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RESEARCH ARTICLE

A geochemical approach to the restoration plans for the Odiel River basin (SW Spain), a watershed deeply polluted by acid mine drainage

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Abstract The Odiel River Basin (SW Spain) drains the central part of the Iberian Pyrite Belt (IPB), a world-class example of sulfide mining district and concomitantly of acid mine drainage (AMD) pollution. The severe AMD pollution and the incipient state of remediation strategies implemented in this region, coupled with the proximity of the deadline for compliance with the European Water Framework Directive (WFD), urge to develop a restoration and water resources management strategy. Furthermore, despite the presence of some reservoirs with acid waters in the Odiel basin, the construction of the Alcolea water reservoir has already started. On the basis of the positive results obtained after more than 10 years of developing a specific passive remediation technology (dispersed alkaline substrate (DAS)) for the highly polluted AMD of this region, a restoration strategy is proposed. The implementation of 13 DAS treatment plants in selected acid discharges along the Odiel and Oraque sub-basins and other restoration measurements of two acidic creeks is proposed as essential to obtain a good water quality in the future Alcolea reservoir. This restoration strategy is also suggested as an economically and environmentally sustainable approach to the extreme metal pollution affecting the waters of the region and could be considered the starting point for the future compliance with the WFD in the Odiel River Basin.

Keywords Odiel River Basin · Alcolea reservoir · European Water Framework Directive · Acid mine drainage · Dispersed alkaline substrate

Introduction

Odiel River basin

The Odiel River has the largest drainage basin in the Huelva province (SW Spain), with an area of 2330 km^2 and a fluvial network of 1149 km of streams (Sarmiento et al. 2009a). The Odiel basin can be divided into three main sub-basins: Odiel, Oraque, and Meca (Fig. 1), with areas of 1401, 612, and 317 km^2, respectively.

The Odiel basin is mainly underlain by materials from the Iberian Pyrite Belt (IPB), one of the largest sulfide provinces in the world (Sáez et al. 1999) that has been mined since the third millennium BC (Nocete et al. 2005) until the present days. This ancient mining has created a huge number of abandoned mine sites that generate a severe metallic pollution by acid mine drainage (AMD) in the Odiel River, causing a poor ecological and chemical quality of its waters (Sarmiento et al. 2009a).

Owing to the severe pollution of the Odiel River, it shows a low regulation and the largest reservoirs in the basin are Olivargas (29 hm^3) and Sancho (58 hm^3), which regulate the Olivargas and Meca rivers, respectively (Fig. 1), and both are affected by AMD (Sarmiento et al. 2009b). While the former

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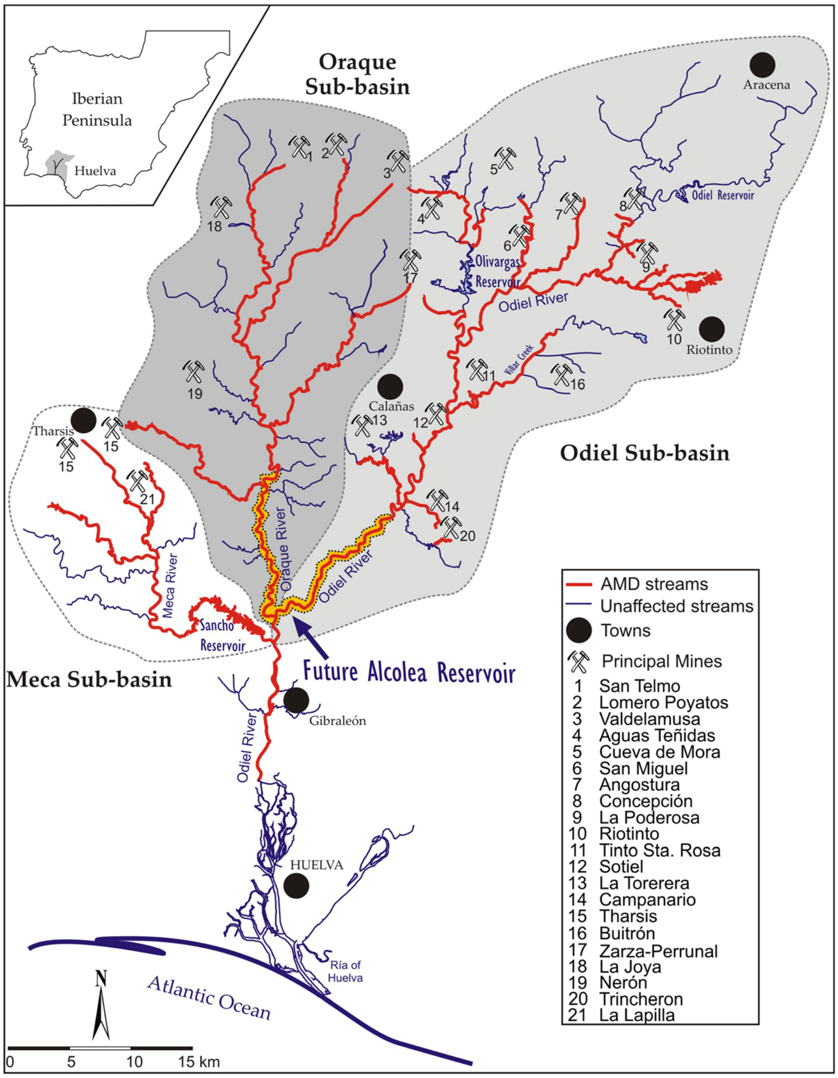

