MNA and in situ reactive barrier approaches for groundwater contaminated by petroleum hydrocarbons

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Abstract Monitored natural attenuation (MNA) is fast becoming the preferred remedial option for groundwater contaminated by petroleum hydrocarbons. Contaminant plumes (mainly BTEX) are anticipated to extend typically <100 m, stabilize and then contract. However, some well-documented hydrocarbon plumes are >300 m long. Other BTEX plumes show signs of surging ahead after apparent stabilization. It is important to understand the controls on plume length and long-term behaviour if MNA is to be reliably applied. Factors such as source strength, aquifer geology (especially as it influences transverse dispersion), and electron acceptor type and availability are significant. Where MNA is not appropriate and rapid clean up of plume and source is not possible or too expensive, in situ plume control might be entertained. Five pilot and full scale in situ permeable reactive barrier systems are discussed. Design rationale, cost, performance, and potential applications are presented.

Key words BTEX; funnel-and-gate; monitored natural attenuation; permeable reactive barrier

INTRODUCTION

Monitored natural attenuation (MNA) has become an established remedial approach at least in North America (Wiedemeier et al., 1999). MNA is attractive mainly because of a perception of lower clean-up costs. However, MNA remedies leave in place much of the contaminated soil/groundwater that was the primary reason for remedial action. While MNA is expected to result in lower remedial costs, it is difficult to argue that the environmental liability associated with still-contaminated groundwater and soil can be devalued.

Another plume risk management approach is to intervene to limit the potential exposure of receptors to groundwater contaminants. Plume cut-off can be attained with groundwater extraction (so-called pump-and-treat or P&T), in situ bioremediation using injection wells (reactive barrier wells or RBWs) or permeable reactive barrier (PRB) technologies designed to remove the risky chemicals while permitting continued groundwater flow.

Issues for MNA

The longevity of the monitored natural attenuation remedy remains largely untested at least in the peer-reviewed literature. Three issues are troublesome:
- Unrecognized critical chemicals (e.g. methyl-tert-butyl ether or MTBE). MNA strategies adequate for BTEX plumes may not provide sufficient protection from MTBE impacts of water supply wells.
- Changes in the source zone (e.g. spillage of ethanol-fuels where MNA for normal gasoline spills had been initiated). Ethanol may enhance the persistence of BTEX, putting nearby receptors at greater risk.
- Changes in electron acceptor or electron donor availability. For example, Fe(III) in aquifer sediment may be consumed, removing an important electron acceptor to support biodegradation of BTEX. Continuing BTEX contamination may undergo less bio-attenuation without this electron acceptor and the BTEX plume may expand unexpectedly, especially if monitoring has not continued.

**IN SITU PERMEABLE REACTIVE BARRIER (PRB) APPROACHES**

Various pilot- and full-scale projects have now demonstrated the successful in situ treatment of a wide range of contaminants using permeable reactive barrier technology (RTDF, 2001). Table 1 provides a summary of some of the PRBs used with petroleum hydrocarbon contamination. Some basic designs are illustrated in Fig. 1. The simplest, lowest cost PRBs use a line of wells transverse to the groundwater flow direction, termed reactive barrier wells or RBWs. These are used to introduce remedial agents (e.g. oxygen from the oxygen-releasing magnesium peroxide compound, ORC®, (Chapman et al., 1997)) into the contaminated groundwater. RBWs make minimal effort to control the reactive zone and depend on the usually weak lateral dispersive mixing to spread the remedial addition into the contaminated groundwater flowing between the wells (Fig. 1(a)). Consequently, the wells need to be sufficiently close for lateral dispersion to deliver remedial chemicals to the plume (Fig. 1(b)). An intermediate approach is to introduce the remedial additions across the width of the contaminant plume, by periodically injecting remedial solutions and pumping them across the plume width. This can be done either through the natural aquifer material or through a trench of permeable material (a true PRB) installed across the width of the plume (Fig. 1(c)). The more expensive and highly-engineered PRBs use groundwater flow barriers and engineered in situ treatment zones (e.g. trench-and-gate by Bowles et al. (1999); funnel-and-gate by Morkin et al. (2000)). The “funnel” or permeable “trench” directs groundwater to an in situ, semi-passive treatment system, termed the “gate” (Fig. 1(d, e)).

Chapman et al. (1997) found limited success with the RBWs using ORC® placed in closely-spaced treatment wells (Case 1). Maximum treatment was about 70% of the influent BTEX. However, along flowpaths where BTEX was <5 mg l⁻¹, nearly complete removal was noted for the 132 day experiment. They also noted that much more oxygen was consumed than needed to degrade the BTEX removed. This was attributed to high biological oxygen demand (BOD) exerted by uncharacterized, non-BTEX organics and dissolved Fe(II).

