



In-situ remediation of acid mine drainage using a permeable reactive barrier in Aznalcóllar (Sw Spain)

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ABSTRACT

Following on the accident occurred in Aznalcóllar in 1998, whereby a huge amount of acid mine drainage and heavy metal-bearing pyritic sludge was released to the Agrio river valley with the subsequent contamination of groundwater, a subsurface permeable reactive barrier (PRB) was installed to mitigate the long-term impacts by the spillage. The PRB material consisted of a mixture of limestone and vegetal compost. A particular characteristic of the Agrio aquifer is its high water flow velocity (0.5–1 m/d), which may pose difficulties in its remediation using PRB technology. The present study reports the 36-month performance of the PRB. Vertical differences in water velocity were observed within the PRB, with the deeper part being slower and more effective in neutralizing pH and removing heavy metals (Zn, Al, Cu). On the other hand, partial sulfate removal appeared to be restricted to the bottom of the PRB, but with no apparent influence on downgradient water quality. The results are finally compared with the other four reported existing PRBs for AMD worldwide.

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1. Introduction

A major environmental concern regarding mining activities worldwide is the contamination posed by the so-called acid mine drainage (AMD) originated from the biochemical oxidation of pyritic minerals in both abandoned and active mines. Upon exposure to atmospheric oxygen and water, these minerals oxidize to form an acidic, heavy metal and sulfate-rich drainage that, following the abandonment of sites, improper disposal, landfill leachates or accidental spills, can infiltrate through the soil degrading the quality of the groundwater. Because of its harmful effects on the natural ecosystems, considerable efforts have been made to mitigate ecological damage posed by AMD-contaminated groundwater.

Permeable reactive barriers (PRB) for groundwater treatment have emerged in the last two decades as a promising alternative to conventional pump-and-treat approaches, which are costly and not always effective at restoring sites to background conditions. A PRB consists of an engineered zone of reactive material buried in a narrow trench such that contaminated groundwater is treated as it flows through the reactive material [1]. The selection of the reactive material is crucial: it must be chemically effective to eliminate the

target contaminant(s) and must maintain an adequate permeability to ensure flow through the PRB. If hydraulic conductivity is too low or if the PRB clogs over time, water will not flow through it and will not be treated. If preferential flow paths develop in the reactive material, most of the water will flow through these zones, and residence time may be too short to achieve an adequate level of treatment. There are currently over 200 PRBs installed worldwide for different scenarios of contamination, but most of them rely on zero-valent iron (ZVI) and only a few on other materials (modified zeolites, limestone, organic substrates, activated carbon...) [1,2].

PRBs for AMD biological remediation are based on sulfate-reducing bacteria (SRB), which under favourable conditions convert sulfate to sulfide by the oxidation of organic carbon. Bacterially in situ generated sulfide can then precipitate dissolved metals [3–6].

Even though considerable laboratory-based research has been performed on this approach [3–6], to our knowledge only four full-scale PRB (besides the one reported in this study) have been installed until today [7–10]. Clearly, the use of PRB for the remediation of AMD-contaminated groundwater is still at the very early stage of application.

The PRB reported here was motivated by the mining accident occurred in the Aznalcóllar pyritic mine (Spain), probably the most serious environmental accident recorded in Spanish history [11]. On the 25th April 1998, a retention wall of a tailing dam of the

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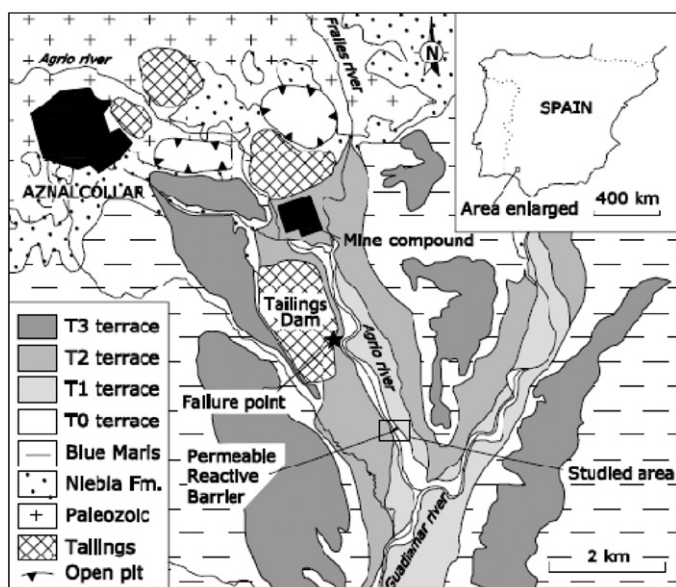


Fig. 1. Study area with geologic and geomorphologic formations.

mine collapsed resulting in the release of approx. 4 million m³ of AMD and 2 million m³ of toxic mud rich in heavy metals [11–13]. Over the following days the spill flowed 40 km downstream the Agrio and Guadimar rivers covering a zone about 800 m wide along them [11] and threatening the Doñana National Park, a UN World Heritage Area and important RAMSAR site. A total area of 4286 ha was covered by a mud layer averaging 7 cm thickness [14]. Extensive cleanup measures began immediately after the accident, e.g. construction of walls to retain the flood, withdrawal of mud and dead fauna, construction of a water treatment plant, among others. Despite these efforts and further cleanup operations in 1999 and 2000, large areas of soil and sediment still remained contaminated [12–14].

Many studies have reported the long-term effects caused by the spillage on the local soils [12–15], groundwater [16], biota [17] and fluvial geomorphology and hydrology [18]. In order to mitigate some of these long-term effects, the installation of a PRB was proposed based on the only PRB for AMD reported in the scientific literature at that time [7]. The PRB in Aznalcóllar was, thus, the second of its kind and, as such, it represented a challenging approach in the field of in situ remediation.