Fig. 1 Odiel River basin, with its three sub-basins, the main mining districts, and the location of the future Alcolea reservoir

presents circum-neutral pH values and low metal concentrations, being used for drinking water supply after treatment, the latter shows a pH between 3 and 4 and high concentration of toxic elements (Sarmiento et al. 2009b) and has been classified as an extreme case of surface water pollution worldwide (Cánovas et al. 2016). Despite this fact, the construction of two reservoirs is planned in areas with a higher degree of mining pollution. The Alcolea reservoir (247 hm^3), with a final budget of almost €164 million, is the most advanced project, and its construction has already begun. Nevertheless, the water of the reservoir will be acidic if remediation measures are not put into practice (Olias et al. 2011).

On the other hand, the Odiel River merges with the Tinto River in a common estuary called Ría of Huelva (Fig. 1). The great ecological and social importance of this estuary is reflected in the protection legal figure of "biosphere reserve" given to the lower section of the Odiel estuary from UNESCO in 1983. However, the upper section of the estuary has pH values close to 3.6 and high concentration of dissolved metals, which inflict a high environmental impact in the estuarine system (Cánovas et al. 2007; Nieto et al. 2007).

European Water Framework Directive

The Directive 2000/60/EC of the European Parliament, so-called Water Framework Directive (WFD) (EU Commission 2000), established a communitarian frame of action in the scope of water policy. It was approved with the aim of merging in a unique legal text the regulations established in multiple norms regarding the aquatic environment and the control and prevention of pollution. Its main objective is to achieve a good ecological and chemical quality of all European waters by 2015.

Nevertheless, the WFD allows the deadline prolongation in cases of technical feasibility, when improvements within the timescale would be economically unsustainable and if natural conditions do not foster the timely improvement. These conditions are met in the Odiel River basin due to the severe and widespread metal pollution. For these reasons, the regional

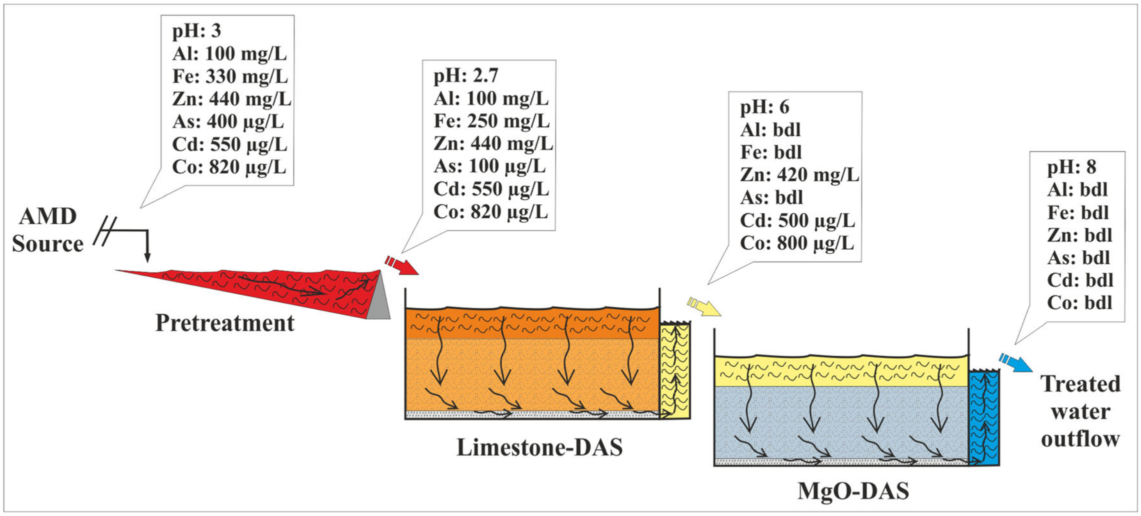

Fig. 2 Sketch of a basic DAS treatment plant illustrating its performance. Major chemical composition and pH values in the output of the different steps from the pilot-scale passive treatment system implemented in Monte Romero abandoned mine (Macías et al. 2012a, b)

authorities published the "Water Resources Management Plan", proposing to extend the deadline for 2021 and 2027 to perform remediation measures and to be in compliance with the WFD. According to economical and environmental criteria this document proposes the use of passive treatment systems as the most feasible and sustainable option to be implemented in these restoration strategies.

Remediation strategies

AMD pollution can be treated by active or passive technologies (Johnson and Hallberg 2005). An active treatment implies the use of energy and continuous addition of chemicals, whereas passive treatments rely on gravity forced water flow and biogeochemical reactions. AMD at abandoned mine sites is generally treated by the use of passive technologies (Younger et al. 2002). Conventional passive treatments (e.g., anoxic limestone drains, vertical flow wetlands, aerobic wetlands) have been successfully employed in coal mine districts affected by AMD (Younger et al. 2002). However, its use in the AMDs at the IPB or similar sites around the world is highly discouraged because the high acidity and metal content of these waters quickly promote clogging, thus losing the reactivity of the alkalinity-generating material employed (Ayora et al. 2013).

