L	25	–	100	100
Cd	μg/L	8	30	5	10
Co	μg/L	67	–	–	50
Ni	μg/L	36	–	–	–
Pb	μg/L	13	–	50	–

3.2 Critical Review of the Study on Water Quality in the Dam Project

The Environmental Impact Declaration of the Alcolea Dam states (BOE 2000): *Mine contamination in the Odiel River is high during the whole year except in flood periods. The construction of a storage reservoir allows the waters running during the year to be mixed with those of floods, reducing, initially by dilution and then by decantation, the contaminant load of the whole, having checked in the large dams existing in the area, such as those of the Chanza and Olivargas rivers, that the heavy metals carried by the water are deposited in the bottom, which results in output water for supply with admissible contaminant values*.

Although it is true that this dilution process caused by the less mineralized water of the floods occurs, it has not been confirmed that it is enough to balance the acidity transported by the river. Especially when the two reservoirs mentioned in the Environmental Impact Declaration cannot be compared to that of Alcolea, since the degree of mining affection in their drainage basins is much lower than that of the Odiel River. The Chanza reservoir, located to the west of the Odiel River basin had a mean sulfate content of 45 mg/L in 2008 (data from the Spanish water quality network) because its drainage network has only one AMD-affected creek (Delgado et al. 2009). Moreover, this declaration does not address the Sancho reservoir, which has similar characteristics to that of Alcolea (highly contaminated input) and presents poor quality water which would be unfit for agricultural use.

The study on water quality in the Alcolea reservoir (DGOHCA 1996), based on the water quality analyses in Sotiel (see Fig. 1) from 1973 to 1988 (102 analyses), shows that the quality parameters for the reservoir water will be those shown in Table 3. These figures are obtained from the mean concentrations of elements for very large flows (>10 m^3/s) and for lower flows, and subsequently the water input to the reservoir is estimated under each of these hydrological conditions. Finally, the results are reduced by 20%, since the river contamination between Sotiel and Gibraleón decreases approximately at this rate (DGOHCA 1996). Table 3 also provides maximum pre-treatment water values for household usage according to Spanish law, and recommended values for irrigation from Ayers and Westcot (1985).

The calculations performed in this study contain numerous errors; nevertheless, the results agree with ours in that they show water characteristics worse than those found by us for an imaginary reservoir located in Gibraleón (Table 3) and than those in the Sancho reservoir (Table 2). According to these values, sulfate concentration would be almost 2.4 times that of the Sancho reservoir. Therefore, the acidity and contaminant load which the Alcolea reservoir will receive (in relation to its volume), will be 2.4 times higher and its conditions much worse.

Despite these values, the dam Project considers that the water will be usable due to the 'improving effects of difficult assessment not included in this study' (DGOHCA 1996):

> The reduction of mining activity, the regeneration of mine slag heaps and dumps and the source control of the present contaminant sources carried out by the Environmental Agency of the Andalusian Government.

These measures, carried out in the 1990s, involved blocking the galleries that discharged leachates, adding limestone to acidified rivers, covering slag heaps with impermeable materials, etc. Some of these measures may have been effective locally, however most of them were poorly planned and designed, and did not achieve any results. Sáinz et al. (2003) have clearly shown that these performances have not achieved any reduction in the amount of contaminants carried by the Odiel River into the Ría of Huelva.

> Decantation of heavy metals that will systematically occur in reservoirs, whose process will be activated with the increase in the water pH.

First of all, for decantation to occur, metal precipitation must take place first. Below pH value 4.5, the only metal that undergoes an important precipitation is Fe, as can be checked in the Sancho reservoir (Sarmiento et al. 2009b; Galván et al. 2009); the rest will remain dissolved in the water. Therefore, as has been discussed before, if pH is lower than that observed in the Sancho reservoir, this effect will be limited and will not cause a significant improvement of the water quality.

> Inhibiting the activity of the bacteria which catalyze the acidic reaction of metal sulfides as pH increases. This inhibition may reduce the formation of acid importantly, with the inhibition threshold estimated, according to the research, at around pH 4.5 to 5, and with maximum bacteria activity having a pH close to 2.5.

This effect will not occur as it is based on a conceptual error: there is no sulfide oxidation in the reservoir; this takes place in the mining areas. Therefore, there will be no inhibition of the *activity of bacteria which catalyze the acidic reaction of sulfides*. On the other hand, if the reducing conditions are reached in the bottom of the reservoir, the inverse process may occur, that is, sulfate reduction and sulfide precipitation, which produce alkalinity. This aspect, which is positive as regards water quality, must be investigated, as it will depend on the characteristics of the reservoir which controls the duration of the process of thermal stratification and, as a result, the existence of an anoxic layer on the bottom.

The arrangement of outlets at a level close to the water line of the reservoir, so that well oxygenated and decanted surface water will be derived at all times.

As mentioned before, if a pH close to neutrality is not reached, most of the toxic elements will remain dissolved. As a result, despite taking water from the surface, its quality will continue to be highly inadequate, as can be checked in the vertical profiles carried out in the Sancho reservoir (Sarmiento et al. 2009b).

