Biobaroriers for groundwater treatment: a review
A. Careghini, S. Saponaro and E. Sezenna

ABSTRACT
Biobaroriers (BBs) are a new type of in situ technology for the remediation of contaminated groundwater. In recent years, this remediation technique has been more and more used in place of traditional Pump & Treat systems or other in situ technologies both in the USA and Europe. This work reviews the main experiences of BBs. The literature contains reports about tests and application at different scales (laboratory, pilot and full scale), which have been analyzed according to the aim of the study, the operative conditions adopted, the filling material, the inoculation procedure, the electron acceptor and the nutrient delivery systems. Operative conditions were extremely varied. Lab scale experiments pointed out good results in terms of pollutant removal efficiency. Pilot scale tests and full-scale applications confirmed the results obtained at lab scale, but also pointed out the importance of design for a proficient remediation system. The experiences underlined some possible critical issues: (a) the filling material must ensure proper hydraulic properties, but it also must be capable of keeping biomass in the reactive zone; (b) inoculation is a critical step and measurements should be carried out to check the initial distribution of microorganisms and its evolution over time; (c) electron acceptor and nutrient supply is usually required, but oxygenation into anaerobic aquifers can be critical.

Key words | biobarrier, groundwater, remediation

INTRODUCTION
Groundwater resources are highly vulnerable to contamination due to events such as accidental spills, unsatisfactory disposal of chemicals, agricultural practices, mining activities, etc. Petroleum and chlorinated solvents are reported as the most relevant contaminants for groundwater in Europe and in the USA; heavy metals frequently affect groundwater too. As far as petroleum hydrocarbons are concerned, groundwater is usually contaminated by short- to medium-chain alkanes, monoaromatic hydrocarbons (BTEXs: Benzene, Toluene, Ethylbenzene, Xylenes), PolyAromatic Hydrocarbons (PAHs), and oxygenated compounds used as gasoline additives (Methyl Tert-Butyl Ether – MTBE, Tert-Butyl Alcohol – TBA, ethanol, etc.). The most distributed chlorinated solvents affecting groundwater are trichloroethylene (TCE), tetrachloroethene (PCE), vinyl chloride (VC), etc. The behavior of these pollutants in the environment depends on their physical–chemical characteristics (e.g. density, vapor pressure, Henry’s constant, organic carbon–water partition coefficient, etc.), geology and hydrogeology at the site (e.g. aquifer thickness, porosity, hydraulic conductivity, hydraulic gradient, etc.) and the physical–chemical characteristics of groundwater (pH, redox potential, dissolved oxygen (DO), temperature, etc.) (U.S. EPA 2004; EIONET 2007; U.S. EPA 2007; AFCEE 2008; Farhadian et al. 2008; Thiruvenkatachari et al. 2008).

Excavation and multi-phase extraction have been the remediation options applied in the source zones for years, but recently the application of in situ chemical oxidation has increased considerably. Dissolved plume areas have been treated using Pump & Treat (P&T) systems, but the application of in situ techniques is increasing. This trend is confirmed by U.S. EPA (2010) reporting about 83 P&T remediation projects and 101 in situ treatments for the period 2005–2008. Among the in situ projects, bioremediation, chemical treatments, air-sparging and Permeable Reactive Barriers (PRBs) were the most used.

PRBs are passive systems based on placement of a permeable reactive medium to intercept the contaminated plume and to transform pollutants into less harmful or...
less mobile species. They have several advantages compared with traditional P&T systems and other in situ technologies, due to the low costs associated with operation and maintenance and the low impact on the activities carried out at a site (Yerushalmi et al. 1999; Blowes et al. 2000; Scherer et al. 2000; Miller et al. 2001; Xenidis et al. 2002; Thiruvenkatachari et al. 2008). PRBs can be suitable to treat many types of organic or inorganic pollutants (chlorinated solvents, petroleum hydrocarbons, heavy metals, etc.), according to the removal mechanism and the reactive medium selected. Until recently this kind of system was based most on physical or chemical mechanisms to promote degradation, precipitation or sorption of the dissolved contaminants. Different reactive media have been used, such as zero-valent iron for dechlorination or reduction of metallic species, activated carbon for sorption of organic pollutants, limestone for metal precipitation, etc.

Biological PRBs, also known as ‘biobarriers’ (BBs), are a new type of permeable barrier based on biological processes to degrade organic pollutants or to precipitate inorganic species (U.S. EPA 2004; Saponaro et al. 2009; ITRC 2011). A BB can be described as such when biodegradation occurs through a more permeable filling material replacing part of the natural aquifer. Therefore, more traditional in situ biostimulation or bioaugmentation, or the injection of edible/vegetable oils in groundwater to promote biodegradation without the creation of a more permeable zone within the aquifer cannot be considered a BB system (Borden 2008). The advantage of a BB is that limitations due to soil heterogeneities, hydraulic conductivity and/or biomass attachment/detachment can be reduced. Usually a selected biomass is seeded into the reactive zone, but applications based on growth on the filling material of microorganisms selected from the aquifer are also included (U.S. EPA 2004; Saponaro et al. 2009; ITRC 2011).

BB configurations and design

A BB, like all types of PRBs, is defined as ‘a continuous in situ permeable treatment zone designed to intercept and remediate a contaminant plume’ (ITRC 2011). BB systems can be considered as in situ biofilters with microorganisms attached to the filling material (Vesela et al. 2006; Lyew et al. 2007). Degradation of organic pollutants can occur through direct metabolism, cometabolism or reductive dehalogenation based on the contaminants of concern, the microorganisms and the electron acceptors/donors. Inorganic pollutants can be treated as well, through microorganisms able to promote changes in metal speciation or other mechanisms (e.g. nitrification–denitrification for ammonium). Two main configurations are available for PRBs (Figure 1), the Continuous PRB (C-PRB) and the Funnel & Gate PRB (F&G-PRB), regardless of the removal mechanism. A C-PRB consists of a continuous wall, entirely filled with the filling material, intercepting the plume perpendicularly to the groundwater flow. The F&G-PRB is composed of impermeable funnels to direct the groundwater flow through the reactive gate, resulting in a wider capture area. PRB height must cover the contaminated depth; the bottom of the barrier can be keyed into an impermeable aquitard to avoid possible underflow of contaminated groundwater (Xenidis et al. 2002; Thiruvenkatachari et al. 2008; ITRC 2011).

