Metal retention mechanisms for the Aznalcóllar permeable reactive barrier (SW Spain)

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Abstract

A permeable reactive barrier, consisting of a mixture of compost and calcite gravel, was built in Aznalcóllar (SW Spain) to treat acidic groundwater containing zinc, aluminium and copper. Monitoring results show that practically no dissolved sulphate is reduced as water flows through the barrier, which has a residence time of about 1 to 2 days. Despite this lack of bacterial activity significant metal removal is achieved, making it clear that most of the metal retention can not be attributed to bacterially mediated sulphate reduction but to other mechanisms. In a laboratory study, a packed column was operated to evaluate the potential of municipal compost and calcite to promote sulphidogenesis in the remediation of a synthetic mine water at high flows (>0.5 m/d, 0.47 days average residence time). Results showed that acidity was neutralised and that metals were significantly removed. Rather than precipitation as metallic sulphides, metal removal was found mainly to be due to the combined result of precipitation as metal-oxyhydroxides, co-precipitation with these secondary phases, and sorption onto compost surfaces. The two latter mechanisms are especially significant for Zn: it can be roughly estimated that before saturation of compost sorption sites, 60% of the influent Zn was removed by co-precipitation with Fe- and Al-oxyhydroxides and 40% by sorption onto

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compost. Sorption onto compost is only expected for the first months of the field barrier operation.

1   Introduction

A major environmental concern regarding abandoned and active mines throughout the world is the treatment of acid mine drainage (AMD), which is produced from chemical and biological oxidation of residual sulphide minerals. A recent economically attractive technology for the *in-situ* treatment of AMD is the permeable reactive barrier (PRB), where a reactive material is emplaced underground in the path of the contaminant plume (Blowes et al., 2000). This material must be chemically effective to eliminate contaminants and must maintain a permeability at least equal to the surrounding aquifer material to ensure preferential flow through the barrier. The biological approach to the treatment of AMD is based on the use of sulphate-reducing bacteria (SRB) which, under favourable conditions, convert sulphate to sulphide by the oxidation of organic carbon (Benner et al., 1997). Bacterially *in-situ* generated sulphide can precipitate dissolved metals, while bicarbonate production can increase the pH of the acidic water.

The present paper investigates the feasibility of remediating AMD by using vegetable compost in combination with calcite. This study is part of the research work concerning the mine tailings spillage of the Aznalcóllar Mine (Spain) in April 1998, when a tailings pond dam failed catastrophically. The spread of mine wastes over the Agrio river valley instigated the installation of an organic-based PRB. As described below, no significant sulphate reduction is detected across the barrier. The lack of the activity of SRB could be attributed to the limited degradability of the current carbon source (Waybrant et al., 1998; Chang et al., 2000; Béchard et al., 1994; Gibert et al., 2003). Despite this lack of bacterial activity significant metal removal is achieved in the Aznalcóllar barrier, making it clear that most of the metal retention can not be attributed to bacterially mediated sulphate reduction, but to other mechanisms. These mechanisms are presumed to include metal precipitation as oxyhydroxides and carbonates (Dvorak et al., 1992), co-precipitation with these precipitates (Cravotta and Trahan, 1999; Song et al., 2001) and sorption onto the organic substrate (Machemer and Wildeman, 1992; Gibert et al., 2003). However, much uncertainty remains in identifying these processes, and papers comparing their contribution are scarce (Machemer and Wildeman, 1992).

Due to the complexity of the in-situ barrier system, laboratory column experiments were carried out with the same materials and under controlled conditions to be representative of the Agrio aquifer, with a view to interpreting the behaviour of the PRB in Aznalcóllar. The laboratory experiments were carried out in three stages: (1) a compost-based mixture was evaluated in a column experiment from a chemical point of view. Since results suggested that diverse mechanisms other than metallic sulphide precipitation were taking place, further experiments were focused on highlighting the contribution of (2) co-precipitation of metals with Fe- and Al-oxyhydroxides and (3) sorption of metals onto the compost substrate.

2   Performance assessment of the Aznalcóllar PRB

2.1   Barrier installation

The contaminant plume of the Agrio river alluvial aquifer was characterised by a pH lower than 4, and high concentrations of Zn (15 mg/L), Al (10 mg/L), Cu (1 mg/L) and SO_4^{2-} (1000 mg/L). The aquifer consists of gravels, sands and silts excavated in a base of marls.