The aim of the present study is to report the performance of the PRB installed in Aznalcóllar during three years of operation. From a broader perspective, and given the still scarce data on full-scale PRB for AMD remediation worldwide, the goal of the present study is contributing to a better understanding of such systems and aid future design for other PRB applications.

2. Materials and methods

2.1. Site characterisation

Aznalcóllar is located in the province of Seville (SW Spain) within the Iberian Pyrite Belt. Mining extraction activities before the accident were performed in two open pits north of the mine compound, while process residues were deposited in a 30 hm³ tailing dam on the terraces of the Agrio river south of the mine compound and 3 km upstream from the confluence with the Guadimar river (Fig. 1). It was a section of the eastern wall of this pond that collapsed resulting in the massive release of AMD and toxic mud over the Agrio and Guadimar river floodplains.

The geology and hydrology beneath the Agrio river have been described previously [16,19,20]. Briefly, the geologic setting consists of Paleozoic materials overlain by conglomerates and calcarenites dating from the Upper Miocene ages, blue marls from the Upper Miocene and Lower Pliocene, sandy silts from the Middle Pliocene, Plio-Quaternary sands and Holocene marsh clays and, overlying all of these, are the alluvial deposits of the Agrio and Guadimar fluvial systems, which are made up of silt, sand and gravel deposits. Close to the PRB site, the alluvium consists of an upper gravel layer, a silt layer and a lower gravel layer [20].

Groundwater flow at the site is in a southerly direction in the alluvium along the watercourse of the Agrio river, with a hydraulic conductivity ranging from 10 to 400 m/d. The estimated groundwater flow is high (0.5–1 m/d), representing a notable distinct characteristic compared to other AMD-contaminated groundwaters treated by PRB. The average hydraulic gradient was found fairly flat (0.1%), which is expected of highly permeable media [16,19,20]. The values of such hydrodynamical parameters are fairly variable due to seasonal fluctuations and the complexity and heterogeneity of the geologic setting.

Site investigations conducted by many previous studies revealed that both soil and groundwater severely suffered from a high loading of acidity, heavy metals (primarily Zn but also Cu and to a lesser extent Al, Pb, Co, Cd and Mn), As and sulfate. With regards to groundwater beneath the Agrio river to be treated by the PRB, it was found to be characterized by a pH around 4.0 and high concentrations of Zn (15 mg/L), Al (15 mg/L), Cu (1 mg/L) and SO₄²⁻ (1000 mg/L). Unlike other sites contaminated by AMD, Fe and As were not found to be of concern (groundwater concentrations <1 mg/L and <10 µg/L, respectively) [19].

2.2. Construction of the PRB

The site investigation carried out for the location and orientation of the PRB, as well as its installation, has been reported in detail previously [20]. Surface mapping and geophysical exploration, boreholes drilling, trenching, vertical electrical sounding, hydraulic testing and water sampling provided data converging on a simple geological model based on three terraces that gave rise to the final design and installation of the PRB. For its construction, sheet piling was driven into the ground and keyed into the aquitard (the blue marls formation), to break any hydraulic connection between the trench and the aquifer. A trench was then excavated with a conventional backhoe, filled with the reactive materials and covered with local low-permeability sediment in order to prevent atmospheric oxidation of the filling materials. Finally, the sheet piles were extracted.

Subsequent subsurface data demonstrated that the internal structure of the Agrio alluvial deposits did not follow the simple model derived from the initial site investigation but a much more complex one, questioning the initial conceptual grounds that served as basis for the design of the PRB. Basically, it was found that an intermediate silt layer initially believed to correspond to one of the three terraces did in fact belong to another terrace. As a result, the new data showed that the PRB failed to intercept the whole saturated thickness, leaving untreated a portion of groundwater flow to the west [20]. Design flaws (e.g. improper hydraulic characterisation of a site prior to PRB installation) have been reported to be the most common cause of PRB failures according to an extensive review on PRB performances [2].

2.3. Configuration of the PRB

The PRB was designed to span 110 m, the full width of the river Agrio floodplain and to be divided into 3 modules (each 30 m long perpendicular to groundwater flow, 1.4 m thick parallel to ground-