The design of a BB is based on three main sequential steps (NAVFAC 2004):

- Site characterization to get information about site geology and hydrogeology (aquifer depth and thickness, hydraulic conductivity, effective porosity, hydraulic gradient, groundwater flow direction, water table fluctuation) and physical-chemical characteristics of groundwater (pollutant concentrations, pH, redox potential, dissolved

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**Figure 1** | Continuous (a) and Funnel & Gate (b) barriers (U.S. EPA 1998).
oxygen, nutrients, temperature, hardness, concentrations of iron, manganese, sulfate, etc.).

- Laboratory scale tests, consisting of: (a) batch tests, to select the proper biomass and conditions for the biological process, and (b) column tests, to estimate the hydraulic conductivity and the longitudinal dispersivity of the BB filling material, the pollutant retardation coefficients in the system, and the biodegradation kinetic constants. Table 1 summarizes the experimental conditions reported in the literature.
- 3D numerical modeling to select the optimal BB location and size; this in turn affects the pollutant residence time in the reactive zone. This step also helps assess the BB effect on water flow, taking into consideration the site-specific groundwater hydraulics.

**Filling materials**

A suitable medium for a BB must ensure optimal growth conditions for microorganisms and exhibit high hydraulic conductivity compared with the surrounding aquifer to avoid groundwater by-pass. Other issues to keep in mind are: (a) long-term stability; (b) environmental compatibility (no release of by-products or harmful compounds); (c) safety during construction, maintenance and monitoring; (d) availability and cost. Geotextiles (polypropylene fleece and natural coconut fiber) have been recently proposed, but up to now, granular filling materials have been the most tested (Xenidis et al. 2002; Vesela et al. 2006; Jechalke et al. 2010).

Di Lorenzo et al. (2005) used pumice granulates in the particle size range 0.4–0.6 mm, resulting in an excellent microbial binding capacity.

Liu et al. (2006) used expanded perlite in the particle size range 2–3 mm, which was chosen for its high porosity, poor reactivity and low cost.

Saponaro et al. (2009) used commercial quartz sand for concrete manufacturing in the particle size range 0.355–0.6 mm; this medium was homogeneous, inert and suitable as a biomass support; however, the low hydraulic conductivity (2.2 × 10^-6 m/s) limited the applicability to low-permeability aquifers. Also, Yeh et al. (2010) used inert sand (Ottawa standard sand in the particle size range 0.6–0.85 mm), reporting the same advantages but also a higher hydraulic conductivity (2.9 × 10^-4 m/s) due to the particle size distribution selected. Sand was used also by Teerakun et al. (2011), but no information was given about particle size distribution and/or hydraulic conductivity.

Yerushalmi et al. (1999) compared stainless steel pieces (0.6 × 0.6 cm, average particle density 5.13 g/ml) as an inert filling with granulated peat moss (in the particle size range 4–7 mm) as a reactive filling. The sorption capacity of peat moss resulted in retardation of gasoline pollutants through the medium, but no significant difference in the residual pollutant concentrations was observed between the two. These results suggested that biodegradation was the major mechanism removing the contaminants from water and that both materials were suitable for BB applications. A peat material (70% biogreen reed sedge, 20% sphagnum peat and 10% cocoa fiber) was used by Guerin et al. (2002) for its high sorption capacity on petroleum hydrocarbons. High removal efficiencies were measured for the organic pollutants being treated.

Leglize et al. (2006) used activated carbon (particle size range: 0.85–1.1 mm) and pozzolan (particle size range: 2–3 mm), coated or not with heavy fuel oil to improve PAH sorption. All materials were able to keep the biomass in the system and support growth. Coating of pozzolan increased the sorption capacity, but the mineralization rates were slowed down.

Vesela et al. (2006) tested keramzit (ceramic granulate) as an inert filling and oxyhumolite (oxidized young lignite) as an adsorptive filling. Sorption on oxyhumolite was negligible, resulting in no significant difference in the residual pollutant concentrations between oxyhumolite and keramzit. However, oxyhumolite was able to support biofilm growth if combined with limestone and gravel.

Plant mulch is more and more used as filling material to promote anaerobic microbial degradation of chlorinated solvents or heterocyclic nitramines, because it is composed of structural polymers (such as cellulose and hemicellulose) whose degradation can provide metabolic intermediates to support the process (AFCEE 2008; Shen et al. 2010). BBs based on the use of plant mulch are usually called ‘biowall’.

Hardwood bark mulch was used by Seo & Bishop (2008) and Seo et al. (2009). The sorption capacity of the mulch prevented fast migration of hydrocarbons or chlorinated solvents and helped the BB to overcome the initial lag phase in the biofilm production (Wei & Seo 2010).