After more than 10 years of research and development of conventional passive treatment technologies in the acidic and metal-rich AMD from the IPB, a new design of alkaline passive treatment has been optimized for this type of waters. This novel treatment, known as dispersed alkaline substrate (DAS), comprises an inert wood shaving matrix, to supply high porosity and reduce the clogging problems, mixed with a fine-grained alkaline reagent to increase the substrate reactivity, which induces an increase of water pH after dissolution. A detailed explanation of the different laboratory and field experiments based on DAS passive treatment system can be looked up in Caraballo et al. (2009, 2011a), Macías et al. (2012a, b), and Ayora et al. (2013).

The good hydraulic performance of the DAS reactive substrate has been widely verified by mineralogical and geochemical approaches (Caraballo et al. 2011b), and a new potential economic source of metals by the exploitation of the DAS solid waste has been suggested (Pérez-López et al. 2011; Macías et al. 2012c). All these studies have demonstrated that the DAS system successfully treats metal-rich AMD from the IPB. Figure 2 shows the general performance of the DAS system as well as the chemical composition of waters and the removal efficiency obtained in each treatment step.

Objectives

The challenge of implementing the WFD fosters the development of new water treatment approaches. The directive encourages the use of modeling methods to optimize all stages of the treatment process, from characterization of background values and assessment of impacts to identification of the main restoration tasks for the improvement of water quality. The current study is based on the previous principles. The main aim of this work is to provide the basis for a future restoration planning in the Odiel basin.

Methodology

Data collection and treatment

A critical bibliographic review of the hydrochemistry of the main water courses comprising the Odiel and Oraque subbasins was performed (Asta et al. 2010; Cánovas et al. 2007; Galván et al. 2009; Grande et al. 2010; Sanchez-España et al.

Table 1 Real values before and after acid inputs and modeling values without DAS treatment in the end of each polluted sector of the Odiel and Oraque sub-basins

	Flow rate (L/s)	pH	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	SO_4 (mg/L)	Zn (mg/L)
Odiel sub-basin								
Odiel pre-AMDs real[a]	110	8.7	0	30	0	0	10	0
Odiel final sector real[a]	n.a.	3	13	51	5	18	512	9
Odiel final sector modeled	124	3	21	36	7	60	558	10
Seca pre-AMD real[b]	n.a	7.2	0	17	0	0	30	0
Seca post-AMD real[a]	n.a.	5.6	3	5	3	1	69	0
Seca final sector modeled	10.4	6.3	2	17	1	0	79	0
Escalada pre-AMD real[a]	22.6	8.2	0	28	0	0	10	0
Escalada post-AMD real[a]	18	3.7	5	36	1	11	282	1
Escalada final sector modeled	24.1	4.7	1	33	2	90	380	1
Olivargas pre-AMD real[a]	n.a.	7	0	8	0	0	35	0
Olivargas post-AMD real[a]	n.a.	4.9	1	8	0	2	32	0
Olivargas final sector modeled	11	4.5	3	33	0	1	245	0
Villar pre-AMD real[a]	n.a.	6.5	0	25	0	0	109	0
Villar post-AMD real[a]	n.a.	2.8	32	122	4	15	1024	26
Villar final sector modeled	11.4	4.4	6	45	3	107	503	9
Aguas Frias pre-AMD real[b]	n.a.	7.2	0	17	0	0	30	0
Aguas Frias post-AMD real[a]	30	3.2	9	45	1	39	483	9
Aguas Frias final sector modeled	11.3	3.3	5	33	1	38	345	6
Galaparosa pre-AMD real[a]	n.a.	7.4	0	15	0	0	63	0
Galaparosa post-AMD real[a]	16	5.2	4	34	1	6	252	5
Galaparosa final sector modeled	11	4.5	4	40	2	6	314	4
Oraque sub-basin								
Gonzalo pre-AMD real[b]	n.a.	7.2	0	17	0	0	30	0
Gonzalo post-AMD real[a]	2	2.6	756	110	4	3951	13,783	4
Gonzalo final sector modeled	12	2.6	55	16	0	218	1069	0
Pelada pre-AMD real[a]	n.a.	6.4	0	5	0	0	38	0
Pelada post-AMD real[a]	18	3.3	11	51	1	4	440	3
Pelada final sector modeled	15	3.2	17	163	0	116	1303	5
Tamujoso pre-AMD real[b]	n.a.	7.2	0	17	0	0	30	0
Tamujoso post-AMD real[a]	5	2.5	39	39	7	213	1336	7
Tamujoso final sector modeled	12	4.2	45	43	4	383	1498	8
Panera pre-AMD real[b]	n.a.	7.2	0	17	0	0	30	0
Panera post-AMD real	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Panera final sector modeled	13.6	2.7	200	56	22	314	3729	58

n.a. not analyzed

[a] Sarmiento (2007)

[b] Sarmiento et al. (2009a)

2005a, b; Sarmiento 2007). The dataset employed in this study can be consulted in Appendix Table 3. The chemical composition of the most relevant AMD discharges (mine adits and shafts, pit lakes and acid reservoirs outputs, and spoil heap leachates) was obtained from Sanchez-España et al. (2005a, b), Sarmiento (2007), and Asta et al. (2010). Hydrochemical data of the main creeks and rivers suffering from low level of pollution (or none) by AMD were obtained from Sarmiento (2007). When hydrochemical data of non-affected streams were not available, background values for these area provided by Sarmiento et al. (2009a) were used. This dataset was geochemically modeled by the code PHREEQC Interactive 2.15.0 (Parkhurst and Appelo 1999). The thermodynamic database WATEQ4F (Ball and Nordstrom 1991) was enlarged with the solubility constants (Ks) for schwertmannite according to Bigham et al. (1996) and Yu et al. (1999).