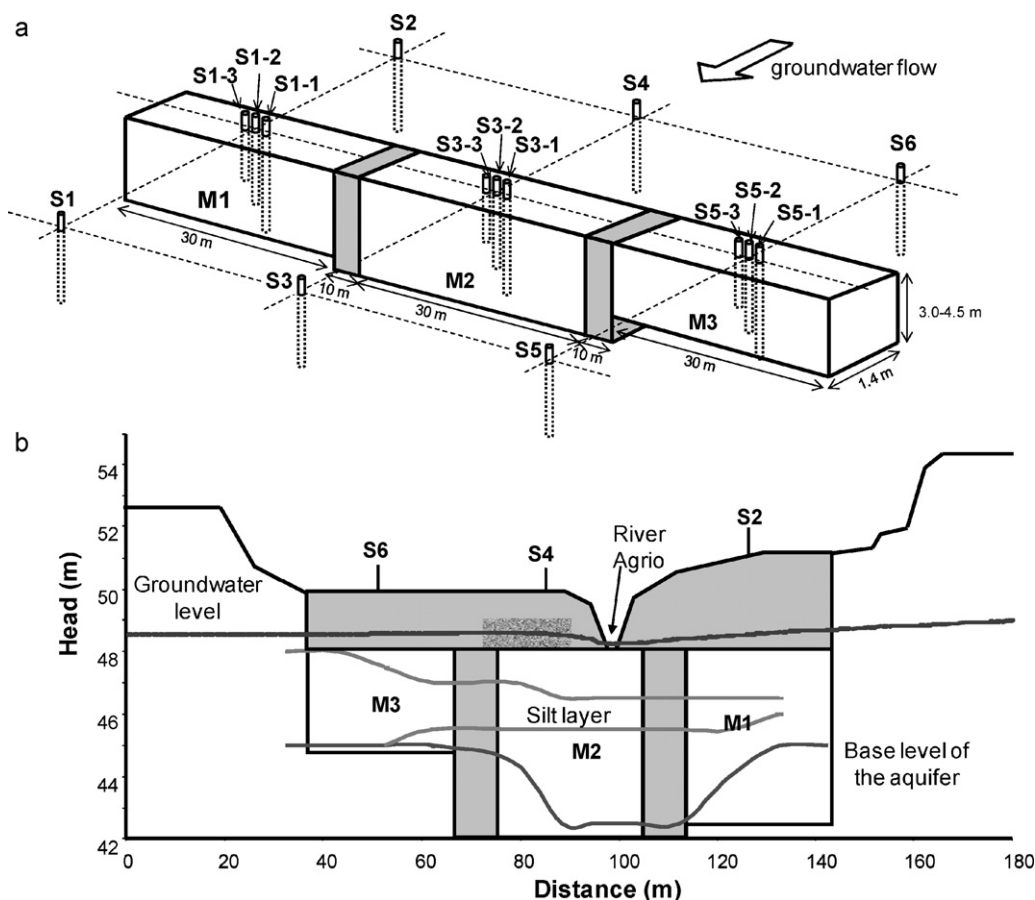


Fig. 2. Conceptual scheme of the PRB; (a) 3D-sketch of the PRB showing the position of the monitoring wells up- and down-gradient and within the PRB (not to scale), (b) cross section of the PRB system.

water flow, and on average 6.0 m deep) separated by 10 m long non-reactive sections of low hydraulic conductivity (clayey soil) (Fig. 2a). The three modules of the PRB penetrated the underlying marls by about 0.5 m (Fig. 2b) and were filled with different filling materials and proportions (Table 1).

The filling materials consisted of limestone, two organic substrates (of different origins i.e. vegetal-gardening compost and sewage sludge) and ZVI. Limestone (in the form of chips 1–2 cm diameter) was used to raise pH, to precipitate some metals as (oxy)hydroxides and to create suitable conditions for SRB [3,21,22]. The organic substrate was added to provide an electron donor to sustain SRB activity [3,6]. ZVI (in the form of iron cuttings of variable size, but thickness below 1–2 mm) was added in the central module (M2) in order to better achieve reducing conditions suitable for the SRB [23,24]. Additional reasons of adding ZVI is that ZVI corrosion can (1) enhance SO_4^{2-} reduction by generating $\text{H}_2(\text{g})$, which can be utilized by some SRB species as an electron donor [6,23,24] and (2) favor the formation of iron (oxy)hydroxides with excellent sorptive properties for the removal of other species present in groundwater [24,25]. The presence and proliferation of SRB was anticipated on

the basis that SRB are ubiquitous in the environment and can proliferate under suitable conditions (i.e. presence of a carbon source and sulfate, absence of oxygen). This hypothesis was corroborated by exhaustive laboratory work carried out to simulate the PRB in Aznalcóllar [22,23,25]. The expected reactions involved by using the materials described are summarized in Table 2.

2.4. Monitoring of the PRB

A sampling network was installed to monitor the performance of the PRB. Three transects of wells oriented perpendicular to groundwater and parallel to the PRB were installed upgradient (wells S2, S4 and S6), inside (wells S1, S3, S5 with hyphenated numbers) and downgradient (wells S1, S3, S5) the PRB (Fig. 2a). Transects delimited by wells S2–S1, S4–S3 and S6–S5 ran through modules M1, M2 and M2, respectively, as shown in Fig. 2a. The monitoring wells within the PRB consisted of piezometer nests to enable water sampling at three different depths (3.0, 4.0 and 5.0 m bgl). In their identification name shown in Fig. 2a, the hyphenated number indicates the depth of the piezometer (number 1 referring to the deepest one and number 3 to the shallowest one). Hydraulic conductivity of the reactive modules was measured by slug tests and data treated using the Theis and Cooper-Jacob methods and the software packages “Mariaj” and its user interface “Epebo” [26]. Tracer tests were performed to verify groundwater flow using inorganic (NaCl, LiBr, KBr, KI) and organic (uranine, rodamine, Gd-DTPA, piranine, eosine) species and data obtained were interpreted following Carrera and Walter’s approach and using the software package Trazador [27]. Monitoring for groundwater hydrology and chemistry was conducted with decreasing frequency from monthly

Table 1
Filling materials and proportions within each module of the PRB in Aznalcóllar.

Filling material	M1	M2	M3
Limestone chips	60%	60%	60%
Sewage sludge	5%	–	–
Vegetal compost	35%	35%	40%
Zero-valent iron cuttings	–	5%	–
Hydraulic conductivity (m/d)			
PRB	<0.1	1.0	0.6

Table 2
Reactions involved by the filling materials of the PRB for the mitigation of AMD.