Both Shen et al. (2010) and Lu et al. (2008) used plant mulch composed of shredded bark mulch, cotton gin compost and sand as filling material in their experiments. In Shen et al. (2010), the amount on a volume basis of the different materials (50% shredded bark mulch, 10% cotton gin compost, 40% sand) was based on a previous study (Shen & Wilson 2007).
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<tr>
<td>Leglize et al. (2006)</td>
<td>100 ml flasks, filled with 50 ml pollutant solution and different amounts (0.05–10 g) of solid materials. Temperature: 28 °C.</td>
<td>Water artificially contaminated with phenanthrene (PHE) (1 mg/l).</td>
<td>(1) Activated carbon (AC) (0.85–1.1 mm); (2) Pozzolan (2–3 mm) not coated (Pz) or coated (PzF) with heavy fuel oil.</td>
<td>–</td>
<td>PHE sorption on the matrices did not reduce mineralization. The degradation rates were significantly higher with AC and Pz than without the filling material. Lower PHE mineralization rates were observed using PzF.</td>
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<td>Liu et al. (2006)</td>
<td>600 ml flasks filled with 200 ml mineral solution and 20 ml inoculum. Temperature: 20 °C.</td>
<td>Water artificially contaminated with MTBE (130 mg/l).</td>
<td>Not used</td>
<td>Aerobic process. ORCs added to the mineral solution + air sparging (10 min) before starting the experiment.</td>
<td>The best ORC composition was studied varying the ratio among CaO₂, KH₂PO₄ and (NH₄)₂SO₄; the effect of pH on biodegradation was also assessed. CaO₂: KH₂PO₄ : (NH₄)₂SO₄ was finally set to 1.0:2.0:2.6 on weight basis, because it was able to keep pH values in the optimal range for MTBE biodegradation.</td>
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<td>Choi et al. (2007)</td>
<td>120 ml bottles filled with 95 ml polluted solution and 5 ml inoculum. Room temperature (about 25 °C). Duration: 16–23 d</td>
<td>Water artificially contaminated with 2,4,6-trichlorophenol (TCP) (21–139 mg/l) or phenol (11–60 mg/l)</td>
<td>Not used</td>
<td>Anaerobic process (degradation under iron-reducing conditions).</td>
<td>Anaerobic digested sludge from a municipal wastewater treatment plant was used as the inoculum. Microbes were not able to degrade TCP. Phenol up to 28.5 mg/l was completely removed after 8 d of operation; 16 d were necessary to remove phenol at 60 mg/l.</td>
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<td>Saponaro et al. (2009)</td>
<td>1,100 ml flasks filled with 270 ml contaminated water and 30 ml inoculum. Temperature: 25 °C.</td>
<td>Water artificially contaminated with commercial gasoline. Main pollutants: MTBE (950 mg/l), benzene (8 mg/l) and toluene (21 mg/l).</td>
<td>Not used</td>
<td>Aerobic process. Oxygen from air in the flask headspace (800 ml).</td>
<td>Pollutant concentration, microbial density and dissolved oxygen were measured at 0, 3, 6, 10 and 13 d of incubation in biotic and abiotic tests. First-order degradation constants were obtained.</td>
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<td>Yeh et al. (2010)</td>
<td>250 ml flasks filled with 100 ml mineral medium and 5 ml inoculum. Temperature: 30 °C.</td>
<td>Water artificially contaminated with benzene and toluene. Concentrations tested for each compound: from 20 to 320 mg/l.</td>
<td>Not used</td>
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<td>Inhibitory degradation effects were observed for concentrations exceeding 80 mg/l.</td>
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<td>Shen et al. (2010)</td>
<td>60 ml bottles filled with 50 ml of sterile basal medium, 1.5 ml of dechlorinating enriched culture and filling material. Temperature: 25 °C Duration: 300 d</td>
<td>Water artificially contaminated with TCE (3.2 mg/l)</td>
<td>Sand (10 g d.w.), shredded tree mulch (3 g), shredded cotton gin trash (0.3 g)</td>
<td>Anaerobic process (reductive dehalogenation)</td>
<td>Microcosms were prepared using intact plant materials or dried-water extracts from plant materials or dried-solvents extracts. They were inoculated with an enriched culture selected from TCE-contaminated groundwater. Only microcosms with the intact plant material exhibited substantial removals of TCE (removal efficiency: 99.9%). By-products (cis-DCE, VC, ethylene) were observed and degraded during the test duration.</td>
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Lab scale – Column tests

Yerushalmi et al. (1999)  
Column length: 25 cm, column height: 20 cm; column width: 10 cm. Flow rate: 500–9,300 ml/d. Room temperature (about 25 °C)  
Water artificially contaminated with gasoline (3.7–74 mg/l). (1) granulated peat moss (4–7 mm); (2) protruded stainless steel.  
Aerobic process. Air sparging in the feeding tank before gasoline addition.  
The oxygen supplied was not enough to support complete aerobic biodegradation, so that also anaerobic processes occurred. Gasoline removal efficiency was between 86.6 and 99.6% in the peat moss-packed BB and between 94 and 99.9% in the stainless steel-packed one. Most removal occurred in the first few centimetres of the barrier. Adsorption also occurred in the peat moss-packed barrier. BTEXs did not exceed 15.8 and 5.7% of the effluent's organic content in the peat moss-packed and in the stainless steel-packed barrier respectively.

Kao et al. (2003)  
Column length: 30 cm, column diameter: 4.8 cm. Flow rate: 250 ml/d. Duration: 90 d Temperature: 23 °C.  
Groundwater artificially contaminated with PCE (1.0 mg/l). Columns 1, 3, 4, 6 and 7: aquifer material (silty sand) from a TCE/PCE-contaminated aquifer. Column 2: sludge cake Column 5: ORC.  
Test carried out using seven sequential continuous-flow columns with different fillings materials. Activated sludges from an industrial wastewater treatment plant were used as the microbial inoculum. Insignificant removal of PCE occurred in the first two columns due to the lack of carbon source in column 1 and the high pH value in column 2.
PCE degradation occurred in columns 3 and 4, with 98% removal efficiency at the end of column 4. Negligible removal of PCE was observed in the aerobic layers. By-products (TCE, cis-DCE, VC) were detected in column 3, but they were completely removed at the end of column 7. Accumulation of VC was observed in anaerobic layers.

A linear relationship between toluene removal rate and the loading rate was obtained, resulting in 99% removal efficiency. A toluene-degrading biofilm grew on pumice. Oxygen was not enough to support complete degradation, so that nitrate was postulated as the additional electron acceptor.