Conceptual design of the geochemical model

A geochemical model is proposed to predict the water chemistry under two different scenarios: (1) baseline conditions and (2) after passive treatment implementation. The geochemical modeling of baseline conditions is only performed for validation purposes by comparing modeled to measured values of different parameters (Table 1).

The geochemical model applied to the Odiel River consists in a mixing model using the "MIX" PHREEQC data block, which defines mixing fractions of aqueous solutions. Mixing fractions were obtained from data reported in literature. The model is subsequently improved by applying some geochemical constraints using the "EQUILIBRIUM PHASES" data block, which allows phase assemblages to react with an aqueous solution. These geochemical constraints are based on a previous analysis of the saturation state of main minerals commonly found in AMD environments relative to water samples. In this way, all mineral phases found oversaturated relative to water in each sample were forced to reach equilibrium, i.e., schwertmannite, jarosite, and ferrihydrite for Fe minerals; basaluminite, alunite, amorphous $Al(OH)_3$, and gibbsite for Al minerals; and some soluble salts such as gypsum, melanterite, and copiapite.

Equilibrated waters are subsequently mixed with downstream discharge and so on. Modeled values are compared with those

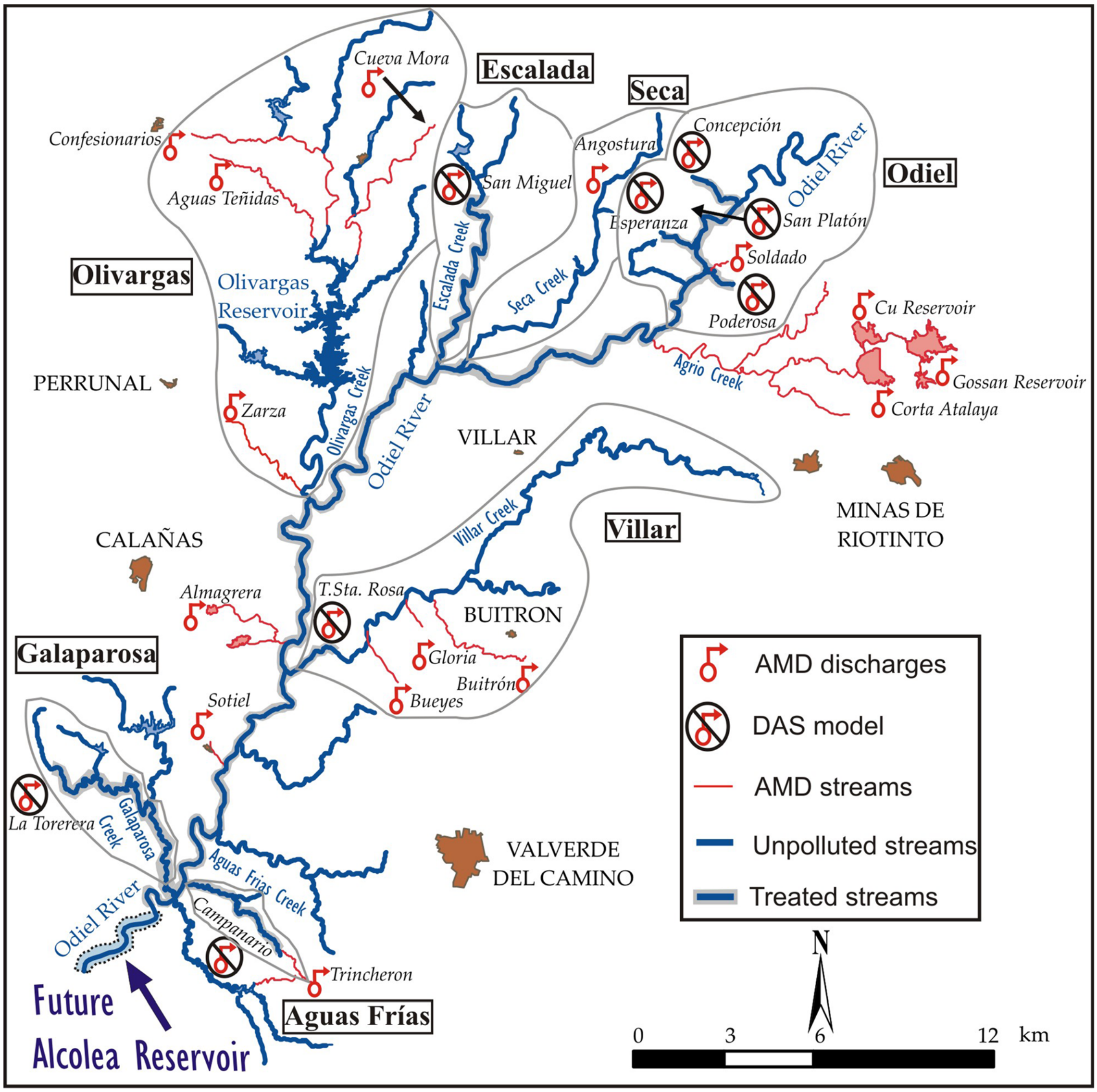

Fig. 3 Odiel sub-basin with the main AMD discharges. Some DAS treatment plants are strategically planned in this sub-basin (DAS model in the figure legend)