Material	Purpose
Limestone $\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	Increase of alkalinity and neutralization of pH
Organic substrate $2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$ $\text{M}^{2+} + \text{H}_2\text{S} \rightarrow \text{MS} + 2\text{H}^+$	Microbial reduction of SO_4^{2-} by SRB Precipitation of M^{2+} with generated H_2S
Zero-valent iron (ZVI) $\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2$ $\text{SO}_4^{2-} + 4\text{H}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$ $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$	Better achievement of reducing conditions for SRB Generation of H_2 as electron donor for SRB Formation of Fe-(oxy)hydroxides with sorptive properties for the removal of species by co-precipitation.

intervals during the first year, to three month intervals during the third year. Field monitoring comprised the determination of water levels in the piezometers and groundwater sampling for quality analysis (pH, Eh, dissolved oxygen, heavy metals, As, SO_4^{2-} and S^{2-}).

2.5. Chemical analysis

Groundwater samples for laboratory analysis were stored at 4 °C until analysis within 10 days following established QC/QA protocols. Heavy metals, S and As were measured by inductively-coupled plasma mass spectroscopy (ICP-MS) (VG Plasma Quad PQ2). S^{2-} was analysed by colorimetry following the methylene blue method [28]. Solid fractions from within the PRB were withdrawn after two years of installation for examination by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analyser (JEOL 6450, EDX-LINK-LZ5) and by X-Ray Diffractometry (XRD) (Bruker D5005) with Cu $\text{K}\alpha$ radiation. Sulfate-reducing bacteria enumerations were also quantified using standard spread plate-count technique according to Standard Methods [28].

3. Results and discussion

3.1. Hydraulic performance

The groundwater head generally ranged between 34.3 and 35.0 m above sea level, with up-gradient heads being slightly higher than down-gradient, indicating that flow progressed in the expected direction through the PRB. Fig. 3 shows the evolution of groundwater head within M2. It also shows the variability of groundwater head attributable to seasonal conditions and/or sporadic rainfall events, with raises following heavy and sustained rainfalls during the period 5–7 months and after approximately 17 and 29 months after the PRB installation. The rainfall events eroded the stream bed and enhanced the hydraulic connection of the Agrio

river to the lower gravel layer [29], which in turn led to increases of groundwater flow. This must be borne in mind in interpreting the water quality in the sections further below.

The hydraulic conductivity of each module was measured by slug tests soon after the PRB installation and was found to be <0.1 m/d for M1, 1 m/d for M2 and 0.6 m/d for M3 (Table 1), which are lower than that of the aquifer (10–400 m/d). Tracer test showed that groundwater was flowing through modules M2 and M3, while the flux through M1 was diverted to M2 and the western end of M3 (where some conductive terrace was still present), indicating that the hydraulic conductivities of M2 and M3 were sufficiently high to allow groundwater flow through them. Lack of flow through M1 was confirmed by tracer tests. Tracers injected upstream of M1 took more than one month to arrive at the downstream well. The low conductivity of M1 was probably due to the fact that the fine grained sewage sludge used as additional filling material, although added in a low percentage (5%) (Table 1), clogged the pores and prevented a good hydraulic connection within the module. Because M2 and M3 showed very similar performances, in the following only the evolution of M2 will be described, and discussions (unless otherwise stated) apply to both M2 and M3.

Average residence time (t_R) within M2 and M3 of the PRB was estimated from groundwater flux (calculated from the hydraulic conductivity and the hydraulic gradient using Darcy's law and found to average $0.3 \text{ m}^3/\text{m}^2/\text{day}$) and the effective porosity within the PRB (estimated to be 0.1–0.4). Calculated t_R generally ranged between 1 and 2 days.

3.2. Basic water quality parameters

Values of pH, Eh and DO in groundwater entering the PRB spanned from 3.9 to 4.0, +100 to +400 mV and 5 to 8 mg/L, respectively (Fig. 4). Within the PRB, these values strongly depended on the vertical location of the sampling points. Groundwater sampled from the deeper monitoring wells S-3-1 and S-3-2 (at depths 4.0 and 5.0 m, respectively) showed neutral or even basic pH (mostly ranging between 7 and 8) and reducing and hypoxic conditions (E_h ranging generally between –100 and –250 mV and DO between 0.5 and 2 mg/L) (Fig. 4). These environmental conditions appeared to be appropriate for SRB activity to develop. However, groundwater sampled from the shallowest part of the PRB (well S-3-3 at a depth of 3.0 m) showed pH values around 4.5 (only slightly above the inlet pH) and oxidant conditions (E_h values between +100 and +300 mV and DO concentrations between 5 and 7 mg/L) (Fig. 4).

The pH pattern suggested that preferential flows might be occurring within the PRB, with higher flow rates in the upper part of the PRB in such a way that, due to a lower residence time, calcite dissolution could not raise pH to at least neutral values. Equal reasoning could be made for organic matter oxidation and subsequent decrease in Eh and DO. A similar heterogeneous behavior in a zero-valent PRB is reported by other studies [30]. Cores extracted from the PRB after three years of operation showed that in the shallowest

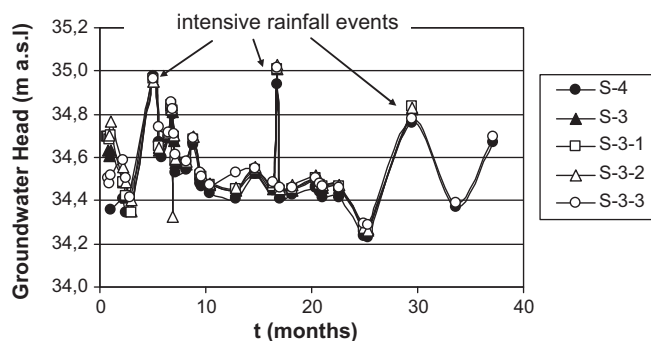


Fig. 3. Evolution of groundwater head in wells upgradient (S-4, ●), downgradient (S-3, ▲), and within the PRB in decreasing depths: bottom (S-3-1, □), middle (S-3-2, △) and top (S-3-3, ○) of the module M2.