The Aznalcóllar PRB (110 m wide x 1.4 m thick x 4 to 8 m deep) was installed across the floodplain of the Agrio river, 1 km downstream of the Aznalcóllar tailings dam. Construction was completed in September 2000. The PRB consists of 3 modules (30 m wide each) separated by 10 m wide modules of low permeability clayey soil (Carrera et al., 2001). The barrier fill comprised limestone chips (1-2 cm diameter), iron cuttings (variable size, but thickness below 1-2 mm), and organic composts from two different origins (compost-1: gardening compost + sewage sludge; compost-2: gardening compost only). The following volumes of materials were used in each module of the barrier:
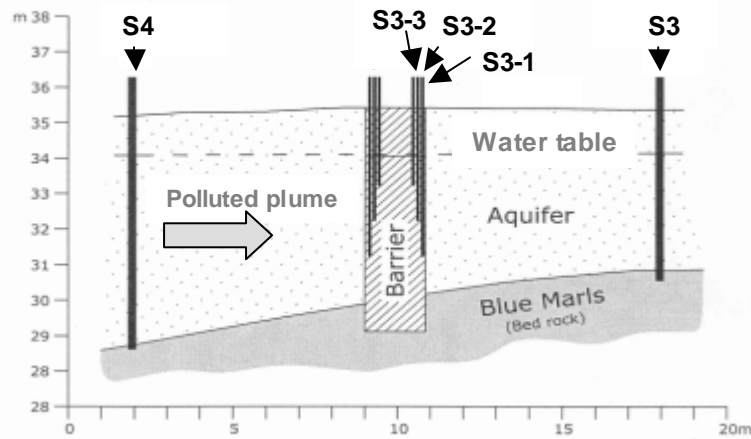
Fig. 1. Cross section of the Aznalcóllar PRB and distribution of monitoring boreholes in the central section of the barrier.

Western barrier (right margin): 60% limestone + 40% compost-1
Central barrier: 60% limestone + 35% compost-2 + 5% iron
Eastern barrier (left margin): 60% limestone + 40% compost-2.

The fill was covered with clayey soil, in order to place the reactive material where the groundwater flux is expected to be largest, and to protect the organic matter and iron from atmospheric oxidation. A comprehensive sampling network was installed both within and up- and downstream of the barrier, as illustrated in Figure 1.

2.2 Results

The evolution of pH through the barrier gives a good overall indication of its behaviour (Fig. 2). Field determinations of pH indicated that the barrier effectively removed acidity from groundwater during the first three months of operation (until January 2001). Over this period, pH downstream of the PRB was raised to near neutral values, but then dropped to pH 4, concurrent with a very significant flood event on the Agrio river. After the flood, the pH gradually increased again, recovering to near pre-flood values. The evolution of pH within the barrier was heterogeneous. Whereas the bottom and middle boreholes showed pH between 7 and 9 for the entire monitor-

ing period, the top borehole showed an evolution similar to the downstream pH with values between 4 and 5. The reason may be that the top borehole was initially located within the barrier material, but later it became surrounded by the clayey barrier cover due to consolidation of the barrier infill. The fact that the downstream borehole S-3 (Fig. 1) displayed a much lower pH than the barrier boreholes is somewhat paradoxical. This is attributed to the influence of the river on the aquifer and to mixing of treated water with water flowing around the PRB.
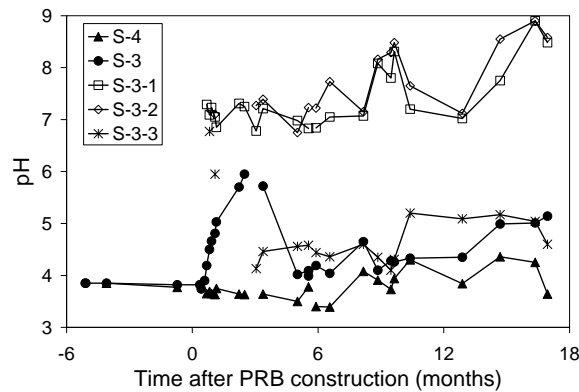

Fig. 2. Evolution of pH upstream (S-4: solid triangles), downstream (S-3: solid circles) and inside the central section of the Aznalcóllar barrier (open symbols): top (S-3-3), middle (S-3-2) and bottom (S-3-1).