measured in real conditions in each sub-basin for validation purposes. Finally, the sample procedure is followed to perform a mixing model including the operation of different DAS plants located at strategic points in each sub-basin. The model was performed during high and low flow rate scenarios, but for the sake of simplicity, only results obtained during the extremely pollutant scenario, when the lowest flows are recorded, are presented.

Results and discussion

Validation of the model

As can be seen in Table 1, the validation of the model evidences some differences between modeled and measured values in different points. For instance, modeled Fe values are commonly higher than those measured (e.g., Odiel River; Table 1). These differences can be mainly attributed to the limitation of the model to consider reactive transport processes along the channels. Dispersion, diffusion, and transient storage may play an important role in element transport in these watercourses, especially during low flow rate scenarios such as that modeled. The higher residence time of water could enhance intense Fe precipitation processes that are not considered by the model. Another weak point of the model could be the inability to reflect the Fe oxidation processes catalyzed by bacterial activity. While Fe(II) remains dissolved at pH values of Odiel waters, Fe(III) is prone to precipitate. The model also disregards evaporative processes that play a key role in temporal storage of acidity and metals in semiarid

Table 2 Real values and model with DAS plants implemented values in the end of each polluted sector of the Odiel and Oraque sub-basins

	Flow rate (L/s)	pH	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	SO_4 (mg/L)	Zn (mg/L)
Odiel sub-basin								
Odiel final sector real[a]	n.a.	3	13	51	5	18	512	9
Odiel modeling with DAS	124	8.1	0	50	0	0	305	0
Escalada post-AMD real[a]	18	3.7	5	36	1	11	282	1
Escalada modeling with DAS	24.1	8.2	0	31	0	0	187	0
Villar post-AMD real[a]	n.a.	2.8	32	122	4	15	1024	26
Villar modeling with DAS	11.4	6.3	0	147	0	0	445	0
Aguas Frias post-AMD real[a]	30	3.2	9	45	1	39	483	9
Aguas Frias modeling with DAS	11.3	6.5	0	121	0	0	350	0
Galaparosa post-AMD real[a]	16	5.2	4	34	1	6	252	5
Galaparosa modeling with DAS	11	6.6	0	72	0	0	266	0
Oraque sub-basin								
Gonzalo post-AMD real[a]	2	2.6	756	110	4	3951	13,783	4
Gonzalo modeling with DAS	12	8.4	0	315	0	0	929	0
Pelada post-AMD real[a]	18	3.3	11	51	1	4	440	3
Pelada modeling with DAS	15	6.3	0	82	0	0	351	0
Tamujoso post-AMD real[a]	5	2.5	39	39	7	213	1336	7
Tamujoso modeling with DAS	12	6.6	0	304	0	0	1074	0
Panera post-AMD real[b]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Panera modeling with DAS	13.6	8.3	0	386	0	0	1687	0

n.a. not analyzed

[a] Sarmiento (2007)

[b] Sarmiento et al. (2009a)

AMD-affected catchments (e.g., Cánovas et al. 2008). This could also cause differences between modeled and measured values of not only Fe but also pH, Al, sulfate, Mg, and Ca.

On the contrary, when real data show a lower degree of AMD pollution than the modeled ones (e.g., Galaparosa creek in Table 1), it could be due to diffuse sources of pristine waters that cause dilution process and are not being taken into account in the model. Despite the differences observed in the validation processes, the same procedure was applied including selected DAS treatment plants as a preliminary approach for the restoration of the catchment.

Restoration strategy of the Odiel and Oraque sub-basin based on passive remediation systems

On the basis of the results obtained after the successful implementation of the DAS remediation technology in a highly metal polluted AMD at the IPB (Fig. 2), the remediation effect of several DAS treatment plants strategically located in the Odiel and Oraque sub-basins was modeled. The model did not include the Meca sub-basin because the main contributors correspond to diffuse sources (i.e., spoil heaps, low-grade ore stockpiles, leaching heaps), and thus, the application of DAS technology would not be cost-effective. The main limiting factors for the real implementation of a DAS passive treatment in the field were the flow rate (5 L/s is the maximum flow rate that the treatment can economically treat) and the geographic situation of the discharge. Another key limiting factor to decide the suitability of implementing a DAS treatment at a specific site is the chemistry of the waters after the mixture. To this respect, the hydrochemical threshold was employed to consider that a water has good chemical quality if pH >6 and toxic metals are absent.