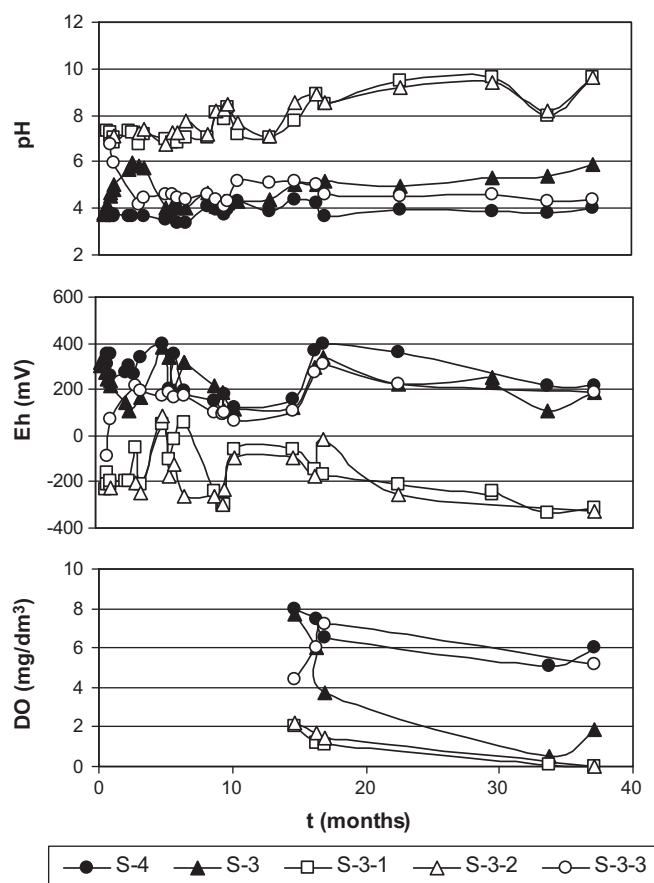


Fig. 4. pH, Eh and DO levels in groundwater in wells upgradient (S-4, ●), downgradient (S-3, ▲), and within the PRB in decreasing depths: bottom (S-3-1, □), middle (S-3-2, △) and top (S-3-3, ○) of the module M2.

part of this section calcite gravel and compost had been insufficiently mixed, creating zones of pure calcite with a high hydraulic conductivity. This evidence confirmed the above hypothesis on short residence times and incomplete (bio-) geochemical reaction in this part of the PRB.

The pH of the downgradient groundwater (well S-3) was found to be generally low (around 5). This could be an indication that groundwater flow through the shallowest part of the PRB was much higher than that through the deeper part of the PRB and, thus, dominated the final pH in the downgradient side of the PRB.

3.3. Heavy metals

Groundwater entering the PRB showed concentrations of Zn, Al and Cu of 20, 15 and 1.2 mg/L, respectively. These values gradually decreased over the 3-year monitoring period to 4, 2.5 and 0.25 mg/L (Fig. 5). High variations of inlet groundwater composition due to seasonal variations are often reported for other PRBs [7,8,10].

Regardless of the entrance concentration, vertical trends also in the removal of heavy metals were observed within the PRB. The extent of the removal was clearly inversely correlated with pH: higher metal concentrations were found at lower pH (well S-3-3) and, conversely, lower metal concentrations were found at higher pH (wells S-3-1 and S-3-2). Thus, while no apparent removal of metals was observed in the shallowest well (S-3-3), Al, Zn and Cu concentrations in deeper wells (S-3-1 and S-3-2) were found at concentrations mostly <0.05 mg/L (metal removal >95%).

Downgradient Al, Zn and Cu concentrations were lower than upgradient concentrations, with average removal percentages of

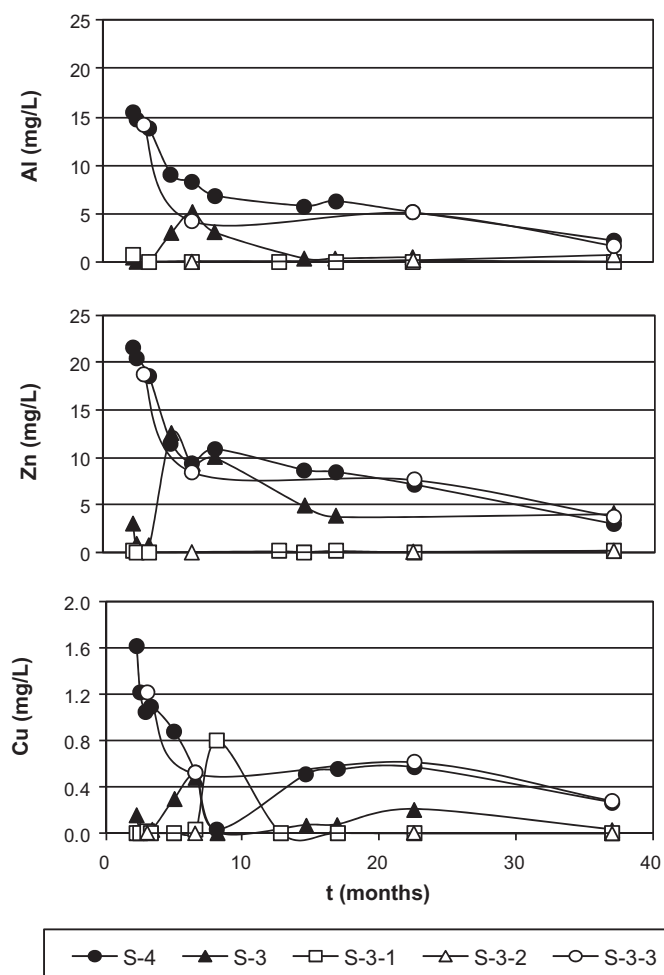


Fig. 5. Zn, Al and Cu concentrations in groundwater in wells upgradient (S-4, ●), downgradient (S-3, ▲), and within the PRB in decreasing depths: bottom (S-3-1, □), middle (S-3-2, △) and top (S-3-3, ○) of the module M2.