The systematic improvement which occurs when mixing the Odiel water with other waters coming from different sources (water from the Guadiana–Chanza–Piedras system), with different characteristics and without the contamination problems typical of this river.

Here it is being assumed that the water will not be useful unless it is mixed with good quality water. However, as mentioned before, some elements such as Mn do not precipitate as hydroxides even at pH 10, so a large proportion of clean water would be necessary to reduce the values for these contaminants. Moreover, another difficulty would be that the precipitated elements should be separated from the water using a coagulation/decantation and/or filtering system. All of these factors contribute to making the mixture with better quality water to seem an unfeasible alternative.

4 Conclusions

The first question that comes to us after the displayed analysis of the results is: How is it possible for an investment of €164 million into a dam (and its associated distribution channels) to take place without a thorough study of the water quality that will be obtained?

The answer to this question must be that there is a strong political will to carry out this hydraulic work without taking into account any technical or scientific conditioning factors. Using data from WCD (2000), it is obtained that Spain has more large dams per capita than any other country in the world. While the authorities speak about a new water policy, reservoirs are still considered in Spain a source of economic development for a region, like in the developing world (Shah and Kumar 2008). Alternative sources of supply along with management measures based on efficiency and saving are still ignored. Political parties often use water as their weapon to win votes using perverse funding, i.e., using public funds for infrastructures of little interest, which are harmful in economic and environmental terms (Llamas 2008).

On the other hand, also the ecologist groups often ignore the studies when analyzing any performance in the environment and present strong opposition to any development measures, without a thorough analysis of the impacts and benefits (Wasimi 2010). Within this context, it is essential that the authorities base their hydrological planning (and the use of the economic resources that it entails) on technical studies rather than on political issues that result in the construction of unsuccessful or unnecessary works and in a large waste of economic resources and environmental actives.

In the case of Alcolea, a scientific study on the contaminant input that the reservoir will receive is necessary, since this is not known thoroughly. Moreover, not all elements decrease at the same rate during floods and some can even increase (Cánovas et al. 2008). On the other hand, an analysis of the self-depuration processes which occur in similar systems (such as the Sancho reservoir) and the factors that control them is also necessary.

Considering all this, a model needs to be created to predict the water quality in the reservoir. Since the construction of the dam has already begun, efforts should be aimed at source performances for remediation of acidic leachates. The model could be applied to predict changes in the water quality in the reservoir with various scenarios of contaminant reduction by remediation performances, so that the actions are addressed at treatments with larger impact on the reservoir water quality.

Another possibility would be to provide water active treatment measures by means of neutralization at the reservoir. Though perfectly feasible from a technical point of view, the volume of water to be treated is extremely high (131 hm^3/year) and it is not likely that the end users of the water will be able to cover this cost. Moreover, source treatment measures for contamination are preferable because they will also contribute to the recovery of the water quality, and ecological conditions, in creeks downstream.

Acknowledgements The authors wish to thank the Environmental Council of the Andalusia Regional Government and the Spanish Ministry of Science for the funding of several research projects about AMD-contamination in the Odiel River basin. The original manuscript was notably improved thanks to the comments and suggestions of two anonymous reviewers.

References

Achterberg EP, Herzl VMC, Braungardt CB, Millward GE (2003) Metal behaviour in an estuary polluted by acid mine drainage: the role of particulate matter. Environ Pollut 121:283–292

Ayers RS, Westcot DW (1985) Water quality for agriculture. FAO Irrigation and Drainage Paper 29 Rev.1, Roma, p 174. Available at http://www.fao.org/docrep/003/T0234E/T0234E00.htm#TOC. Accessed 22 April 2010

Berger AC, Bethe CM, Krumhansl JL (2000) A process of natural attenuation in drainage from a historic mining district. Appl Geochem 15:655–666

Blowes DW, Ptacek CJ, Jambor JL, Weisener CG (2004) The geochemistry of acid mine drainage. In: Lollar BS (ed) Treatise on geochemistry vol. 9: environmental geochemistry. Elsevier, Oxford, pp 205–262

BOE (2000) Resolución 2595 de 21 de enero de 2000, de la Secretaría General de Medio Ambiente, por la que se formula declaración de impacto ambiental sobre el proyecto de presa de Alcolea (Huelva). Bol Of Estad 33:5922–5925

Braungardt CB, Achterberg EP, Elbaz-Poulichet F, Morley NH (2003) Metal geochemistry in a mine-polluted estuarine system in Spain. Appl Geochem 18:1757–1771

Cánovas CR (2008) La calidad del agua de los ríos Tinto y Odiel. Evolución temporal y factores condicionantes de la movilidad de los metales. Ph.D. thesis. University of Huelva. Available at http://hdl.handle.net/10272/604. Accessed 22 April 2010

Cánovas CR, Olías M, Nieto JM, Sarmiento AM, Cerón JC (2007) Hydrogeochemical characteristics of the Tinto an Odiel rivers (SW Spain). Factors controlling metal contents. Sci Total Environ 373:363–382