Odiel sub-basin

This is the largest drainage network in the Odiel basin and the main contributor to the projected Alcolea reservoir (Fig. 1). Almost 20 abandoned mines are located in this sub-basin with around 23 point AMD discharges (Fig. 3). The modeled water quality for each sector after DAS plant implementation is shown in Table 2. The absence of DAS systems in some AMD sites is due to natural attenuation of pollution after mixing with unpolluted streams (e.g., Angostura AMD in Seca creek, Fig. 3) or DAS-treated effluents (e.g., Zarza discharge in Odiel

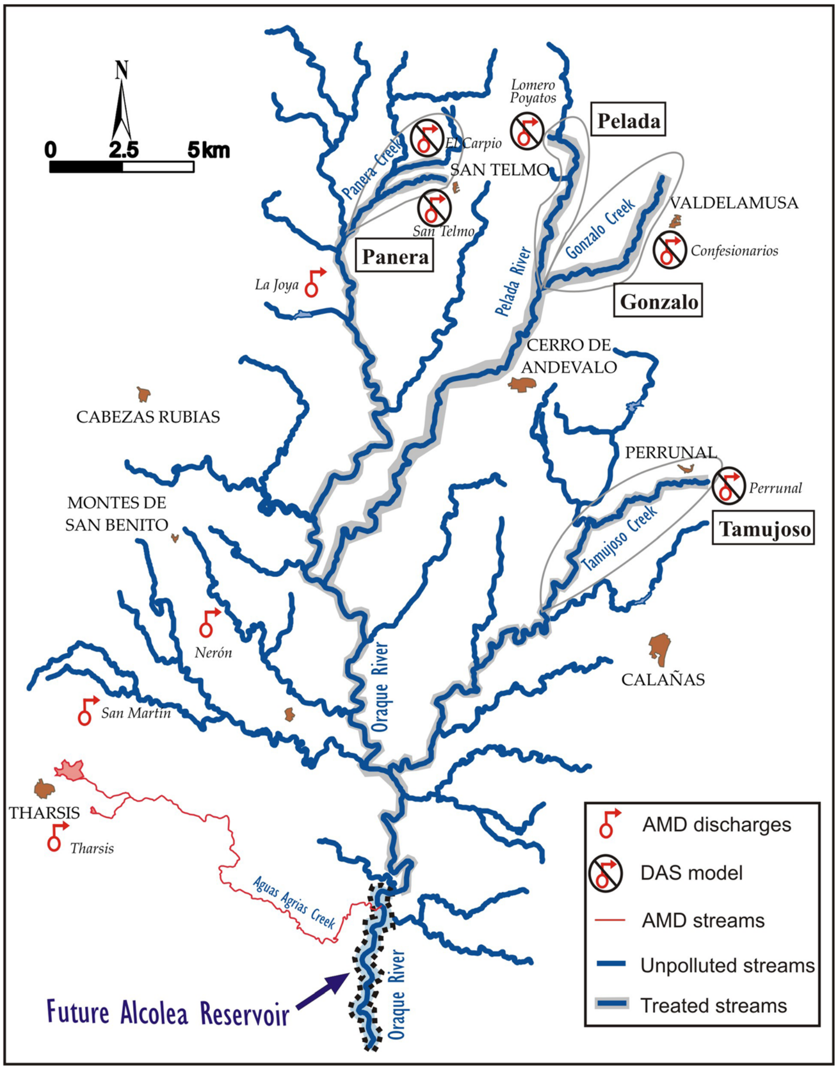

Fig. 4 Oraque sub-basin with the main AMD discharges. Some DAS treatment plants are strategically planned in this sub-basin (DAS model in the figure legend)

River, Fig. 3); therefore, the implementation of DAS systems in these points would be needless.

Taking into account these practical considerations, we considered the strategic implementation of eight DAS treatment plants in the Odiel sub-basin (Fig. 3). In this sense, two of these proposed plants (Concepción and Esperanza) are currently working financed by the EU LIFE+ program (LIFE-ETAD project, www.life-etad.com) and the national government, respectively. This must be considered a first step to improve the water quality in the river, because only 8 of the 23 acid discharges are treated. It is necessary to remind that despite these remediation efforts, several acidic streams would not be still in compliance with the WFD regulations.

Notwithstanding, this restoration strategy for the Odiel sub-basin would not have the proposed beneficial effect in the main course of the Odiel River after the confluence with the Agrio creek (Fig. 3). This acid creek presents an average pH of 2.8 (minimum of 2.58 and maximum of 3.18), mean concentrations of 429 mg/L for Al (minimum of 133 mg/L and maximum of 1140 mg/L), and 264 mg/L as average for Fe (minimum of 57 mg/L and maximum of 554 mg/L). The mean flow rate is 873 L/s, with 20 and 5040 L/s as minimum and maximum values, respectively; these data were obtained from 11 samplings in both dry and wet periods and just before its confluence with the Odiel River (Sarmiento 2007). The pollution sources that affect this creek come from the Ríotinto mining district. Some of these sources present very high flow rates (e.g., 90 L/s from Corta Atalaya pit lake or 220 L/s from Cu Reservoir tailing impoundment; Sanchez-España et al. 2005a). This flow rates preclude the use of a DAS treatment system or any other passive treatment systems. In this area, other measures must be taken. Nevertheless, at the present time, the Riotinto mine is working, and according to the environmental conditions imposed by the regional authorities, acidic discharges must be reduced by 20% before the third exploitation year, 50% before the sixth year, and totally before the tenth year. The mine company is currently facing this issue by active treatment technologies, while the decommissioning project considers the DAS passive technology to treat the acid waters.