80%, 47% and 76%, respectively. This result demonstrated that, despite the channelized flow, the PRB showed a considerable capacity of metal removal. However the removal percentages during rainfall events were notably lower, particularly during the period 5–7 months after installation (removal percentages of 45%, 5% and 36% for Al, Zn and Cu, respectively). Clearly, removal efficiency for Zn was lowest among the metals evaluated. Limited Zn removal in comparison with other metals such as Al and Cu has been reported in previous studies [25,31].

3.4. Sulfate and sulfide

Upgradient sulfate concentration was initially around 1100 mg/L and tended to gradually decrease to 400 mg/L towards the end of the monitoring period (Fig. 6).

Irrespective of the upgradient value, a significant decrease in sulfate was only observed in the lower part of the PRB (wells S-3-1 and S-3-2) where sulfate was detected at levels between 50 and 400 mg/L. This corresponded to an average sulfate removal percentage of 43%, suggesting that relatively strong sulfate reducing conditions developed in this part of the PRB. In contrast, sulfate in the upper part of the PRB (well S-3-3) remained unaffected by the passage through the PRB. Sulfide concentrations were found below detection limits (0.48 mg/L), which was indicative that generated S^{2-} , if any, rapidly precipitated in the presence of heavy metals.

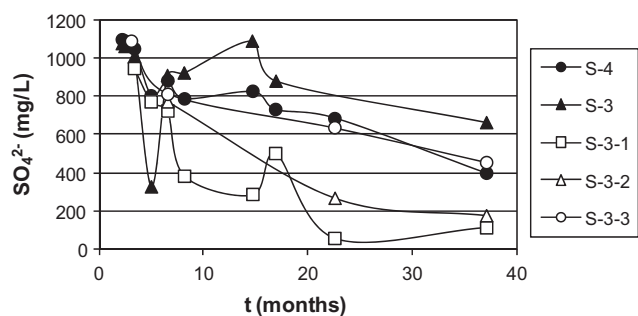


Fig. 6. Sulfate concentrations in groundwater in wells upgradient (S-4, ●), down-gradient (S-3, ▲), and within the PRB in decreasing depths: bottom (S-3-1, □), middle (S-3-2, △) and top (S-3-3, ○) of the module M2.

The occurrence of SRB activity in the lower part of the PRB was in accordance with pH and Eh values recorded at this depth (Fig. 4) and further corroborated by preliminary microbiological analysis, which showed higher SRB populations (around 1×10^4 cell/g, with a maximum up to 1×10^6 cell/g) in the bottom part of the SRB (S-3-1) than in other parts of the PRB (always $<6 \times 10^3$ cell/g). Better reducing conditions achieved and/or maintained at deeper locations of similar systems have been reported and are attributed to the prevention of air intrusion [8,32].

Downstream sulfate concentration did not seem to be influenced by the partial removal of sulfate in the lowest part of the PRB and it was globally indistinguishable from upgradient concentrations of the PRB. This finding again suggests that most of groundwater flows through the upper part of the PRB whereas it is quasi stagnant in the lower part of the PRB.

3.5. Mechanisms in the performance of the PRB

In views of the results the mechanisms responsible for the removal of heavy metal within the PRB were found to be likely more related to pH increases (i.e. precipitation as metal (oxy)hydroxides and co-precipitation onto them) rather than to sulfide generation. SEM-EDX analysis of solid cores from the PRB corroborated these mechanisms by showing throughout “armoured” calcite (Fig. 7a) with a pervasive coating layer composed of amorphous Al-(oxy)hydroxide (and Fe-(oxy)hydroxide where ZVI was used) and amorphous Al-S-Fe hydroxide (Fig. 7b), as made evident by the presence of the Al, O, Fe and S peaks in the associated EDX diagrams (not shown). These precipitates served as a secondary phase for sorption of dissolved metals such as Zn and Cu. In fact Zn was detected on their surfaces. The amorphous nature of the precipitates prevented any identification by XRD.

This finding was in agreement with previous extensive laboratory-scale work mimicking the PRB conducted to elucidate the mechanisms taking place within it but under more controlled conditions [23,25,33]. In these studies, Al, Zn and Cu were found to be partially or totally precipitated at circum-neutral pH as metal (oxy)hydroxides and carbonates. Additionally, Zn was also removed through co-precipitation onto Al-(oxy)hydroxide (and to a lesser extent onto Fe-(oxy)hydroxide where ZVI was used) [23,25]. The occurrence of the combined effect of precipitation as metal (oxy)hydroxides and co-precipitation onto new formed phases as major mechanisms for metal removal under similar conditions has been reported by other researchers [6,10,21,30].

Sorption onto the compost surface is an additional mechanism presumed to account for Zn and Cu removal in non-sulfate reducing conditions according to our previous work [23,25,33] and other published studies using a large list of organic substrates [3,6,24,30], but no conclusive data on this point are available from the PRB in

Aznalcóllar. Identification and quantification of this mechanism is a subject for future investigations.