Cánovas CR, Hubbard CG, Olías M, Nieto JM, Black S, Coleman ML (2008) Hydrogeochemical variations in the Río Tinto during flood events. J Hydrol 350:25–40

Clayton LA, Bolis JL, Wildeman TR, Updegraff DM (1999) A case study on the aerobic and anaerobic removal of manganese. In: Filipek LH, Plumlee GS (eds) The environmental geochemistry of mine waters. Rev Econ Geol 6B:515–526

Davis RA, Weltiy 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, Jiménez A, Borrego J, Díaz Curiel JM (2009) Time evolution of an AMD affected river chemical makeup. Water Resour Manag 23:1275–1289

Delgado J, Sarmiento AM, Condesso de Melo MT, Nieto JM (2009) Environmental impact of mining activities in the southern sector of the Guadiana basin (SW of the Iberian Peninsula). Water Air Soil Pollut 199:323–341

DGOHCA (1996) Estudio de la calidad del agua almacenada en la presa de Alcolea. Anejo n° 5 del Proyecto de la Presa de Alcolea, Dirección General de Obras Hidráulicas y Calidad del Agua, p 91

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

Galván L, Olías M, Fernández de Villarán R, Domingo-Santos JM, Nieto JM, Sarmiento AM, Cánovas CR (2009) Application of the SWAT model to an AMD-affected river (Meca river, SW Spain). Estimation of transported pollulant load. J Hydrol 377:445–454

Kleinmann RLP (1989) Acid mine drainage in the United States—controlling the impact on streams and rivers. In: 4th World Congress on the Conservation of the Built and Natural Environments, University of Toronto, pp 1–10

Leblanc M, Morales JA, Borrego J, Elbaz-Poulichet F (2000) 4,500 years old mining pollution in southwestern Spain: long-term implications for modern mining pollution. Econ Geol 95:655–662

Llamas MR (2008) Aspectos éticos de los conflictos del agua. Rev R Acad Cienc Exactas Fís Nat Ser A Mat 102:161–184

Nieto JM, Sarmiento AM, Olías M, Cánovas CR, Riba I, Kalman J, DelValls TA (2007) Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environ Int 33:445–455

Nocete F, Alex E, Nieto JM, Sáez R, Bayona MR (2005) An archaeological approach to regional environmental pollution in the south-western Iberian Peninsula related to Third millenium BC mining and metallurgy. J Archaeol Sci 32:1566–1576

Nordstrom DK, Ball JW (1986) The geochemical behavior of aluminium in acidified surface waters. Science 232:54–56

Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ (eds) The environmental geochemistry of mine waters. Rev Econ Geol 6A:133–160

Olías M, Nieto JM, Sarmiento AM, Ceron 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

Olías M, Cánovas CR, Nieto JM, Sarmiento AM (2006) Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (South West Spain). Appl Geochem 21:1733–1749

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2)—a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water-Resources Investigations Report 99-4259. Denver, p 312

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

Sáinz A, Ruiz F (2006) Influence of the very polluted inputs of the Tinto–Odiel system on the adjacent littoral sediments of southwestern Spain: a statistical approach. Chemosphere 62:1612–1622

Sáinz A, Grande JA, de la Torre ML (2003) Analysis of the impact of local corrective measures on the input of contaminants from the Odiel River to the Ría of Huelva (Spain). Water Air Soil Pollut 144:375–389

Sánchez España J, López Pamo E, Santofimia Pastor E, Aduvire O, Reyes J, Barettino D (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain). Appl Geochem 20:1320–1356

Sánchez España J, López Pamo E, Santofimia Pastor E, Reyes Andrés J, Martín Rubí JA (2006) The impact of acid mine drainage on the water quality of the Odiel river (Huelva, Spain): evolution of precipitate mineralogy and aqueous geochemistry along the Concepción–Tintillo segment. Water Air Soil Pollut 173:121–149

Sarmiento AM (2007) Estudio de la contaminación por drenajes ácidos de mina de las aguas superficiales de la cuenca del río Odiel (SO España). Ph.D. thesis. University of Huelva. Available via UMI ProQuest http://proquest.umi.com/pqdweb?did=3&Fmt=2&clientId=40400&RQT=309&VName=PQD. Accessed 22 April 2010

Sarmiento AM, Nieto JM, Olías M, Cánovas CR (2009a) Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel river basin (SW Spain). Appl Geochem 24:697–714

Sarmiento AM, Olías M, Nieto JM, Cánovas CR, Delgado J (2009b) Natural attenuation processes in two water reservoirs receiving acid mine drainage. Sci Total Environ 407:2051–2062
Shah Z, Kumar MD (2008) In the midst of the large dam controversy: objectives, criteria for assessing large water storages in the developing world. Water Resour Manag 22:1799–1824
Wasimi SA (2010) Planning for a large dam project: the case of Traverston crossing dam. Water Resour Manag (in press). doi:10.1007/s11269-010-9591-2
WCD (2000) Dams and development: a new framework for decision making. World Commision on Dams. Earthscan Publication Ltd, London, p. 404