BB composed of 2 layers: the first one to oxygenate the polluted water, the second one to biodegrade pollutants. MTBE removal was 50%. Significant accumulation of TBA was observed in first period of operation, but concentrations decreased after 100 h thanks to biomass acclimation to TBA.

Columns were packed with a mixture of mulch and pea gravel (70 and 30% on volume basis); this ratio optimized requirements related to porosity/hydraulic conductivity and the amount of electron donor. No RDX and HMX were detected in the effluent; RDX intermediates in the effluent under steady state conditions was less than 2% of the influent RDX mass. No adsorption of RDX, HMX or intermediates occurred on the column-bed material.

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<td>Choi et al. (2007)</td>
<td>Three sequential columns, 30 cm each (column 1 and 2) and 80 cm (column 3); column diameter: 2.64 cm (column 1 and 2) and 10 cm (column 3). Flow rate: 100–215 ml/d in columns 1 and 2; 245–400 ml/d in column 3. Duration: 240 d. Room temperature (about 25 °C).</td>
<td>Water artificially contaminated with 2,4,6- TCP (100–120 mg/l)</td>
<td>Columns 1 and 2: Fe powder (&lt;150 μm) coated with Pd and sand (50:50 on volume basis). Column 3: sand (0.3–0.6 mm)</td>
<td>Columns 1 and 2: chemical process. Column 3: anaerobic biodegradation of phenol under iron-reducing conditions.</td>
<td>Multi-layer barrier: (1) chemical reductive dechlorination, (2) by-products biodegradation. Only phenol was detected in the effluent from column 2. The BB was able to remove completely phenol at 9.4 mg/l within the column residence time (7–8 d); phenol removal efficiency decreased to 66–85% with phenol inlet concentrations of 14–28 mg/l. The residence time necessary for phenol biodegradation was longer than for 2,4,6-TCP chemical dechlorination.</td>
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<td>Seo &amp; Bishop (2008)</td>
<td>Column length: 30 cm, column diameter: 3.8 cm. Flow rate: 3,670 ml/d. Duration: 210 d. Room temperature (about 25 °C).</td>
<td>Water artificially contaminated with naphthalene (20 mg/l).</td>
<td>Hardwood bark mulch</td>
<td>Aerobic process. Hydrogen peroxide solution 0.8% (v/v) pumped through the column at 34.8 ml/d.</td>
<td>High removal efficiency (99.99%) was observed in biotic columns. The oxygen delivery system was not able to ensure aerobic conditions through the whole column: after 100 d of operation, OD was less than 1 mg/l at the first sampling port. Naphthalene removal occurred most through the initial 6 cm of the column, where aerobic conditions were established, but significant removal was also achieved using nitrates as electron acceptor. Significant amount of extracellular polymeric substance was detected, increasing the sorption capacity of the barrier.</td>
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<td>Seo et al. (2009)</td>
<td>Column length: 30 cm, column diameter: 3.8 cm. Flow rate: 3,670 ml/d. Duration: 150 d. Room temperature (about 25 °C).</td>
<td>Water artificially contaminated with PHE and pyrene (PYR). Pollutant concentrations: 0.6–0.9 mg PHE/l and 0.07 mg PYR/l</td>
<td>Hardwood bark mulch</td>
<td>Aerobic process. Hydrogen peroxide solution 0.8% (v/v) pumped through the column.</td>
<td>Aerobic biomass selected from sewage sludge. In some tests surfactant addition was carried out after 50 d. 99.9% removal efficiency for both the monitored PAHs was achieved in 150 d without surfactants. When the surfactant was used, (continued)</td>
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<td>Saponaro et al.</td>
<td>Column length: 120 cm, column diameter: 11 cm. Flow rate: 220 ml/d. Duration: 40 d. Room temperature (about 25°C). Water artificially contaminated with commercial gasoline; main pollutants: MTBE (950 mg/l), benzene (8 mg/l) and toluene (21 mg/l). Quartz sand (355–600 μm).</td>
<td>(when surfactant was not used), 15 mg PHE/l and 3–5 mg PYR/l (when surfactant was used).</td>
<td>Aerobic process. MgO₂ addition in the feeding tank. Daily injection of 15 ml solution of MgO₂ (0.27 mg/l) at each sampling port.</td>
<td>Two kinds of tests: (1) uninoculated columns; (2) columns inoculated with selected aerobic biomass. Removal up to 47.7% for MTBE and 90% for benzene and toluene at the end of the inoculated columns. No significant removal observed in the uninoculated tests. TBA was observed in both columns, which was biodegraded through the column length only in inoculated columns. MgO₂ additions ensured aerobic conditions (dissolved oxygen &gt;2.0 mg/l).</td>
<td>the removal efficiency was 80–98% for PHE and 28–91% for PYE after 25 d from the surfactant addition, but they dramatically decreased in the following 90 d (8–30%). Mulch sorption capacity decreased due to the surfactant addition; AC was suggested as an additive to mulch.</td>
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<td>Shen et al.</td>
<td>Column length: 46 cm, column diameter: 15 cm. Flow rate: 200 ml/d. Duration: 5 years (ongoing). Groundwater contaminated with TCE, with further addition up to a final concentration of 2.5 mg/l. Shredded tree mulch (50% v/v), cotton gin compost (10% v/v) and sand (40% v/v).</td>
<td></td>
<td>Anaerobic process (reductive dehalogenation).</td>
<td>Removal efficiencies of TCE between 99.3 and 96.5% during 5 years of operation. Rate of mulch degradation was slower than those observed in batch tests; the lower surface area of mulch used in the column test delayed degradation. The theoretical operational time for the mulch biowall was 10–13 years.</td>
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<td>Teerakun et al.</td>
<td>Column length: 30 cm, column diameter: 5 cm (for column 1 and 4) and 10 cm (for column 2 and 3). Flow rate: 64 ml/d. Duration: 80 d. Temperature: 20°C. Water artificially contaminated with TCE (500 mg/l). Column 1: iron powder (425–850 μm) and sand (50:50 by weight); Column 2: sand; Column 3: sand (79% w/w) and 1 cm³ cubes of organic-carbon-inducer-releasing material (OCIRM, 21% w/w) Column 4: sand.</td>
<td></td>
<td>Column 2: anaerobic process (reductive dehalogenation). Column 3: aerobic process thanks to OCIRM composition (CaO₂).</td>
<td>The system was composed of 3 sequential columns (ZVI, anaerobic BB, aerobic BB). Anaerobic and aerobic sludges from a wastewater treatment plant were used as inoculum. TCE removals by ZVI, anaerobic and aerobic columns were 42, 16 and 25% respectively, with overall removal efficiency of 83%.</td>
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<td>Yeh et al. (2010)</td>
<td>Column length: 64 cm, column height: 20 cm; column width: 19 cm. Flow rate: 4,970 ml/d. Duration: 100 d. Room temperature (about 25 °C).</td>
<td>Water artificially contaminated with BTEXs (30 mg/l each).</td>
<td>Ottawa standard sand; ORC added (CaO₂, cement, sand, KH₂PO₄, K₂HPO₄, NaNO₃).</td>
<td>Aerobic process. ORC layer (2 cm long) located 20 cm far from water inlet.</td>
<td>Sand inoculated with selected aerobic biomass. High removal efficiency for toluene (80–99%), p-xylene (70–95%) and ethylbenzene (60–90%), low removal for benzene (30–60%). Two shock-loading events were tested, resulting in lower removal efficiencies. ORC was effective to keep aerobic conditions, but the ORC layer had to be replaced after 40 d of operation. The best ORC configuration had CaO₂ 40% w/w.</td>
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<td>Vesela et al. (2006)</td>
<td>Drainage trench + in situ bioreactor (chamber I, followed by chambers II and III in parallel) + recharge gallery. Flow rate: 430–720 l/d.</td>
<td>BTEX, chlorobenzenes, naphthalene, nitro-derivatives, phenols, TCE, Total Petroleum Hydrocarbons.</td>
<td>(1) Keramzit in chamber II (2) Oxyhumolite in chamber III.</td>
<td>Aerobic process. Chamber I equipped with an aeration segment at the base.</td>
<td>Removal from 57.3 (for naphthalene) to 99.9% (nitro-derivatives, BTEX). Adsorption on oxyhumolite was not a significant removal mechanism, but this material was suitable to support biofilm growth when combined with limestone and gravel.</td>
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<td>Lu et al. (2008)</td>
<td>Continuous wall (length: 139 m; height: 7 m; width: 0.5 m).</td>
<td>TCE (6.04 mg/l).</td>
<td>Plant mulch (shredded bark mulch, cotton gin compost).</td>
<td>Anaerobic process (reductive dehalogenation).</td>
<td>TCE removal efficiency within the biowall was about 99% after one month of operation. The concentration of by-products (cis-DCE, VC) increased downgradient of the biowall. Dehalococcoides was detected within the biowall.</td>
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<td>Guerin et al. (2002)</td>
<td>Funnel &amp; Gate configuration.</td>
<td>Water contaminated with dissolved petroleum hydrocarbons. Monitored compounds: BTEX (up to 25 mg/l), n-alkanes (up to 1,000 mg/l).</td>
<td>Peat materials.</td>
<td>Aerobic process. Air sparging system (0.9 m³ air/h).</td>
<td>Contaminated site in South Eastern Australia. Oxygen was added by air injections upgradient of the reactive zone. Removals between 54 and 96% for the different pollutants over 10 months (overall efficiency: 72%). The contribution of the different mechanisms (adsorption, biodegradation) on pollutant removal still not studied.</td>
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Ahmad et al. (2007) used pine bark mulch (4.75–1 mm) mixed with pea gravel (9.5–4.75 mm); the mulch to pea gravel ratio of 70%:30% (vol./vol.) optimized porosity, hydraulic conductivity and the amount of electron donor.