3.6. Comparison with other reported PRB for AMD remediation

As mentioned above, there are only four other reported PRB for AMD remediation worldwide (apart from the one described here). Though the principles and design of these five PRBs are comparable in general terms, their performances differ considerably and variations in the extent of contaminant removal and in the nature of precipitates occur from site to site. This difference is likely due to dissimilarities in PRB hydraulics, the type of organic substrate used as filling material, the chemistry of the inflow water, and the local hydrogeologic setting. Table 3 presents an inventory of the existing biological PRBs for AMD treatment to facilitate comparisons among them.

Basically, the five PRBs are successful in neutralizing pH and removing heavy metals from groundwater within the PRB (general pH increases from 3–4 to 7 or even higher, and metal concentration decreases from many hundreds or thousands mg/L to few mg/L).

However, more variability is found in the removal of SO_4^{2-} . Organic substrate degradability and residence time (t_R) are reported as key factors on SRB activity and can, thus, explain the differences observed between PRBs [4,5,22,31].

Many different organic substrates (mulch, compost, sawdust, sewage sludge, manure, ...) have been thoroughly researched at a laboratory scale with different degrees of success, their degradability being recognized to control the sulfate reduction activity [3–6,22–25,31]. Attempts to predict the degradability of a raw organic material have been performed [22], but it is still an open issue and the selection of an organic substrate is done on an empiric basis by comparing performances of different candidates [4–6].

With regards to the t_R , laboratory studies have emphasized the importance of providing a sufficient time to ensure good contact between the water and the organic substrate and enable a sustained SRB activity to develop [22,31]. Experiences from full-scale PRBs seem to be in agreement with this trend. Although data are not always available and comparison are often difficult between PRBs, lower t_R indeed seem to limit the SO_4^{2-} reduction extent (Table 3).

For the PRBs in Vancouver (Canada) [8] and Charleston (USA) [9], either t_R or SO_4^{2-} removal are not reported and, thus, SO_4^{2-} removal cannot be discussed in terms of t_R . Among the remaining PRBs, the highest sulfate removal percentage (25–78%) with documented t_R is reported for the PRBs at Sudbury, where the average t_R is as high as 90 days [7,34]. SEM and XRD analysis of solid cores from this PRB showed that precipitation of metal sulfides was a major sink for Fe (the most abundant metal) and SO_4^{2-} [35,36]. This finding was corroborated by high increases of SRB populations within the PRB compared to the upgradient aquifer [7,36]. However, even for this case, which is characterized by an extremely high t_R , a decline of 30% in the sulfate removal was observed after 3 years of operation [34]. The PRB in Vancouver, which operates with a t_R of 6 days, does not report any percentage removal of SO_4^{2-} , but analysis of groundwater within the PRB showed a significant increase in sulfide concentration (0.61–0.70 mg/L) and geochemical modeling indicated supersaturation with respect to many metal sulfides (e.g. FeS, Fe_{1+x}S , Fe_3S_4 , CuFeS_2 , CuS , ...), with the formation of some of these minerals being confirmed by XRD analysis [8].

Both PRBs in Shilbottle (UK) and Aznalcóllar (Spain) operate at high flow rates and low t_R (between 0.4 and 3 days), which undoubtedly does not favor sulfate removal. Though an initial sulfate removal of 40% was reported for the former of these PRBs [10], “a reductive environment was only marginally achieved in some areas at the base of the PRB bottom” and “both the small or negligible amount of S removed and the high Al removal make the actual processes occurring in the PRB closer to treatment systems based

Table 3
Compilation of the existing biological PRB for AMD treatment worldwide.

Location (and year of installation)	Filling Components	Dimensions (m) ^a	t_R (d)	Upgradient			Within the PRB			Downgradient			Ref.
				pH	Metal (mg/L)	SO ₄ ²⁻ (mg/L)	pH	% Metal removed ^b	% SO ₄ ²⁻ removed ^b	pH	% Metal removed ^b	% SO ₄ ²⁻ removed ^b	
Sudbury, Ontario, Canada (1995)	Municipal compost (20%) Leaf mulch (20%) Wood chips (9%) Pea gravel (50%) Limestone (1%)	W = 20 T = 4 D = 3.5	90 (60–165)	4–6	Fe (200–2000) Ni (0.12–30)	2500–5200	6.7 ^c	56–91 ^c	25–78 ^{c,f}	6.5 ^c	38–94 ^c	7–56 ^c	[7,34]
Vancouver, British Columbia, Canada (1997)	Leaf compost (15%) Pea gravel (84%) Limestone (1%)	W = 10 T = 2.5 D = 6.5	6	6.39	Cu (0.6–10.7) Zn (2.4) Cd (0.015) Co (0.005) Ni (0.013)	n.a.	6.86	>95	n.r.	6.63	“... oxidation of sulfides downgradient the PRB leads to a re-contamination of the groundwater after the passage through the PRB”.		[8]
Charleston, South Carolina, USA (2002)	Leaf compost (30%) Zero-valent iron (20%) Pea gravel (45%) Limestone (5%)	W = 7.9 T = 1.8 D = 4.1	n.a.	3.16–4.24	Zn (2.64–1060) Fe (83.4–10500) Al (69.1–2710) As (0.261–206) Cd (0.003–1.44) Ni (0.048–2.12) Pb (0.032–4.08)	1800–49500	6.20–9.28	>98	83–99		“Because pyritecontaining fill was present on the down gradient side of the PRB, groundwater exiting thePRBwas subject to rapid recontamination”		[9]
Shilbottle, United Kingdom (2003)	Compost horse manure and straw (25%) Green compost (25%) Limestone (50%)	W = 180 T = 2 D = 3	0.4–1.7	<4	Fe (10–800) Mn (5.4–227) Al (16–862))	8700	n.r.	10–87	40 ^f	n.r.	n.r.	n.r.	[10,37]
Aznalcóllar, Spain (2000)	Vegetal com post (35–40%) ^d Sewage sludge (0–5%) ^d Limestone (60%) ^d Iron (0–5%) ^d	W = 110 T = 1.4 D = 3.0–7.5	1–2	4	Zn (20) Al (15) Cu (1)	1000	5 ^e	50–98 ^e	0–43 ^e	4–6	47–80	~0	This study

^a Dimensions: W (width), T (thickness), D (depth).