Oraque sub-basin

The Oraque sub-basin is subjected to fewer acid inputs than the Odiel with only nine mines generating AMD in its drainage network (Fig. 4). Moreover, some of the polluting sources (La Joya, Nerón, and San Martín) do not cause any relevant depletion in the quality of the surrounding waters (Fig. 4). On the contrary, some other mines like San Telmo and Perrunal generate extreme metal-polluted AMDs (Appendix Table 3).

To improve significantly the water quality of the Oraque River network drainage, the installation of only five DAS treatment plants would be necessary (Fig. 4 and Table 2). This remediation strategy would also imply the remediation of almost all the acid discharges characterized in this region, implying the restoration of practically all the sub-basin. However, a similar situation than the one already explained for the Agrio creek in the Odiel sub-basin can be observed for the Aguas Agrias creek in the Oraque sub-basin (Fig. 4). This creek is affected by several acid discharges from the Tharsis mines, whose flow rates are too high for passive remediation. Sanchez-España et al. (2005a) identified a discharge from a waste rock pile leaching 15 L/s. The implementations of active treatments or other measures such as isolation with impervious covers to reduce the drainage generation are recommended as the most feasible measurements for this creek.

Conclusions

The main objective of the WFD is to achieve a good ecological and chemical quality for all European waters by 2015. Compliance with these regulations in the Odiel River basin seems to be impossible. The Andalusia Regional Government has proposed 2021 and 2027 as new deadlines for the application of the WFD, but even with these new deadlines, the magnitude and ubiquity of the AMD pollution in this region make the WFD economically and socially unfeasible. We propose a rational use of the economic, energetic, and natural resources to improve considerably the water quality in the Odiel River basin, although the WFD regulations were not completely met.

Thirty-two AMD discharges from 30 different mines located in the Odiel and Oraque sub-basins were modeled. The validation of the model evidenced some limitations (i.e., inability to model reactive transport processes, biological oxidation of Fe, and evaporative processes of waters) to accurately predict the chemical composition of water during mixing. According to our simulation, the existence of diffuse sources could also be inferred, so the performance of tracer injection tests together with synoptic samplings in these watercourses is highly encouraged.

The restoration strategy proposed in this work is based not only in the model calculated including the DAS treatment technology but also on a detail comprehension of the AMD problematic in the region and of the different passive and active treatment technologies available to date. The implementation of 13 DAS treatment plants to remediate some affordable acid discharges located along the two sub-basins would produce the recovery of 128 km of streams, and it would be a first step in the basin restoration. Also, a significant decrease in the acid inputs of the future Alcolea reservoir is expected. Nevertheless, the elimination of the acid inputs of the Agrio creek from the Río Tinto mines, which is currently conducted by active technologies by the mine company, is essential to obtain a good water quality in the future Alcolea reservoir. However, if these measures are not maintained along the time (e.g., due to the close of the mine), the costs of these technologies would be unaffordable by the regional authorities and other restoration measures may be conducted in the Agrio creek (i.e., waste dump isolation with impervious covers to mitigate the AMD generation and the deviation of the Agrio creek to the Tinto River basin). On the other hand, the reopening of mines due to the increase of the Cu price in the international markets can be other interesting opportunity to reduce the enormous contaminant load reaching the drainage network of the Odiel River due to the obligation of mining companies to face inherited environmental liabilities.