Lyew et al. (2007) compared peat, perlite, pouzzolana, pumice and granular activated carbon (GAC), in terms of sorption capabilities on MTBE and biomass (pure culture) attachment. GAC was the most effective in sorbing the pollutant, but had the worst behavior toward microorganism attachment. The best immobilization capacity was found for perlite, which also ensured the proper water flow thanks to its porosity.

Some authors suggested reusing waste materials (modified fly ash, compost, waste tire rubber scrap, etc.), which would help improve waste management, but additional research must be carried out to understand their long-term impact on aquifers (Doherty et al. 2006; Boni & Sbaffoni 2009; Lee et al. 2010).

Inoculation

Injection of enriched cultures is a common practice in BBs, regardless of the scale (Yerushalmi et al. 1999; Liu et al. 2006; Seo et al. 2009; Teerakun et al. 2011). Di Lorenzo et al. (2005) inoculated the columns recirculating a suspension (biomass concentration on dry weight basis: 1.2 mg/ml) at 8 ml/h for a week. Choi et al. (2007) recirculated a mixture of inoculum and nutrient medium for 10 d. Saponaro et al. (2009) recirculated a suspension for 4 d at 62 l/d and at 12 l/d in the following 20 h. Yeh et al. (2010) injected BTEX-degrading strains from the polluted site, at first at the inlet port of the column (31, 4.62 × 10⁶ Colony Forming Units (CFU) per ml), then at each sampling port (200 ml, 8.49 × 10⁹ CFU/ml). In NAVFAC (2004), selected cultures were injected into the aquifer at a concentration of 2 mg Total Suspended Solids per litre.