The evolution of the metal concentrations (Al, Zn and Cu) matched that of pH, the higher the downstream pH the lower the metal concentration (Fig. 3a-c). Initially, metal concentrations in the downstream borehole decreased, then they rose concurrent with the Agrio river flood. Finally, the concentrations decreased again. As described for pH, the deep boreholes within the barrier (S-3-1 and S-3-2) showed very low metal concentrations. It is interesting to note that metal concentrations in the upstream borehole showed a gentle decrease with time. A distinct characteristic of the acidic waters in the Agrio river aquifer is the low Fe concentration (<1 mg/L in the upstream boreholes) and thus Fe has been omitted from the present discussion.
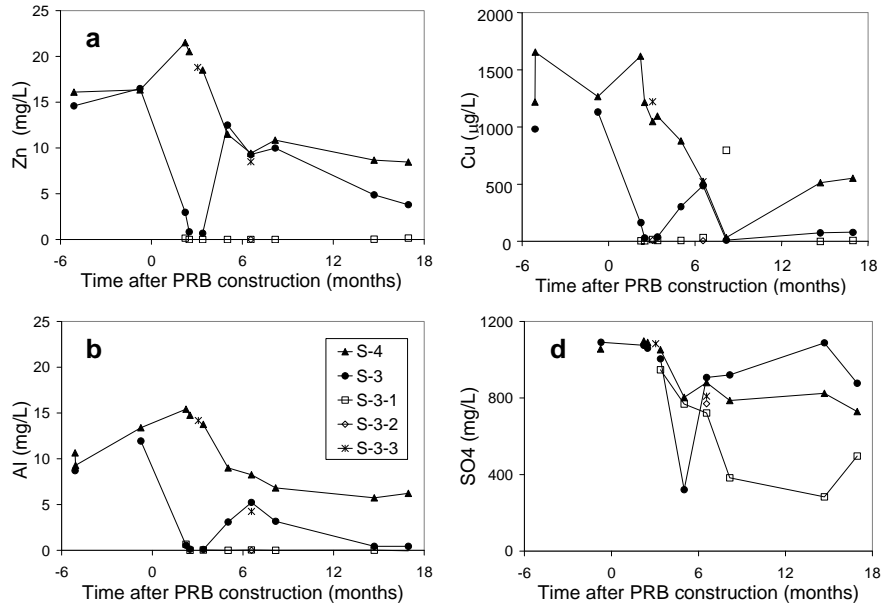
Fig. 3. Zn (**a**), Al (**b**), Cu (**c**) and SO_4^{2-} (**d**) evolution upstream (S-4: solid triangles), downstream (S-3: solid circles) and inside the central section of the Aznalcóllar barrier (open symbols): top (S-3-3), middle (S-3-2) and bottom (S-3-1).

The downstream concentration of sulphate was similar to that upstream (Fig. 3d). As described for metals, a gentle decrease of the input sulphate concentration was observed with time. A significant depletion of sulphate in the outflow was only observed in one sample after 5 months. With respect to the monitoring inside the barrier, no decrease was observed in the limited data collected from the middle and top parts of the barrier (S-3-2, S-3-3). However, a significant decrease in sulphate concentration was observed in the bottom of the barrier (S-3-1, Fig. 3). This may be due to low local flux and reducing conditions, with no apparent influence on the bulk downstream concentration.

Microbiological studies were carried out on organic matter samples from different parts of the barrier. The population of SRB was lower than $<10^{-6}$ cells/g, too low for biologically mediated processes to be significant. This was confirmed by H_2S analyses which were always below detection limits (15 μM), and Eh measurements were rarely below –150 mV.

The acidity of the water, A (mol/L), was calculated as follows:

$$A = 3*Fe \text{ (mol/L)} + 3*Al \text{ (mol/L)} + 10^{-pH} \qquad (1)$$

The percentage of metal and acidity removal was calculated according to:

$$\% \text{ removal} = (M_{up} - M_{down}) / M_{up} * 100 \tag{2}$$

where M_{up} and M_{down} are metal concentration or acidity up- and downstream of the barrier.

A very high capacity for acidity and metal removal was observed immediately after the barrier construction (Fig. 4). The efficiency of the barrier dropped rapidly during and after the heavy rain event. These parameters recovered slowly during the following months, attaining values between 60 and 90 %.
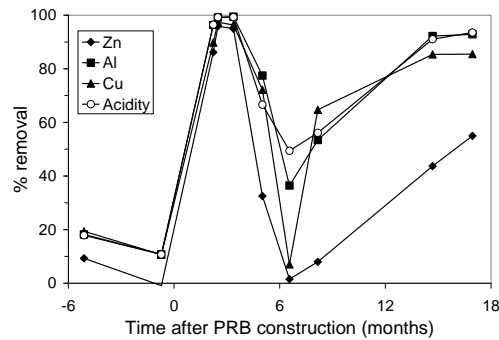

Fig. 4. Evolution of relative metal and acidity removal in the central section of the Aznalcóllar barrier.