^b Referred to the upgradient concentration entering the PRB.

^c percentages roughly estimated from Figures shown in [7,31].

^d Composition variable depending on the module.

^e Depending on depth within the PRB.

^f Sulfate removal percentage decreasing considerably with time.

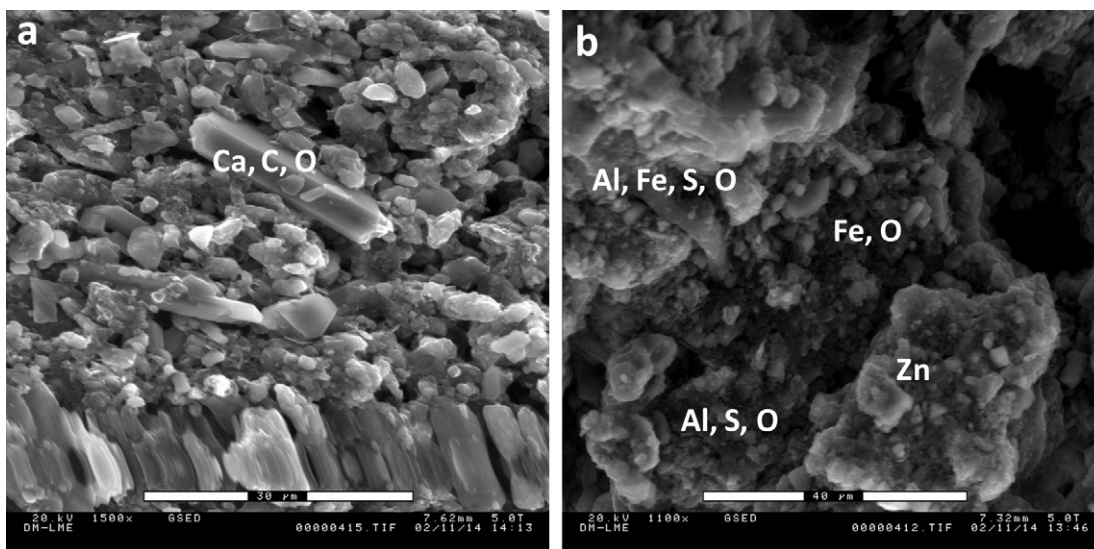


Fig. 7. SEM image for a solid core extracted from M2 showing calcite (a) with a pervasive coating layer composed of amorphous Al-(oxy)hydroxide and amorphous Al-S-Fe hydroxides with Zn on their surface (b).

on the use of alkaline substrates rather than systems using organic matter” [37]. More conclusively, the authors add that “the low residence time of the water within the PRB appears to be the reason for the absence of a more reducing and less acidic environment in the reactive substrate” [37]. The metal removal in this case was mainly due to precipitation as (oxy)hydroxides and carbonates (e.g. schwertmannite and goethite) [37]. These patterns are very similar to those observed in Aznalcóllar. In both PRBs calcite dissolution and not sulfate reduction was the main acidity neutralization process and driver for metal removal, probably due to the relatively low residence time.

4. Conclusions

PRB is a growing technology, which is gaining general attention in the field of AMD-contaminated groundwater remediation thanks to the opportunities it offers in the mitigation of acidity, heavy metals and sulfate. Together with the successes achieved by the existing PRBs of such nature, however, also hindrances are reported.

A common failure is design flaws (e.g. improper hydraulic and/or geological characterization of a site prior to PRB installation), which can give rise to a sequence of events from limited capture of the plume, diversion and partial or total by-pass of the groundwater around the PRB and, overall, loss of hydraulic control. This can further be complicated when climatic conditions can vary considerably over the year and so do the aquifer hydrologic conditions, in particular following heavy and sustained rainfalls. From a chemical point of view, limited sulfate reduction is a second drawback often reported. This limited sulfate reduction is probably due to poor degradability of the organic substrate used and/or to too short residence time within the PRB.

The PRB in Aznalcóllar reported here proved to be successful in neutralizing pH and removing heavy metals from groundwater (Al, Zn and Cu removals >96%, >95% and >98%, respectively). However, hindrances related to design flaws and limited sulfate reduction were encountered. The former was due to an improper initial characterization of the aquifer that led to a PRB design that, in retrospect, resulted to be not the most efficient at capturing the contaminated plume. The latter was probably due to the too short residence time within the PRB that resulted in a limited SRB activity. As discussed above, these findings agree with those reported on other PRB for AMD.

Clearly, biogeochemical processes and fluid flow through PRBs need to be better understood. This knowledge would clearly enable to assess the long-term effects, in particular if pore clogging occurs within the reactive zone and, if so, how it compromises the performance of the PRB. Considering the expansion of the PRB technology, it is foreseen that more data will be generated within the coming years and will provide a good base for better identifying benefits and limitations of this technology.

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