The distribution of the inoculated biomass was often considered as uniform within the bioactive volume of the barrier and constant over time. However, a homogeneous distribution of biomass by injection is difficult to achieve, because bacterial cells tend to concentrate near the injection points, sometimes clogging the wells (Streger et al. 2002). Actually, laboratory tests and field studies demonstrated the variability of microbial populations in both space and time (Thullner et al. 2002; Sandrin et al. 2004). Lesser et al. (2010) assessed the variability in space in the aerobic treatment at the Naval Base Ventura County, Port Hueneme (CA, USA), where high biodegradation rates of MTBE were measured close to the bioaugmented region. The placement of pre-incubated filling materials during BB construction can overcome problems related to biomass distribution.

Seki et al. (2006) investigated the effects of bioclogging through one-dimensional and two-dimensional inoculated flow cells. After 9 d of operation, the hydraulic conductivity decreased by 50% in the one-dimensional test. In the two-dimensional test, the overall hydraulic conductivity did not change significantly, but tracer tests pointed out preferential flow paths within the cell, reducing the retention time of water within the barrier.

The measurement of the biomass attached to the filling medium should be carried out to verify the inoculation effectiveness. This was estimated as Volatile Solids (loss weight at 600 °C) or by scanning electronic microscopy (Di Lorenzo et al. 2005). Protein assays on liquid samples were
also used (Di Lorenzo et al. 2005; Seo et al. 2009). Saponaro et al. (2009) estimated the concentration of biomass in the inoculated columns by mass balance, measuring the microbial density in the suspension before injection and after recirculation.

Electron acceptors and nutrient delivery

BBs can be divided into aerobic and anaerobic systems according to the final electron acceptors used by the microorganisms. Anaerobic BBs can work to dechlorinate organic compounds, to reduce and precipitate some metallic species or to remove nitrate and sulfate, whereas aerobic BBs are usually thought to biodegrade organic compounds such as short- to medium-length chain alkanes, monoaromatic solvents, light polycyclic aromatic hydrocarbons and MTBE (Scherer et al. 2000; Mackay et al. 2002). Among these, BTEXs and MTBE can be mineralized either under aerobic or under anaerobic conditions, though the rate and the extent of biodegradation is quite different for the different compounds under the different conditions, MTBE being the most recalcitrant (Stocking et al. 2000; Pruden et al. 2001; Nava et al. 2007; Farhadian et al. 2008). Moreover, it was verified that MTBE anaerobic degradation was too slow in view of field scale applications (Fayolle et al. 2003; U.S. EPA 2004; Nava et al. 2007; Farhadian et al. 2008; Youngster et al. 2008; Jechalke et al. 2010). When either aerobic or anaerobic biodegradation can occur and the rate and the extent of biodegradation are sufficient to achieve the remediation target, anaerobic treatments should be preferred in order to avoid oxygen supply (Yerushalmi et al. 1999; Liu et al. 2006).

For aerobic treatments, DO is to be higher than 2 mg/l, but values above 4 mg/l usually result in higher removal efficiencies. In order to supply oxygen to aquifers, in-well delivery systems or diffusive delivery systems were proposed, the choice to be based on site-specific hydrogeological and geochemical conditions (Scherer et al. 2000; Wilson et al. 2002; Thiruvencatchari et al. 2008; Zhu et al. 2009; Johnson et al. 2010).

In a column test, Yerushalmi et al. (1999) sparged air into the feeding tank to get oxygen at the saturation level (DO = 8 mg/l) in the inlet gasoline-contaminated water; no further oxygenation was carried out. Oxygen was enough to support aerobic biodegradation throughout 3 cm of packed soil, where pollutant removal was 92%. Anaerobic biodegradation (by sulfate-reducing bacteria) took place in the remaining part of the column, where pollutant removal was below 8%. Di Lorenzo et al. (2005), who used the same approach, pointed out that oxygen was not enough to explain the measured toluene removal, which in fact occurred also via nitrate reduction. Guerin et al. (2002) reported on a funnel and gate PRB, designed and built to treat groundwater contaminated with TExs and n-alkanes. The gate consisted of a sparging unit emplaced in basaltic scoria, followed by blended peat materials. Air injection was performed in the gate in continuous mode at 0.9 m³/h, but no information was given about hydraulic conductivity variations due to air injection. Johnson et al. (2010) recommended oxygen delivery via pulsed gas flow to increase DO levels (as high as 30–40 mg/l) while not altering the natural groundwater flow rate and direction. The use of oxygen rather than air is also advantageous in reducing pollutant volatilization (Salanitro et al. 2000).