3   Laboratory column experiments

3.1   Experimental set-up and methodology

The reactive mixture consisted of 40% (v/v) vegetal compost (189 g), 50% crushed natural calcite (755 g) and 10% river sediment (378 g). River sediment acted as the SRB source, compost was the provider of the organic carbon and calcite was used as the pH neutralising agent. The materials were mixed and homogeneously packed in the column (diameter of 5 cm and length of 50 cm), resulting in an estimated porosity of 0.35.

A synthetic acidic water, prepared on the basis of the groundwater composition in the Agrio aquifer was used, to ensure constant composition throughout the experiment. Its chemical composition was Fe(II) (10 mg/L),

Zn (20 mg/L), Cu (20 mg/L), Al (10 mg/L), SO_4^{2-} (1000 mg/L). Metals and anions were added as sulphates and chlorides, and pH was adjusted to 2.80 by HCl addition. Despite the low Fe concentration in the Agrio aquifer groundwater, Fe(II) was added to account for the dissolution of Fe^0 fragments and Fe-minerals in the barrier.

This synthetic water was kept in a closed vessel with low oxygen by bubbling nitrogen and was gravity fed into the column at an average flow rate of 0.5 ml/min, which equals a Darcy velocity of 0.73 m/d (0.47 days average residence time).

3.2   Water and solid analysis

All pH measurements were made routinely using a Hamilton combination pH electrode coupled to a Crison GLP22 pH meter. Eh was measured using a tubular platinum electrode paired with an Ag/AgCl-reference electrode. Fe, Zn, Cu and Al were measured spectroscopically by ICP-MS (VG Plasma Quad PQ2) and ICP- AES (Spectra). Sulphate was measured by liquid ion chromatography (ALLIANCE model Waters 2690) coupled to an electrical conductivity detector (Waters 996). Dissolved sulphide was determined using an Ag/AgS electrode. On completion of the experiment, fractions of precipitate were sampled from the inlet of the column and examined by scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyser (JEOL 6450, EDX-LINK-LZ5).

3.3   Results

As shown in Fig. 5, the removal efficiency of heavy metals was very high during the first 100 pore volumes, with measured concentrations in the effluent lower than 0.150 mg/L (retention levels >99%). From 100 pore volumes on, Zn showed an exceptional behaviour, with an increase in the outlet Zn concentration, which attained a maximum of approximately 8 mg/L. Al concentration was always below detection limit (0.010 mg/L). Outflow pH approached neutrality from the beginning of the experiment, SO_4^{2-} concentration was not found to decrease and HS^- concentration was always below detection limits (0.005 mg/L). These results, combined with the positive Eh values (around 400 mV), made it evident that no bacterial activity was occurring.
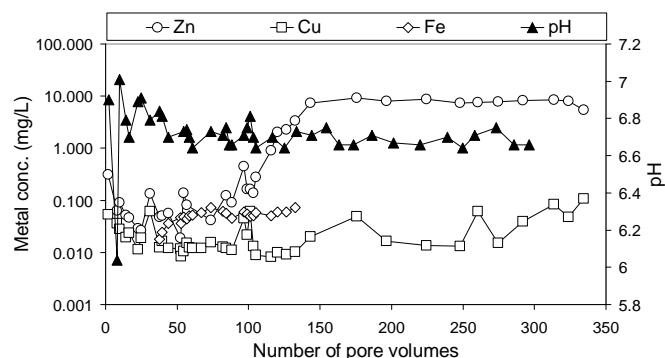
Fig. 5. Evolution of pH and metals concentrations in the outflow of the column experiment.

SEM analysis of the precipitates showed the presence of an amorphous layer of Zn-containing Fe- and Al-oxyhydroxides on the surface, and also the presence, although to a lesser extent, of secondary gypsum. The ability of Fe- and Al-oxyhydroxides to act as secondary sorbent phases and to incorporate heavy metal and metalloids through co-precipitation has been reported by numerous previous studies (Machemer and Wildeman, 1992; Cravotta and Trahan, 1999; Amos and Younger, 2003; Gibert et al., 2003).