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Appendix

Table 3 Database employed in this study after the bibliographic critical review

Name	Type	Flow rate (L/s)	pH	Pe	Alk	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	SO_4 (mg/L)	Zn (mg/L)
Concepción[a]	Pit lake	2.8	3.1	12	bdl	157	78	13	1089	1	177	46	9	5117	111
San Platón[b]	Mine adit	2	2.5	10	bdl	247	108	69	1780	3	85	5	25	5850	227
Esperanza[b]	Mine adit	2.2	2.7	10	bdl	152	103	39	965	4	100	3	25	3710	24
Soldado[b]	Mine adit	2	2.5	11	bdl	33	31	5	147	2	30	1	19	800	8
Poderosa[a]	Mine adit	5	2.1	10	bdl	232	53	122	1330	2	46	6	13	5690	550
Odiel[a]	Polluted river	n.a.	2.9	13	bdl	13	51	5	18	2	41	3	23	512	9
Corta Atalaya[b]	Pit lake	90	2.7	10	bdl	1810	325	183	1290	bdl	1800	251	11	23,300	463
Cu Reservoir[b]	Reservoir output	220	4.6	8.1	bdl	30	382	18	4	10	87	7	94	1670	12
Agrio[a]	Polluted creek	873	2.8	12	bdl	429	236	58	264	3	684	84	42	7016	122
Angostura[b]	Mine adit	0.4	2.7	12	bdl	57	27	21	127	1	100	3	11	1250	6
Seca[a]	Polluted creek	n.a.	5.6	n.a	bdl	3	5	3	1	1	42	1	9	69	bdl
San Miguel[b]	Mine shaft	1.5	2.3	9.5	bdl	265	112	21	1426	bdl	251	23	11	5890	13
Cueva Mora[b]	Mine adit	3.5	3.3	9.5	bdl	125	288	3	511	2	181	22	22	n.a.	125
Aguas Teñidas	Mine shaft	2	3.1	10	bdl	34	89	8	162	1	87	8	24	1370	51
Escalada[a]	Polluted creek	18	3.7	9	bdl	5	36	1	11	1	24	2	14	282	1
Zarza[b]	Mine adit	1	3.6	10	bdl	57	266	2	37	2	247	49	32	2160	4
Olivargas[a]	Polluted creek	n.a.	4.9	7.9	bdl	1	8	bdl	2	1	5	1	7	32	bdl
Gloria[b]	Mine adit	1	2.8	11	bdl	46	90	77	183	2	47	6	26	1310	3
Tinto Santa Rosa[c]	Mine adit	1.4	3.1	10	bdl	79	173	20	796	2	143	45	26	2939	64
Villar[a]	Polluted creek	n.a.	2.8	12	bdl	32	122	4	15	2	77	23	32	1024	26
Sotiel[a]	Mine adit	n.a.	3.1	n.a.	bdl	20	65	3	38	3	78	26	14	819	47
Trincheron[b]	Mine adit	0.3	3.2	12	bdl	27	237	4	142	2	228	32	52	2050	5
Campanario[b]	Mine shaft	1	2.6	9.9	bdl	54	123	10	771	3	88	16	27	2780	52
Aguas Frías[a]	Polluted creek	30	3.2	13	bdl	9	45	1	39	1	42	6	18	483	9
Torerera[a]	Mine adit	1	2.8	11	bdl	62	263	15	88	1	218	68	50	2591	39
Galaparosa[a]	Polluted creek	16	5.2	8.4	bdl	4	34	1	6	1	25	4	20	252	5
Confesionarios[b]	Spoil heap	2	2	12	bdl	273	14	1	1115	bdl	110	1	9	5230	bdl
Gonzalo[a]	Polluted creek	2	2.6	11	bdl	756	110	4	3951	bdl	385	22	26	13,783	4
Lomero Poyatos[b]	Mine adit	5	2.7	10	bdl	57	529	1	408	12	483	11	74	4240	16
Pelada[a]	Polluted river	18	3.3	11	bdl	11	51	1	4	1	43	2	18	440	3
Perrunal[b]	Mine adit	2	2.9	8.2	bdl	317	177	27	2369	4	145	44	39	9130	46
Tamujoso[a]	Polluted creek	5	2.5	10	bdl	39	39	7	213	2	30	4	23	1336	7
El Carpio[b]	Mine adit	1.6	2.8	11	bdl	70	75	5	300	1	100	4	13	2030	15
San Telmo[b]	Spoil heap	2	2.5	11	bdl	1192	215	132	2004	bdl	567	82	31	21,380	342
Odiel[a]	Unpolluted river	110	8.7	6.3	190	bdl	30	bdl	bdl	1	11	bdl	10	10	bdl
Seca[d]		n.a	7.2	6.8	91	bdl	17	bdl	bdl	1	11	bdl	16	30	bdl

Table 3 (continued)

Name	Type	Flow rate (L/s)	pH	Pe	Alk	Al (mg/L)	Ca (mg/L)	Cu (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)	SO_4 (mg/L)	Zn (mg/L)
	Unpolluted creek														
Escalada[a]	Unpolluted creek	22.6	8.2	6.2	155	bdl	28	bdl	bdl	1	12	bdl	15	10	bdl
Olivargas[a]	Unpolluted creek	n.a.	7.1	7.6	26	bdl	8	bdl	bdl	1	4	bdl	7	35	bdl
Villar[a]	Unpolluted creek	n.a.	6.5	6.1	64	bdl	25	bdl	bdl	1	16	bdl	15	109	bdl
Aguas Frías[d]	Unpolluted creek	n.a.	7.2	6.8	91	bdl	17	bdl	bdl	1	11	bdl	16	30	bdl
Galaparosa[a]	Unpolluted creek	n.a.	7.4	6.5	51	bdl	15	bdl	bdl	1	11	bdl	13	63	bdl
Gonzalo[d]	Unpolluted creek	n.a.	7.2	6.8	91	bdl	17	bdl	bdl	1	11	bdl	16	30	bdl
Pelada[a]	Unpolluted river	n.a.	6.4	6.8	70	bdl	5	bdl	bdl	1	8	bdl	11	38	bdl
Tamujoso[d]	Unpolluted creek	n.a.	7.2	6.8	91	bdl	17	bdl	bdl	1	11	bdl	16	30	bdl
Panera[d]	Unpolluted creek	n.a.	7.2	6.8	91	bdl	17	bdl	bdl	1	11	bdl	16	30	bdl

n.a. not analyzed, *bdl* below detection limit, *Alk* alkalinity in milligram per liter as $CaCO_3$ equivalents

[a] Sarmiento (2007)

[b] Sanchez-España et al. (2005a)

[c] Asta et al. (2010)

[d] Sarmiento et al. (2009a)

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