Diffusive delivery systems can ensure proper DO levels in groundwater with less disturbance to aquifers (Wilson et al. 2002). At Vandenberg Air Force Base (CA, USA), Mackay et al. (2002) performed a field test using a pressurized cylindrical releaser (coil of silicone tubing wound around a PVC support) to diffuse oxygen through the walls of the tubing and then dissolve into groundwater. Oxygen-releasing compounds (ORCs) (e.g. magnesium peroxide, calcium peroxide, sodium percarbonate, etc.) are passive systems as well. Specific commercial products were developed to inject as slurry or to locate as filter socks in passive wells. Hicks et al. (2001) injected ORCs as slurry within the source area and in the plume to oxygenate groundwater contaminated by MTBE and BTEXs. The DO levels increased from 0.16–0.64 to 6.2 mg/l, allowing aerobic biodegradation to take place. Some ORCs can increase groundwater pH significantly, which must be buffered in order to avoid inhibitory effects on the microbial activity. Kao et al. (2005) used 500 g of a mixture composed of cement, CaO₂, sand, fly ash, NH₄Cl, K₂PO₄ and water (ratio: 1.4:1.5:0.7:1.3:0.7:0.8:2 by weight) to ensure aerobic conditions over a 3-month period in a multiple flow-column test. DO concentrations were very high (about 35 mg/l) in the first weeks of operation and were above 2 mg/l in the aerobic columns for the whole experimental duration. High pH values (9.5) were also observed in the first month of operation, which decreased to about 8 in the subsequent 2 months, a more appropriate value for a biological treatment. Liu et al. (2006) used CaO₂ mixed with KH₂PO₄ and (NH₄)₂SO₄ to balance pH and nutrients; pH values in the range 6.5–8.5 (in place of 12.1 using CaO₂ alone) and DO at about 20 mg/l were achieved using the weight ratios CaO₂:KH₂PO₄:(NH₄)₂SO₄ = 1:0.2:0.2:6. In a column test, Yeh et al. (2010) used an ORC layer (mixture of sand, cement, 40% CaO₂, KH₂PO₄, K₂HPO₄, NaNO₃ and water) 2 cm thick, placed before the bioreactive zone.
DO levels at about 8 mg/l were achieved at first, but DO decreased with time, so that the ORC layer had to be replaced every 40 d. Saponaro et al. (2009) saturated the inlet water with MgO2 and injected 15 ml a day of MgO2 (0.27 mg/l) through each sampling port of the soil column. MgO2 addition ensured aerobic conditions while neutral pH values were measured over the entire column. Teerakun et al. (2011) used 1.0-cm3 cubes composed of binding cement, CaO2, sand, sugarcane bagasse, fly ash and water at ratio: 1:5:1.5:0.2:0.2:1.5:2 (by weight). The DO level was above 5 mg/l in the effluent of the column for the entire duration of the experiment, but pH strongly increased (up to 11.0).

Some authors (Seo & Bishop 2008; Tiehm et al. 2008; Seo et al. 2009) proposed hydrogen peroxide injection. In general, dilute solutions are recommended to avoid negative effects on the biomass, resulting in high volumes to ensure proper DO levels (Scherer et al. 2000).

Oxygenation of anaerobic aquifers with high contents of dissolved iron or manganese can be challenging because of possible precipitation of metal oxides. This decreases permeability in the areas close to the delivery system and clogs the well screens. Some authors proposed ex situ treatments for the removal of iron/manganese and re-injection of the aerated water just before the BB reactive zone (Scherer et al. 2000; Tiehm et al. 2008; Zhu et al. 2009).

Anaerobic mechanisms, like reductive dehalogenation, do not require electron acceptors (provided by chlorinated contaminants of concern), but require electron donors. The use of biodegradable filling materials, such as mulch, sludge cake or sugarcane bagasse, can provide the required electron source (Kao et al. 2003; Ahmad et al. 2007; AFCEE 2008; Lu et al. 2008; Shen et al. 2010; Teerakun et al. 2011).

Nutrients and possible co-substrates are usually injected into groundwater as aqueous solutions through injection wells. The injection points are located upgradient from the reactive zone (Scherer et al. 2000; Thiruvenkatachari et al. 2008).

**Multi-layer barriers and innovative configurations**

The presence of pollutants biodegradable under different redox conditions might require multi-layer BBs to ensure and/or to optimize the removal of each compound. For instance, groundwater contaminated by both chlorinated solvents and petroleum hydrocarbons could be treated sequentially using an anaerobic layer for the reduction of chlorinated solvents and an aerobic layer to mineralize petroleum hydrocarbons and the dechlorination by-products (Kao et al. 2003; Bastiaens et al. 2005; Thiruvenkatachari et al. 2008; Lee et al. 2010; ITRC 2011).

Multi-layer barriers can also be composed of a chemical barrier followed by a biological one. Choi et al. (2007) obtained satisfactory results using a multi-layer barrier to promote chemical reductive dechlorination of 2,4,6-trichlorophenol (TCP) in two columns filled by microscale iron powder coated with palladium (Pd) and the degradation of by-products in a following anaerobic column filled with sand. Teerakun et al. (2011) proposed a ZVI-filled barrier (iron powder, 425–850 μm) followed by an aerobic BB and an aerobic BB to treat high concentration of TCE in groundwater (500 mg/l), obtaining removal efficiencies of 42, 16 and 25% in the three sequential zones.

A multi-layer barrier can be suitable also for the treatment of groundwater contaminated by landfill leachate. Van Nooten et al. (2008) studied a system composed of biological nitrifying and denitrifying layers to remove ammonium; in a second period of the experiment, the denitrifying layer was replaced with an activated carbon layer to remove organic halogens and chemical oxygen demand (COD) from groundwater. Ammonium was oxidized to nitrite up to 98% and then removed by denitrification, whereas organic halogens and COD were efficiently removed (66 and 49% respectively) by sorption on activated carbon.

The functionality of the multi-layer systems can be affected by the physical–chemical characteristics of groundwater flowing out of the previous layers and must be taken into account in design and operation. Chen et al. (2011) demonstrated an enhanced degradation of benzene and toluene downgradient of a ZVI barrier due to the TCE by-products, but it was also adversely affected by high pH values (10.5).

New types of BB are under study. Electricigenic Permeable Reactive Barriers (EPRBs) are an innovative type of anaerobic BB based on the microbial fuel cell concept. Electricigenes are used in these systems because they can oxidize organic compounds to carbon dioxide with an electrode serving as the sole electron acceptor; then electrons flow through the electrode to a final electron acceptor, usually oxygen. EPRBs are composed of two units: (1) the underground bioreactive zone that acts as the anode, and (2) the near-to-ground unit to allow cathodic oxygen reduction. Wires and water keep these units electrically connected, overcoming the limitations due to the electron acceptor delivery in groundwater. Moreover, electric current is produced (Zhu et al. 2009).

**Modeling**

Modelization of BBs does not differ from modelization of classic PRBs. Many works are available in the literature on modeling PRB systems. Usually, numerical models are
used to simulate groundwater flow and pollutant transport for different remediation scenarios (Gupta & Fox 1999; Das 2002; Elder et al. 2002; Burger et al. 2007; Johnson et al. 2008; Liu et al. 2011). Analytical models can be useful for preliminary evaluations, but they are not suitable to design full-scale systems (Craig et al. 2006).