An essentially full-scale trench-and-gate (T&G) system was installed at an operating gas plant in Alberta in September 1995 (Case 2). Details are provided by Bowles et al. (2000). Two, 30-m long collection trenches of about 5 m depth conveyed groundwater from the low permeability aquifer into a sequence of three gates where air
Table 1 Summary of selected permeable reactive barriers (PRBs) used with petroleum hydrocarbons.

<table>
<thead>
<tr>
<th>Case no. and reference</th>
<th>PRB system</th>
<th>Fig. 1</th>
<th>Contaminant</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chapman et al., 1997</td>
<td>RBW</td>
<td>(b)</td>
<td>BTEX</td>
<td>Oxygen addition using ORC®</td>
</tr>
<tr>
<td>2. Bowles et al., 2000; Granger, 1997</td>
<td>T&amp;G</td>
<td>(d)</td>
<td>Natural gas condensate (BTEX)</td>
<td>Oxygen sparging; ammonia addition via diffusive tubing; P via dissolution of phosphates</td>
</tr>
<tr>
<td>3. Gorman, 1995; Austrins, 1997</td>
<td>F&amp;G</td>
<td>(e)</td>
<td>BTEX + styrene</td>
<td>Oxygen (+ ammonia) sparging of gravel-filled gate</td>
</tr>
<tr>
<td>4. Lauzon, 1998; Kerr, 2001</td>
<td>F&amp;G</td>
<td>(e)</td>
<td>Naphthalene</td>
<td>Nitrate addition in cassette gate</td>
</tr>
<tr>
<td>5. Morkin et al., 2000</td>
<td>F&amp;G</td>
<td>(e)</td>
<td>BTEX and chlorinated ethenes</td>
<td>Fe° for reduction of Cl-ethenes; oxygen sparging to volatilize and biodegrade BTEX</td>
</tr>
</tbody>
</table>

Fig. 1 Schematic layouts of permeable reactive barriers, including reactive barrier walls (RBWs).

sparging supported volatilization and biodegradation of the target BTEX. Treated water flowed into an infiltration gallery which had about 1.5 times the infiltration area of the collection gallery to ensure no mounding within the T&G system. The first culvert was equipped with an air sparging system, a spiralled micropore hose anchored to the base; the second culvert could be divided into two parallel compartments; and the third culvert could also be equipped with a back-up biosparge system. In terms of treatment of BTEX effluent, treated water usually contained <1 µg l⁻¹ BTEX. With addition of phosphate via dissolution of apatite minerals, much higher fluxes of BTEX could be remediated.

For Case 3, the funnel was composed of steel sheet piling sections driven through a sand fill aquifer just to or into the confining layer. The gate itself consists of a 1.07-m
diameter, 5.3-m deep zone of backfilled pea-gravel installed with the aid of a removable caisson. Embedded within the gravel are a series of five "u"-shaped, 2.5-cm OD diameter steel pipes. The horizontal sections of pipe had holes to release $O_2$ gas or $NH_3$ gas. During gas sparging, direct gas phase contact was limited to about 20% of the gate volume, probably because of the development of preferential flow paths within the pea gravel. Sparge-induced groundwater mixing occurred after the injection and significantly increased the volume of gate groundwater to which $O_2$ or $NH_3$ was provided. It was apparent that sufficient $O_2$ was not being provided since residual BTEX plus styrene (i.e. BTEXS), typically 10+ mg l$^{-1}$, was still found in gate groundwater. Clearly, with the unexpectedly high BTEXS concentrations, even sparging with oxygen and enhancing biodegradation rates through $NH_3$ sparging, was not able to remove the BTEXS completely.

The F&G in Case 4 is in the Borden sand aquifer. It was comprised of Waterloo Barrier™ sealable sheet piling and the gate makes use of a novel cassette system with four removable sections. A naphthalene plume was successfully treated using nitrate as the electron acceptor. Nitrate was released from about 1 kg cement blocks manufactured with nitrate. The capture of the plume by the gate is currently being evaluated. It appears that capture was adequately anticipated from initial modelling. While encouraging, it must be noted that the aquifer is the world's most studied and is very simple.

Case 5 is a unique sequential treatment gate installed at Alameda NAS, California, USA. Granular iron is contacted by contaminated groundwater and chlorinated ethenes are dechlorinated. Next, groundwater flows through an open cassette in which $O_2$ gas is sparged. A combination of volatilization and biodegradation removes >99.9% of the BTEX and chlorinated ethenes reaching the biosparge zone.

Selected aspects of the five PRBs are compared in Table 2.