The solubility of Zn is significantly affected by solution pH because of the formation of solid phases. At pH 6.8, the value reached in the outflow of the column experiment, almost all Zn is expected to remain in solution. This is in strong contrast with the Zn profile obtained in Fig 5, with marginal outflow concentrations during the first 50 days and concentrations reaching around 8 mg/L (which from a total concentration of 20 mg/L corresponds to a 60% retention) from this time on. These findings suggest that alternative mechanisms must be speculated to explain the partial depletion of Zn from the contaminated water. These mechanisms are hypothesised to be co-precipitation onto Fe- and Al- oxyhydroxides and sorption onto compost, and will be discussed further.

3.4   Discussion: metal retention processes

Co-precipitation with Fe- and Al- oxyhydroxides

Additional column experiments were carried out to test Zn and Cu removal by precipitation/co-precipitation in a calcite column system. Three col-

umns (hereafter referred as A, B and C) were filled with 20 g of calcite, and each one received a synthetic water containing (A) Zn, (B) Zn and Fe, and (C) Zn and Al. The metal concentrations were in the range 10-20 mg/L. All these solutions were acidified to a pH of 3.0 (by HCl addition) and prepared in a sulphate (1000 mg/L) and carbonate (60 mg/L) medium to meet the same conditions as in the previous column experiment. For comparative purposes, an analogous set of column experiments was conducted with metallic solutions containing Cu instead of Zn. These feed waters were pumped through the columns at a flow rate of 0.036 mL/min which equals a Darcy velocity of 0.59 m/d (0.15 days average residence time). At the end of the experiments, precipitates were retrieved for SEM and XRD analysis.

Results showed dissolved Zn concentration in the outflow from column A averaged concentrations of 14 mg/L (85% of the inflow content). The 15% removal of Zn may be caused by Zn precipitation at the prevalent pH, which is supported by the detection of hydrozincite ($Zn_5(CO_3)_2(OH)_6$) by XRD analysis.

Outlet Zn concentrations were much lower for columns B (9 mg/L, 50%) and C (3.5 mg/L, 25%), suggesting that co-precipitation of Zn onto Fe- and Al- oxyhydroxides was occurring. Zn would thus have more capacity to co-precipitate with aluminium than with iron. SEM analysis of precipitates from columns B and C corroborated this mechanism by showing a pervasive coating layer composed of amorphous Fe-oxyhydroxide and Al-oxyhydroxide respectively, with Zn on their surfaces.

For Cu columns, similar patterns were obtained with pH values stabilised at around 6.8. In sharp contrast to Zn columns, Cu concentrations for the three columns were lower, with outflow concentrations below 1,5 mg/L (removal levels of >86%), suggesting that Cu removal is basically governed by its precipitation induced by the increase of pH and that Fe and Al are not significantly involved in the Cu removal.

Sorption onto vegetal compost

Sorption onto the compost surface is a second mechanism presumed to account for metal removal in these systems. This phenomenon has been reported to be important, in non-sulphate-reducing conditions, for a large list of organic substrates (Machemer and Wildeman, 1992; Aderhold et al., 1996).

A set of batch equilibrium experiments was conducted in order to test the ability of compost to adsorb Zn and Cu on its surface. Experiments were conducted at a fixed pH (6.5 for Zn and 5.5 for Cu, the latter being

lower to prevent Cu precipitation as hydroxide), which was checked and adjusted periodically to the desired value. A sulphate (300 mg/L) and carbonate (60 mg/L) medium was provided to each batch experiment to better simulate conditions of the experiment described in section 3.1.

In Fig. 6 equilibrium metal concentrations in the solid phase (Γ in mg/g compost) are plotted versus concentrations in the solution (c_L). The amounts of metal taken up by compost were determined through a mass balance from liquid-phase measurements.

These data of sorption of Zn and Cu onto compost can be modelled by a non-competitive Langmuir-type adsorption isotherm:

$$\Gamma = (b\, c_L\, \Gamma_{max})/(1 + b\, c_L) \tag{3}$$

where Γ_{max} is the maximum adsorption capacity of the adsorbent and b is the apparent affinity constant. Experimental Γ and c_L data were used to determine the constants (Γ_{max} and b) from a linearised form of equation (3) and using least-square regression analysis. The curves in Fig. 6 were generated from Langmuir model equations, using the constants obtained above.
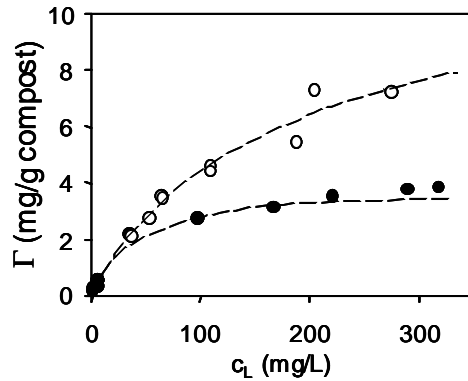

Fig. 6. Constant pH equilibrium uptake isotherms for Zn (solid circles) and Cu (open circles) onto compost. Curves are based on the Langmuir model with appropriate constant values.