Guerin et al. (2002) and Li & Benson (2010) used the modular finite difference groundwater flow model MODFLOW and the three-dimensional transport model MT3D. Saponaro et al. (2010) used MODFLOW to reproduce the natural steady-state flow field and MT3DMS to simulate BTEX and MTBE plumes. Plume capture capabilities of the proposed BB were assessed with the particle-tracking code MODPATH; RT3D was used to check the DO requirement and the ORC effectiveness. Bioclogging should be taken into account in the models.

Field applications

Tiehm et al. (2008) reported on a pilot plant study of a BB located in Offenbach (Germany) for the remediation of groundwater contaminated by BTEXs (up to 12 mg/l) and PAHs (up to 4.8 mg/l). The treatment was composed of three sequential steps: precipitation of iron (III), aerobic biodegradation, and sorption on GAC. Hydrogen peroxide was used to supply oxygen. With a 72 h-residence time, removals above 99% were reached for the major contaminants. The full-scale project cannot be considered a conventional BB, because the treatment was performed in a modular system with three separated bioreactors.

Vesela et al. (2006) described a pilot test carried out in East Bohemia (Czech Republic) to treat groundwater contaminated by many different organic pollutants (BTEXs, Total Petroleum Hydrocarbons, chlorobenzenes, naphthalene nitro-derivatives, phenols and TCE). The system was composed of a drainage trench (length: 13 m; width: 1.0–1.5 m; depth: until the impermeable clay layer at about 2.6–3.0 below ground surface), an in situ bioreactor (2.0 × 1.2 × 4.8 m³) and a recharge gallery. The in situ bioreactor was composed of three chambers, the first of which (I) was equipped with an aeration system, and was followed by chamber II and chamber III (not inoculated biofilter units) connected in parallel. Different filling materials were used in the chambers. The flow rate through the bioreactor varied between 430 and 720 l/d; the average water retention time was 129 h in chamber I and 16 h in chambers II and III. During 1 year operation, the results showed high effectiveness on organics, resulting in average removals of 57% for naphthalene and 99.9% for nitro-derivatives and BTEXs.

Lu et al. (2008) described a pilot scale BB installed in Oklahoma (USA) to treat TCE contamination of groundwater. Anaerobic degradation removed about 99% of TCE, but by-product (cis-DCE, VC) concentrations increased downgradient of the BB.

Guerin et al. (2002) reported on a full-scale application of a F&G BB in South-Eastern Australia to remediate groundwater contaminated by white spirit petroleum hydrocarbons. The gate consisted of a sparging unit located in a layer of porous basaltic scoria, upgradient of a blend of peat materials. The funnels consisted of 0.75 mm thick high-density polyethylene membranes. Inoculation was not performed. The system was designed to intercept the groundwater flow just downgradient of the spill location and from areas affected by lateral migration of the plume. The water table level remained constant over 10 months of operation. Hydraulic conductivity tests pointed out a large variability in the hydraulic properties of the filling material, resulting in preferential flow paths. Based on pollutant concentrations collected through the monitoring period, the BB system was effective in treating groundwater.

Critical issues, recommendation and BB future

The experimental activities carried out to test BB feasibility at different sites pointed out some critical issues, which suggest a few recommendations.

Design and operation must consider whether different types of pollutants are dissolved in groundwater, which might require different conditions for biodegradation. Possible by-products should be included in the list of long-term monitored parameters to avoid new uncontrolled plumes or prevent toxic effects on biomass (U.S. EPA 2004).

A non-homogeneous and/or excessive growth of microorganisms can lead to microbial induced clogging (bioclogging), potentially affecting the BB performance. Bioclogging preferentially occurs around the aeration systems (air or oxygen injection wells, ORC filter socks, etc.) or nutrient injection points and can be enhanced by the degradation of the biopolymers often used for trench construction (Zolla et al. 2009; ITRC 2011). The local decrease of permeability and/or the creation of preferential flow paths can result in the water flow bypass of the reactive zone or in insufficient oxygen/nutrients supply to the microorganisms (Seki et al. 2006). In order to prevent these effects, injections of small amounts of air or nutrients at different locations within the barrier are to be preferred (Seki et al. 2006).

If reactive materials are used as filling material, the operational lifetime must be carefully assessed to avoid long-term
failure of the BB system. In particular, mulch or compost longevity spans from 5 to 10 years in biowall applications; periodic replacement of the organic substrate might be necessary. Injection of fluid substrates (such as emulsified vegetable oils) has been recommended to avoid more invasive actions at the site (AFCEE 2008; Shen et al. 2010; ITRC 2011).

Finally, traditional monitoring systems based on arrays of screened wells might not be suitable to evaluate the performance of BBs. Wilson et al. (2008) used multilevel sampler transects, based on a mass performance of BBs. Wilson of screened wells might not be suitable to evaluate the performance of BBs. Wilson et al. (2008) used multilevel sampler transects, based on a mass flux approach, resulting in more realistic results. The traditional monitoring system could be acceptable if multilevel-screened wells were used instead of long-screened wells.

In spite of these issues, BBs have several advantages compared with traditional groundwater remediation systems and other in situ technologies. Aerobic, anaerobic or multi-layer barrier systems can be developed in order to treat groundwater affected by different kinds of pollutants, such as chlorinated organic compounds, oxidized metallic species, nitrate, sulfate, short- to medium-length chain alkanes, monoaromatic solvents, light polycyclic aromatic hydrocarbons and MTBE. Limitations due to in situ soil heterogeneities, hydraulic conductivity and/or biomass attachment/detachment are reduced. Costs for operation and maintenance as well as the impact on site activities are low.

These undoubted advantages give BBs broad prospects of application worldwide in the near future and next decade.

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