**CHOOSING MNA AND PRBS**

The choice of clean-up remedy will be situation-specific. One screening approach is to identify the "drivers" for clean up. These are often one or more of: time, cost, distance to plume limit or regulatory boundary. If time is the driver for remediation, neither MNA and permeable reactive barriers (PRBs) are likely to be appropriate. Source clean up (dig and dump, vapour extraction, etc.) and plume extraction using P&T are the current choices, although the efficacy of P&T for rapid clean up is doubtful. There will be situations where rapid clean up is not technically feasible or where time can be traded for cost savings. When cost becomes the driver, MNA should be the general choice. Where time is available but MNA is not technically feasible or is too risky (e.g. the plume will be too close to the regulatory boundary), in situ remediation and pump and treat are the likely remedies.

PRBs typically have higher initial costs with potentially lower operation costs than P&T. Cost advantages over P&T are very dependent on ongoing operational costs and financial discount rate. PRB design variants continue to appear, so technically better and lower cost systems are anticipated. While considerable experience with P&T has accumulated, longer-term performance/cost information for PRBs is still accumulating as this technology moves from the demonstration stage to maturity.
Table 2 Comparison of five PRBs. Note that BTEXS is BTEX plus styrene.

<table>
<thead>
<tr>
<th>Case</th>
<th>Target compounds</th>
<th>Electron acceptor</th>
<th>Nutrients</th>
<th>Aquifer $K$ (m s$^{-1}$)</th>
<th>Capture cross section (m$^2$)</th>
<th>Cost of design and installation</th>
<th>Treatment Conc. reduction (g l$^{-1}$)</th>
<th>Flux reduction (g year$^{-1}$)</th>
<th>Major remaining uncertainties</th>
<th>Potential application in the petroleum industry</th>
<th>Challenges for cost-effective, full scale application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BTEX</td>
<td>O$_2$ from ORC®</td>
<td>none</td>
<td>$10^{-4}$</td>
<td>5</td>
<td>US$ 12 000</td>
<td>$10^7$</td>
<td>$3 \times 10^{-6}$</td>
<td>Long-term performance</td>
<td>Cut off a small plume in a shallow aquifer</td>
<td>Longevity and cost of ORC®</td>
</tr>
<tr>
<td>2</td>
<td>BTEX</td>
<td>Sparged O$_2$</td>
<td>Diffused NH$_3$, solid P0$_4$-</td>
<td>$10^{-7}$ (est.)</td>
<td>480</td>
<td>US$ 60 000</td>
<td>$60 \text{ mg l}^{-1}$</td>
<td>2200</td>
<td>Long-term performance</td>
<td>Contain a large source area in a shallow, low $K$ aquifer</td>
<td>Variable ground water flux</td>
</tr>
<tr>
<td>3</td>
<td>BTEXS</td>
<td>Sparged O$_2$</td>
<td>Sparged NH$_3$</td>
<td>$3 \times 10^{-6}$</td>
<td>25</td>
<td>US$ 25 000</td>
<td>$45 \text{ mg l}^{-1}$</td>
<td>200</td>
<td>Treatment capacity, long-term cost and performance</td>
<td>Contain a small source area or plume in a shallow aquifer</td>
<td>Non-uniform oxygen delivery</td>
</tr>
<tr>
<td>4</td>
<td>Naphthalene</td>
<td>NO$_3$ from cement</td>
<td>none</td>
<td>$7 \times 10^{-5}$</td>
<td>20</td>
<td>US$ 67 000</td>
<td>$1 \text{ mg l}^{-1}$</td>
<td>$&lt;10 \mu g l^{-1}$</td>
<td>Treatment mechanism, long-term performance</td>
<td>Contain a small source area or plume in a shallow aquifer</td>
<td>Uncertain reaction, expensive cassette system</td>
</tr>
<tr>
<td>5</td>
<td>BTEX, chlor. ethers</td>
<td>Sparged O$_2$</td>
<td>none</td>
<td>$2 \times 10^{-5}$</td>
<td>40</td>
<td>US$ 140 000</td>
<td>$1.5 \text{ mg l}^{-1}$</td>
<td>320</td>
<td>Long-term performance</td>
<td>Construction costs and longevity of sparge $K$</td>
<td></td>
</tr>
</tbody>
</table>

Although there is an obvious need to consider a combination of techniques for efficient site clean up, there is little well documented experience. For example, MNA would be a useful "polishing" for more active treatments, especially PRBs. Perhaps plume "hot spots" could be attacked with aggressive PRBs or P&T, while MNA would be sufficient to remediate lower concentrations. A useful concept is to only design active site clean up to the point where MNA can then meet the site-specific remedial objectives. For example, this may require no or only partial NAPL source removal, a very attractive concept given the difficulty in finding and remediating NAPL sources.

Acknowledgements Field projects have been supported by a variety of agencies and companies, especially the National Sciences and Engineering Research Council of Canada, the American Petroleum Institute, Gasrep, Capp, Shell Canada and UK, and by the US Department of Defense through the Advanced Alternative Technology Demonstration Facility. Dr J. F. Devlin provided critical data interpretation and insight.

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