The Langmuir model yielded values of Γ_{max} of 3.9 and 12.1 (mg/g compost) for Zn and Cu respectively. These values were comparable to those reported by other studies with a broad range of organic substrates (Allen and Brown, 1995; Veglio et al., 2002).

Contribution of mechanisms in Zn removal

Results from the previous co-precipitation and sorption tests can be applied to interpret the profile of Zn concentration over the column experiment in Fig. 5. Initially Zn removal can be attributed to the combined effect of co-precipitation with Fe- and Al-oxyhydroxides and sorption onto compost, resulting in marginal concentrations in the outflow (below 1 mg/L). Gradually the compost sites became occupied until, at day 50, saturation occurred, with the subsequent rise of Zn concentration in the outflow to levels around 8 mg/L. From this moment, Zn did not continue to adsorb onto compost but continued to co-precipitate with fresh Fe- and Al-oxyhydroxides. Fig. 7 shows the contribution of each mechanism in the Zn removal over the experiment. It can be roughly estimated that during the first 50 days approximately 60% of the influent Zn was removed by co-precipitation with Fe- and Al-oxyhydroxides and 40% by sorption onto compost.
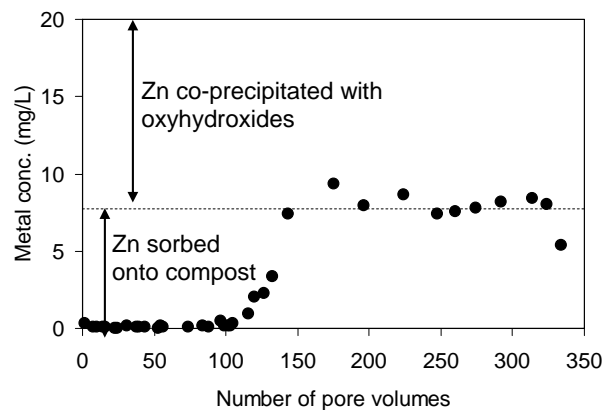

Fig. 7. Contribution of co-precipitation with Fe- and Al- oxyhydroxides and bio-sorption onto compost in the Zn removal over the experiment.

4   Conclusions

From the comparison of the field scale barrier and the column experiment, the following conclusions can be drawn:
- Both in the field and laboratory studies, compost was found to be too poor at providing nutrients to promote and sustain bacterial ac-

tivity, since SO_4^{2-} inflow concentration is not significantly reduced, no significant populations of SRB were found in the barrier material, no HS^- is detected, and Eh remains higher than 400 mV throughout the column experiment.

- Acidity neutralisation occurred immediately both in the field barrier and in the column experiment and was due to calcite dissolution. Acidity neutralisation was less efficient in the field barrier because of the greater grain size (lower reactive surface) and because groundwater partly bypasses the PRB.

- In the column experiment pH was always higher than 6, and aluminium and iron removal was practically complete, as an amorphous oxyhydroxide. In the field barrier, Al removal was strictly linked to pH variation and its efficiency increased as pH approached 5.

- In the column experiment, before saturation of compost sorption sites occurred, 60% of the influent Zn was removed by co-precipitation with Fe- and Al-oxyhydroxide and 40% by sorption onto compost. Once sorption sites of compost were saturated (100 pore volumes), co-precipitation appeared to be the only mechanism responsible for the Zn removal.

- In the field barrier, the removal of Zn and Cu was practically complete during the first three months, then dropped due to a flood, and increased again to values between 60% and 90%. According to the results of the column experiments, initially Zn retention occurred due to sorption onto compost and co-precipitation with Al-Fe-oxyhydroxides (100 pore volumes of the barrier are washed in 6 months). Then removal dropped due to the exhaustion of adsorption sites and/or pH decrease, and further retention was only due to co-precipitation.

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